INDUSTRIAL ORGANIC CHEMICALS

INDUSTRIAL ORGANIC CHEMICALS

Second Edition

HAROLD A. WITTCOFF
Scientific Adviser, Nexant ChemSystems Inc.; Vice President of Corporate Research, General Mills, Inc. (ret.)

BRYAN G. REUBEN
Professor Emeritus of Chemical Technology
London South Bank University

JEFFREY S. PLOTKIN
Director, Process Evaluation and Research Planning Program,
Nexant ChemSystems Inc.

WILEY-INTERSCIENCE
A John Wiley & Sons, Inc., Publication

Copyright © 2004 by John Wiley & Sons, Inc. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400, fax 978-646-8600, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services please contact our Customer Care Department within the U.S. at 877-762-2974, outside the U.S. at 317-572-3993 or fax 317-572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print, however, may not be available in electronic format.

Library of Congress Cataloging-in-Publication Data:
Wittcoff, Harold.
Industrial organic chemicals.—2nd ed. / Harold A. Wittcoff, Bryan G. Reuben, Jeffrey S. Plotkin.
p. cm.
Includes index.
ISBN 0-471-44385-9 (Cloth)
1. Organic compounds—Industrial applications. I. Reuben, B. G. II. Plotkin, Jeffrey S. III. Title.
TP247.W59 2004
661.8—dc22 2003023097

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

OTHER BOOKS BY THE AUTHORS

The Phosphatides, by Harold A. Wittcoff, Reinhold, New York, 1950.

The Chemical Economy, by Bryan G. Reuben and Michael L. Burstall, Longman, London, 1973.

Industrial Organic Chemicals in Perspective, Part 1: Raw Materials and Manufacture, Part 2: Technology, Formulation, and Use, by Harold A. Wittcoff and Bryan G. Reuben, Wiley, New York, 1980.

Industrial Organic Chemistry, an ACS tape course, by Harold A. Wittcoff, ACS, Washington DC, 1984.

The Pharmaceutical Industry—Chemistry and Concepts, an ACS tape course, by Harold A. Wittcoff and Bryan G. Reuben, ACS, Washington DC, 1987.

The Cost of "Non-Europe" in the Pharmaceutical Industry, *Research in the Cost of "Non-Europe," Basic Findings Vol. 15*, by Michael L. Burstall and Bryan G. Reuben, Commission of European Communities, Luxembourg, 1988.

Pharmaceutical Chemicals in Perspective, by Bryan G. Reuben and Harold A. Wittcoff, Wiley, New York, 1990.

Cost Containment in the European Pharmaceutical Market, by Michael L. Burstall and Bryan G. Reuben, Marketletter, London, 1992.

Implications of the European Community's Proposed Policy for Self-Sufficiency in Plasma and Plasma Products, by Bryan G. Reuben and Ian Senior, Marketletter, London, 1993.

Outlook for the World Pharmaceutical Industry to 2010, by M. L. Burstall and B. G. Reuben, Decision Resources, Waltham MA, 1999.

Organic Chemical Principles and Industrial Practice by M. M. Green and Harold A. Wittcoff, VCH Wiley, Weinheim, Germany, 2003.

Outlook for the World Pharmaceutical Industry to 2015, by M. L. Burstall and B. G. Reuben, Decision Resources, Waltham MA, 2004.

To our wives, Dorothy, Catherine, and Marisa, and to our children,
grandchildren, and great-grandchildren.

ACKNOWLEDGMENTS

We gratefully acknowledge the help of Professor Maurice Kreevoy, who reviewed the chapter on catalysis and offered many helpful suggestions. Mrs. Denise Phillips searched the literature diligently for us. We thank Ms. Carol Conti of Nexant ChemSystems Inc. for many insights about the supply and demand situation for many of the large volume petrochemicals and plastics. We are particularly grateful to Nexant ChemSystems Inc., whose numerous multiclient reports provided detailed information about reaction conditions and production economics. And we are grateful to our wives, who gave us encouragement at all stages of this enterprise.

CONTENTS

CHAPTER 3 CHEMICALS AND POLYMERS FROM ETHYLENE 100

CHAPTER 12 CHEMICALS FROM COAL 399

CHAPTER 13 FATS AND OILS 411

CHAPTER 14 CARBOHYDRATES 435

CHAPTER 17 SUSTAINABILITY AND GREEN CHEMISTRY 567

PREFACE

In the preface to the first edition, we expressed the hope that we could comment on the chemical industry's evolution in 10 years time. Dramatic changes have motivated us to compress this time frame. There have been unprecedented restructuring, severe and complicated feedstock problems, and massive shifts of capacity to developing countries, whose economic and political stability is in doubt. Possible terrorist activity dictates elaborate safety and security procedures, and the design of plants with small inventories is a priority.

In the years since the last edition, one of us (HAW) has increased his tally of courses on the fundamentals of the industry to 300 in 28 countries. To increase our cover, particularly of the patent literature, we have invited Dr. Jeffrey S. Plotkin, Director of the Process Evaluation and Research Planning program at Nexant ChemSystems Inc., to join us as co-author.

PREFACE TO THE FIRST EDITION

In the early 1970s, one of us (BGR) wrote a book celebrating the rapid growth of the adolescent chemical industry. The organic chemicals industry at the time was growing at four times the rate of the economy. It was indicated nonetheless that “trees do not grow to the sky.” In 1980, in another book, we both declared the industry to be middle-aged with slow or zero growth. In this totally revised and expanded version of our earlier book, we reflect that the industry, at any rate in the developed world, is showing many of the illnesses of late middle-age.

The problems have arisen first from the undisciplined building of excess capacity with consequent fierce competition and low prices. Second, the entry of numerous developing countries into the industry has exacerbated the situation (Section 1.3.6), and third, there has been much stricter government legislation (Section 1.3.7). There is massive worldwide restructuring and continual shifting of commodity chemical manufacturing to areas other than the United States, Western Europe, and Japan. The Middle East and Southeast Asia are the principal new players in the game. Perhaps this trend will continue and the present developed world will in the future confine itself to the manufacture of specialties, but the economic and political forces at work are more complex than that. We hope to be able to discuss their resolution in another edition in about 10 years’ time.

Meanwhile, some things have not changed. The organic chemicals industry is still based on seven basic raw materials all deriving from petroleum and natural gas. The wisdom of teaching about the chemical industry on the basis of these seven building blocks has been confirmed by the fact that, since the publication of our first book, one of us (HAW) has delivered by invitation 200 courses in 27 countries on the fundamentals of the industry based on this pattern. Most of these courses are for industrial personnel but academia has not been neglected.

Furthermore, some changes have been positive. For example, there have been exciting new processes such as the development of metallocene catalysts (Section 15.3.12). Section 4.6.1 describes new methyl methacrylate processes that give a potentially cheaper product, that do not produce ecologically undesirable ammonium hydrogen sulfate by-product or (in another process) that eliminate the use of dangerous hydrogen cyanide.

In this book, our main objective is still to present the technology of the organic chemicals industry as an organized body of knowledge, so that both the neophyte and the experienced practitioner can see the broad picture. Nonetheless, we have expanded its scope to include not only new processes but many apparently less important reactions that are significant because they give rise to the more profitable specialty chemicals. The lesser volume chemicals have been clearly delineated as such, and the reader who wishes to see the industry on the basis of its large tonnage products can omit these sections.

We hope this book will be useful both to college students who have studied organic chemistry and to graduates and industrial chemists who work in or are interested in the chemical industry. Even though much of the chemistry has remained the same, the change in the way the industry looks at its problems provides ample justification for our offering this edition as a fresh perspective on industrial organic chemicals.

LIST OF ACRONYMS AND ABBREVIATIONS

ABS	Acrylonitrile-butadiene-styrene
ACS	American Chemical Society
AFC	Alkali fuel cell
AMOCO	Formerly American Oil/Standard Oil of Indiana, now owned by BP
AO	Acid Optimization
APPE	Association of Petrochemicals Producers in Europe
ARCO	Formerly Atlantic Richfield Oil Company, now owned by Lyondell
BASF	German chemical company: formerly Badische Anilin und Soda Fabrik
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BP	British Petroleum
BPA	Bisphenol A
Btu	British Thermal Units (see appendix 2)
BTX	Benzene-toluene-xylene
CAA	Clean Air Act
CEFIC	Centre Européen des Fédérations de L'Industrie Chimique
CFCs	Chlorofluorocarbons having no hydrogen atoms
CHP	Combined heat and power
CIA	UK Chemical Industries Association
CIS	Commonwealth of Independent States (formerly USSR)
CMA	Chemical Manufacturers' Association
CMC	Carboxymethylcellulose
CMRs	Carcinogens, mutagens, and reprotoxins
CNI	Chemical News Intelligence
COCs	Cyclic olefin copolymers
CRG	Catalytic rich gas
DCC	Deep catalytic cracking
DDT	Bis(chlorophenyl)trichloromethylmethane
DEA	Diethanolamine
DMF	Dimethylformamide

DMSO	Dimethyl sulfoxide
DSM	Dutch chemical company; formerly Dutch State Mines
EDTA	Ethylenediaminetetraacetic acid
ENI	Italian chemical company: Ente Nazionale Idrocarburi (Enichemi is a subsidiary)
EP	Ethylene-propylene (rubber)
EPA	Environmental Protection Agency
EPDM	Ethylene-propylene-diene-monomer
EVA	Ethylene-vinyl acetate
EVC	European Vinyls Corporation
FCC	Fluid catalytic cracking
FDA	Food and Drug Administration
GATT	General Agreement on Trade and Tariffs
GLA	Gamma-linolenic acid
GMP	Good Manufacturing Practice
GTL	Gas-to-liquid
HTE	High throughput experimentation
HCFCs	Hydrochlorofluorocarbons
HCN	Hydrocyanic acid and Hydrogen cyanide
HDPE	High-density polyethylene
HIPS	High-impact styrene
HMDA	Hexamethylenediamine
HMDI	Hexamethylene diisocyanate
HMSO	Her Majesty's Stationery Office
ICI	UK Chemical Company; formerly Imperial Chemical Industries
IFP	Institut Français de Pétrole
IPDI	Isophorone diisocyanate
IR	Infrared
ISP	International Specialty Products
IUPAC	International Union of Pure and Applied Chemistry
KA	Ketone/alcohol
LAB	Linear alkylbenzene
LDPE	low-density polyethylene
LLDPE	Linear low-density polyethylene
LPG	Liquid petroleum gas
LVN	Light virgin naphtha
M/F	Melamine-formaldehyde
MBS	Methyl acrylate-butadiene-styrene
MCFC	Molten carbonate fuel cell
MDI	4,4-Diphenylmethane diisocyanate
MEK	Methyl ethyl ketone; 2-butanone
MOI	Mobil Olefin Interconversion
MON	Motor Octane number
MTBE	Methyl *tert*-butyl ether
MTG	Methanol to gasoline
MTO	Methanol to olefins
MTP	Methanol-to-propylene
NAICS	North American Industry Classification System
NPRA	National Petroleum Refiners Association
OSHA	Occupational Safety and Health Act
P/F	Phenol-formaldehyde
PAFC	Phosphoric acid fuel cell
PAMAM	Poly(amidoamine)
PAN	Peroxyacetyl nitrate
PBBs	Polybrominated biphenyls

PBDEs	Polybrominated diphenyl ethers
PBT	Persistent bioaccumulative toxic
PDJ	Patents and Design Journal
PEEK	Poly(ether ether ketone)
PEMFC	Polymer electrolyte-proton exchange membrane fuel cell
PEN	Poly(ethylene naphthalate)
PERP	Process Evaluation and Research Planning
PET	Poly(ethylene terephthalate)
PIMM	Process Integrated Management Methods
PMDA	Pyromellitic dianhydride
PO	Propylene oxide
POX	Noncatalytic partial oxidation
PTA	Pure terephthalic acid
PTFE	Polytetrafluoroethylene
PVC	Poly(vinyl chloride)
REACH	Registration, Authorization, and Evaluation of Chemicals
RIM	Reaction injection molding
RIPP	Chinese Research Institute of Petroleum Processing
RON	Research Octane number
SABIC	Saudi Arabia Basic Industries Corporation
SAN	Styrene-acrylonitrile
SAPO	Silicaaluminophosphate
SBR	Styrene-butadiene rubber
S-B-S	Styrene-butadiene-styrene
S-E-B-S	Styrene-ethylene-butylene-styrene
S-E-P-S	Styrene-ethylene-propylene-styrene
SHOP	Shell Higher Olefins Process
SI	Système International
S-I-S	Styrene-isoprene-styrene
SMDS	Shell Middle Distillate Synthesis
SNG	Substitute natural gas
SOFC	Solid oxide fuel cell
SOHIO	Was Standard Oil of Ohio; now part of BP
TAME	*tert*-Amyl methyl ether
TBA	*tert*-Butylbenzaldehyde
TDI	Toluene diisocyanate
THF	Tetrahydrofuran
TMA	Trimellitic anhydride
TNT	Trinitrotoluene
TPA	Terephthalic acid
U/F	Urea-formaldehyde
UOP	Universal Oil Products
USGC	United States Gulf Coast
USGS	United States Geological Survey
USSR	Union of Soviet Socialist Republics (Soviet Union), now CIS
UV	Ultraviolet
VGO	Vacuum gas oil
vPvBs	Very persistent bioaccumulative toxic chemicals
WIPO	World Intellectual Property Organization

CHAPTER 0

HOW TO USE INDUSTRIAL ORGANIC CHEMICALS, SECOND EDITION

Industrial Organic Chemicals, published in 1996, was an updated, expanded, and completely rewritten version of volume I of a two-volume set, *Industrial Organic Chemicals in Perspective*, published in 1980. Volume I of the set described where industrial organic chemicals came from; volume II described how they were used. Two decades later, chemicals still come from the same sources, but there are many new processes to be described. The application of chemicals has changed much less, and a revision of volume II is not planned. This second edition of the 1996 book is warranted by the numerous changes the industry has undergone in a short time. We discuss many new processes and improvements in many older ones.

0.1 WHY THIS BOOK WAS WRITTEN AND HOW IT IS STRUCTURED

The petrochemical industry provides well over 95% by tonnage of all organic chemicals. It grew rapidly in the 1950s and 1960s. Many new processes and products were introduced. Large economies of scale proved possible. The prices of chemicals and polymers dropped so that they could compete with traditional materials. Cheerfully colored plastic housewares, highly functional packaging, shampoos that tolerated hard water and easy care garments of synthetic fibers were no longer exciting new technology. Instead they had become an accepted and routine part of modern life.

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

By the 1970s, growth was leveling off. The first and second oil shocks increased the price of crude oil, and hence of its downstream products. Economies of scale suffered a hiatus to rise again in the late 1990s with the announcement of 2.2 billion lb of ethylene per year steam crackers and a 3.5 billion lb per year methanol plant. In 2004, SABIC announced plans for a 2.9 billion lb/year cracker. The industry had matured. As its technology became better known, developing countries started their own petrochemical industries, competing with the developed countries and thus depressing profitability. Furthermore, the impact of the industry on the environment became evident.

In the 1980s and early 1990s, new products were no longer the name of the game, in part because the 1960s and 1970s had provided an arsenal of them to attack new applications. Also, the industry became subject to strict government monitoring. Expensive toxicity testing was required before a new compound could be introduced. (Section 1.3.7).

Rather than developing bigger, better plants to manufacture novel chemicals, the industry became concerned with lessening pollution, improving processes, and developing specialty chemical formulations and niche products that could be sold at higher profit margins. Research and development became highly process oriented, in part to find less polluting processes, and in part to combat maturity and gain an edge over competition with money-saving technology. Examples are given in the foreword and throughout the book.

Chapter 1 shows how the chemical industry fits into the overall economy and then defines the industry in terms of its characteristics.

Chapter 2 describes where organic chemicals come from and then shows how the major sources, petroleum and natural gas, provide seven basic chemicals or chemical groups from which most petrochemicals are made. The basic building blocks comprise olefins—ethylene, propylene, and the C_4 olefins (butadiene, isobutene, 1- and 2-butenes); aromatics—benzene, toluene, and the xylenes (*ortho*, *meta*, *para*); and one alkane, methane. Chapter 2 explains how the olefins derive primarily from steam cracking and secondarily how C_3 and C_4 olefins come from catalytic cracking, and how the aromatics derive primarily from catalytic reforming in the United States but from steam cracking in Europe. Methane occurs as such in natural gas. The chapter emphasizes the important interface between the refinery and the petrochemical industry and the relationship between feedstock flexibility and profitability.

Chapters 3 and 4 describe the chemistry of ethylene and propylene. They are the most important of the seven building blocks and are treated accordingly.

Chapters 5 and 6 deal with the C_4 and C_5 olefins. Chemical usage of C_4 olefins (excluding methyl-*tert*-butyl ether for gasoline) is an order of magnitude less than that of ethylene and propylene, and the major C_4 applications are in synthetic rubbers. The C_5 compounds and their derivatives are only used in much lower volume and are not included in the seven basic building blocks. They are nonetheless an important source of isoprene for a synthetic analogue of natural rubber (Section 15.3.10) and for thermoplastic elastomers (Section 15.3.8).

Chapters 7–9 describe the chemistry of the aromatics—benzene, toluene, and the xylenes. Benzene has been overshadowed by ethylene and propylene since the 1960s but is still the third most important of the building blocks.

Chapter 10 describes the chemistry of methane, a relatively unreactive molecule, which nonetheless is the source of synthesis gas ($CO + H_2$) for ammonia and methanol manufacture. Acetylene is discussed here, since it may be made from methane. Very important 50 years ago, its significance has been steadily diminished by chemistry based on ethylene and propylene.

Chapter 11 is devoted to the growing industrial chemistry based on alkanes other than methane. The substitution of alkanes for olefins, which depends on sophisticated catalyst development, could change industrial chemistry profoundly in the future.

Chapters 12–14 deal with non-petroleum sources of chemicals—coal, fats and oils, and carbohydrates. The chemical industry in the nineteenth and early twentieth centuries was based on chemicals derived from coal tar or coke oven distillate. Today, this is a specialty area, and our major interest in coal focuses on its conversion to synthesis gas. This would be the first stage in building a coal-based chemical industry should petroleum and natural gas be depleted.

The chemistry of fats and oils (Chapter 13) is reflected in the surfactant area and in numerous specialty performance products. Carbohydrate-based chemicals (Chapter 14) are also largely specialties.

Since over one-half of all organic chemicals manufactured end up in polymers, Chapter 15 is devoted to polymerization processes and polymer properties. Chapter 16 deals with the all-important subject of catalysis without which there would hardly be a chemical industry. Chapter 17 discusses the vital issue of sustainability, and the emergence of “green” chemistry, a topic that dominates the books published on industrial chemistry since 1990.

It is these new processes and attitudes that provided the incentives for this new volume, but we have also expanded its scope to include many apparently less important reactions, which are significant because they give rise to the more profitable specialty chemicals. We hope it will be useful both to university students who have studied organic chemistry and to graduates and industrial chemists who work in or are interested in one of the most remarkable industries of the twentieth century and, if we may anticipate a little, the twenty-first century.

We intend each chapter to be self-sufficient, hence there is inevitably a degree of repetition. We have tried to minimize this by extensive cross-referencing and hope the reader will be tolerant of the repetition that remains.

0.2 NORTH AMERICAN INDUSTRY CLASSIFICATION

The US government provides statistics on all branches of industry, dividing them according to the North American Industry Classification System (NAICS). Each major segment of the economy is classified under a number between 1 and 99 (Table 1.1). Manufacturing industries are classified under numbers 31–33 and the chemical and allied products industry falls within this category at 325. Statistics for subsegments of the industry are provided under four, five, or six digit numbers. Thus 3252 is *Resins, synthetic rubbers & artificial & synthetic fibers and filaments*, 325211 is *Plastics materials and resins*, 325212 is *Synthetic rubber*, and 32522

Artificial & synthetic fibers and filaments. We have relied on these data, although it is never possible to obtain up-to-date figures. Thus the material published in 2002 contains information for 2000. Statistics from other sources are often more up-to-date but are less authoritative (Section 0.4.5).

The industries that form the chemical and allied products industries are shown in Table 1.2. Although at times one might wish for even more detailed information, the North American Industry Classification provides a wealth of it. Other countries do not have comparable databases; many have Standard Industrial Classifications, but none provides so much information. The classifications in other countries rarely correspond to those in the United States or to each other, and analysts wishing to tackle official statistics should be aware of the pitfalls.

0.3 UNITS AND NOMENCLATURE

The widespread adoption of the SI (Système International) system of units based on the meter, the kilogram, and the second has worsened rather than improved the plethora of units used in the chemical industry. Three kinds of tons are in common use—the short ton (2000 lb), the metric ton or tonne (1000 kg or 2204.5 lb), and the long ton (2240 lb). U.S. Statistics are usually given in millions of pounds, which are at least unambiguous, and we give all our figures either in these units or in tonnes. In addition, we try to quote figures in the units actually used by industry—petroleum is measured in barrels, benzene in gallons, mixed xylenes in gallons, and (incredibly) *p*-xylene in pounds—to give conversions in better known units. A table of conversion factors is given in Appendixes 2 and 3.

Similarly, in naming chemicals, we tend to use the names conventional in industry rather than the more academic nomenclature of the International Union of Pure and Applied Chemistry (IUPAC). Thus we write hydrogen not dihydrogen; ethylene, acetylene, and acetic acid; not ethene, ethyne, and ethanoic acid.

Industry makes no effort to use consistent nomenclature. Ethene and propene are universally known as ethylene and propylene and would scarcely be recognized by their IUPAC names. The C_4 olefins, however, are frequently referred to as butenes rather than butylenes and we have followed this style. We use trivial names wherever industry does. Thus we refer to $C_6H_5CH(CH_3)_2$ as cumene, the name by which it is bought and sold, rather than the more informative names of isopropylbenzene, 2-phenylpropane, or (1-methylethyl)benzene. The term ethanal would be likely to be misread or misheard in industry as ethanol, and the compound is known as acetaldehyde. So important is trivial nomenclature that the pharmaceutical industry could not exist without it.

We regret the lack of consistency that the use of trivial nomenclature entails, but we feel it best serves our aim of communicating with chemical industry personnel and preparing students to enter the industry.

0.4 GENERAL BIBLIOGRAPHY

In many ways, the greatest service that a book like this can provide is to introduce the student to the industrial chemical literature. We follow each chapter with an annotated bibliography that lists some of the standard literature on the subject of the chapter, cites the sources of much of our own information, and adds occasional notes to matters discussed in the chapter. Two of the authors of this book received their basic education many years ago, and we have listed unashamedly the books that influenced us, aged though they may be. We have omitted some of the truly obsolete material. References to early work, as well as more recent material, may be found in *Kirk–Othmer* and other encyclopedias, and in B. G. Reuben and M. L. Burstall, *The Chemical Economy*, Longman, London, 1974. Relatively few books have been written recently on the chemical industry and much can still be gained from the old ones.

0.4.1 Encyclopedias

The most important single reference work is R. E. Kirk and D. F. Othmer, *Kirk–Othmer's Encyclopedia of Chemical Technology*, Volumes 1–25, 4th ed., J. I. Kroschwitz and M. Howe-Grant, Ed., Interscience, New York, 1991–1998. *Kirk–Othmer* provides comprehensive and well-referenced coverage of almost every aspect of industrial chemistry. New articles appear on the web (www.mrw.interscience.wiley.com/uric or www.mrw.interscience.wiley.com/kirk) and these will eventually be included in a 5th edition. The earlier volumes of the first, second, and third editions are inevitably dated, but provide information not readily available from other sources. If a subject is not treated in the new edition, it is always worth consulting the older one.

The Encyclopedia of Polymer Science and Engineering, 2nd ed., J. I. Kroschwitz, Ed., (17 volumes plus supplement and an index volume) Interscience, New York, 1985–1989, provides comprehensive coverage of polymer chemistry. It is well referenced but weak on technology. The first edition (called *The Encyclopedia of Polymer Science and Technology*) comprised 15 volumes and was published between 1964 and 1971. As with *The Encyclopedia of Chemical Technology*, the earlier edition still contains valuable material. Part 1: Volumes 1–4 of the 3rd ed. (reverting to the original title, H. F. Mark, Ed.) had been published by June 2003.

The Encyclopedia of Chemical Processing and Design, J. J. McKetta, Ed., Dekker, New York, has a chemical engineering orientation. It had run to 68 volumes by 1999. As publication started in 1976, it is perhaps inevitable that the approach is inconsistent. Individual articles are worthwhile but the content is unpredictable.

The only encyclopedia to rival *Kirk–Othmer* is *Ullmann's Encyclopedia of Industrial Chemistry*, W. Gerhartz, Ed., Wiley-VCH, Weinheim. It was first published in 1914 and this, the 6th ed., appeared as a 40-volume set in October 2002. A rapid inspection suggests rigorous editorial control, with well-indexed chapters following a standard pattern. It has a more international approach than *Kirk–Othmer.*

An ambitious undertaking is the *Dictionary of Scientific and Technical Terms*, S. P. Parker, Ed. The 4th ed. was published by McGraw-Hill in 1989. Two newer ventures are R. D. Ashford, *Dictionary of Industrial Chemical Properties, Production and Uses*, 2nd ed., Wavelength, London, 2002, and A. Comyns, *Encyclopedic Dictionary of Named Processes in Chemical Technology*, CRC Press, Cleveland OH, 1999.

Some consulting companies publish reports on a continuing basis that contain a wealth of up-to-date information on chemistry, engineering, and markets of numerous industrial chemicals. These are, however, quite expensive and are usually found only in industrial libraries, the subscriber agreeing to keep the information confidential. One such program is entitled *Process Evaluation and Research Planning (PERP Program)* Nexant Inc./Chemsystems, 44 South Broadway, White Plains, NY 10601-4425, which covers in depth the chemistry, engineering, and market data for many of the basic petrochemicals as well as important specialty chemicals. A less in-depth compendium but one that covers a greater breadth of subjects is the *Chemical Economics Handbook*, Stanford Research Institute, Menlo Park, CA.

0.4.2 Books

Before the spectacular growth of the chemical industry after World War II, three classic books appeared that encompassed much of what was done up to 1950. These books have been repeatedly revised and updated and, although they seem old-fashioned in some ways, they are certainly worthy of mention. The oldest is *Riegel's Handbook of Industrial Chemistry*, 9th ed., J. A. Kent, Ed., Van Nostrand–Reinhold, New York, 1992. Riegel first appeared in 1928 and is now a multiauthor survey of the chemical and allied products industry. R. N. Shreve and N. Basta, *The Chemical Process Industries*, 6th ed., McGraw-Hill, New York, 1994, was first published in 1945 and covers many of the process industries such as cement and glass as well as the mainstream chemical industry. *Faith, Keyes and Clark's Industrial Chemicals* first appeared in 1950. The fourth and most recent edition was revised by F. A. Lowenheim and M. K. Moran and was published by Wiley-Interscience in 1975. It is now out of print. It provides details of manufacture and markets for the 140 most important chemicals in the United States and is significant because of its interdisciplinary approach, which has never been repeated.

Another volume of note is *Chemistry and the Economy*, M. Harris and M. Tischler, Eds., American Chemical Society, Washington DC, 1973. Although old, it provides an excellent overview of the impact of chemical technology on the economy. It describes how industrial chemistry interfaces with numerous industries, gives insight into the makeup of the chemical industry, and provides numerous historical facts that tend to humanize the industry. The book is good reading for students as well as for practicing chemists and engineers.

In the 1970s, interest increased in the teaching of industrial chemistry in colleges and universities. There is still a long way to go to impress the academic community with the important role that industrial chemistry has played not only in the application of chemical technology but also in the development of new knowledge. Nonetheless, a number of important books were published.

One of the first books on industrial organic chemistry was J. K. Stille, *Industrial Organic Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1968. This small volume, now out of print, contains a wealth of material about the industry as it existed prior to 1970 and is written from the interesting perspective of an academic organic chemist.

The Chemical Economy, B. G. Reuben and M. L. Burstall, Longman, London, 1974 is a guide to the technology and economics of the chemical industry and provides an overview of the industry emphasizing organic chemicals. It is biased somewhat toward European practice and contains annotated bibliographies.

Basic Organic Chemistry V: Industrial Products, J. M. Tedder, A. Nechvatal, and A. H. Jubb, Eds., Wiley, Chichester, 1975, is the fifth volume of a series on organic chemistry, but the title is somewhat misleading as the book can stand by itself as a textbook on industrial organic chemistry. It comprises a multiauthor survey, oriented toward chemistry rather than technology and toward British practice. Insufficient references are given. The book is a mine of information for the specialized reader and has been reprinted but not revised.

C. A. Clausen, III, and G. Mattson, *Principles of Industrial Chemistry*, Wiley-Interscience, New York, 1978, is aimed at chemists and is a collection of case studies providing an enthusiastic introduction to chemical process principles, process development, and various commercial aspects of the chemical industry. A more recent collection is E. Lister and C. Osborne *Industrial Chemistry Case Studies*, Royal Society of Chemical Education Division, London, 1998.

A. L. Waddams, *Chemicals from Petroleum*, 4th ed., John Murray, London, 1978, was a pioneering account of petrochemicals and provides an insight into the relationship of the refinery to the chemical industry.

Among the important books dealing specifically with the organic chemicals industry is P. Wiseman, *An Introduction to Industrial Organic Chemistry*, 2nd ed., Halsted Press, New York, 1979. It is well organized, well written, and is oriented toward the pure chemistry that provides a base for technology. The same author provided *Petrochemicals*, Ellis Horwood, Chichester, 1986.

J. Wei, T. W. F. Russell, and M. W. Swartzlander, *The Structure of the Chemical Processing Industries*, McGraw-Hill, New York, 1979, is similar in structure to *The Chemical Economy (loc. cit.)* but deals primarily with the economic structure of the industry and much less with technology.

At the end of the 1970s appeared our two-volume work, H. A. Wittcoff and B. G. Reuben, *Industrial Organic Chemicals in Perspective, Part I: Raw Materials and Manufacture*, and *Part II: Technology, Formulation and Use*, John Wiley & Sons, Inc., New York, 1980. Part I concentrated on the production of organic chemicals from seven major building blocks, while Part II dealt with the downstream sectors of the chemical industry, detailing the chemistry that was involved in the use of chemicals for plastics, fibers, elastomers, surface coatings, adhesives, surface active agents, pharmaceuticals, solvents, lubricating oils, plasticizers, agrochemicals, food chemicals, and dyes and pigments. Both volumes were reprinted by Krieger, FL, in 1990.

The 1980s and early 1990s saw some new editions but relatively few new books on industrial organic chemistry. W. S. Emerson, *Guide to the Chemical Industry: R&D, Marketing and Employment*, Wiley-Interscience, New York, 1983, reprinted by Krieger, FL, 1991, provides useful insights into how the industry functions, but the technical part contains several unfortunate errors.

Chemicals are discussed from the point of view of the consumer in an interesting and original book, B. Selinger, *Chemistry in the Market-Place*, 5th ed., Australian National

University Press, Canberra, 1998. Selinger is a pioneer of the Australian consumer movement and chaired a committee on toxic waste disposal. He describes the formulation of many domestic products together with the reasons for the various additives and the theory behind them. An explanation of everyday chemicals whose presence in products may puzzle consumers is to be found in G. R. Lewis, *1001 Chemicals in Everyday Products*, 2nd ed., John Wiley & Sons, Inc., New York, 1999. It describes in dictionary format many chemical products, mixtures such as creosote and general terms such as hallucinogen, together with the answers to "consumers" chemical questions'.

An English translation of the 4th ed. of K. Weissermel and H. J. Arpe, *Industrial Organic Chemistry*, VCH, Frankfurt appeared in 2003. Like the 1976 first edition, it is beautifully laid out, easy to follow, highly accurate, and concentrates on the upstream large tonnage processes.

H. Szmant, *Organic Building Blocks of the Chemical Industry*, John Wiley & Sons, Inc., New York, 1989, contains a wealth of information even about small tonnage chemicals and emphasizes practice at the end of the 1980s. It lists the prices at the time of publication of all the chemicals it mentions and illustrates vividly the adding of value as chemicals further and further downstream of the oil refinery are produced.

P. J. Chenier, *Survey of Industrial Chemistry*, 3rd ed., Kluwer Academic-Plenum, New York, 2002, contains well-written thumbnail sketches of about a hundred industrial organic chemicals plus a few inorganics. It describes some economic aspects of the industry but is strongly United States oriented and lacks an international dimension. *Handbook of Chemicals Production Processes*, R. A. Meyers, Ed., McGraw-Hill, New York, 1986, describes lucidly 40 industrial processes, divided between organics, inorganics, and polymers.

S. Matar and L. F. Hatch, *Chemistry of Petrochemical Processes*, 2nd ed., Gulf Professional Publishing, Boston, 2001 is a competent exposition of petrochemicals, weak on social and economic implications but redeemed by excellent flow diagrams. Regrettably the 2nd ed. is changed only slightly from the first.

C. A. Heaton has edited two books of note: *An introduction to Industrial Chemistry*, 2nd ed., Blackie, London 1991, and *The Chemical Industry*, 2nd ed., Blackie, London, 1993. The UK Society of Chemical Industry published *The Chemical Industry*, D. H. Sharp and T. F. West, Eds., Ellis Horwood, London, 1981, to celebrate their centenary. It contains "a glance back and a look ahead at problems, opportunities and resources . . ." *Industrial Chemistry, vol. 1*, E. Stocchi, Ellis Horwood, London, 1990, appeared to be the start of a series but was largely devoted to inorganic chemicals and no further volumes have yet appeared. The Industrial Chemistry Library is a somewhat off-beat series, publishing books on topics generally neglected. For example, G. Agam, *Industrial Chemicals, their Characteristics and Development*, Elsevier, Amsterdam, The Netherlands, 1994, deals entertainingly with the things that academic chemists in general do not know about formulations, specifications, standards, assays, scale-up, safety, patents etc. In the same series is *The Roots of Organic Development*, J.-S. Desmurs and S. Ratton, Eds., Elsevier, Amsterdam, The Netherlands, 1996.

An historical perspective of the chemical industry that is interesting for anyone who is engaged in it as well as to academics who want insight into how basic chemistry is translated into technology is P. H. Spitz, *Petrochemicals: The Rise of an Industry*, Wiley, New York, 1988. This book can be highly recommended. Other histories include F. Attalion, *The History of the International Chemical Industry*, University of Pennsylvania Press, PA, 1991, and H. L. Roberts, *Milestones in 150 years of the Chemical Industry*, P. J. T. Morris, Ed., Royal Society of Chemistry, London, 1991. Morris has also edited *From Classical to Modern Chemistry: the Instrumental Revolution*, Royal Society of Chemistry, London, 2002, which deals with the impact that advances in instrumentation, especially in environmental analysis and process control, have had on what chemists and chemical engineers do and how they think about their subject. The UK Chemical Industries Association has produced *Development of the UK Chemical Industry: a Historical Review*, CIA, London, 2000.

In mid-2003 M. M. Green and H. A. Wittcoff, published *Organic Chemical Principles and Industrial Practice*, Wiley-VCH, Weinheim, 2003. As its name indicates, it relates the theory of organic chemistry to the important industrial reactions that derive from that theory, and how these in turn impact on daily living.

0.4.3 Journals

A serious student of the chemical industry must follow the trade press. New products and processes, changes in the structure and prospects of the industry, take-overs and trades, mergers and demergers, as well as economic trends, can all be followed.

A selection of news magazines for English-speaking readers includes *Chemical and Engineering News* (weekly, ACS, Washington, DC); *Hydrocarbon Processing* (monthly, Gulf Publishing, Houston, TX); *Chemical Week* (weekly, Chemical Week Associates, New York, there are European and US editions); *European Chemical News* (weekly, Reed Business Information, London); *Modern Plastics* (Chemical Week Associates, New York), *Chemistry and Industry*, (fortnightly, Society of Chemical Industry, London); *Chemistry in Britain*, (monthly, Royal Society of Chemistry, London) relaunched in January 2004 as *Chemistry World*; *Manufacturing Chemist* (weekly, Morgan Grampian, London); and *Chemical Market Reporter* (weekly, Schnell Publishing, New York). *European Chemical News* provides US and European prices of the major bulk chemicals. A sister publication, *Asian Chemical News*, was started in 1994. *Chemical Marketing Reporter* carries a comprehensive tabulation of US list prices of almost all widely sold chemicals.

CHEMTECH (monthly, ACS, Washington, DC) replaced *Industrial and Engineering Chemistry* in 1971 and was founded by Ben Luberoff as an ideas magazine rather than a news magazine. It aimed to be conceptual and at the same time to humanize chemistry. Luberoff retired and subsequently died in 2001. The journal was renamed *Chemical Innovation* in 2000 but, without Luberoff's dynamism, it ceased publication by the end of 2001.

0.4.4 Patents

Patents are a device whereby the government grants inventors the sole right to exploit their inventions for 17 years in the United States (until recently), 20 years in the European Community and similar periods in other countries. In return, the inventors disclose details of their inventions in their patent specifications. Recent legislation in the United States has extended the life of a pharmaceutical patent to 22 years under certain circumstances and similar patent term restoration has been enacted in Europe. As a result of the GATT (General Agreement on Tariffs and Trade) negotiations, the United States has extended patent protection for 20 years; however, the time clock starts from the date of application instead of issuance.

Patents lie at the heart of a developed society. It is difficult to see how innovation could take place if innovators were not rewarded for their efforts. "I knew that a country without a patent office . . . was just a crab," said Mark Twain, "and couldn't travel any way but sideways or backwards." Meanwhile, the patent literature has grown exponentially. In the United States, it took about 200 years to amass four million patents, the four millionth having been issued in 1976. It took only 15 years to accumulate one million more patents and US Patent 5,000,000 was issued on 19 March 1991 to L. O. Ingram *et al*. It described the use of modern biotechnology to produce one of the oldest synthetic organic chemicals—ethanol.

Patent specifications are a major source of technical information. They often disclose information at a much earlier date than the scientific literature; sometimes they are the only source of such information. Negative results often appear in patents but not in scientific journals, and knowledge of what has been tried without success may save the working scientist much time.

Academic scientists shun patents because the introductions and claims are written in legal jargon with long convoluted sentences. Librarians shun them because they are published as individual items and are difficult to collect and bind. They have, however, one overwhelming advantage. They are classified by subject and can be subscribed to in this way, a copy of a US patent costing $3.00. They may also be obtained free on the Internet.

Patent applications are numbered consecutively as they are received by the US Patent Office (US serial number) and, when the patent is granted, it is assigned another number (US patent number). Other patent offices do the same.

Brief accounts of patents appear in the chemical trade literature. *Chemical Abstracts* publishes a numerical patent index that lists each patent number together with its corresponding Chemical Abstracts abstract number, country of origin, and serial number. It also provides a worldwide list of major patent offices and their addresses. *Chemisches Zentralblatt* (Akademie Verlag, Berlin) offers a similar service together with a guide to its use. (*Chemisches Zentralblatt: das System*). Derwent (Thomson/Derwent, 14 Great Queen Street, London WC2 5DF, UK) publishes analyses and abridgements of patents from every country classified by subject, and provides monthly bulletins, for example, *Organic Patents Bulletin* and *Pharmaceutical Patents Bulletin.* Derwent has contributed greatly to making patent literature available.

The *Official Gazette*, copies of patents, coupon books (a convenient way to pay for copies), listings of patents by subject, copies of foreign patents, and much other information may be obtained from the Commissioner of Patents and Trademarks, Washington, DC 20231. Although many official and commercial organizations exist to help the student of the patent literature, a thorough search can be conducted only at the National Patent Library, Washington, DC.

In the United Kingdom, the equivalent of the *Official Gazette* is the *Patents and Design Journal (PDJ)*, and it and other information are available from the Patent Office, Concept House, Cardiff Road, Newport, NP10 8QQ. The departure of the Office from London has been compensated for by a Central Inquiry Unit, telephone 0845 9500505, web site www.patent.gov.uk. A thorough search can be carried out at the British Library (Patents Section), 96 Euston Road, London NW1 2DB.

Information on subject codes and many other aids to patent searching may be found in *Kirk–Othmer* (cited in Section 0.4.1). Highly praised for its clarity and sound advice is *The Business of Invention*, P. Bissel and G. Barker, Wordbase, Halifax, West Yorkshire, UK.

Access to patents has been simplified greatly by computerized searching of patent databases of which Derwent, *Chemical Abstracts, Inpadoc* and *esp@cenet* are the most important (Section 0.4.6). The United States (www.uspto.gov), European (www.european-patent-office.org/inpadoc) and British Patent Offices (gb.espacenet. com) are all on line. Delphion Research, founded in 2000, has established an intellectual property network that can be subscribed to at a variety of levels ranging from full premier membership to a one-day pass. It enables one to perform text searches of United States, European, and Japanese patents, plus other intellectual property resources. Searching can be done by patent number or subject. WIPO, the World Intellectual Property organization, based in Geneva, produces many CD-ROM and online publications dealing with the state-of-play of patents throughout the world. This has become more important as more countries have come into line with the GATT (General Agreement of Trade and tariffs) regulations.

Although use of these databases requires skill, the user is rewarded by the access these bases provide to vast amounts of information. It is said that the Japanese have been able to accomplish a great deal in the chemical industry because of their skill in reading and interpreting patents. As the industry becomes more and more competitive, it is important to monitor trends, to know what other companies are doing and to avoid duplication. The patent literature can contribute more than any other source to “knowing what your neighbor is doing,” an important concept in today’s technical world where an inventor can bring a new frame of reference to someone else’s invention to create new and unanticipated goods and services.

0.4.5 Statistics

Students of the commercial side of the chemical industry will require access to statistics of production and consumption. Comprehensive US statistics were formerly published annually by the US International Trade Commission as *Synthetic Organic Chemicals: United States Production and Sales.* Publication ceased after 1994 on the spurious grounds that the data were available from other sources. The National Petroleum Refiners Association (NPRA) took over some of the operation and makes the information available to members.

Figures for the major chemicals plus much information about companies, employment, and related topics are published more rapidly in *Chemical and Engineering News* at the end of June or the beginning of July of the subsequent year. Thus the data for 2001 were published in the June 24, 2002 edition. An important major source is the annual *Guide to the Business of Chemistry*, American Chemistry Council., 1300 Wilson Blvd., Arlington,VA 22209.

On a worldwide basis, The United Kingdom Chemical Industries Association (CIA has a quite different meaning in the US) (www.chemical-industry.org.uk); King's Buildings, Smith Square, London SW1P 3IJ) publishes statistical reviews, notably *Basic International Chemical Industry Statistics 1963–1996*, London, 1997, and *Main World Chemical Markets by Geographic Area, 1996–2010* (Published occasionally; formerly *Chemical Industry Main Markets*). The former provides charts and tables for Western Europe, the United States, and Japan.

The Chemical Industry in 2000: Annual review, production and trade statistics, 1997–1999, United Nations, New York, 2001, is the latest of an annual compilation by the Economic Commission for Europe. Until 1988, it was published as the *Annual Review of the Chemical Industry*. *Chemical Industry Europe*, United Business Media international information services, Tonbridge, 2001, is a CD-ROM containing industry statistics.

Detailed statistics may be obtained rather belatedly from Government sources in most countries. In the United Kingdom, disaggregated figures appear relatively quickly in the *Business Monitor*, HMSO, London, and are summarized in, for example, *Business Monitor, Report on the Census of Production*, summary volumes published occasionally, HMSO, London.

In Europe, too, many useful data and some comments are published by the industry association CEFIC (Centre Européen des Fédérations de l'Industrie Chimique) and by their subsidiary APPE, the Association of Petrochemicals Producers in Europe, who produce an annual *Activity Review* of exceptional interest. CEFIC often does not provide hard copy, but their material is easily available online at www.cefic.org and www.petrochemistry.net. They have as members a range of associations dealing with lower olefins, aromatics, acetyls, acrylonitrile, amines, ethanol, acrylic monomers, plasticizers and intermediates, fuel oxygenates, ethylene oxide and derivatives, methanol, phenol, propylene oxide and glycols, oxygenated solvents, hydrocarbon solvents, styrene, and coal tar chemicals. Each contributes its own reports.

CEFIC has produced a splendid interactive flowsheet, tracing the steps that turn crude oil into petrochemicals and petrochemicals into everyday products. It is to be found at www.petrochemistry.net/flowchart//index.htm.

0.4.6 CD-ROM and On-Line Databases

When the authors of this book were starting in the chemical industry, information about the industry was sparse in the United States and practically nonexistent in Europe. Hoffman la Roche in 1967, at the time the world's largest pharmaceutical company, published no accounts, investment figures, or costs. They declared a profit of \$9.3 million and stated "The result for the year 1966 again shows improvement over the year before. Sales and earnings have increased in approximately equal proportions . . . the volume of investment was again large and will hardly diminish in the foreseeable future." Assiduous marketers would spend their time trying to pick up fragments of information and weave them into a coherent pattern. The difficulty was to obtain the information in the first place. Since then, legal requirements for disclosure have forced companies to publish more about their activities, and the advent of CD-ROM, on-line databases and the internet have meant that the problem today is not to obtain information but to sift what is reliable from what is dubious or just plain wrong.

Available databases are listed in the *Gale Directory of Databases*, M. Faerber and M. E. Williams, Eds., Gale Research, Detroit MI, published annually in two volumes, the first dealing with on-line databases and the second with CD-ROM, diskette, magnetic tape, handheld, and batch access database products. The increasing popularity of the internet, its speed, and the improved search engines (we use Google, Yahoo, and Alta Vista) have meant that the CD-ROM disk (updated, say, at monthly intervals) is being displaced by direct online linkage to sites where a subscription is necessary to gain access. Vendors maintain systems for dialing into them. Typical of scores of vendors is STN International, whose United States address is c/o Chemical Abstracts Service, 2540 Olentangy River Road, PO Box 3012, Columbus, OH 43210–0012. In the United Kingdom, access to most scientific databases is through MIMAS, Manchester Computing, University of Manchester, Kilburn Building, Oxford Road, Manchester M13 9PL. The most important databases are those of the Institute of Scientific Information (ISI), known as the *ISI Web of Knowledge* (www.isinet.com/isi). Starting with a science citation index, they now also operate social science, and arts and humanities indexes.

Chemical information is widely available. Sources of online patent information are listed in Section 0.4.4. Online technical information may be obtained from Chemical Abstracts and the Science Citation Index via ISI. Information on markets and technology is provided by *Promt*, a University of Pittsburgh database. Engineering information, once listed in the Engineering index, is now available from *Ei Compendex, Ei Compendex Plus*, and *Ei Chemdisc*. As far as we know, these are still CD-ROM-based and originate from Palo Alto, CA, Dialog Information Services. For commercial information, we rely heavily on *Chemical News Intelligence* (CNI) and *Insite Pro*. The former is an arm of Reed Business Information, which publishes numerous magazines and journals, and abstracts only Reed's information. *Insite Pro* is available through Dialog and abstracts many magazines.

The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 4WF, UK, produces a *Chemical Business Newsbase* dealing with the commercial environment of the chemical industry, which is international but biased toward Western Europe. There is a general business database *ABI Inform Global/ Wall Street Journal*, which abstracts chemical industry journals such as *Chemical and Engineering News*, *Chemical Market Reporter*, *Chemical Week*, and *Modern Plastics*. The coverage is largely North American but there is an invaluable extension called *Business Periodicals Ondisc*, which provides full text of many articles on the main database. *Uncover* (uncweb.carl.org) is a database of multidisciplinary journals, which provides tables of contents. Articles can then be ordered directly or by fax.

BEST (Building Expertise in Science and Technology, Longman Cartermill, Technology Centre, St. Andrews, Fife, Scotland KY16 9EA) is produced by the

British Council and is the official national database of current research and expertise in U.K. universities and colleges. It maintains records of scientists and engineers and what they are doing. It is widely used as a repository of technical information to supplement what one might get out of a patent search.

Finally, and extremely useful, are the Chemical Company Annual Reports that are published online. Among the color photographs of Chief Executive Officers, nuggets of valuable information are often to be found. They can all be accessed by a search engine.

The Internet is a virtual world on its own, and surfing it is a skill that must be learned. Books on it are numerous, and appear so rapidly that it is not worthwhile listing them. We mention S. M. Bachrach, *The Internet: A Guide for Chemists*, ACS, Washington, 1996, because it focuses on chemists' needs, but in general we advise students to spend a couple of hours learning the intricacies of their search engines, so that they can reduce the length and increase the specificity of their searches.

CHAPTER 1

THE CHEMICAL INDUSTRY

The United States, Western Europe, and Japan are the most complex societies that have ever existed. Division of labor has been carried to the point where most people perform highly specialized tasks and rely on many others to provide them with the goods and services they need. In return for these goods and services, they provide their outputs to satisfy the needs of others. All men are brothers in a material sense just as they should be in a moral sense.

The various segments of the economy are interrelated in a complex way. For example, manufacturing industry draws heavily on the output of the mining sector by buying iron ore from which to make steel. In turn, it may convert that steel to machinery to sell back to the mining industry who will use it in mining operations.

1.1 THE NATIONAL ECONOMY

The interdependence of a society's activities may be seen more clearly if its economy is divided into specific industries or groups of industries. Until 1997 this was done according to the standard industrial classification (SIC) of the US Bureau of the Census, but this has now been revised as the North American Industry Classification System (NAICS)(see note at end of this chapter). Table 1.1a shows the main sectors of a developed economy. The manufacturing sector is designated sections 31–33 (Table 1.1b). Each industry within it is allocated a three-digit code number, chemical

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

TABLE 1.1a Main Sectors of a Developed Economy

The Economy	NAICS Classification (1997)
Agriculture, forestry, fishing, and hunting	11
Mining	21
Utilities	22
Construction	23
Manufacturing	31–33
Wholesale trade	42
Retail trade	44–45
Transportation and warehousing	48–49
Information	51
Finance and insurance	52
Real estate and rental and leasing	53
Professional, scientific, and technical services	54
Management of companies and enterprises	55
Administrative and support and waste management and remediation services	56
Educational services	61
Health care and social assistance	62
Arts, entertainment, and recreation	71
Accommodation and food services	72
Other services (except public administration)	81
Public administration	92

manufacturing being 325. Sectors, subsectors and subsubsectors of the industry are then allocated four, five, and six digit numbers, for example, Basic Chemical Manufacturing is 3251, Dyes and Pigments are 32513, and Synthetic Organic Dyes and Pigments are 325132. Broadly speaking, the basic chemical industry (NAICS 3251) isolates or synthesizes chemicals, whereas the allied products industries (NAICS 3252–3259) modify, formulate, and package products based on those chemicals. The NAICS codes for the chemical industry are shown in Table 1.2.

The combined value of shipments is the total sales of the industry. Value added is defined as the value of shipments less cost of raw materials and cost of manufacture (Appendix A). Among the specific items in the cost of manufacture are containers, fuels, purchased electricity, bought-in services, and contract work. It is thus the value added to all the inanimate inputs to an industry by the people working in it. The total value added throughout the economy is the gross national product, the sum of wealth produced by the nation, in this case about $9.5 trillion for the United States in 2001 and $9.7 trillion in 2002.

The manufacturing sector contributed about $2.0 trillion of value added, which was about one-fifth of that year's gross domestic product (GDP). The figure has dropped

TABLE 1.1b Breakdown of Manufacturing Category NAICS 31–33

		Value of Product Shipments ($ billion)	Value Added 1999 ($ billion)[a,b]
311	Food	429.1	177.7
312	Beverage and tobacco products	107.4	68.60
313	Textile mill products	54.85	22.95
314	Other textile products (carpets, curtains etc.)	32.64	14.26
315	Apparel	62.80	30.59
316	Leather and allied products	9.67	4.55
321	Wood products	97.58	38.4
322	Paper	157.5	74.6
323	Printing and related support activities	102.4	62.43
324	Petroleum and coal products	168.1	42.36
325	Chemicals	419.7	229.3
326	Plastics and rubber products	172.4	91.35
327	Nonmetallic minerals	97.50	56.54
331	Primary metals	158.1	66.73
332	Fabricated metal products	256.9	142.5
333	Machinery	277.1	138.8
334	Computer and electronic products	458.5	265.4
335	Electric equipment, appliance and component	119.8	60.46
336	Transportation equipment	675.1	268.5
337	Furniture and related products	72.75	40.30
339	Miscellaneous manufacturing	108.2	66.37
Total		4038.1	1962.6

[a] The latest available statistics when this chapter was prepared (US Census Bureau, Annual Survey of Manufacturers, 2001) were for 1999. However, the relative positions of the various groups remain constant over long periods.

[b] Contrast the value added of the petroleum industry ($42.36 billion) with that of the chemical and allied products industry ($229.3 billion). The chemical industry's value added is 5.4 times as great despite the fact that its sales are less than twice as great. It is this greater value added that motivated the petroleum companies to develop chemical arms.

from about 40% in the past generation. This underscores the point that manufacturing, the traditional means for creating wealth, is no longer the major part of the US national economy and has to a large extent been replaced by services.

In 1991 the chemical industry provided the largest amount of value added among manufacturing industries but, by 1999, with $229.3 billion, it had been overtaken by transportation equipment ($268.5 billion) and computer and electronic products ($265.4 billion).

The transportation equipment industry has the largest total revenue ($675.1 billion) in the United States. The computer and electronics products industry comes second with $458.5 billion followed by food ($429.1 billion) and the chemical industry ($419.7 billion). This is shown in Figure 1.1b.

TABLE 1.2 Chemical Industry 1999 (NAICS 325)

		$ Billion		Percentage	
NAICS		Shipments	Value Added	Shipments	Value Added
325	**Chemical manufacturing**	**419.7**	**229.3**		
3251	**Basic chemicals**	**106.9**	**50.24**	**25.5**	**21.9**
32511	Petrochemicals	16.1	4.5	3.8	2.0
32512	Industrial gases	5.328	3.235	1.3	1.4
32513	Dyes and pigments	6.098	3.171	1.5	1.4
32518	Other basic inorganic chemicals	26.36	18.22	6.3	7.9
32519	Other basic organic chemicals	52.98	21.11	12.6	9.2
3252	**Resins, synthetic rubbers, artificial and synthetic fibers, and filaments**	**62.51**	**27.31**	**14.9**	**11.9**
325211	Plastics materials and resins	44.21	18	10.5	7.8
325212	Synthetic rubber	5.594	2.863	1.3	1.2
32522	Artificial and synthetic fibers, and filaments	12.71	6.442	3.0	2.8
3253	**Pesticides, fertilizers, and other agricultural chemicals**	**21.69**	**10.7**	**5.2**	**4.7**
32531	Fertilizers	10.9	3.668	2.6	1.6
32532	Pesticides and other agricultural chemicals	10.79	7.03	2.6	3.1
3254	**Pharmaceuticals and medicines**	**107.9**	**74.11**	**25.7**	**32.3**
325411	Medicinals and botanicals	11.68	5.127	2.8	2.2
325412	pharmaceutical preparations	81.18	58.62	19.3	25.6
325413	*In vitro* diagnostic substances	9.178	6.649	2.2	2.9
325414	Biological products (except diagnostics)	5.813	3.716	1.4	1.6
3255	**Paint, coatings, and adhesives**	**27.53**	**12.88**	**6.6**	**5.6**
32551	Paints and coatings	19.75	9.114	4.7	4.0
32552	Adhesives	7.777	3.77	1.9	1.6
3256	**Soap, cleaning compounds, and toilet preparations**	**53.27**	**32.48**	**12.7**	**14.2**
325611	Soap and other detergents	16.3	8.824	3.9	3.8
325612	Polish and other sanitation goods	7.945	4.901	1.9	2.1
325613	Surface active agents	4.954	2.407	1.2	1.0
32562	Toilet preparations	24.06	16.35	5.7	7.1
3259	**Other chemical products**	**39.95**	**21.56**	**9.5**	**9.4**
32591	Printing inks	4.719	2.238	1.1	1.0
32592	Explosives	1.08	0.511	0.3	0.2
325992	Photographic film, paper, plate, and chemicals	13.17	7.982	3.1	3.5
	All other miscellaneous chemicals	20.983	10.831	5.0	4.7

Source: Annual survey of Manufactures, U.S. Census Bureau, 5 May 2001.

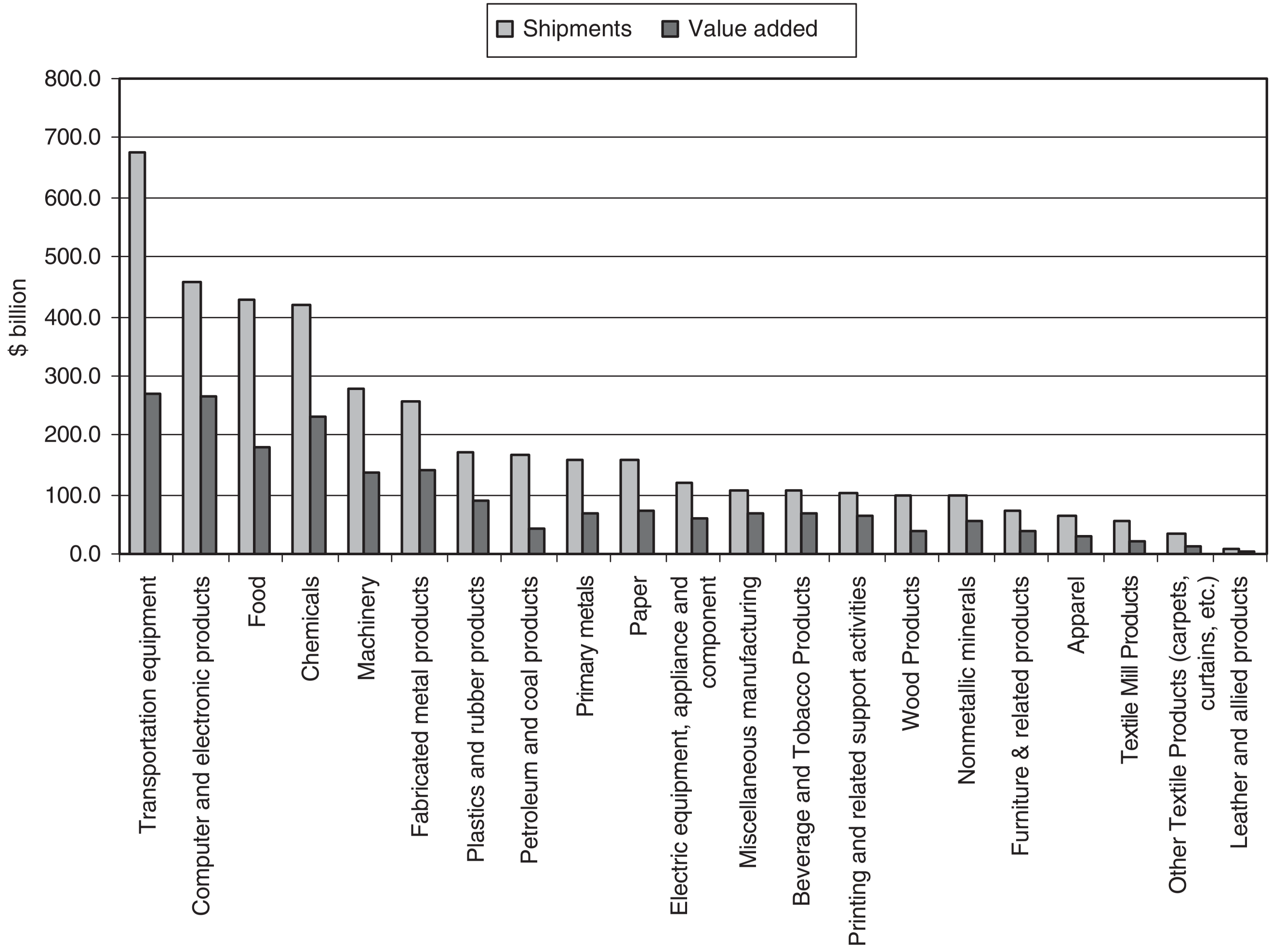


FIGURE 1.1 Shipments and value added in manufacturing industry, United States, 1999.

1.2 SIZE OF THE CHEMICAL INDUSTRY

The world chemical industry produced sales of about \$1700 billion in 2000 and provided jobs for more than ten million people. The division by region is shown in Figure 1.2. The United States accounted for 27% of this business, Western Europe for 29%, and Japan for about 15%. Asia Pacific, a relative newcomer, accounted for about 10% if Japan is excluded. Other regions are much less significant. The U.S. industry had sales of about \$300 billion in 1992 and \$460 billion in 2000. The division by shipments is shown in Table 1.2 and Figure 1.2, which also show the division by value added.

The total chemicals sector in the United States grew by 3.5%/year between 1991 and 2001, but shrank by 1.6% in 2000–2001. The basic chemicals sector grew by only 0.3%/year between 1991 and 2001 and shrank by 12.6% in 2000–2001. Thus the basic chemicals sector showed lackluster performance over the 1990s, and in 2000–2001 showed an unprecedented downturn. The 2002 figures are expected to match those of 2000.

Comparison of the shipments and value added in Figure 1.3 shows that so-called “fine chemicals,” such as pharmaceuticals, pesticides, and toilet preparations make a larger contribution to the chemical industry’s value added than they do to its shipments. They tend to be high-priced products with specialized markets, and their manufacture is less capital- and more labor intensive than the manufacture of the run-of-the-mill general chemicals. Their importance to the chemical industry is best represented by the value-added figure which, for example, emphasizes, the overwhelming importance of the pharmaceutical sector. This importance accounts for 25.7% of shipments but 32.3% of value added.

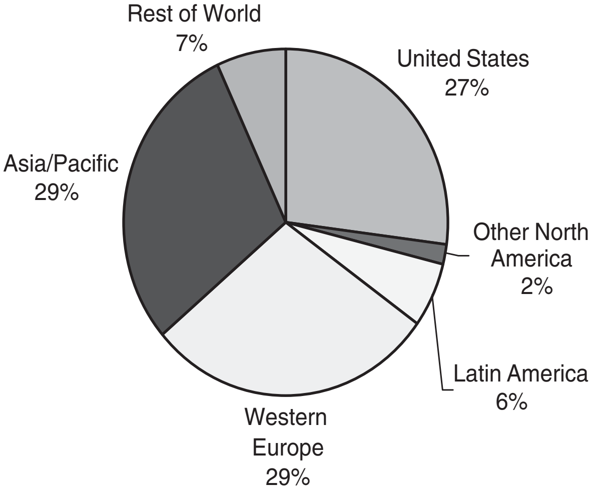


FIGURE 1.2 Division of the global chemical industry by region (2000).

1.3 CHARACTERISTICS OF THE CHEMICAL INDUSTRY

The chemical industry has certain well-defined characteristics that govern its attitudes and its performance. These are listed in Table 1.3 and we shall discuss them in turn.

1.3.1 Maturity

Maturity, highly prized in an individual, is feared in an industry. When we wrote about the chemical industry in 1980 (see notes at the end of this chapter) we stressed its growth. Between 1954 and 1974 the US chemical industry grew at a rate of 8.5–9%. Between 1964 and 1974 the Japanese industry grew at a rate of 11.7%. Western Europe during that period enjoyed a 9.7% growth. In 1976 the US industry,

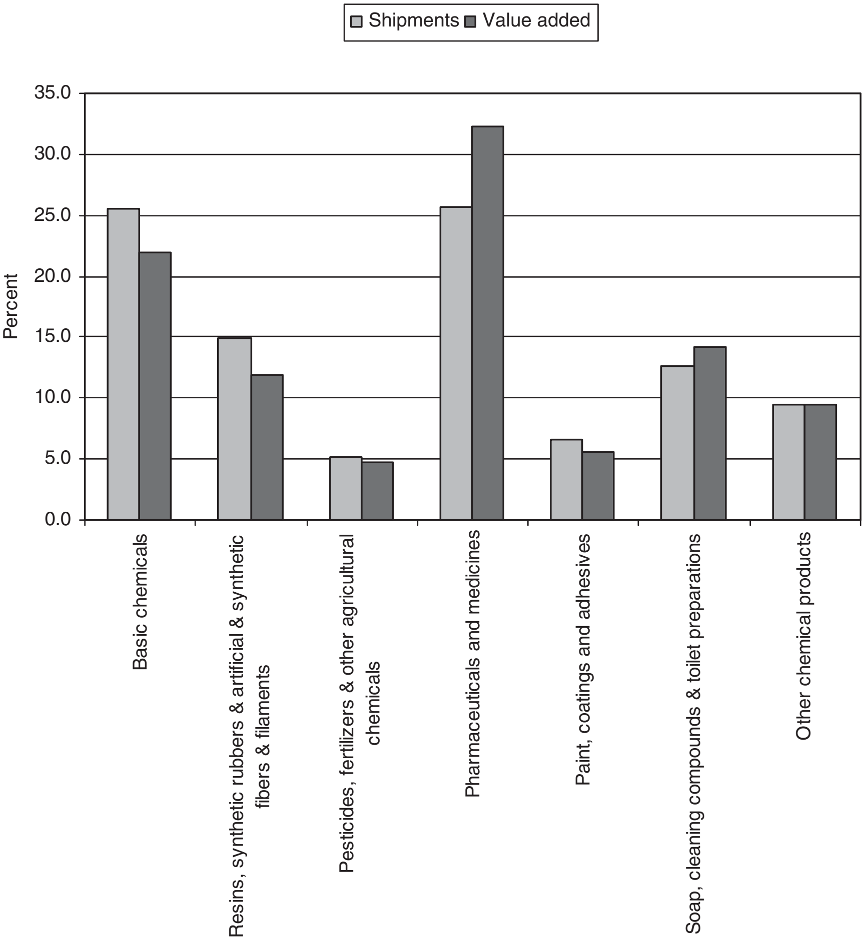


FIGURE 1.3 Subdivisions of the chemical industry by sector and value added.

TABLE 1.3 Characteristics of the Chemical Industry

Maturity and its consequences (restructuring, mergers, demergers, acquisitions)
Participation in international trade
Competition from developing countries
Capital intensity and economies of scale
Criticality and pervasiveness
Freedom of market entry
Strong health and safety regulation
High research and development expenditures
Dislocations

coming out of a recession, grew 17%, although this included 5–8% of inflation. We pointed out that inevitably growth must lessen and that the industry would eventually grow at the rate of the economy as a whole. We pointed out also that government regulations relative to pollution, worker safety, and ecology generally would take its toll on profitability. By the early 1990s, all of this had come to pass. No company could operate in the chemical industry unless it fully understood all the ramifications of maturity, which expresses itself in overcapacity, intense competition, low prices, and low profitability. Ultimately, it leads to restructuring which, between1980 and 1999, involved an estimated $5.25 trillion of assets. All of these things have happened in the chemical industry not only with commodity chemicals, the ones we are mainly concerned with in this volume, but also with specialties.

Maturity occurs because of market saturation, wide diffusion of technology, and low barriers to entry to the industry. Engineering companies are eager to build turnkey plants and train clients to operate them, which encourages overproduction. Maturity is hastened by competition from developing countries, especially those with indigenous sources of petroleum and natural gas and whose governments are eager to industrialize even if the emergent industries need to be subsidized. These issues are discussed below.

For the years 1987–2001, maturity is demonstrated in another way in Table 1.4, which shows the sales in the chemical industries in the United States, Western Europe, and Japan in current dollars and in constant 2000 dollars. Although the sales in current dollars increased appreciably, the corresponding value in constant dollars increased at only 1.8%/year in the United States. The Western European and Japanese industries remained effectively static.

Restructuring is the inevitable result of overcapacity and is well demonstrated with ethylene. By the late 1970s, the capacity for ethylene manufacture far exceeded the demand. Restructuring started in 1986 and at first involved reduction in personnel. The chemical industry in the United States employed about 1.15 million people. This number was cut by 7–8% by attrition, early retirement, and redundancy. Second, and most important, was reduction in productive capacity to bring it in line with demand.

Figure 1.4(*a*) shows what happened relative to United States demand versus capacity for ethylene (see note at end of this chapter). Capacity in 1981 was about 40 million lb.

TABLE 1.4 Sales of the United States, Western European, and Japanese Chemical Industries ($ billion)

	1987	1989	1991	1993	1995	1996	1997	1998	1999	2000	2001
United States											
Current	229.5	298.3	317.1	335.4	386.9	393.6	417.4	416.9	435.4	455	447.8
2000 constant $	347.9	414.3	400.9	399.7	437.2	432	447.8	440.4	450	455	434
Gross operating surplus as % sales[a]		19.8	19.8	20.5	25.6	24.7	25.4	24.7	24		
Western Europe											
Current	302.2	337.7	393.4	373.1	483.7	475.8	456.7	454.5	457.5	470	
2000 constant $	458.1	469	497.4	444.6	546.5	522.2	490	480.2	472.9	470	
Gross operating surplus as % sales[a]		16.4	13.5	13.4	16	15.5	16.2	15.7	15.6		
Japan											
Current	137	160.5	180.4	209.2	248.3	215.9	202.7	172.7	205	207	
2000 constant $	207.7	222.9	228.1	249.3	280.6	237	217.5	182.4	211.9	207	

[a] Gross operating surplus = value added − labor cost (a measure of profitability). These figures based on: Eurostat-SBS & CEFIC–TEA Analysis reported in European Chemical Industry Council's Economic Bulletin, November 2000.

By 1986, this had decreased to about 36 million lb. This 10% cut in capacity coupled with growth in ethylene usage brought demand and production into line. The growth can be attributed first of all to stockpiling of downstream products—ethylene itself cannot be stockpiled—since companies tend to amass materials when a shortage appears imminent, as it does when capacity is being eliminated. But also, when business improves, companies are more prone to invest in new applications and to expand old ones, and this reflected itself in growth for the polyethylenes. In turn, this resulted in growth of ethylene. Thus, the period encompassing 1987 and 1988 was probably the most profitable the chemical industry in the United States has ever enjoyed. The value of shipments between 1987 and 1989 in real terms increased 8.6%. But the honeymoon was over by 1989, for the industry started to debottleneck existing plants and to build new capacity. By 1991, there was again appreciable overcapacity and need for further restructuring.

Capacity and production were more or less in balance again by 1995, and capacity had only gone slightly ahead by 2001, but, as will be described, huge new capacity is planned. The phenomenon of profitability being cyclical is referred to in the industry as "The Old Paradigm," whose components are overbuilding and building at the wrong time. This leads to overcapacity, with much of it coming onstream when business is depressed. There is then intense competition with subsequent low prices and profitability.

Western European capacity and demand were similarly in balance in 1989–1990, as shown in Figure 1.4(*b*), but the construction of new crackers by Fina, Veba, BP and BP ENI, BASF, and Hüls opened up a large gap by 1993–1994. The average European operating rate was down to about 83% of nameplate capacity and, at the time of writing, no new European cracker has since been built. The operating rate limped along at about 92% in the late 1990s, but strong ethylene demands growth of the order of 5%/year in 1999–2002 led to the planning of fresh capacity, illustrated in Figure 1.5. These plans collectively imply a capacity increase of about one-quarter over the 6-year period at a time, but since 2002 there have been indications of a slowing in world demand growth.

Compared with other industries, the chronic overcapacity of the chemical industry is related to its capital intensiveness, with high fixed and low variable costs. There is a large gap between the break-even price of products (when price equals total cost) and the price at which it is rational to shut down a plant (when price falls below cash cost—see Appendix A). Furthermore, because of economies of scale, it may be more economic to run a plant at full capacity even if it means cutting prices. Finally, third world countries see a chemical industry as an acceptable way to industrialize, and some of them (e.g., Malaysia, Saudi Arabia, and Venezuela) have access to cheap indigenous supplies of oil and natural gas. Thus the chemical industry is always inclined to "shoot itself in the foot."

Another problem that exacerbates overcapacity is that the chemical industry participates in the economic cycles (boom and bust) that are part of a capitalist economy. A rise in demand by consumers leads to higher prices and rising profitability in industry, which prompts additional investment to satisfy the demand, and the extra money pumped into the economy fuels further rises in demand. This is the "boom" stage of the cycle. Because building new plants takes time, the increase in supply

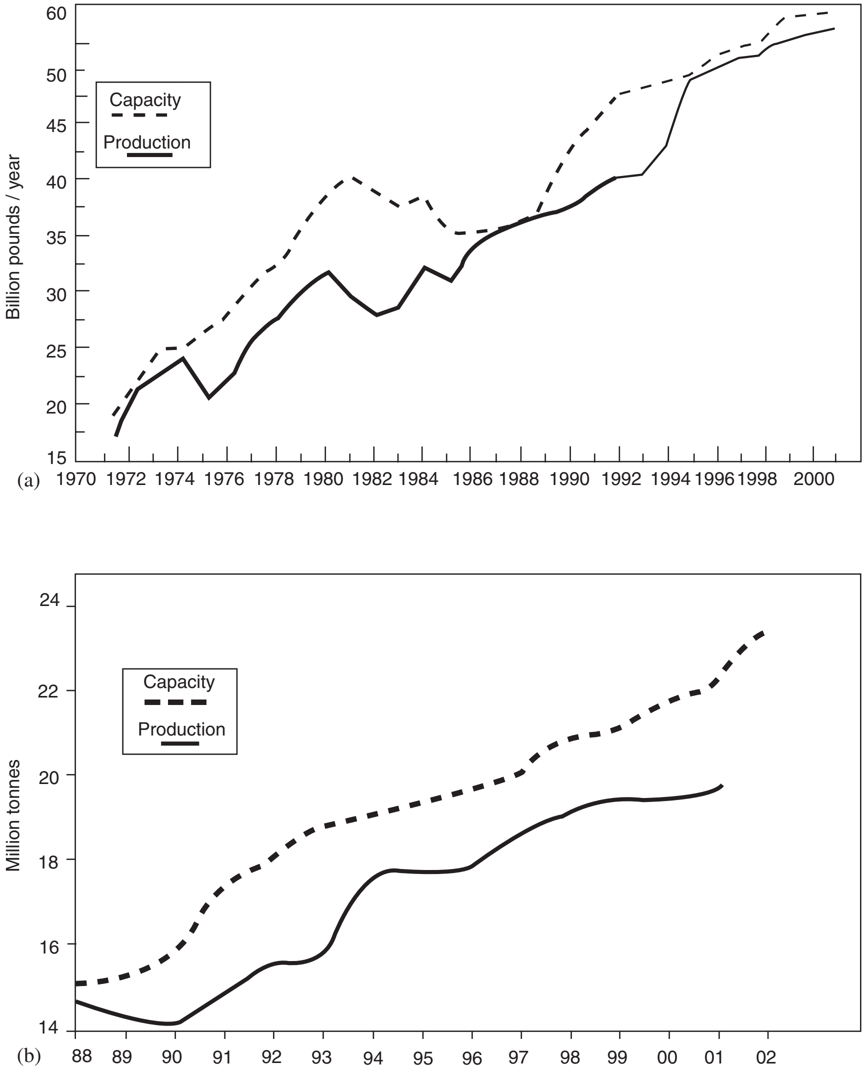
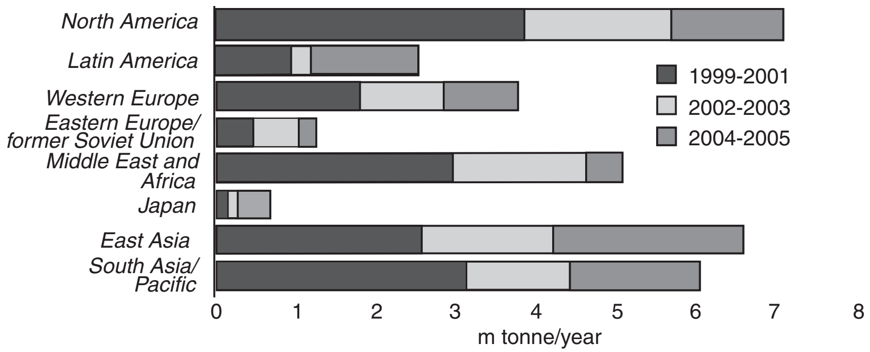


FIGURE 1.4 Capacity for and production of ethylene. (*a*) United States 1971–2001. (*b*) Western Europe 1998–2001. Eastern Germany included from 1991. *Source:* Nexant Chemsystems; APPE.

lags behind the rise in demand. Thus there is usually an overinvestment and the increase in supply causes prices and profits to fall. Investment is cut back, plants are closed (rationalization!), workers are made redundant, and the drop in demand is accelerated. This is the “bust” stage of the cycle and it continues until the overshoot in plant closures leads to an excess of demand once more. The widely quoted figure for length of cycle is 4–5 years from slump through recovery, boom, and recession again. It is taking longer in the depressed period of the early 2000s.



SOURCE: TECNON CONSULTING GROUP

FIGURE 1.5 Ethylene capacity build, 1999–2005. *Source: Eur. Chem. News*, October 2, 2000.

The question for the chemical industry is how to invest the large amount of money made during the boom years, especially as the time taken to build plant means that facilities built at the top of the cycle will come onstream during its decline. Investment in areas outside the chemical industry has been tried unsuccessfully. Nonetheless, Wall Street frowns on accumulating cash, so there is pressure to invest in new facilities. Also, cash makes the company a target for takeover. The company can buy back its own stock, but its price at the top of the cycle will be high. Profitability figures showed a mild boom peaking in 1984 and a major one peaking in 1989. At this point, China stopped buying polyolefins. Shortly afterward the Gulf War started.

The markedly increased profitability (a so-called “fly-up”) in 1994–1995 was caused by accidents in plants all over the world. Three crackers in the United States blew up. In Europe and Southeast Asia, there were similar disruptions, which created a shortage, remembering that a shortage in the chemical business is only a 2–3% shortfall. Plants were soon repaired and the fly-up was over. In 2001, there was a decrease in profitability largely because of the expensive gas ($10/million Btu in January as compared to $0.75 in Saudi Arabia) and cheap imports. The higher oil and gas prices could not be passed on to the consumer because of competition resulting from overcapacity.

1.3.1.1 Realignment of Business Segments

Another aspect of restructuring is realignment of business segments. As an example, Union Carbide had a small, and presumably barely profitable, polyether polyol (Section 4.11.1) business. Carbide sold this business in the early 1980s to ARCO, a major manufacturer of the propylene oxide from which the polyols are made. ARCO not only gained more captive use for its propylene oxide but increased its polyether polyol business well above the critical mass. In spite of this, in 1999 ARCO was bought by Lyondell. Both of these companies had been spun-off by Atlantic Richfield, which later was acquired by BP, itself a union of British Petroleum, SOHIO, and AMOCO. Lyondell, like other petroleum companies, does not look kindly on products that are far downstream from the refinery and sold the polyether polyols business to Bayer. Bayer, one of Germany's big three chemical companies, announced in 2001 its aim "to become known as a pharmaceutical company with a chemical business rather than a chemical company with a pharmaceutical business," but its cholesterol-lowering drug Ciprobay had to be withdrawn from the market after being implicated in a number of deaths. Even though ciprofloxacin had huge success as an antianthrax drug during the scare about unconventional weapons and terrorism, Bayer has felt compelled to demerge into four operating subsidiaries and to sell other operations. Hoechst, another of Germany's big three, demerged itself into twelve separate companies of which Celanese and Aventis (a joint venture with Rhone Poulenc's pharmaceutical business) are the largest.

A restructuring of great impact was the trade in 1992 in which Du Pont took on ICI's European nylon business and ICI received in turn Du Pont's methyl methacrylate business. ICI then decided to reinvent itself as a specialty chemicals company and spun off its pharmaceutical and agrochemical divisions as Zeneca. It then bought a rather old-fashioned portfolio of specialty chemicals from Unilever and sold its heavy chemical assets, mainly to Huntsman, and resold the methacrylate business to a Belgian investment company, Ineos, which is developing it aggressively. Ineos also bought ICI's chloralkali business directly and had grown to a $5 billion company by 2001. ICI was an international company, well placed to capture what profits were available from a commodity operation. It had an "ideal site" at Wilton/Billingham, with a refinery on site plus ethylene pipelines linking it to Grangemouth, Mossmoran, and Tranmere. It was surrounded by user industries, and its feedstocks and products needed only to be pumped over the wall. Britain is still a profitable market for home producers because of the costs of shipping. In 1986, ICI ranked fifth by turnover in the U.K. industrial league table, with a return on capital of 21.9%; in 2000 it was ranked 108th in the United Kingdom with a return on capital of 20.1%. One is bound to ask if the transition, rather than a triumph for shareholder value (which was never achieved), was a failure of commercial nerve. Whatever the case, the shrinking of ICI and demerging by Hoechst, Rhone Poulenc, and Bayer have significantly altered the structure of the European chemical industry (see Section 1.4).

Yet another restructuring is the combination in 1994 of the Montedison and Shell polyolefins businesses to form Montell, which became the world's largest polypropylene producer. Shell then took back the polyethylene business and formed a joint venture with BASF called Elenac. Montedison then sold its remaining share of Montell back to Shell, which became the sole owner. To meet the enhanced polypropylene competition, Hoechst and BASF in turn merged their polyolefins businesses and called the joint venture Targor. Subsequently, Targor and Montell merged to become Basell Olefins. The business is highly polypropylene oriented and Basell in Western Europe was 2.4 times as large as the next largest producer, Borealis. Borealis is itself a joint venture of the Finnish company Neste and the Swedish company Statoil. Neste subsequently left the business by selling its portion to the state-owned petroleum company of Abu Dhabi and the Austrian company OMV. Subsequently, Amoco and Appryl merged their polypropylene businesses in Europe to become somewhat larger than Borealis. These examples typify the enormous amount of restructuring that went on in the chemical industry in the 1990s and early 2000s.

The sad thing is that little if any of this restructuring has enhanced stockholder value or increased profitability. The only thing that could certainly do that is enhanced creativity, but creativity is inhibited by decreased R&D budgets, and researchers are demoralized by repeated takeovers, mergers, buy-backs, and the other activities, with associated cultural change, that financial experts regard as the solution to the industry's problems.

1.3.2 Participation in International Trade

The chemical industry in the United States always had two advantages that made its products cheap not only at home but in the international arena. First, there was ample natural gas, which provided ethane and propane for steam cracking (Section 2.2.1), and it generally was cheaper to crack gas than the liquids, naphtha, and gas oil. Second, the United States had ample supplies of propylene, not only because it is produced in steam cracking, but because the huge capacity for catalytic cracking (more than the rest of the world combined) required by the gasoline industry means that the few percent of propylene produced in this reaction translates itself into billions of pounds of product (Section 2.2.2).

The balance of trade in chemicals in the United States as compared with the European Union and Japan is shown in Figure 1.6. The European Union balance does not include intra-European Union trade, which is much larger. The rise in European and decline in United States trade balances through the 1990s is remarkable, especially in view of the problems of the European petrochemical industry discussed

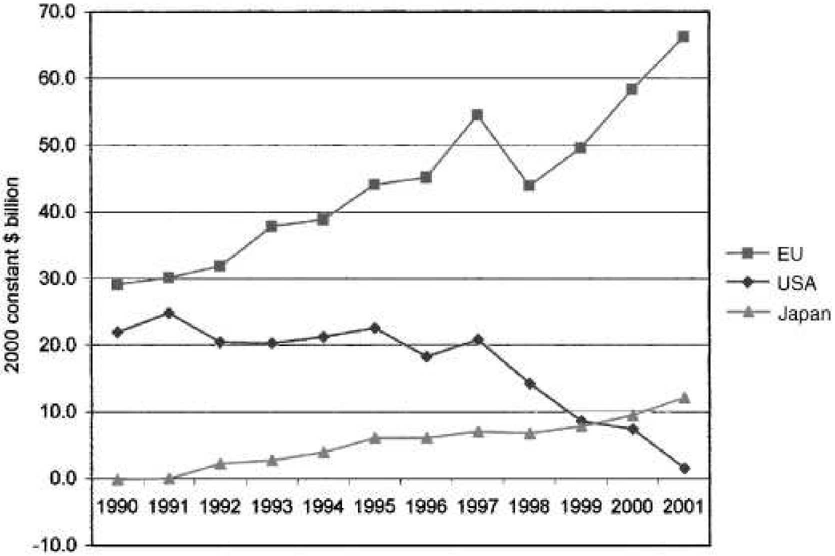


FIGURE 1.6 Chemicals trade surplus 1990–2001 United States, European Union, and Japan.

above. The solitary fall was in 1998 as a result of the southeast Asian crisis. The fact remains that the European Union exports considerably more than the United States: in 1999, exports were \$118 billion against \$68.5 billion imports counting, only trade with countries outside Europe; the United States exported \$72 billion against \$62.2 billion imports. Companies like BASF, Bayer, Degussa, Akzo Nobel, and Enichem are all highly export-oriented. In 1999, Western Europe exported 70% of its production if one counts intra-European trade and 27% if one excludes it. High levels of exports are required if plants are to operate efficiently, even if exports are rarely as profitable as home business.

The balance of trade figures are misleading insofar as the petrochemical industry is concerned. Pharmaceuticals are responsible for 38% of the trade balance and cosmetics for 13%. All basic chemicals make up only 17% and perhaps one-half of these are petrochemicals. Furthermore, many US companies, especially pharmaceutical companies, operate subsidiaries in the European Union to avoid tariffs. Some of them export to the United States and depress its trade balance. The US chemical industry's international investments provide appreciable income from the net earnings of foreign subsidiaries and from the licensing of US technology to those subsidiaries as well as to other companies. Add to this the fact that during the 1990s the euro was exceptionally weak, and hence its chemical exports were cheap, and one has gone a long way to explaining the remarkable performance of the European industry.

This is not to denigrate the role of US exporters. The chemical industry was the largest US exporter in 2000 and had the third largest positive balance of trade, after Aircraft/Aerospace and agricultural commodities. Between 1991 and 2001, the US chemical industry had trade surpluses totaling \$140 billion. Ten percent of US exports are chemicals and amounted to \$80.8 billion in 2002. The US balance of trade dropped over the 1990s because the strength of the dollar meant that imports were cheap, exports expensive, and there was increasing competition from less developed countries including Saudi Arabia and South Korea. By 2000, the balance was negative.

Japan, having based its chemical industry on relatively expensive imported naphtha and having struggled with an expensive yen, cannot compete in the world market, although since the mid-1990s it has enjoyed sales to neighboring countries with expanding economies, primarily China. Freight costs are a significant additional expense in the heavy chemicals business, and Japan's geographical position enables her to compete in the Far East, but this has contributed little to profitability.

1.3.3 Competition from Developing Countries

But what about the future? Natural gas has been discovered in many places in the world and many countries have petroleum. Some, if not most, are eager to enter the chemical business because it promises greater value added than is possible when the gas or oil is used for energy. Thus an awesome list of countries have built or are building chemical industries. The United States, Western Europe, and Japan have longstanding industries. Newcomers in the 1980s included Saudi Arabia, Iran, and other Gulf states, Canada, Mexico, Venezuela, Brazil, Argentina, and other Latin American countries including Trinidad and Chile, the former members of the USSR and other eastern European countries, and the "tiger" economies of Southeast Asia. China, Taiwan, and Korea had to import feedstocks, but Thailand, Indonesia, and Malaysia had indigenous resources. Singapore had no raw materials and no indigenous market, but an excellent infrastructure and stable and relatively honest government. How seriously some of these countries regard the chemical industry is indicated by the statistic that in Taiwan the chemical industry accounts for 30% of manufacturing as opposed to 10% in the United States and Western Europe. Many of these countries enter the chemical business to provide for their own needs. Taiwan and Thailand indicate that they will not be major exporters because they can consume locally most of their production. Korea, Saudi Arabia, and Canada and most other countries have become formidable competitors in the international trade arena. The impact on Western European trade of recent entrants to the petrochemical market, and particularly Canada and Saudi Arabia, is indicated in Figure 1.7, which shows an increasingly unfavorable trade balance in ethylene and benzene derivatives, and a decreasing positive balance in propylene derivatives. These figures are perhaps a better measure of the problems of the European petrochemical industry than the favorable overall trade balance shown in Figure 1.5.

Japan lost its stake in trade of ethylene derivatives very early and indeed this was true of virtually all Japanese chemicals because of expensive raw material and a strong currency. Their slowly increasing trade balance is due largely to the needs of mainland China, where shipments from Japan have lower freight costs. Western Europe, as noted, does not derive much of its huge chemical exports from basic petrochemicals. The United States still maintains a role and it is believed that this will continue through the

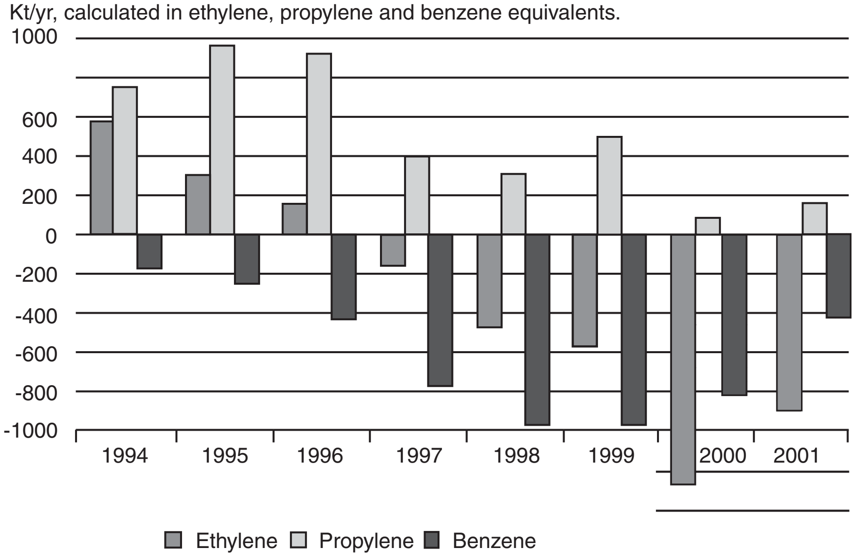


FIGURE 1.7 Western European trade balance in petrochemical derivatives. *Source:* PIMM.

TABLE 1.5 Decline in Production of Petrochemical Ethanol in the United States

	1982	1985	1988	1990	1999	2000	2001
Production (million lb)	1023	573	500	210	210	180	180

year 2005, particularly if gas continues to be available for steam cracking (Section 2.2.1). The situation is unpredictable. Prices of both oil and gas fluctuate. Early in 2001, oil reached \$30/bbl but dropped to \$17.85/bbl. Gas reached \$10/million Btu in the same year, then dropped to \$4, which is still historically high. Prices are affected both by political and economic factors and have been exceptionally volatile in the 2000s. If US gas prices remain high, in the longer term the US olefin derivative industry will largely service domestic markets. It will become an opportunist rather than a base load exporter of commodities, the latter role perhaps passing to developing countries.

The impact a developing country can make is exemplified by the declining production of petrochemical ethanol in the United States. The data are shown in Table 1.5. Admittedly, the use of ethanol as a chemical feedstock is declining, and use of subsidized corn-based ethanol for fuel is increasing. Nonetheless, Saudi Arabia's cheap ethylene can be converted to ethanol and imported into the United States at a cost that makes its domestic manufacture uneconomic. It was predicted that petrochemical ethanol manufacture in the United States would come to an end by the year 2000, but a single producer—Equistar—remains in the field. Dow is said to refine imported Saudi ethanol. Fermentation ethanol will boom if MTBE (Section 5.2.1) is phased out. Current plans are for the US government to subsidize fermentation ethanol as a gasoline additive and the subsidy will primarily go to the alcohol manufacturers, while the farmers will get only 13%. Use of subsidized fermentation ethanol for chemical production is illegal as is the use of petrochemical ethanol in drinks.

As already indicated, numerous other countries have entered the chemical business, but Saudi Arabia is impressive for two reasons. First of all, it has 25% of the world's oil reserves, and second it has a reasonable supply of so-called associated gas (ethane, propane, butanes, and condensate—a cheap C_5+ fraction from certain gas wells), the gas that comes out of the ground when oil is pumped. Since there is no alternative use for this gas in Saudi Arabia, it has zero value at the wellhead. The Saudis took the decision to extract and crack the ethane at an extraction cost of \$0.50–0.75/million Btu (British Thermal Units; 1 Btu = 1.054 kJ) in 2001 and to sell the LPG (propane + butane) on the world market. This provides extremely favorable economics for ethylene production. Iran is possibly less efficient and costs its gas at \$1.25/million Btu. In 2002, the Middle East produced 10 million tonnes of ethylene, two-thirds from Saudi Arabia, one-tenth from Iran and 23% from all other producers, principally Kuwait and Qatar. Production is predicted to exceed 20 million tonnes by 2010.

To become a full player in the world petrochemical market rather than just dealing in ethylene derivatives, the Saudis also built a plant to crack C_3+ and condensate in 1995, and declared that a 30% discount off the lowest world price would be granted on supplies of naphtha, condensate, and liquefied petroleum gas (LPG) used in their newest petrochemical plant. Seven more crackers are planned.

There is no moral reason why developing countries should not take trade away from developed countries when able to do so. Developed countries stay ahead by innovative technology and, once that technology has become mature, anyone is entitled to use it. A problem in developing countries is that small operations frequently undercut costs by ignoring health and safety precautions. Indeed there have been riots in India because dye manufacturers ignored such precautions. In China, diethylene glycol was disposed of by combining it with glycerol, and the mixture sold to companies in Bangladesh and elsewhere who compounded it into fever medicines. Many children died from the poisonous diethylene glycol (see note at the end of this chapter).

This disregard for health and safety does not apply to the billion dollar installations for the manufacture of commodity chemicals where there is frequently a partner or a contractor from the United States, Western Europe, or Japan.

1.3.4 Capital Intensity and Economies of Scale

The chemical industry is capital intensive. It produces huge quantities of homogeneous materials, frequently liquids or gases, which can be manufactured, processed, and shipped most economically on a large scale. This was less so through the nineteenth century until World War II. The early chemical industry used more general purpose equipment and operated batch processes that required little capital investment but had high labor costs. Typical of such processes were the Leblanc route to sodium carbonate and the benezensulfonate route to phenol (Section 4.10).

The petroleum refining industry was the first to convert to continuous operation on a large scale. The engineering developed for the petroleum industry was applied to the chemical industry after World War II. Plant sizes escalated as dramatic economies of scale became possible. The capacity of a typical ethylene cracker rose from 70 million lb/year in 1951 to 1 billion lb in 1972. This was regarded as an upper size limit until the early 1990s when plants with 1.5 billion lb/year capacity were built. Meanwhile, in 2001, BASF/Fina brought on stream a 2 billion lb/year ethylene plant in Port Arthur, TX, and 2.8 billion lb/year is seen as an attainable size. The Port Arthur plant will incorporate a metathesis unit described in Section 2.2.9 to increase propylene production. Even the residual butadiene/butenes will make this the world's largest C_4 olefins plant.

Currently there are few batch processes of any size in operation for commodity chemicals, and substantial economies of scale are a characteristic of the petrochemical industry. They arise not only from improved technology but also from purely geometric factors. The capacity of a great deal of chemical equipment (e.g., storage tanks and distillation columns) varies with its volume, that is the cube of its linear dimensions. The cost, on the other hand, is the cost of a surface to enclose the volume and varies with the square of the linear dimensions. Consequently, cost is proportional to $(\text{capacity})^{2/3}$. This is called the square-cube law. It does not apply to all equipment. The capacity of a heat exchanger depends on its surface area, so cost is proportional to $(\text{capacity})^1$ and there are no economies of scale. Control systems are not affected by capacity at all, so cost is proportional to $(\text{capacity})^0$ and economies are infinite. It is claimed that, for a modern petrochemical plant overall, cost is proportional to $(\text{capacity})^{0.6}$.

Labor costs are a small proportion of petrochemical plant cash costs (HDPE 2.5%, benzene 3.5%, purified terephthalic acid 5.7%, acrylonitrile 7.3%) but they contribute to economies of scale, because they do not increase proportionately to increase in size of the plant. Doubling the size of a unit does not double labor cost. Indeed, because of automation, the labor cost may increase only 10–20%.

The size and complexity of a modern chemical plant demand high capital investment. Although other industries invest more capital per dollar of sales, the chemical industry has the highest investment of current capital. That means that the chemical industry invests more each year than do other capital intensive industries such as mining, where equipment once bought remains in service for many years.

Capital intensity has a number of corollaries. The return on capital is relatively low. Because high capital investment reduces the labor force required, manpower productivity (i.e., value added per employee) is high, while salaries contribute relatively little to costs (of the order of 2.0% for steam crackers), For example, in 1999, in the labor-intensive food manufacturing industry (NAICS 311) the average production worker added value of $156,000 and was paid $23,814. In the basic chemical industry (NAICS 3251) the value added per production worker was $453,000 and the pay $48,600. Thus employers need worry less about pay increases, and labor relations are unusually good. If we take figures for overall industries, the chemical industry ranked third with a value added of $170,000/employee after Tobacco Products ($543,000) and Petroleum and Coal Products ($217,000). At the bottom of the list comes the labor-intensive Apparel and other Textile Products Industry with a figure of only $37,000.

The assets of a company are the estimated value of the plants, land, and other capital goods it owns. Such ratios as assets per employee, sales per dollar assets, and sales per employee are measures both of the capital and labor intensity of an industry.

Generally, the petroleum refining industry has both the highest assets and the highest sales per employee. The chemical industry shows lower figures but still ranks high. The food and clothing industries are usually at the low end of the scale. Service industries with few assets and many employees, such as consulting companies, will show both low assets and low sales per employee.

The move to specialty chemicals has altered these perceptions as far as the overall chemical industry is concerned, although not for the sectors described in this book. Small, high value, low tonnage chemicals are frequently made by batch processes in multipurpose computer-controlled equipment. Such equipment brings some of the advantages of continuous processing to batch processes.

1.3.5 Criticality and Pervasiveness

A chemical industry is critical to the economy of a developed country. In the nineteenth and first half of the twentieth century, a nation's industrial development could be gauged from its production of sulfuric acid, the grandfather of economic indicators. Today one uses ethylene production as a yardstick of industrial sophistication. An advanced economy cannot exist without a chemical industry; neither can a sophisticated chemical industry exist without an advanced economy to support it and to provide the educated manpower it requires. Nevertheless, various developing countries have started to build chemical industries by buying so-called “turnkey” plants constructed by foreign chemical engineering contracting companies and staffing them either with imported foreign labor or with locals who have been educated abroad. Indeed, this is part of the development process.

The chemical industry is an “upstream” industry. It purchases raw materials such as petroleum, natural gas, coal, and metallic, and nonmetallic minerals. It bought about $40 billion worth in 2000 and made from them products that were sold for $460 billion. These products, however, are usually not sold to the final consumer. About one-fifth of them are sold to other firms in the chemical industry for further processing. The remainder are sold to other industries to help them make their own products or sell their services. Makers of plastic packaging, for example, rely on polymers and one-hour photo stores rely on photographic chemicals. Automobile manufacturers use the products of the chemical industry in tires, hoses, safety glass, seat belts, upholstery, bumpers, fenders, and even doors and side panels, as well as many other components. The pattern in 2000 is shown in Figure 1.8. The chemical industry was always said to be its own best customer, but the $93.2 billion intraindustry sales were overtaken in 2000 by the burgeoning health care sector with purchases of $97.2 billion. Thus it is the major purchaser by value, although certainly not by volume. It buys small quantities of high value-added chemicals. Rubber and plastics producers buy large quantities of resins, and the textile industry buys synthetic fibers. Petroleum refiners, who supply much of the industry’s raw materials, also buy back some of its products to aid their own processing.

The chemical industry is not replaceable. There is no other industry that could fulfill its function. It is pervasive and reflected in all goods and services. Not only is the chemical industry here to stay, but it is also a dynamic and innovative industry that has grown rapidly and on which the world will continue to rely in the future.

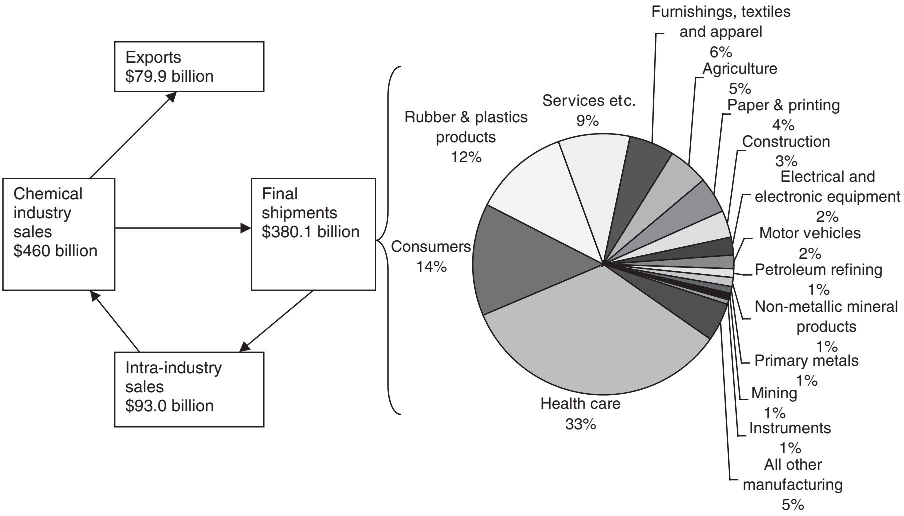


FIGURE 1.8 Who buys chemicals?

Many of the problems concerning pollution and energy have been detected and monitored by chemical methods, and chemistry is playing a part in their solutions.

1.3.6 Freedom of Market Entry

Another characteristic of the chemical industry is freedom of market entry. Anyone who wants to manufacture bulk chemicals may do so by buying "turnkey" plants. Chemical engineering contracting companies have processes for preparation of virtually any common chemical and will build a plant guaranteed to operate for anyone who wishes to invest the money. This was the way that many of the petroleum companies gained entry to the petrochemical business and is also the route followed by developing countries.

The one requirement is large amounts of capital. To enter the basic chemical business requires a bare minimum of \$1 billion. Large sums of money may be required for purposes other than capital investment. In the pharmaceutical industry, large sums are required for research and development, which in the 1990s was of the order of \$500 million per drug. The detergent industry, on the other hand, requires money for massive amounts of advertising. These two industries underscore the importance of large cash flows to support research and development, and merchandising. Thus entry into the chemicals market is free in the sense in which economists use the word, but the expense is such that only governments, oil companies, and other giant enterprises can find the necessary capital.

What has been said about capital applies primarily to very large volume basic chemicals such as the seven petroleum and natural gas-based chemical groups (Table 2.1) and their first-line derivatives. Beyond that there may be other barriers to entry such as lack of necessary technology or reluctance on the part of a patent holder to license technology. An example is Du Pont's process for making hexamethylenediamine by the hydrocyanation of butadiene (Section 5.1.3). Its economics make it the preferred process, but it is not available for license. On the other hand, the Dutch company Akzo was able to enter the Aramid (Du Pont's Kevlar) business, presumably by finding loopholes in the Du Pont patents. Kevlar (Section 9.3.3) is used for fibers that are stronger, weight for weight, than steel and Du Pont finds it profitable, but the business had to be shared with Akzo since the patents were apparently not invincible. The competition was further intensified by DSMs Dyneema, a strong fiber based on very high molecular weight polyethylene and used for body armor.

Downstream operations may provide a barrier to entry. Thus the manufacturers of poly(methyl methacrylate) convert their product to acrylic sheets that are then sold to molders. Potential manufacturers must decide whether they want to gain the expertise that participation in sheet production and its marketing requires. Indeed, will the company's culture allow participation in a business so far removed from basic chemical manufacture?

Low price of the product, and correspondingly low profitability, may deter entry. Furfural (Section 14.1.1) provides a classic example. When introduced many years ago, it was priced so low that it never attracted competition until well into the product's life cycle, and then major competition came not from U.S. companies but from

China. Companies with products whose patents are about to expire often use this technique to discourage other manufacturers. Monsanto used it successfully when one of its herbicides came out of patent. It was able to manufacture it cheaply in a depreciated plant by an optimized process. It was not worthwhile for other companies to invest the fresh capital in order to compete. And, to Monsanto's surprise, the market increased as farmers used more of this cheap herbicide to control weeds in place of the more cumbersome processes of plowing or covering the ground with plastic. Union Carbide similarly exploited the technique with its pesticide carbaryl (Section 10.5.2.5). By pricing it low, it successfully avoided serious competition after the patent had expired.

1.3.7 Strong Health and Safety Regulation

The chemical industry is one of the most highly regulated of all industries. The regulations are intended to protect and improve the worker's and the nation's health, safety, and environment. Chemicals may be toxic or hazardous, that is, they may be liable to poison people fairly quickly or to catch fire or to explode. Some chemicals may appear to damage the environment in ways that are subtle and not well understood. These are the problems that arouse the greatest debate. Long-term ill effects may not be evident or demonstrable in the short term, and in the long term it will be too late to do anything.

The regulatory environment of the chemical industry is subdivided in a number of ways and monitored by various government departments and agencies, some of which are shown in Table 1.6. The on-site problems of regulating the manufacture of chemicals are dealt with mainly by the Department of Labor under the Occupational Safety and Health Act, although the Food and Drug Administration (FDA) sets up standards for Good Manufacturing Practice (GMP), especially in the pharmaceuticals industry. The on-site chemicals may be intermediates that are being processed further, raw materials and end products that are being stored, or effluents that are being discharged into the environment. The GMP is of particular interest in that it not only sets standards for cleanliness, hygiene, and exposure to toxic substances in the pharmaceutical industry, it also insists on specific documentation and demands specific management structures. For example, the heads of production and quality control must be independent of each other.

The absence of major plant accidents in the United States does not mean that the potential for such accidents does not exist. In 1990, the Senate reviewed incidents in the chemical industry and concluded that 17 accidents had released sufficient volumes of chemicals with such toxicity that the potential consequences could have been more severe than Bhopal. They concluded that accident prevention had not been given sufficient attention in existing federal programs.

The intermediate problems of shipping chemicals are regulated by the Department of Transportation, while the problems associated with the off-site use of chemicals are largely the responsibility of the EPA. The off-site chemicals may be materials that are themselves toxic or hazardous, or there may be problems arising from their use or disposal. In the former category come many pharmaceuticals that

TABLE 1.6 Who Monitors the Chemical Industry?

Environmental Protection Agency (EPA)	
Clean Air Act (CAA)	41 pollutants had to be be controlled by 1995; 148 more by 2003. Cost to industry estimated at $25 billion/year.
Federal Insecticide, Fungicide, Rodenticide Act (FIFRA)	
Pollution Prevention Act (PPA)	
Resource Conservation and Recovery Act (RCRA)	Clean up of hazardous and nonhazardous waste sites. Cost to industry $9–60 billion in decade 1990–2000.
Safe Drinking Water Act (SDWA)	Sets standards for 83 chemicals in water.
Clean Water Act (CWA)	Ensures high quality water.
Toxic Substances Control Act (TSCA)	Requires premanufacture notification to EPA of tests on and effects of new products.
Food Quality Protection Act (FQPA)	
Superfund Amendments and Reauthorization Act (SARA)	Clean up of hazardous sites. Mostly funded by taxes in industry.
Comprehensive Environmental Response Compensation and Liability Act (CERCLA)	
Food and Drug Administration (FDA)	
Federal Food, Drug and Cosmetics Act	Sets standards for and evaluates tests of food, drugs, and cosmetics.
Good Manufacturing Practice	Center for Drug Evaluation & Research imposes standards.
Department of Labor	
Occupational Safety and Health Act (OSHA)	Defines hazards in an attempt to prevent industrial accidents. Defines permissible exposure limits for 600 hazardous chemicals.
Department of Transportation	
Hazardous Materials Transportation Act	
Department of Justice	
Chemical Diversion and Trafficking Act (CDTA)	Prevents use of chemicals to make illegal drugs.
Other Departments	
Poison Packaging Prevention Act (CPSC)	
The Emergency Planning and Community Right-to-Know Act	Reporting of production, handling and storage of hazardous materials.
State Laws and Regulations	

are toxic in large doses and in the latter such materials as chlorinated hydrocarbons and nonbiodegradable plastics.

With such a battery of regulatory agencies, the chemical industry might hope that the general public would view its activities benevolently. The reverse is the case, and the chemical industry is regarded with fear and suspicion by many. In fact, it is a remarkably safe industry, with a far better safety record than, for example, the construction, mining, or fishing industries. The truly dangerous activities are such things as smoking cigarettes or crossing the road. The perceived danger of the chemical industry has four reasons. First, people are not familiar with the operations carried out in a chemical plant. The risks inherent in working on high buildings are evident and, when workmen fall from them, the accident is seen as regrettable but inevitable. Second, accidents in chemical plants are infrequent but, when they occur, they are spectacular. At Flixborough in 1974, Bhopal in 1984, and Toulouse in 2001, numerous people were killed instantly. The same applies to airplane accidents, hence many people's fear of flying. If the number of people who are killed on the roads every week instead died simultaneously in a weekend catastrophe, motor vehicles would probably be banned. Third, the chemical industry is an "upstream" industry, and people are unfamiliar with its products and unaware of the extent to which they depend on them. Chemicals are ubiquitous but invisible to the public. Fourth, they worry that they are being poisoned insidiously by the products of the chemical industry without their knowing anything about it.

Whereas one can perhaps avoid being knocked down by a taxicab by taking care, people fear that undetectable chemicals are being ingested with food or water, breathed in with air, or absorbed through the skin. Approximately 100,000 chemicals are manufactured, 30,000 of them at a level greater than 1 tonne/year. These numbers increase by perhaps 300–400 new chemicals each year. Premanufacturing notice under the Toxic Substances Control Act does not allow detailed testing of them all—after all, the FDA only authorizes about 40 new chemical or biotechnological entities per year and that at immense expense. Add to that that the life cycle of many chemicals is not understood. Brominated flame retardants from television sets are said to occur in sperm whale body fat, but how they get there is a mystery (Section 17.2.3.2).

In October 2003, the European Commission adopted a draft regulation under the acronym REACH (Registration, Evaluation and Authorization of Chemicals), to expand regulation from the current 3000 chemicals tested to the 70,000, produced or imported at a total level of more than 1 tonne/year. The degree of testing required varies depending on whether the total production plus imports in Europe is greater than 1, 10, 100, or 1000 tonnes/year, and there are substances of high concern—carcinogens, mutagens, and reprotoxins (CMRs); persistent, bioaccumulative toxins (PBTs); very persistent bioaccumulative toxic chemicals (vPvBs); and endocrine disruptors. The burden of proof of safety is shifted from the regulators to the industry. Authorization will involve about 12 million animal tests, and has set the "green" supporters of chemicals testing at the throats of the equally "green" animal rights activists. The compromise—that testing data be made public so that tests need not be repeated—presents many issues of intellectual property rights. The cost to the European chemcial industry is estimated at $2.6–7.1 billion over the next decade and is seen as a threat to many of the smaller producers.

Whatever happens, there is no practicable way in which so-called "chemicals" can be proved to be absolutely safe, even in the cases where extensive testing has been carried out. A blanket ban on "chemicals" is, however, out of the question. The products of the chemical industry confer benefits. Urban life would be impossible without food preservatives. Pesticides and rodenticides mean that we are able to feed ourselves adequately rather than having our crops destroyed by animal and insect competitors. Fertilizers enhance crop yields. Modern drugs extend our life spans. Synthetic polymers enable us to live much more comfortably than our ancestors. There is no way in which risks can be eliminated completely, but the chemical industry in the developed world is active in testing the toxicity of the products that it manufactures, tracing the sources of pollution, and combating it as demanded by the regulations. The American Chemistry Council, previously the Chemical Manufacturers' Association (CMA), has documented industry's vigorous response to the need for pollution abatement. Which chemicals should be permitted and which banned depends (or should depend) on risk–benefit calculations.

To take a few examples, carbon tetrachloride and chloroform are no longer marketed, but perchloroethylene is still permitted as a dry cleaning solvent. Although the EPA would like to eliminate it, no adequate replacement has come to light, although Micell has launched a chain of dry cleaners who use beverage-grade liquid carbon dioxide and specialty surfactants. Lead tetraalkyls were banned from gasoline because they led to lead bromide dust in the environment. Instead, octane numbers were maintained by an increase in aromatics content. Fears of benzene's carcinogenicity then led to the use of methyl-*tert*-butyl ether as an octane improver. This is now under attack because of contamination of groundwater but, at every stage, attempts have been made to minimize risk.

There is no end to the fears. Chlorinated polymers such as poly(vinyl chloride) (PVC) give dioxins if burned in inefficient incinerators. Many solvent residues are thought to migrate to the stratosphere and damage the ozone layer. Carbon dioxide, the product of every combustion process, is thought to contribute to global warming. Dealing with all these problems comes at a cost. The stringent requirements of the Clean Air Act had the most far-reaching economic impact on the industry, with a cost of $25 billion/year.

The cost-benefit discussion inevitably becomes politicized. When C. Everett Koop, a former US surgeon general, described an environmentalist campaign against diisononyl and di-2-ethylhexyl phthalates as "The Latest Phony Chemical Scare," he was denounced, not because his opponents had powerful evidence of their harmfulness, but because they claimed he was funded by the industry. Koop said bluntly that the greatest health hazards were not trace chemicals but smoking, excessive drinking, drug use, accidents in the home, unprotected sex, poor nutrition, and lack of exercise. Nonetheless, the scare caused most toy manufacturers to remove phthalates from their products.

Certainly there appear to be cases where regulation seems to have got out of hand. Between 1990 and 1993 the United States spent $42 billion on the removal of asbestos from public buildings, compared with the $40.8 billion total budget of the National Institute of Health. It is almost unbelievable that more was spent on the former than on the latter. The harm that asbestos exposure can do to a school child is tiny compared to other causes of death. The annual death rate from asbestos exposure in schools was 0.005–0.093/year per million at risk. The chance of death from high school football was 1–6 per year per million at risk, of drowning (ages 5–14) 27 per year per million at risk and of being run over by a motor vehicle (ages 5–14) 32 per year per million at risk. In assessing the risk from a material, one needs to know both how carcinogenic (or dangerous in other ways) it is and, equally as important, what an individual's chances are of exposure to the material. Thus the FDA has announced that short-fiber asbestos and dioxins, through harmful, provide little danger to the general population. An article by Ames (see note) places the problem of carcinogenicity of chemicals in perspective. Asbestos is harmful only to those who are exposed continually to it in the workplace.

Methyl bromide is an example (Section 17.2.1) where a proposed ban has not yet been implemented because of lack of a reasonable alternative as a soil fumigant. DDT (Section 7.2) is still used in 23 countries because malaria limitation is seen as more important than the thickness of eggshells but, as DDT spreads globally, it will affect people who have taken opposite decisions.

The elimination of benzene from gasoline, mentioned above, was an expensive operation. It costs $150 million/year and saves perhaps 3–4 lives. A life is priceless, but perhaps there are better ways to spend the money. What about vaccinations for poor children or an antiobesity campaign or cheaper medical care for the indigenous elderly? Environmentalists might reply that the chemical industry would not reallocate the funds to other causes anyway, but many of the causes are government funded, and the opportunity for more cost-effective allocation of resources exists.

Steve Rayner, Oxford University's professor of science in society, summed up the fears of the general public: "Most people are perfectly content with an awful lot of science and technology that goes unquestioned. But people resist the feeling of disempowerment at the hands of public and private decision makers, who use technical criteria to dismiss concerns that arise from divergent values. Social ambivalence about the chemicals industry is not simply because people are opposed to chemistry, but to a historical legacy of unscientific waste management. Industry leaders are using science to achieve significant waste reduction and such moves are generally well received by communities and consumers."

The disempowerment of which Professor Rayner writes, however, may express itself in barely rational ways, and an example is the so-called precautionary principle. This has been stated as "When an activity raises threats of harm to human health and the environment, precautionary measures should be taken even if some cause and effect relationships are not fully established scientifically." While that sounds harmless and, indeed, such an approach is already in place as shown by the 1958 Delaney Clause overseeing pesticide residues in food, the new approach is clearly intended to be more stringent. Its opponents feel that extreme environmentalists will no longer have to produce statements of damage caused by particular chemicals to have them banned. The necessity to balance upside benefits against downside risks will be lost. A widespread press campaign against a "chemical" will be sufficient, together with the statement that there is no way a material can be proved to be totally harmless, and you can't be too careful. On such logic, Justice Stoughton was quite right to hang the "witches" of Salem. Threats to human health were certainly attributable to witches even if the cause and effect relationships were not established scientifically.

The precautionary principle has been widely adopted across Europe and has been incorporated into the United Nations Biosafety Protocol regulating trade in genetically modified products. It seems gradually to be working its way into US policy. Much rests on how it is interpreted, and the chemical industry and the general public must hope for a balanced approach.

1.3.8 High Research and Development Expenditures

The chemical industry is research intensive. It hires many graduates, peaking at one time at 13.3% of all scientists and engineers in the United States. In the late 1990s, the figure was reduced to 9%, 5% in the pharmaceutical industry, and 4% in the remaining sectors. That still amounted to 91,000 scientists and engineers, and most of them work in research and development laboratories (see note at the end of this chapter).

Industrial R&D expenditures in the United States increased impressively between 1970 and 1990 in terms of current dollars by about 70%, and chemical R&D had more than doubled. By the 1990s and into the 2000s, the rate of growth of chemical R&D spending had slowed. Figure 1.9 shows expenditure in current and constant (2000) dollars. In basic chemicals, it has remained more or less static at about 3% of sales, while there has been a drop in total industrial R&D spending. Pharmaceutical spending rose from 10.4% of sales in 1990 to 14.5% in 2000, and has increased even more because sales have risen at the same time. Decreased military R&D may be responsible for the lack of buoyancy in chemical companies' spending.

The average research expenditures of the various sectors of the chemical industry are shown in Table 1.7, and the expenditures of some of the top chemical companies in Table 1.8. Pharmaceutical companies such as Merck and Novartis and companies with major pharmaceutical subsidiaries, such as Bayer, spend more on R&D than do the mainline chemical companies, but the table is compiled, as far as possible, to exclude pharmaceutical sales. At the other extreme, the major oil companies are involved mainly with commodity chemicals and spend about 2% of chemical sales on research.

Actually, 3–4% of sales is considered normal for companies that do not have a pharmaceutical arm and are only marginally involved in specialty chemicals. Research-based pharmaceutical companies with few other interests spend 10–25% of sales on research. True specialty chemical companies have budgets about one-third of those of the pharmaceutical companies.

How is the R&D budget spent? Research is a risky and expensive business. Finding the conditions that maximize the cost-effectiveness of an R&D budget preoccupies many managers especially those of pharmaceutical companies. Unfortunately, it is not a science, and success in the laboratory often depends on serendipity. Should a company rely on discoveries emerging from the interests of its researchers, or should it try to satisfy the pull of the marketplace? Should it rely on in-house research or should it "out-source" some of its research and attempt to buy ideas from small entrepreneurial companies? "Technology push" was the initial approach. R&D received a boost from government tax incentives during and immediately after World War II. Much of this

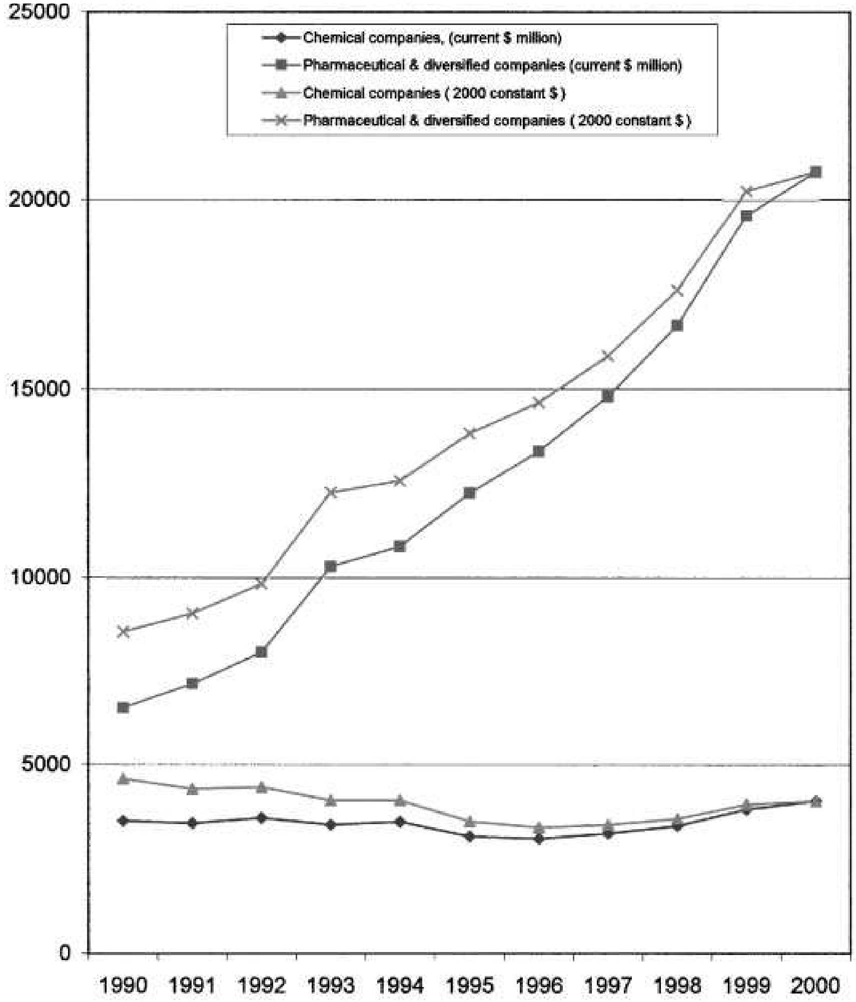


FIGURE 1.9 United States R&D spending.

TABLE 1.7 Research Expenditures in the Chemical Industry by Sector

Sector	Sales ($ billion) 2000	Average Research Expenditure as % Sales
Basic industrial chemicals	5.689	3.6
Fertilizers	0.101	1.0
Specialty chemicals	4.433	4.2
Life sciences (including pharmaceuticals)	19.544	14.5
Consumer products	1.382	2.7
Total	**31.149**	**6.8**

Source: Guide to the Business of Chemistry (cited in Section 0.4.5).

TABLE 1.8 Research Expenditures of Selected Companies, 2000[a]

	Country[b]	Total Sales ($ million)	R&D ($ million)	R&D as % Total Sales
BOC	UK	5,881	818	13.91
Syngenta	CH	6,846	745	10.88
Du Pont	US	31,831	1,776	5.58
Clariant	CH	6,267	245.1	3.91
Dow Chemical	US	23,008	892	3.88
Rohm and Haas	US	6,879	259	3.77
Ciba Specialty Chemicals	CH	5,137	173.5	3.38
Bayer	D	28,534	949.9	3.33
PPG Industries	US	8629	282	3.27
DSM	NL	7453	243.2	3.26
Rhodia	F	6,835	195.3	2.86
Eastman Chemical	US	5,292	149	2.82
Degussa	D	18,672	499.4	2.67
Union Carbide	US	6526	152	2.33
Aventis	F	20,549	468	2.28
ICI	UK	11,747	266.8	2.27
Air Products & Chemicals	US	5,468	124	2.27
Akzo Nobel	NL	12,901	267.2	2.07
Celanese	D	4,797	89.8	1.87
Formosa Plastics	Twn	4,881	86.6	1.77
Henkel	D	11,774	185.2	1.57
Praxair	US	5,043	65	1.29
Air Liquide	F	7,462	87.8	1.18
Solvay	B	8,166	81.1	0.99
Ineos Group	UK	5,000	28.6	0.57
TotalFina Elf	F	105,544	460.7	0.44
BASF	D	333,118	974.8	0.29
Occidental Petroleum	US	13,575	35.9	0.26
Norsk Hydro	Nor	17,821	22.6	0.13
Pharmaceutical companies, 2000				
Roche	CH	10,970	2,030	18.51
Novartis	CH	12,680	2,080	16.40
GlaxoSmithKline	UK	22,210	3,730	16.79
Aventis	CH	14,810	2,590	17.49
Astra-Zeneca	UK-Scand	14,830	2,450	16.52

[a] Chemical and diversified companies.

[b] B = Belgium, CH = Switzerland, D = Germany, F = France, NL = Netherlands, Nor = Norway, Scand = Scandinavia, Twn = Taiwan, UK = United Kingdom, US = United States, C = Canada, J = Japan, Ind = India, SA = South Africa.

research related to finding new materials for which uses could be created. Thus the period between 1940 and 1965 was a time of great discovery. Nylon, other synthetic fibers, and the polymers that provide plastics, elastomers, coatings, and adhesives are examples. Chemicals were also discovered with numerous applications that made industry generally more efficient, such as corrosion inhibitors, electronics chemicals, and food antioxidants.

In the mid-1960s, however, the concept changed to "demand pull." What problems are there in the marketplace that require technical solutions? Market research to answer such questions became a discipline and, for the past 35 years, the industry has talked of "market orientation." Examples of technology push include television, sulfonamides, and lasers. Examples of demand pull include hard-water-compatible detergents, jumbo jets, and automobiles with low-exhaust emission. The isomerization of *m*-xylene to *p*-xylene (Section 2.2.3) is an obvious example of a market-oriented research project. Catalytic reforming gives a mixture of xylenes containing too much *m*-xylene for the market and too little *p*-xylene for conversion to terephthalic acid for polyester production (Table 2.10). Were sufficient *p*-xylene produced to satisfy the market, there would be a huge excess of the other isomers. Originally, a catalyst was developed that would isomerize the residual xylene mixture left after the *p*-xylene had been separated, and *p*-xylene was then separated again by the tedious process described in Section 9 and the residual mixture isomerized and recycled again. But the fast-growing demand from China and East Asia for polyester fabrics led to market pressures that were satisfied by the development of another process based on surplus toluene. A conventional acid catalyst will disproportionate this to benzene and a mixture of xylenes, which must be separated as before. With an unusual zeolite catalyst, however, the major xylene obtained is the *p*-isomer. Section 8.1 describes this sophisticated market-oriented chemistry.

Both "technology push" and "demand pull" should be part of any large company's research plan, although there has been a marked trend to deemphasize the "blue-skies" research that leads to truly novel discoveries. Thus, first generation research was "blue-skies" research. It required little participation by management, and researchers were generally regarded as a group of people difficult to communicate with. It was only when a project reached the development and marketing stages that management was required. Du Pont, General Motors, and IBM are examples of companies that made discoveries and brought them to the marketplace. Second generation research involved going to the marketplace to find out what was needed. This demanded strong participation on the part of the marketing branch, but still little participation by top management.

Today there is a third generation of research managers who recognize that research should be a part of the organization not apart from it. R&D should figure in corporate objectives and should take its direction from these objectives in exactly the same way as any other business function. It should thus help the organization to achieve its overall goal. Indeed it should even help to set goals by managing technology as opposed only to inventing and applying it.

Thus the R&D department has to determine which technologies may be developed internally, which may be obtained through licensing, and which may be obtained through strategic alliances. This is very much like a "make-or-buy" decision in manufacturing. It was obviously better for many companies to license BPs ammoxidation technology (Section 4.8) than to try to work out an acrylonitrile process on their own. Today well over 90% of all acrylonitrile is made by this process. Similarly, when Himont wanted to develop highly sophisticated catalysts for propylene polymerization, it joined forces with Mitsui, for both companies had strong backgrounds in catalyst development, and jointly they could bring these to bear on the objective.

Metallocene catalysts (Section 15.3.12) make possible the synthesis of polymers previously difficult to obtain by Ziegler–Natta catalysis. One example is syndiotactic polystyrene, a high-melting specialty or engineering polymer. Both Dow and Idemitsu developed this polymer but, instead of carrying out competing research and development programs, the companies joined forces. Once the project had passed the pilot plant stage, they parted company, and each pursued its own commercial strategy. Since then, the project has been dropped—a striking example of the difficulty of penetrating the polymer business with a new product.

A sensible R&D strategy avoids duplication but, even so, a large amount of duplication takes place in the world's research laboratories. The patent literature discloses 25 processes for the manufacture of 1,4-butanediol and a similar number for manufacture of propylene oxide. At least 15 companies have worked on the homologation of methanol to higher alcohols, a process that none has commercialized. There are many other examples.

There is also duplication in the competition between companies in the specialty and performance polymers business. Not only is there intercompany competition to sell the same polymer but there is also much interpolymer competition as different polymers vie for use in a given application. In 1993, there were at least 51 companies manufacturing engineering thermoplastic polymers, that is, sophisticated polymers to replace metal. Sixty percent of the business was enjoyed by only five companies: General Electric, Du Pont, Bayer, Hoechst Celanese, and BASF. Another eight companies had 19% of the business; these were Allied, Monsanto, Asahi Chemical, Mitsubishi Gas Chemical, Teijin Seiki, Mitsubishi Chemical, DSM, and Toray. The remaining 21% of the business was the province of 37 companies, none of which had achieved the critical mass required for profitability in the engineering polymer business. On the one hand, this kind of operation leads to a great deal of waste. On the other hand, it may be the concomitant of a competitive capitalist economy. Experience in centrally planned economies, especially in pharmaceuticals research, suggests that without the spur of competition very little is discovered. Having a number of groups trying to get something to work will at least increase the possibility that one of them will succeed.

Of the $23.4 billion spent on chemical and drug industry research in 1999, 9.7% was for basic research, 34.3% for applied research and 56.1% for development. There has always been an academic argument that holds that basic research is the province of the university. This may well be so, but in any laboratory there may be need for theory that has not been developed but is necessary for the solution of a problem. The pursuit of this theory, which in essence is basic research, is appropriate for the industry that requires it in order to fulfill its objectives. This leads to many industry–academic collaborations and to industrially funded research in universities.

Applied research is usually defined as the type of R&D that leads to new uses for existing products or new products that fill needs in the marketplace. The development of a new polymer that absorbs many times its weight of water for use in disposable diapers is a good example of applied research as is the extension of the use of that material to other areas such as agriculture. All the same, very little effort is being expended on new products. One reason for this is that the maturity of the industry does not offer as many opportunities for new products. Also, the many regulations that govern the chemical industry, particularly the Toxic Substances Control Act, (Section 1.3.7) require extensive and expensive testing before a product can be test-marketed. Usually, the risk is deemed greater than the potential benefit. An international report in the year 2000 judged that the chemicals sector was near the bottom of the league in generating growth through innovation, producing just 26% of its turnover from "new" products and services introduced in the past five years.

A major exception is found in the pharmaceutical and agricultural chemical businesses, although even these industries have seen a decline in the rate of innovation. In the 1990s it cost approximately $500 million to develop a new pharmaceutical. The pharmaceutical companies are willing to make such expenditures, however, because of the lure of "blockbuster" drugs whose annual sales may reach a billion dollars with concomitant profits.

The bulk of R&D dollars is spent on applied research and development. This includes work on new and improved processes, finding new uses for existing products, pursuing the analytical activities on which a modern laboratory depends, and solving ecological problems.

Ecological problems—the monitoring and reducing of pollution—have become a major research area in the past generation. One-fifth of new capital expenditures in the 1990s was for pollution abatement and control; approximately the same amount of the R&D budget of a large company is likely to be spent on ecologically oriented projects.

1.3.9 Dislocations

An important concept in today's chemical industry is the ever-present possibility for dislocations. This is particularly important for planners who, all too often, find their scenarios askew because of a dislocation. Dislocations are defined as events over which a given company has no control but which markedly affect that company's business. In planning, one cannot forecast what a dislocation might be. Indeed, if it could be forecast, it would not be a dislocation. But what must be anticipated in planning is that there will be dislocations either for good or ill.

A few examples illustrate the point. The advent of unleaded gasoline made lead tetraalkyls obsolete in the United States. The major manufacturer of these compounds was Ethyl Corp. with a reputed $90 million of profit. That figure rapidly declined to $20 billion and would have been lower had it not been for export sales. Obviously, Ethyl was a victim of a dislocation. This motivated Ethyl to use its skills to expand into a variety of specialized and semicommodity businesses that allowed them to recoup their profits. Thus they became a large supplier of the bulk pharmaceutical, ibuprofen, for sale to packagers, who converted it into a consumer item. Their synthesis involved organometallic chemistry developed for the unrelated area of both lead tetraethyl and α-olefin production.

The same unleaded gasoline dislocation proved to be a windfall for ARCO. ARCOs two-for-one process for the manufacture of propylene oxide and *tert*-butanol (Section 4.11) made available to them large quantities of the latter for which, at the time the plant went on stream, there was very little use. Accordingly the *tert*-butanol was recycled to the starting material, isobutene. The need for octane improvers in unleaded gasoline soon provided a market for it. Dehydration to isobutene and reaction with methanol provided MTBE (Section 2.3.2) and ARCO became the largest single supplier in the United States. Between 1977 and 1993, production rose from virtually nil to about 13 billion lb/year and had reached 20 billion lb by the end of the 1990s. Capital expenditure was conservatively estimated at \$50 billion. There was then another dislocation. Although MTBE functions well as an octane improver, it is water soluble. If there is a leak from a gasoline storage tank in a garage, the MTBE diffuses into the ground water. Gasoline, which is insoluble, does not give this problem. Inspection and repair of hundreds of thousands of gasoline storage tanks was judged impracticable, and instead ethanol was proposed as a replacement for MTBE. The ethanol is to be made mainly by fermentation of corn starch and this requires subsidy (Section 3.9).

A third example also relates to unleaded gasoline. At least one petroleum company announced that it would achieve the desired octane number by removing lead and increasing the aromatics content of their gasoline. A few years later, the Clean Air Act specified that the aromatics content of gasoline must be decreased from about 35% to 25%. Thus the Clean Air Act provided a second dislocation that negated that company's reaction to the earlier dislocation provided by unleaded gasoline.

A fourth example: Phillips Petroleum Company never used the metathesis reaction (Section 2.2.9) to convert propylene into more expensive ethylene and 2-butene which, in turn, may be dehydrogenated to butadiene. One might assume that it did not opt to carry out this interesting chemistry because of the widely held belief in the 1970s that within a 15-year period declining US gas supplies would make naphtha and gas oil the major steam cracking feeds. Accordingly, large quantities of butadiene would become available. The United States has always imported butadiene from Europe because insufficient quantities were produced by the cracking of gas. Actually, naphtha and gas oil never became major feedstocks in the United States chemical business (Section 2.2.1). Saudi Arabia decided to use only the ethane in their associated gas, making large quantities of LPG (propane and butane) available at low world prices. In the late 1990s, the United States used LPG to supplement indigenous ethane and propane and had not found it necessary to switch to liquid feeds. Thus the United States still imports butadiene, a situation that metathesis might have helped to avoid.

Dislocations frequently result from advances in technology. The producers of propylene oxide by the chlorohydrin route suffered a serious dislocation when ARCO announced its new process via *tert*-butyl hydroperoxide (Section 4.7). Every manufacturer except one went out of business. Similarly Monsanto's acetic acid process using methanol and CO closed down every US producer of acetic acid who used acetaldehyde as a starting material.

World events are also dislocations. Booms and slumps, sudden changes in the price of oil or natural gas, political upheavals such as the 9/11 destruction of the twin towers, and the Iraq war all influence the general economic climate and the chemical industry.

The answer to dislocations is the concept of robustness. A robust process is one that can accommodate a variety of dislocations. For example, some companies, uncertain of their feedstock supply, built steam crackers that could operate on gaseous or liquid feedstocks. Their plants cost more than a single feedstock plant would have done, but were sufficiently robust to withstand dislocations in feedstock supply. The fact that the petrochemical business in the United States in 1993 remained relatively profitable is due largely to such flexible crackers. Western Europe suffered because only 5 of its 52 crackers at that time were flexible. This was originally dictated by the lack of availability of gas.

Finally, the chemical business is dynamic. It is affected not only by what it does itself, such as creating new technology, but by what others do around it. Modern managers keep abreast as much as possible with what the rest of the world is doing that might affect their businesses. The development of desk-top computers, the World Wide Web, and specialized databases have provided rapid access to previously undreamed of amounts of data about companies, patents, products, and applications.

1.4 THE TOP CHEMICAL COMPANIES

Table 1.9 provides data about the 50 leading chemical companies in the world in 2000 (see note at the end of this chapter). Pharmaceutical companies have not been included in this list unless they have extensive chemical interests.

Many of these chemical companies have nonchemical activities, the proportion of chemical sales being given in the penultimate column. Chemical arms of petroleum companies include TotalFina Elf, Royal Dutch Shell, ExxonMobil, Lyondell, and BP. Thus ExxonMobil is the fourth largest chemical company in the United States, even though its chemical sales are only 9.2% of the total for the company. For many years the three largest chemical companies in the world were the three arms of the pre-World War II German company, I.G. Farbenindustrie. This giant company was divided into three companies, BASF, Bayer, and Hoechst, after World War II. In 1995 Hoechst, troubled by the difficulties of the heavy chemicals industry in Europe in the 1990s, demerged its entire company into 12 independent companies. The flagship was supposed to be the pharmaceutical sector, which merged with the pharmaceutical sector of Rhone Poulenc. The latter company similarly demerged its petrochemical operation. The new pharmaceutical company was called Aventis and its chemical operations rank 33rd in the table. In 1993, ICI demerged its pharmaceuticals, agrochemicals, and specialty businesses to form a new company, Zeneca. Zeneca then merged with the Scandinavian firm Astra to give AstraZeneca, ranked 45 in the table in 1999. It has since sold its agrochemical interests to BASF. In general, the profitability of companies selling specialties is higher than that of those making commodity chemicals, and the profitability of US companies is higher than that of other companies. Table 1.9 broadly illustrates these trends.

Du Pont and Dow occupied the second and third places respectively in Table 1.9. Since the Dow–Union Carbide merger in 2001, however, the joint company has had higher sales than Du Pont. Dow is an efficient company with highly integrated processes and high annual chemical sales per chemical employee ($480,000), a figure

TABLE 1.9 The Top 50 Companies Worldwide by Chemical Sales, 2000

Rank		Country[a]	Chemical Sales ($ million)	Chemical Operating Profit as % Chemical Sales	Chemical Sales as % Total Sales
1	BASF	D	30,790.5	8.5	93
2	Du Pont	US	28,406.0	11.3	89.2
3	Dow Chemical	US	23,008.0	9.8	100
4	ExxonMobil	US	21,503.0	5.4	9.2
5	Bayer	D	19,295.2	9.5	67.6
6	TotalFina Elf	F	19,203.1	7.8	18.2
7	Degussa	D	15,584.1	4	83.5
8	Royal Dutch Shell	UK/NL	15,205.0	5.4	10.2
9	ICI	UK	11,746.7	7.4	100
10	BP	UK	11,247.0	6.8	7
11	Akzo Nobel	NL	9,364.3	8.2	72.6
12	Sumitomo Chemical	J	9,354.3	8	96.8
13	Mitsubishi Chemical	J	8,976.7	4.2	55.4
14	Mitsui Chemicals	J	8,720.3	5.8	100
15	Huntsman	US	8,000.0		100
16	General Electric	US	7,776.0	24.7	6
17	Chevron Phillips	US	7,633.0		100
18	Dainippon Ink & chemicals	J	7,512.7	5.4	82.5
19	Equistar	US	7,495.0	4.5	100
20	DSM	NL	7,295.0	8.5	97.9
21	Henkel	D	7,215.8	8.3	61.3
22	Sabic	SA	7,119.8	22.8	100
23	Syngenta	CH	6,846.0	10.1	100
24	Rhodia	F	6,835.3	6.7	100
25	Sinopec	China	6,791.6	4.3	17.4
26	Air Liquide	F	6,590.1	15.6	88.3
27	Union Carbide	US	6,526.0	9.1	100
28	Toray Industries	J	6,303.3	5	63.2
29	PPG Industries	US	6,279.0	13.7	72.8
30	Clariant	CH	6,266.6	10.7	100
31	Reliance Industries	Ind	6,232.1	19.9	100
32	Rohm and Haas	US	6,004.0	5.5	87.3
33	Aventis	F	5,792.3	−3.1	28.2
34	ENI	I	5,544.5	−6	12.6
35	Eastman Chemical	US	5,292.0	10.6	100
36	Asahi Chemical	J	5,249.4	5.4	43.6
37	Air Products & Chemicals	US	5,238.3	17.1	95.8
38	Solvay	B	5,145.6	8.3	63
39	Ciba Specialty Chemicals	CH	5,137.4	12.9	100
40	Norsk Hydro	Nor	5,088.7	3.5	28.6
41	Praxair	US	5,043.0	24.2	100

TABLE 1.9 (*Continued*)

Rank		Country[a]	Chemical Sales ($ million)	Chemical Operating Profit as % Chemical Sales	Chemical Sales as % Total Sales
42	Ineos Group	UK	5,000.0		100
43	Formosa Plastics	Twn	4,881.0	18.1	100
44	Celanese	D	4,797.3	1.6	100
45	BOC	UK	4,694.9	15.1	79.8
46	Honeywell/Allied Signal	US	4,055.0	8.2	16.2
47	Lyondell	US	4,036.0	10.9	100
48	Nova Chemicals	Can	3,916.0	18.4	100
49	Monsanto	US	3,885.0	28.3	70.7
50	Occidental Petroleum	US	3,795.0	4.6	28

[a] For key, see Table 1.8.

Source: C & EN July 23, 2001, p. 24.

exceeded among the large companies only by BP ($500,000), Lyondell ($980,000), and Union Carbide ($510,000, 1999 data). Du Pont is known for supporting its marketing operations with strong technical service. In the 12th position is Sumitomo, the Japanese company with highest chemical sales, followed by the largest Japanese chemical company, Mitsubishi Kagaku, formed from a merger between Mitsubishi Kasei, which occupied 14th position in 1991, and Mitsubishi Petrochemical. Japanese companies are relatively small and their profitability is the lowest in the industry. State-owned companies like ENI are among the least profitable, in part because inefficient operations are often maintained simply to provide employment.

Although the chemical industry is proliferating around the world, the largest companies are still concentrated in the United States, Western Europe, and Japan. In Table 1.9, 13 countries are represented, notably Belgium (1 company), Canada (1), Switzerland (3), Germany (5), France (4), India (1), Italy (1), Japan (6), Netherlands (3), Norway (1), Saudi Arabia (1), Taiwan (1), United Kingdom (4), United States (18), and joint United Kingdom/Netherlands (1). In the first edition of this book, we said that future lists may well include companies from the Middle East and Southeast Asia, and two indeed occur. Other relative newcomers include Huntsman, Ineos (aquired interests of Inspec who got them from ICI), Sinopec, Syngenta (agrochemical interests of Astra-Zeneca and Novartis), and Nova Chemicals.

1.5 THE TOP CHEMICALS

Table 1.10 lists the 50 most important chemicals by volume manufactured in the United States in 2000. We have also listed the production figures for 1977 and 1993, which we gave in our earlier edition, and the rate of growth over the intervening years. The rank order would be more or less the same in any developed country.

TABLE 1.10 Top 50 Highest Volume Chemicals in the United States, 2000, 1993, and 1977

Rank Order				Production (billion lb)			Growth 1993–2000	Growth 1977–1993
2000	1993	1977	Chemical	2000	1993	1977	%/year	%/year
1	1	1	Sulfuric acid	87.28	80.31	68.8	1.2	1.0
2	2	6	Nitrogen	62.78	65.29	24.04	−0.6	6.4
3	3	4	Oxygen	56.61	46.52	31.86	2.8	2.4
4	4	5	Ethylene	55.40	41.25	24.65	4.3	3.3
5	5	2	Lime	44.32	36.8	37.78	2.7	−0.2
6	6	3	Ammonia	33.10	34.5	32.35	−0.6	0.4
7	11	13	Propylene	31.83	22.4	12.56	5.1	3.7
8	8	7	Chlorine	26.45	24.06	21.3	1.4	0.8
9	10	10	Phosphoric acid	25.79	23.04	15.6	1.6	2.5
10	7	8	Sodium hydroxide	24.20	25.71	21	−0.9	1.3
11	12	9	Sodium carbonate	22.59	19.8	15.97	1.9	1.4
12	13	15	Ethylene dichloride	21.85	17.95	10.48	2.8	3.4
13	18	14	Benzene	21.19	12.32	11.25	8.1	0.6
14	9	–	Methyl *tert*-butyl ether	19.17	24.05		−3.2	
15	17	23	Vinyl chloride	18.95	13.75	5.81	4.7	5.5
16	14	11	Nitric acid	17.59	17.07	14.77	0.4	0.9
17	15	12	Ammonium nitrate	16.49	16.79	13.97	−0.3	1.2
18	16	16	Urea	15.32	15.66	8.99	−0.3	3.5
19	20	26	Carbon dioxide	14.76	10.69	4.45	4.7	5.6
20	19	18	Ethylbenzene	13.16	11.76	7.3	1.6	3.0
21	21	20	Methanol	12.18	10.54	6.46	2.1	3.1
22	22	19	Styrene	11.92	10.07	6.82	2.4	2.5
23	35	35	Potash (as K_2O)	9.92	3.31	0	17.0	
24	26	24	Hydrochloric acid	9.55	6.45	5.13	5.8	1.4
25	23	25	Terephthalic acid (includes dimethyl terephthalate)	9.22	7.84	5	2.3	2.9
26	24	21	Formaldehyde (37% by weight)	8.85	7.61	6.08	2.2	1.4
27	28	32	*p*-Xylene	8.75	5.76	3.02	6.2	4.1
28	29	27	Ethylene oxide	8.53	5.68	4.42	6.0	1.6
29	27	17	Toluene	8.34	6.38	7.73	3.9	−1.2
30	32	33	Cumene	8.25	4.49	2.64	9.1	3.4
31	30	30	Ethylene glycol	5.95	5.23	3.47	1.9	2.6
32	31	28	Ammonium sulfate	5.74	4.8	3.82	2.6	1.4
33	33	37	Phenol	4.85	3.72	2.38	3.9	2.8
34	34	34	Acetic acid	4.73	3.66	2.58	3.7	2.2
35	38	31	Butadiene	4.43	3.09	3.19	5.3	−0.2
36	36	41	Propylene oxide	3.98	3.3	1.9	2.7	3.5
37	37	29	Carbon black	3.62	3.22	3.48	1.7	−0.5
38	41	44	Acrylonitrile	3.42	2.51	1.64	4.5	2.7

TABLE 1.10 (*Continued*)

Rank Order 2000	1993	1977	Chemical	Production (billion lb) 2000	1993	1977	Growth 1993–2000 %/year	Growth 1977–1993 %/year
39	40	48	Titanium dioxide	3.09	2.56	1.36	2.7	4.0
40	39	45	Vinyl acetate	3.06	2.83	1.6	1.1	3.6
41	42	40	Acetone	2.98	2.46	2.14	2.8	0.9
42	44	39	Cyclohexane	2.31	2	2.34	2.1	−1.0
43	45	46	Sodium silicate	2.16	1.97	1.56	1.3	1.5
44	43	38	Aluminum sulfate	2.14	2.23	2.32	−0.6	−0.2
45	48	36	Calcium chloride	2.07	1.4	2.42	5.7	−3.4
46	46	43	Adipic acid	1.96	1.56	1.85	3.3	−1.1
47			Aniline	1.87				
48	50	49	*n*-Butanol	1.84	1.33		4.7	
49	49		Caprolactam	1.69	1.36		3.2	
50			Sodium chlorate	1.64				

Sulfuric acid heads the list by a large margin as befits its position as an economic indicator, although its maturity means that its growth has been slow. Though it has many applications, about 45% is used for phosphate and ammonium sulfate fertilizers. Of the first 15 chemicals, only five—ethylene, methyl *tert*-butyl ether, propylene, benzene, and ethylene dichloride—are organic. Four are associated with the fertilizer industry—sulfuric acid, nitrogen, ammonia, and phosphoric acid. Oxygen is used by the steel industry and for welding. Sodium carbonate is important in the glass industry. Most of these chemicals are also used to make organic chemicals, but their main markets lie elsewhere. Chlorine has a number of uses including the bleaching of paper, as a disinfectant, and as a component of organic compounds, most important of which is vinyl chloride whose precursor is ethylene dichloride. Many chlorine compounds, however, are now considered ecologically undesirable, as is the use of chlorine for bleaching paper and disinfecting swimming pools.

The three most important organic chemical building blocks, ethylene, propylene, and benzene, occupy positions 4, 7, and 13. The majority of remaining chemicals in the top 50 are organic, and these form the backbone of the so-called heavy organic chemical industry. Heavy organics are defined as large volume commodity chemicals such as ethylene and propylene as opposed to specialty chemicals such as dyes and pharmaceuticals. Some of the chemicals have only one very large use. For example, the major use for ethylene dichloride (No. 12) is to make vinyl chloride (No. 15). The major use for ethylbenzene (No. 20) is to make styrene (No. 22). *p*-Xylene (No. 27) is converted primarily into terephthalic acid (No. 25). Cumene (No. 30) is converted to phenol (No. 33) and acetone (No. 41). Cyclohexane (No. 42) is used primarily to make adipic acid (No. 46) and caprolactam (No. 49).

Many of the top 50 chemicals are monomers for polymers, including ethylene, propylene, vinyl chloride, styrene, terephthalic acid, formaldehyde, ethylene oxide, ethylene glycol, phenol, butadiene, propylene oxide, acrylonitrile, vinyl acetate, adipic acid, and caprolactam.

Comparison of the 2000 with the 1977 data shows the maturity of the chemical industry. Only four chemicals have dropped out of the list since 1977, notably isopropanol, acetic anhydride, sodium tripolyphosphate, and petrochemical ethanol (Nos. 42, 47, 49, and 50, respectively, in 1977). Isopropanol has been hit by the reduction in use of acetone as a solvent as a result of legislation on air pollution, and Exxon has quit the isopropanol → acetone business. Acetone demand can now be entirely satisfied by the coproduct material from the cumene–phenol process (Section 4.9). Acetic anhydride has suffered as a result of the decline of the cellulosics industry (Section 14.3). Sodium tripolyphosphate has diminished in importance with the marketing of low-phosphate detergents and regulations banning its use in some states and limiting it in others. Synthetic ethanol has been affected by imports from Saudi Arabia (Section 1.3.3).

These products were near the bottom of the top 50 anyway, so their dropping out need be little more than a small fluctuation in demand. What products have replaced them? The most significant is methyl *tert*-butyl ether for unleaded gasoline, which we have mentioned repeatedly, and which now occupies position 14, although it has dropped from No. 9 in the 1993 rankings and is expected to drop further. The other newcomers are the fertilizer, potassium chloride (No. 23), which is mined rather than manufactured, caprolactam (No. 49), and *n*-butanol. The appearance of caprolactam indicates a slight shift in the United States from nylon 6,6 to nylon 6 (Sections 7.2 and 7.3).

Not only has the composition of the top 50 remained largely unchanged, but the rank order has varied less than might be expected. The average chemical has changed rank order by fewer than five places since 1977 and 2.5 places since 1993. Chemicals produced at this level usually grow at about the rate of the gross national product, say 2 or 3%/year. The top 50 itself has grown at 2.3%/year. Some of the exceptions are noteworthy. Ethylene and propylene have grown faster than the GNP particularly since the late 1980s because of the growth of high and linear low-density polyethylenes, α-olefins, and polypropylene. Butadiene has shrunk because its major use is to make styrene–butadiene rubber (Section 5.1) for tires. Because cars in the United States were smaller over this period, less rubber was required for tires. The spare tire in automobiles has been practically eliminated, and radial tires last longer and require less synthetic and more natural rubber. This trend may be reversed with the advent of the monstrous sport utility vehicles (SUVs). There has been an embarrassing excess of butadiene in Western Europe, where it is produced in much larger quantities than in the United States, because liquids are steam cracked there as opposed to gas in the United States (Section 2.2.1). Solvent applications for chemicals have decreased generally because of the more stringent requirements to prevent air pollution.

NOTES AND REFERENCES

The *US Chemical Industry Statistical Handbook* contains general information about the chemical industry including sales, volumes, pollution and environmental problems, and trends. It is published by the American Chemistry Council, 1825 Connecticut Ave., Washington, DC 20009. Information is also published annually in *Fortune, Chem. Eng. News, Chem. Week*, and *Chem. Insight* (Quadrant House, The

Quadrant, Sutton, Surrey SM2 5AS). Other guides are listed at www.loc.gov/rr/scitech/scirefguides/chemicalindustry. The American Chemical Society has a website, www.chemistry.org that gives links to sources of industrial data, usually, let it be said, to the relevant issues of *Chem. Eng. News*, which is an ACS publication.

The Economic Contributions of the Business of Chemistry, American Chemistry Council, 2001, reviews the impact of the chemical industry and applies input–output analysis to show the way in which chemistry contributes both to employment and to consumer products, web site www.cmahq.com. *Guide to the Business of Chemistry*, American Chemistry Council, published annually, provides detailed statistics about the sector. CEFIC, The European Chemical Industry Council, Avenue E. Van Nieuwenhuyse, 4 - Box 2, B-1160 Brussels, Belgium has a web site at www.cefic. org. It produces an annual petrochemical review at www.petrochemistry.net. *Economic Bulletin* is a free publication issued three to four times a year by Ecostat, the TEA (Trade and Economic Affairs) Department of CEFIC.

Few books are published on nonscientific aspects of the chemical industry because geographers, economists, and related professionals rarely understand the chemistry. K. R. Payne, *The International Petrochemical Industry: Evolution and Location*, Blackwell, Oxford, 1991, is a worthwhile exception.

Section 1.1 Table 1.1 is based on the US Bureau of the Census, Annual Survey of Manufactures, 2001. The NAICS 1997 classification in Table 1.1 is located at www.census.gov/epcd/www/nais.html and there are links comparing the 1997 classification with older ones and with the 2002 update. Figures 1.1 and 1.3 are based on the US Bureau of the Census. www.census.gov/epcd/www/naicstab.htm

Section 1.2 The world shares of chemical production (Fig. 1.2) and various other statistics in this section come from *The Economic Contributions of the Business of Chemistry*, American Chemistry Council 2001.

Section 1.3 The question of why the chemical industry continually builds excess capacity is discussed in more detail in *When Markets Quake*, J. L. Bower, Harvard Business School Press, Boston, MA, 1986. Bower, who is a Professor at the School, does not arrive at a solution to the problem of “feast and famine” beyond the two obvious and unpopular concepts of cartelization and strict government control.

Section 1.3.1 For comments on the growth of the chemical industry prior to 1980 see *Industrial Organic Chemicals in Perspective, Part One: Raw Materials and Manufacture*, H. A. Wittcoff and B. G. Reuben, John Wiley & Sons, Inc., New York, 1980, pp. 20–21.

Figure 1.5 is taken from *Eur. Chem. News*, October 2, 2000. Bayer’s plans for restructuring appeared in P. L. Short, *Chem. Eng. News*. January 14, 2002, p. 11. Chemical Market Associates Inc. (CMAI) has developed a technique for studying the boom-bust cycle called SWOT analysis (Strengths, Weaknesses, Opportunities, Threats). See W. Weinrauch, *Hydrocarbon Processing*, May 2001, pp. 21–27 and visit www.cmaiglobal.com.

Section 1.3.1.1 The plethora of realignments, mergers, acquisitions and spin-offs can be followed in the business supplements of the press. A more detached view may be obtained from D. Inglis, *Mergers and Acquisitions in the Chemical Industry*, Inform Chemicals, London, 2000. The Bayer restructuring was described in C&EN, January 14, 2002, p. 11.

Section 1.3.2 Figure 1.6 is based on Chapter 6 of www.cefic.be/factsandfigures for 2002. They, in turn, cite the National Chemical Federations (NCF) & Cefic-ITC Analysis. *Chem. Week*, January 2, 2002, p. 2 quotes a trade deficit of ~$2.5 billion for the United States in 2001 and 2002. The 2002 figures indicate exports of $80.8 billion and imports of $83.6 billion. The Cefic figures were in euros but have been converted by the authors to constant dollars.

Section 1.3.3 Ethylene production in the Middle East is reviewed by A. H. Tullo, *Chem. Eng. News*, March 17, 2003, pp. 25–26, and R. Brown, *Chem. Mkt. Reporter*, April 7, 2003, p. 2/1. Our experience of neglect of safety precautions in the third world is anecdotal and dated, but see R. H. King and B. G. Reuben, *J. Chem. Educ.*, **68**, 480–482, 1991. A visit to Hong Kong in 1997 also produced first-hand experience of neglect by small enterprises.

Section 1.3.4 Economies of scale are discussed in more detail in "Economies of Scale or Diminishing Returns," B. G. Reuben, *Process Eng.*, November, 1974, p. 100. At that time, the capacity of steam crackers had reached a plateau, but has since surged ahead. Labor costs vary depending on whether they are direct costs or involve the maintenance staff, security staff, sales staff, and so on. The lowest figure we have seen allowed labor as 0.5% of total costs on an ethylene cracker. The BP/ICI olefins 6 cracker at Wilton, Teesside, UK (Now purchased by Huntsman) employed fewer than 100 people in the mid-1970s, all pictured in *Cracker*, ICI Schools Liaison Section, Welwyn, 1980. As one moves further downstream from ethylene, the proportion of costs attributable to labor rises.

Section 1.3.5 Figure 1.8 is based on *The Economic Contributions of the Business of Chemistry*, American Chemistry Council, Washington, DC, 2001, p. 17.

Section 1.3.7 Table 1.8 is adapted from American Chemistry Council's *Guide to the Business of Chemistry* 2001, p. 166. The most interestingly written books on plant safety are by Trevor Kletz, doyen of British safety engineers. His best-known book is *What Went Wrong? Case Histories of Process Plant Disasters*, 4th ed., Gulf Publishers, Houston TX, 1998. Recently published are *An Engineer's view of Human Error*, 3rd ed., IChemE, Rugby, 2001 and *Learning from Accidents*, Gulf Professional, Oxford, Boston, 2001. His autobiography, *By Accident—A life preventing them in Industry*, PFV, London, was published in 2000. The quoted risks of asbestos are adapted from an article in *Science*, January 19, 1990. The attempts to track the life cycle of chemicals, especially persistent organic pollutants, were reviewed by A. J. S. Rayl, *The Scientist*, September, 2002, pp. 16–18. Details of Good Manufacturing Practice in the United States can be found at www.fda.gov/cder/dmpq. Our copy of the European regulations (perhaps updated now) is *Good Manufacturing Practice for Medicinal Products*, Commission of the European Communities, Luxembourg, 1992.

Data on the chemical industry and its contribution to pollution abatement can be obtained from the American Chemistry Council, Government Relations Department, Washington, DC. The CMA indicated in a bulletin issued in 1992 that pollution from the chemical industry had decreased 60% and that the industry in 1990 had spent $3.8 billion on pollution abatement. This was five times the 1975 level. Cost for pollution abatement in the year 2005 in 1990 constant dollars is estimated to be $11 billion, mostly as a result of the CAA. In the early 1990s, ~20% of all capital investment of the industry was directed toward pollution abatement and pollution control.

Bruce N. Ames' article on cancer risks and how tests for carcinogens should be interpreted will be found in *CHEMTECH* **19**, 591 (1989). He points out that modern sophisticated analytical techniques can detect carcinogens in natural as well as manmade substances and amazingly that they are ubiquitous in the former.

There are innumerable articles on improving the image of the chemical industry, which reflect the lack of a simple solution. We note three articles in *Chem. Ind.*, October 1, 2002, by Steve Rayner (p. 17), Simon Robinson (p. 20) and Rachel Newton (p. 24).

The European Commission's REACH proposals are outlined by E. Johnson and R. Heinen, *Chem. Ind.*, June 16, 2003, p. 12. See also the preceding article, p. 10.

"The New Uncertainty Principle" is described by D. Appell, *Sci. Am.*, January 2001. A conference on the principle was held at Harvard in 2000 and is to be found at www.cid.harvard.edu/cidbiotech/bioconfpp. C. Everett Koop's attack on phony chemical scares appeared in the *Wall Street Journal*, June 22, 1999 and there was a counterblast at www.mindfully.org.pesticide.

Section 1.3.8 R&D statistics appear annually in *Chem. Eng. News*. We have drawn here on the issue of October 29, 2001, pp. 29ff. The effect of government regulations on research and development expenditures has been described for General Motors in an article by P. F. Chenea, *Res. Manag.*, March 22, 1977.

About 65% of all chemists and chemical engineers in industry are employed by companies who are not in the chemical industry but require the services of chemists. Polaroid, 3M, Bell Telephone, and IBM are examples.

"Technology push" inventions are quite rare and tend to be solutions in search of a problem. See J. Schmookler, *Invention and Economic Growth*, Harvard University Press, Boston, 1966.

The gloomy and possibly exaggerated assessment of the decline in chemical industry innovation appeared in *Innovation and Growth: a Global Perspective*, PricewaterhouseCoopers, 2000, summarized in *Chem. Ind.*, January 10, 2000, p. 3.

Section 1.4 Table 1.9 is based on *Chem. Eng. News*, July 23, 2001, p. 24. Table 1.10 comes from *Chem. Eng. News*, various issues, and the *Guide to the Business of Chemistry.*

The order of sales of companies from several countries can change with currency value fluctuations. For this reason, sales are not an absolute indication of size. Also, it is sometimes difficult to separate chemical from nonchemical operations. Thus order of magnitude becomes more important than actual ranking.

The listing of the top chemical companies in the world is from *Chem. Eng. News*, July 23, 2001, p. 24.

Section 1.5 The highest volume chemicals are listed yearly in the *Guide to the Business of Chemistry* and *Chem. Eng. News.* For 1993 they will be found in the issue for July 4, 1994, pp. 30–36, and for 2000 in the issue for June 25, 2001, pp. 42ff. These issues contain a wealth of information about the chemical industry worldwide.

CHAPTER 2

CHEMICALS FROM NATURAL GAS AND PETROLEUM

Where do industrial organic chemicals come from? Table 2.1 provides a guide. Natural gas and petroleum are the main sources. From them come seven chemical building blocks on which a vast organic chemical industry is based. These are ethylene, propylene, the C_4 olefins (butenes and butadiene), benzene, toluene, the xylenes (*ortho*, *meta*, and *para*), and methane. The olefins—ethylene, propylene and butadiene, and the butenes—are derived from both natural gas and petroleum. The aromatics, benzene, toluene, and xylenes, are derived from petroleum and to a very small extent from coal. Methane comes from natural gas.

Whether natural gas fractions or petroleum are used for olefins varies throughout the world depending on the availability of natural gas and the demand for gasoline. Both light and heavy naphthas (Table 2.2) are petroleum fractions that can be cracked to make olefins. They can also be used for gasoline. In the United States demand for gasoline is higher than for other petroleum fractions. Consequently, the price of naphtha has traditionally been high and the chemical industry has preferred to extract ethane and propane for cracking to olefins from what has hitherto been abundant natural gas. This is dictated by linear programming techniques that define the appropriate mix of feeds to maximize profitability in the crackers in the United States, 58% of which are able to handle gases or liquids. The precipitous rise in gas prices in 2001 severely disturbed steam cracker economics. In early 2003, there was another increase in gas prices. The United States has always been an important exporter of ethylene derivatives because of the availability of cheap gas. There is hardly a

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

TABLE 2.1 Sources of Organic Chemicals

- Natural Gas and Petroleum
  - Ethylene (Chapter 3)
  - Propylene (Chapter 4)
  - Butenes and butadiene (Chapter 5)
  - Benzene (Chapter 7)
  - Toluene (Chapter 8)
  - Xylenes (Chapter 9)
  - Methane (Chapter 10)
- Coal (Chapter 12)
  - Synthesis gas (CO and H_2) (see also Chapter 10)
  - Acetylene[a]
- Fats and Oils (Chapter 13)
  - Fatty acids and derivatives
- Carbohydrates (Chapter 14)
  - Cellulose
  - Starch
  - Sugars
  - Gums

[a] Although coal is the traditional source of acetylene, much of it is currently produced either from methane or as a byproduct in ethylene production (Section 10.3).

possibility that US gas will ever be cheap enough to compete in international derivatives' trade with the cheap gas of the Middle East and of other parts of the world. Thus the role of the United States in this trade was being questioned in the early 2000s.

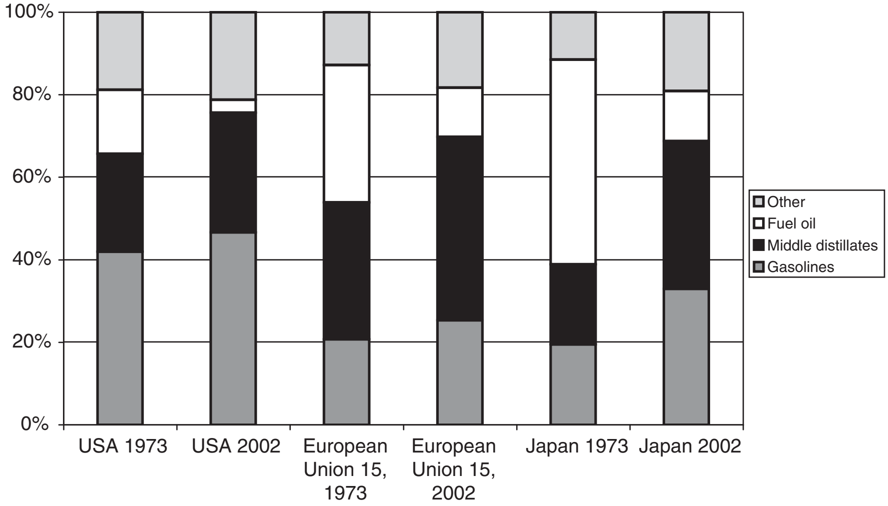
In Western Europe and Japan the demand for gasoline is lower because on a per capita basis there are half as many cars as in the United States. These cars are smaller and are driven shorter distances. Thus in Western Europe more naphtha is produced than is required for gasoline. Also, natural gas is less abundant, even with the North Sea discoveries, and contains less ethane. Consequently, naphtha has been the important European raw material for the manufacture of olefins. This is equally true in Japan, which lacks resources of either natural gas or oil. In the late 1990s and 2000s, naphtha has been a more attractive feedstock because it produces more propylene than does ethane or propane (Table 2.7) to help assuage the propylene shortage. On the other hand, the rise in oil price has diminished its appeal.

Figure 2.1 illustrates the difference in demand for refinery products in the United States, Western Europe, and Japan. Since 1965, gasoline has represented about 45% of the US oil barrel, although it dropped between 1969 and 1981, reaching a low of 40.7% in 1979 at the time of the Iran-Iraq war. The 2002 figure was 46.6%. In Europe, the proportion remained steady at about 20% until 1973 then rose to a peak of 29.7% in 1990 reflecting the replacement of fuel oil by natural gas, which did not come onstream on a large scale until the 1970s. The figure had dropped by 2002 to 25.3%.

TABLE 2.2 Crude Oil Distillation

Fraction	Boiling Point Range	Comments
1. Gases		
Methane (65–90%) ethane, propane, butane	$<20°C$	Similar to natural gas. Useful for fuel and chemicals. Also obtained from catalytic cracking and catalytic reforming. Some of it flared because of cost of recovery. *n*-Butane, however, is practically always recovered.
2. Naphtha		
Light naphtha (C_5,C_6 hydrocarbons)	70–140°C	Naphtha is predominantly C_5–C_9 aliphatic and cycloaliphatic compounds. May contain some aromatics. Base for gasoline. Useful for both fuel and chemicals. Light naphtha now considered undesirable in gasoline because catalytic reforming yields benzene, which is toxic and has a relatively low octane number.
Heavy naphtha (C_7–C_9 hydrocarbons)	140–200°C	
3. Atmospheric gas oil		
Kerosene	175–275°C	Contains C_9–C_{16} compounds useful for jet, tractor, and heating fuel.
Diesel fuel	200–370°C	Contains C_{15}–C_{25} compounds, mostly linear. Useful for diesel and heating fuels. Gas oil is catalytically cracked to naphtha and may be steam cracked to olefins.
4. Heavy fractions		
Lubricating oil	$>370°C$	Used for lubrication.
Residual or heavy fuel oil	$>370°C$	Used for boiler fuel. Vacuum distillation gives vacuum gas oil for catalytic cracking.
Asphalt and "resid"		Used for paving, coating and structural applications.

What was once a straightforward raw material supply situation has become complicated by the discovery of natural gas in many parts of the world in the 1970s and 1980s. Dramatic discoveries in Siberia mean that the CIS possesses a large share of the world's natural gas reserves. Gas fields have also been discovered in Canada, New Zealand, the Arabian peninsula (particularly Qatar), Malaysia, Trinidad, and North Africa. In Venezuela and the Middle East, particularly Saudi Arabia, large quantities of associated gas (the gas that accompanies oil deposits as opposed to that occurring in separate gas fields) are available. In many of these countries, particularly Canada and Saudi Arabia, this gas has become the basis for new chemical industries. The economic consequences of these developments will be discussed further in Section 2.2.1.1.



Middle distillates = kerosenes and gas and diesel oils.
Fuel oil includes bunker crude for ships.
Other = refinery gas, LPG, solvents, petroleum coke, lubricants, bitumen, wax, refinery fuel, and losses

Source: BP Statistical Review of World Energy

FIGURE 2.1 Patterns of oil consumption.

Probably 95% by weight of the organic chemicals the world uses comes from petroleum and natural gas, and we therefore devote most of our space to them. In addition, we consider what might happen if petroleum supplies are exhausted in the next 50–60 years. The reserves/current production ratio in 1999 was 41 years for oil and 61.9 years for gas. These figures have *risen* from 31 and 41 in 1967 but the oil figure went through a peak of 44 years in 1989 and has since declined. On the other hand, huge natural gas deposits were discovered in the 1970s and 1980s, most of them in remote locations. The oil equivalent of these reserves is about four times current petroleum reserves. How to commercialize the so-called remote or stranded gas reserves, when the gas is not readily transportable, is a key problem for the chemical and energy industries (Section 10.7). There is a need for strategies for the future. The glut of oil and gas in the 1980s and 1990s clouds the inevitability of the development of future shortages.

A less important current source of chemicals is coal. Coal was historically important, and much of the progress in the chemical industry until World War II was motivated by the availability of coal. Indeed the famous English chemist, W. H. Perkin, could claim to have founded the organic chemical industry in 1865 when, while trying ineptly to synthesize quinine, he obtained a dye with a mauve color from coal tar intermediates. So important was Perkin's dye that its color gave its name to a period of history known in literature as the "mauve" decade.

The decline of coal coincided with the rise of petrochemicals. However, reserves of coal are much greater than those of oil. If petroleum becomes scarce, will coal come into its own again? Is it a realistic part of an alternative strategy? The so-called C_1 chemistry (Sections 10.5, 10.6) that developed in the 1960s and 1970s when petroleum shortages loomed large assumed that it would, if the industry was willing to provide the tremendous capital investment a switchover would require. Recent discoveries of natural gas, however, mean that any switchover will be considerably delayed. One prediction has been that by 2015 natural gas will be a more important source of energy than petroleum.

The third and final source of organic chemicals is the group of naturally occurring, renewable materials of which triglycerides (fats and oils) and carbohydrates are the most important. Although they account at present for only a few percent by weight of the products of the chemical industry, there has been much discussion of how they might be used to replace nonrenewable fossil materials (oil, coal, natural gas) if the latter ran out. We review some of this chemistry also.

The third group includes hundreds of more obscure natural products that make contributions to specialized segments of the chemical industry. Examples of such materials are sterols, alkaloids, phospholipids, rosin, shellac, and gum arabic. Their contribution to the chemical industry in terms of value or weight is very small but they are irreplaceable for products such as certain pharmaceuticals, flavors, and fragrances.

2.1 PETROLEUM DISTILLATION

To gain an idea of how petroleum is used as a source of chemicals, we must see what happens in a petroleum refinery. Let us consider a simple refinery (Table 2.2; Fig. 2.2) in which crude oil, a sticky, viscous liquid with an unpleasant odor, is separated by distillation into various fractions.

The first most volatile fraction consists of methane and higher alkanes through C_4 and is similar to natural gas. These are dissolved in the petroleum. The methane and ethane can be separated from the higher alkanes, primarily propane and the butanes. The methane/ethane mixture is called “lean gas” from which the ethane can be separated if required. The C_3/C_4 mixture, called liquefied petroleum gas (LPG), may be used as a petrochemical feedstock (Section 2.4) or a fuel. These and other fractions from oil and natural gas are known by various abbreviations summarized in Table 2.3. Butane is also separated for use in gasoline for volatility control, although Government regulations in the United States have decreased this application because the butane contributes to ozone layer destruction. Butane is used to a lesser extent as a raw material for chemicals (Section 5.3.1). Some gas contains C_5, C_6, and even higher liquids. This mixture is called a condensate. It resembles light naphtha (Section 2.2.1.2) and can be used in similar applications.

In the past, the high cost of compressing or liquefying and shipping these refinery gases has dictated that most of them be flared. As the price of natural gas increases, however, shipping of methane in refrigerated tankers may eventually become commonplace. Alternatively, methane may be converted to methanol, which is a useful organic

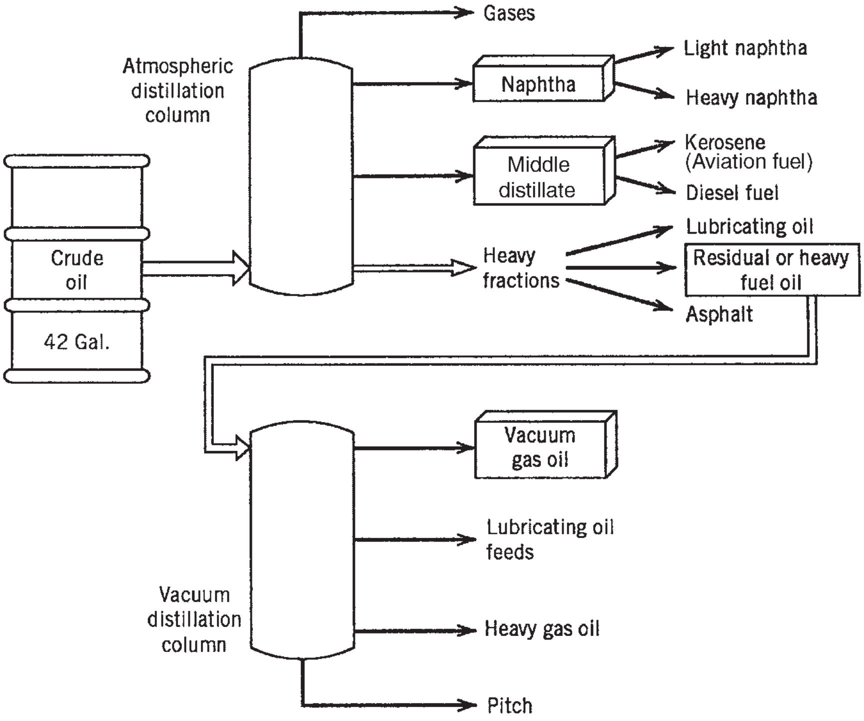


FIGURE 2.2 Crude oil distillation.

chemical building block (Section 10.5) and is more easily shipped. Meanwhile, much refinery gas is still flared even in the United States.

The second fraction comprises a combination of light naphtha or straight run gasoline, and heavy naphtha, and is of particular importance to the chemical industry. The term naphtha is not well defined, but the material steam cracked (Section 2.2.1) for

TABLE 2.3 Petroleum and Natural Gas Abbreviations

Abbreviation	Meaning	Composition
NG	Natural gas	Methane plus small amounts of ethane and propane
LNG	Liquefied natural gas	Liquid methane plus small amounts of ethane and propane
NGL	Natural gas liquids	Ethane and propane condensed from natural gas
Lean gas		Methane and ethane from natural gas
LPG	Liquefied petroleum gas	Liquid propane and butane from associated gas from oil wells
Condensate	A C_5+ fraction from certain oil wells	Similar in composition to light naphtha

chemicals generally distills between 70 and 200°C and contains C_5–C_9 hydrocarbons. Naphtha contains aliphatics as well as cycloaliphatic materials such as cyclohexane, methylcyclopentane, and dimethylcyclopentane. Smaller amounts of C_9+ compounds such as polymethylated cycloalkanes, and polynuclear compounds such as methyldecahydronaphthalene may also be present. Like the lower alkanes, naphtha may be steam cracked to low molecular weight olefins. Its conversion by a process known as catalytic reforming into benzene, toluene, and xylenes (BTX) (Section 2.2.3) is, in the United States, its main chemical use. Catalytic reforming is also a source of aromatics worldwide, although in Western Europe benzene and toluene are mainly derived from pyrolysis gasoline, an aromatics fraction that results from steam cracking of naphtha or gas oil (Section 2.2.1).

Light naphtha, with its octane number raised by addition of lead alkyls, was at one time used directly as gasoline; hence its alternate name, "straight run gasoline." It contains a large proportion of straight-chain hydrocarbons (*n*-alkanes), and these resist oxidation much more than branched chain hydrocarbons (isoalkanes), some of which contain tertiary carbon atoms. Consequently, straight run gasoline has poor ignition characteristics and a low octane number of about 60. It is of little use in gasoline for modern high compression-ratio automobile engines, and its properties are even worse if it is unleaded. Isomerization (Section 2.2.7) of its components to branched compounds increases its octane number and thus its utility. Chemically, however, its significance is like that of naphtha, for it can be cracked to low molecular weight olefins. It does not perform well in catalytic reforming, giving large amounts of cracked products and small amounts of benzene. Benzene is no longer a welcome constituent of gasoline because of its toxicity and relatively low octane number. The situation is summarized in Figure 2.3.

As noted above, international practice has differed. The United States has preferred to crack ethane and propane from natural gas, while the rest of the world has cracked naphtha. The rising price and predicted shortages of natural gas in the United States projected in the 1970s led to an increased interest in liquid feedstock cracking. The preferred liquid feedstock is naphtha, which has traditionally been preempted in the United States for gasoline manufacture. Accordingly, gas oil steam cracking was developed. This was not considered when natural gas was cheap and plentiful, because cracking of gas oil to olefins is accompanied by tar and coke formation. The predicted price rises and shortages, however, motivated techniques for ameliorating this latter problem, and it is now possible to crack gas oil as well as naphtha. The industry has been loathe to do so because it is usually more economic to crack ethane and propane. They are easier to handle, provide fewer coproducts, and much less coke.

From the 1980s onward, the switch to liquid feedstocks lost momentum for three reasons. First, US natural gas production was maintained. Although reserves are being depleted—the reserves/production ratio was down to 8.8 years in 1999—production was scarcely down from the 1973 peak. This reserves/production figure is the same as that in 1993, reflecting a number of new discoveries partly by "wildcatters" and the exploitation of unconventional gas reserves—gas from "tight" (low permeability) sands, sandstones and carbonates, coal seams, shales, and ultradeep

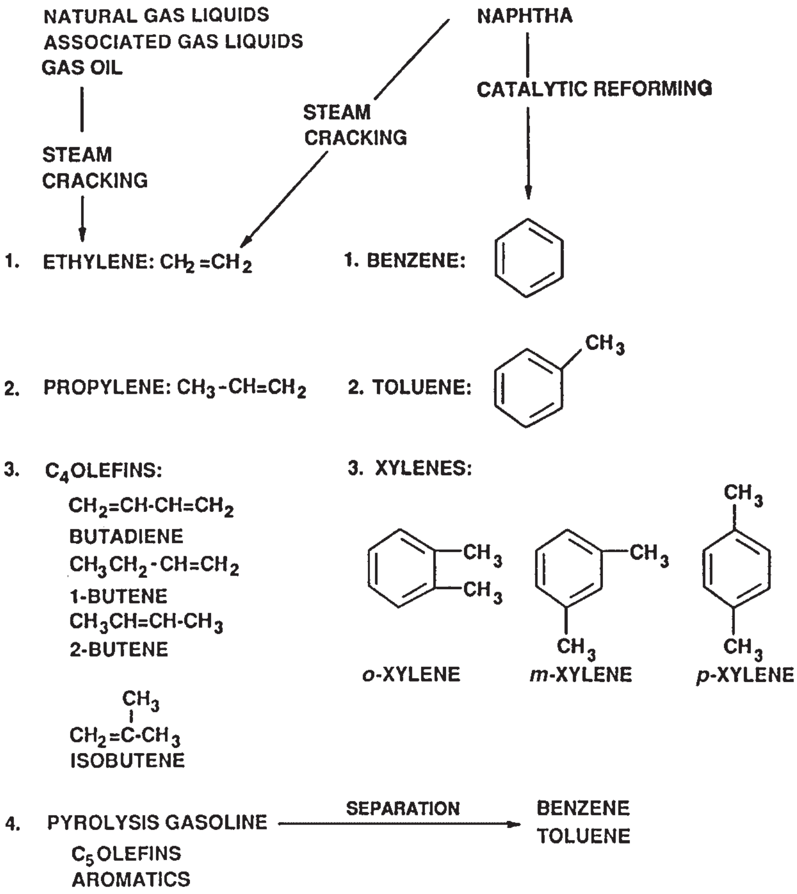


FIGURE 2.3 Steam cracking and catalytic reforming.

(>15,000 ft) reservoirs. Such resources constituted an estimated 30% of natural gas supply in the lower 48 US states in 2000. Price rises stimulated drilling activity. The number of active drilling rigs at the end of 2000 was 879, more than double the cyclical low point of 362 in April 1999 and three times the 1991 low point of 260. Second, natural gas discoveries in Canada meant that cheap natural gas could be imported and in 1999 was about 14% of consumption. Third, Saudi Arabia decided that its first cracker would crack ethane only, making LPG (propane–butane) mixtures available on the world market (see note to Section 2).

Thus, as indicated in Table 2.4, the percent of gaseous feed cracked in the United States has decreased much less than predicted. The sharp rise in gas prices in 2000 (up to $10/million Btu from a typical value of $2.50) led to the closure of 30% of US crackers and was expected to lead to a switch to naphtha but, again, this did not occur. Naphtha was also expensive, and there was a shortage.

TABLE 2.4 Feedstocks for Ethylene—USA *versus* Western Europe

	1982		1985		1995		2001	
Feedstock, % of total	USA	WE	USA	WE	USA	WE	USA	WE
Naphtha[a]	20	90	21	86	20	71.9	30	75.1
Gas oil						10.5		8.8
Ethane/propane	80		79		80	5.5	70	6.5
Ethane/propane/butane/ Crude C_4 streams		10		14		10.6		8.5
Refinery gas						1.5		1.1

[a] Includes gas condensates.
US = United States; WE = Western Europe.

Because of availability of gas from the North Sea, the percentage of gas cracked in Western Europe doubled by 1995, but even so, the predominant feedstock in Europe will continue to be liquids. Gaseous feedstocks are not readily available even though the crackers could be modified to use them. Many crackers in the United States are flexible. If the price of propylene or butadiene goes up, more liquids can be cracked; indeed the optimum ratio of feedstocks is determined at frequent intervals by linear programming.

The situation in Japan approximates that in Western Europe except that even less gaseous feed is cracked and what is cracked comprises almost entirely butane. The liquid feed is entirely naphtha, and it is not expected that gas oil will be cracked in the foreseeable future.

Two decades ago this discussion of world sources of ethylene would have sufficed. By the mid-1980s, however, the impact of the production of ethylene in other parts of the world, primarily the Middle East and Canada, was being felt, and these two giants have been joined by many Asian, South and Central American, and eastern European countries (Section 1.3.3). The availability of ethylene derivatives from third world sources had caused exports from Japan and Western Europe to decrease markedly by the late 1980s. By 1995, the new producers enjoyed a much larger share of the world's ethylene derivatives export business. The United States still participates in trade of ethylene derivatives as long as it is able to crack gas or condensate. As indicated earlier, this capability was threatened in the early 2000s.

To summarize, the two reactions in Figure 2.3—steam cracking and catalytic reforming—are the basis for much of the world's petrochemical production, valued in 2000 at about $1500 billion. The three main raw materials are ethylene, propylene, and benzene, while the C_4 olefins, methane, toluene, and the xylenes, are important but to a lesser degree. Methane is an important source of the fertilizer, ammonia, as well as of organic chemicals, primarily methanol. Its most important reaction is the formation of synthesis gas, from which ammonia and methanol are made. In principle, naphtha may also be used for this (Section 10.4) although it seldom is.

Referring to Figure 2.2, we see that kerosene is a fuel for jet aircraft, tractors, and for domestic heating and has some applications as a solvent. Gas oil is further refined into diesel fuel and light fuel oil of low viscosity for domestic use. Its use as feed for cracking units for olefin production has already been mentioned. Both the kerosene and gas oil fractions may be catalytically cracked to gasoline range materials (Section 2.2.2). Actually, the term gas oil is applied to two types of material, both useful for catalytic cracking. One is so-called atmospheric gas oil which, as its name indicates, is produced by atmospheric pressure distillation. The other is vacuum gas oil, which results from the vacuum distillation of residual oil from the heavy fraction. It has a much higher boiling range of 430–530°C.

Residual oil (Fig. 2.2) boils above 350°C. It contains the less volatile hydrocarbons together with asphalts and other tars. Most of this is sold cheaply as a high-viscosity heavy fuel oil (bunker oil), which must be burned with the aid of special atomizers. It is used chiefly on ships and in industrial furnaces.

A proportion of the residual oil is distilled *in vacuo* at 0.07 bar to give, in addition to gas oil as mentioned above, fuel oil (b.p. $< 350°C$), wax distillate (350–560°C), and cylinder stock ($>560°C$). The cylinder stock is separated into asphalts and a hydrocarbon oil by solvent extraction with liquid propane in which asphalts are insoluble. The oil is blended with the wax distillate, and the blend is mixed with toluene and methyl ethyl ketone and cooled to $-5°C$ to precipitate “slack wax,” which is removed by filtration. The dewaxed oils are purified by countercurrent extraction with such solvents as furfural, which remove heavy aromatics and other undesirable constituents. The oils are then decolorized with Fuller’s Earth or bauxite and are blended to give lubricants.

Part of the vacuum distillate and the “slack wax” can be further purified to give paraffin and microcrystalline waxes used for candles and the impregnation of paper. The petroleum industry is constantly trying to find methods by which the less valuable higher fractions from petroleum distillation can be turned into gasoline or petrochemicals. Table 2.5 gives an indication of the values of the various fractions relative to the cost of crude oil.

TABLE 2.5 Value of Various Oil Fractions

Product	Typical Ratio of Value of Product to Cost of Crude Oil in the United States[a]
LPG	1.1 to 1.4
Motor gasoline	1.4 to 1.5
Naphtha	1.2 to 1.3
Gas oils	1.15 to 1.3
Jet kerosene	1.3 to 1.4
Vacuum gas oil	0.95 to 1.05
Heavy fuel oil	0.6 to 0.7

[a] European figures are similar, but gas oil prices tend toward the top of the range and naphtha/motor gasoline toward the bottom.

2.2 PETROLEUM REFINING REACTIONS

The production of chemical feedstocks from petroleum is inextricably associated with the production of gasoline and other fuels. Sometimes these two industries compete for raw materials, and sometimes they complement each other. The chemical industry is a junior partner because it consumes only about 6% of refinery output in the United States and rarely more than 8% anywhere else. On the other hand, because it produces premium, higher added-value products, it can compete with other consumers in buying those raw materials it needs. The chemical industry can compete successfully because the petrochemicals and the industrial and consumer products made from them represent very high “value added” as compared to the value of the starting materials. In order to understand this competition and the operation of a petroleum refinery, we must examine the chemical processes that follow the physical process of distillation.

We have already noted that straight run gasoline has too low an octane number for high compression-ratio engines. A major objective of a petroleum refinery is to raise this number. It is achieved by way of the reactions summarized in Table 2.6, most of which either modify a petroleum fraction or provide the raw material for another reaction that will give compounds with an improved octane number. In a modern refinery, these reactions as well as distillation take place under computer control. Conditions and output are varied according to the ever-changing demands of the market and the composition of the feedstock, which in turn may vary from day to day and storage tank to storage tank.

2.2.1 Steam Cracking

Steam cracking, derived from the thermal cracking process introduced as early as 1912, involves the use of heat, but no catalyst. From naphtha feedstocks, it yields mainly C_2, C_3, and C_4 olefins and an aromatic fraction called pyrolysis gasoline. Because the olefins are not useful in gasoline, it has long since been superseded for gasoline production by catalytic cracking. It is, however, the mainstay of the petrochemical industry. The insignificance of chemicals’ production compared with that of gasoline is illustrated by the fact that only 9% of total US cracking capacity is steam cracking. The rest is catalytic cracking.

There is little similarity between the old thermal cracking and modern steam cracking processes. The early process required a heavy feedstock and a relatively low temperature and high pressure to maximize gasoline production and minimize gas formation. The new process uses light liquid or gaseous feedstocks (Section 2.1), a high temperature (650–900°C), and a low pressure to maximize the yield of low molecular weight gases. Since it is inconvenient to operate a plant below atmospheric pressure because a small leak could lead to the formation of explosive hydrocarbon–air mixtures, the partial pressure of reactants is reduced by addition of steam as an inert diluent. The steam also serves (Section 10.4) to reduce coke formation in the reactor tubes.

TABLE 2.6 Petroleum Refining Reactions

Cracking

*__Steam Cracking__: Converts *n*-alkanes, cycloalkanes, and aromatics in oil, or ethane, propane, butane and higher hydrocarbons in natural gas into ethylene, propylene, butenes, and butadiene. The products are primarily for the chemical industry.

*__Catalytic Cracking__: Produces molecules with 5–12 carbon atoms suitable for gasoline from larger molecules. Facilitates formation primarily of branched-chain molecules and of some aromatics.

Hydrocracking: Upgrades heavy crudes by converting them to more volatile products. Uses catalysts together with hydrogen, which prevents "coke" formation on the catalyst and converts objectionable sulfur, nitrogen, and oxygen compounds to volatile H_2S, NH_3, and H_2O.

Polymerization

Combines low molecular weight olefins into gasoline-range molecules known as polygas with H_2SO_4 or H_3PO_4 catalysts. It is not widely used today, but there is renewed interest because, if methyl *tert*-butyl ether (MTBE) is phased out, it can be used to produce isooctene from the surplus isobutene. This compound can be used as such or hydrogenated to isooctane, which will somewhat enhance octane number in unleaded gasoline. A more appropriate term would be oligomerization, since oligomers, not polymers, are formed.

*Alkylation

Combines an olefin with a paraffin (e.g., propylene with isobutane) to give branched-chain molecules. Both H_2SO_4 and HF are used as catalysts and solid catalysts are being adopted. Very important in achieving high octane number in lead-free gasoline.

*Catalytic Reforming

Dehydrogenates both straight-chain and cyclic aliphatics to aromatics, primarily BTX over platinum-alumina or rhenium-alumina catalysts. Most widely used refinery reaction in the United States.

Dehydrogenation

Cracking and reforming are basically dehydrogenations. Other dehydrogenations include conversion of ethylbenzene to styrene, butenes to butadiene, and propane to propylene.

Isomerization

Used to convert straight-chain to branched-chain compounds—for example, *n*-butane to isobutane for alkylation, *n*-pentane to isopentane, and *n*-hexane to isohexane in low-boiling naphtha. Other refinery isomerizations include *o*-xylene and *m*-xylene to mixed xylenes (Chapter 9).

Coking

Used to remove metals from a refinery steam. Heat in the absence of air "cracks-off" hydrocarbons. The metals stay behind in the "coke."

Hydrotreating

Like hydrocracking, converts sulfur, nitrogen, and oxygen in petroleum fractions to the gases, H_2S, NH_3, H_2O. Uses hydrogen from other refining processes such as reforming. Can be applied to heavy feedstocks.

---

*An asterisk indicates most important processes.

The hydrocarbon feedstock is vaporized, if not gaseous to begin with, mixed with steam, and the mixture passed through tubes about an inch in diameter through a furnace heated by oil and gas burners. The residence time is short—between 30 and 100 milliseconds—to minimize coking, which is potentially a major problem since coke and hydrogen are thermodynamically the favored products.

The product gases emerge at about 800°C. As they are to be distilled at low temperatures, they have to be cooled by 900°C with minimum waste of heat—a classic chemical engineering problem. Throughout the process, series of heat exchangers conserve the heat used in the early stages and the "coolth" in the later ones. Initially, the gases are quenched to about 400°C in a heat exchanger and the heat used to raise steam to power the turbines of the centrifugal compressors used in the refrigeration process. They are then cooled from 400°C to a little above 100°C in a spray tower cooled by a stream of fuel oil. Additional fuel oil condenses. Some of the fuel oil is removed from the bottom of the spray tower as a product and the remainder cooled and recycled. Further cooling to ambient temperature condenses pyrolysis gasoline plus the steam that was originally added to the feedstock, and these are simply separated in a decanter.

The gases are then scrubbed with ethanolamines (Section 3.11.6.4) to remove acid gases such as carbon dioxide and hydrogen sulfide and dried with molecular sieves. The drying is important because ice is highly abrasive and would damage the low-temperature equipment. The remaining gases are compressed to 40 bar and condensed in a cascade of refrigeration units. Cracking processes only became economically viable because of the development of centrifugal compressors that run the refrigeration processes more cheaply and efficiently than reciprocating compressors. They are the greatest contribution of mechanical engineering to the chemical industry. The condensed gases are then distilled in a column called a demethanizer, which carries on top a condenser cooled to -95°C with liquid ethylene. Methane and hydrogen are the top products, and the C_2+ products emerge as a liquid at the bottom.

This bottom stream is distilled again in a deethanizer in which the C_2 components pass overhead and the C_3–C_5 hydrocarbons form the bottom product. The C_2 fraction is partially hydrogenated to convert small amounts of acetylene to ethylene. The advantage of carrying out the hydrogenation at such a low temperature is that the acetylenic triple bond is selectively hydrogenated. At higher temperatures, double and triple bonds would be indiscriminately reduced. The importance of removing acetylene is that, when polymerized with ethylene, it gives a polymer containing double bonds, which cross-link to give a nonlinear product. The ethylene–ethane mixture is distilled to give an ethylene top product that may be further purified to give polymer grade ethylene, and an ethane bottom product that is recycled.

A depropanizer column separates the C_3 and C_4 streams, and a debutanizer separates the C_4s from C_5s. The latter are combined with the pyrolysis gasoline stream from the first column. The C_3 stream is treated in the same way as the C_2 stream to remove propyne (Section 4.6.1).

2.2.1.1 Choice of Feedstock

The above basic process may be modified depending on the feedstock. Not surprisingly, the products of steam cracking are affected by this as well as by reaction conditions. Modern crackers operate under severe conditions (high-temperatures, low-residence times), and in the last quarter century the typical ethylene yield by weight from fairly severe cracking of a naphtha feedstock has been approximately doubled from about 16 to 31%. As ethylene is the premium product, this is a major advance.

The effect of feedstock is illustrated in Table 2.7. The yield of ethylene decreases and the yield of the coproducts increases as the molecular weight of the feed increases. The economics associated with the use of the different feedstocks depend crucially on the value of the coproducts. Although the cracking of gas has traditionally been the most economical process, there are times when naphtha cracking is preferred because the coproducts are high in price. This is particularly true in Europe where a propylene shortage started to develop in the early 1990s and has continued into the 2000s. The United States is isolated from such a shortage by the large amounts of propylene produced in catalytic cracking (Section 2.3.3). Europe and Japan do not have this reservoir because their lower use of gasoline requires fewer catalytic crackers.

Pyrolysis gasoline is an important product obtained from the cracking of liquids, and the heavier the liquid the more pyrolysis gasoline is produced. It contains aromatics and thus is an important source of benzene and toluene in Europe and Japan. The pattern is shown in Figure 2.4. Much of the toluene converted to benzene also comes from steam cracking. Pyrolysis gasoline is a much less important source of these chemicals in the United States where catalytic reforming is more widely practiced.

TABLE 2.7 Coproduct Yield per 100 lb Ethylene

	Ethane	Propane	Butane	Naphtha	Atmospheric Gas Oil	Vacuum Gas Oil
Feedstock required (lb)	120	240	250	320	380	430
Ethylene (yield %)	80	42	38	31	26	23
Propylene	3	50	40	50	55	60
Butadiene	2	5	9	15	17	17
Other C_4 olefins	1	3	17	25	18	18
Pyrolysis gasoline	2	15	18	75	70	65
Benzene	1	5	6	15	23	24
Toluene	neg.[a]	neg.[a]	3	10	12	12
C_5 olefins	neg.[a]	neg.[a]	1	7	8	7
Other	1	10	8	43	37	22
Fuel oil	neg.[a]	2	4	10	70	125
Other[b]	17	65	62	45	50	45

[a] Negligible = neg.

[b] Mainly hydrogen and methane.

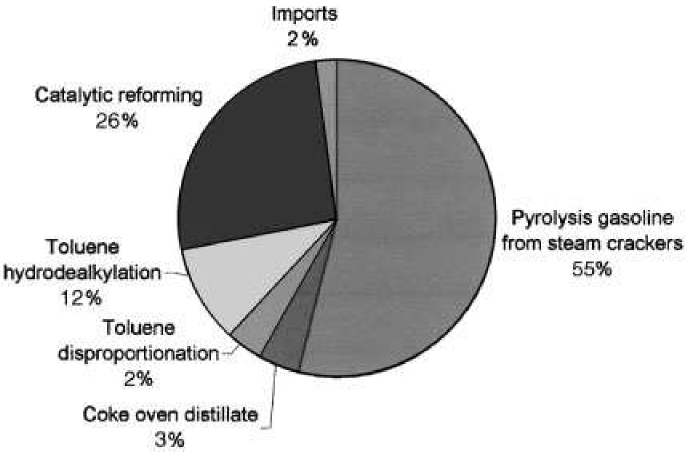
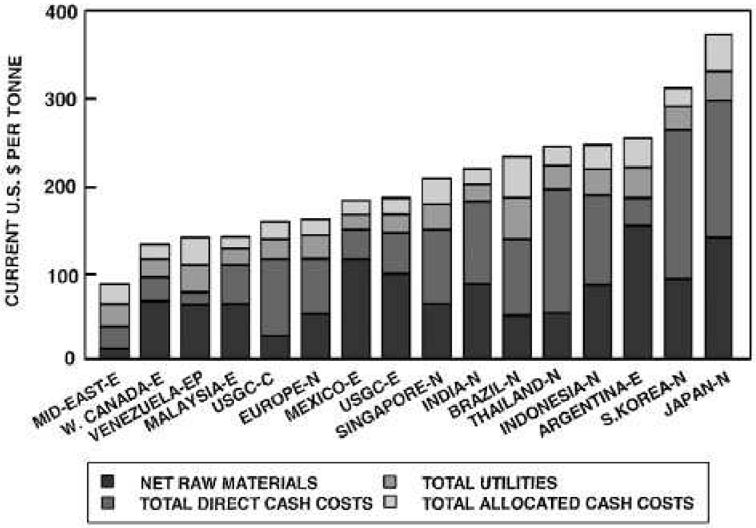


FIGURE 2.4 Sources of benzene in Western Europe, 2001.

2.2.1.2 Economics of Steam Cracking Figure 2.5 shows the relative costs of production of ethylene in 2000 from various feedstocks in various countries. For those unfamiliar with costing terminology, a summary is provided in Appendix A.

The cost of building a plant depends on the chosen feedstock, the degree of flexibility demanded, and the location. In spite of all the engineering ingenuity, elaborate separation processes are costly to build and operate. Ethane crackers, such as



FEEDSTOCK CODE: E=ETHANE, N=NAPHTHA, EP=ETHANE/PROPANE MIX, C=CONDENSATE, USGC = United States Gulf Coast

Source: Nexant Chemsystems

FIGURE 2.5 Ethylene cash cost of production, 2000.

those used in Saudi Arabia (Section 2.1) produce so few byproducts that separation is simple; naphtha and gas oil crackers are more complicated and consequently more expensive. Crackers are cheapest for light feedstocks. They are smaller per tonne of ethylene capacity because they produce fewer coproducts. They also require less elaborate separation processes. Thus, the capital cost of a plant to crack various feedstocks increases in the following order: ethane $<$ ethane/propane $<$ light naphtha $<$ full-range naphtha $<$ gas oil. Light naphtha in this context usually means "condensate," a cheap C_5+ fraction from certain gas wells. It is also called "natural gasoline" and, to add to the confusion, is frequently called simply naphtha. Flexible crackers that can operate on any feedstock are more expensive but involve lower risk. Crackers in developing countries are 10–15% more expensive, in spite of cheap labor, because of the lack of scientific and engineering infrastructure and the need to import many components.

Figure 2.5 does not include interest on finance or corporate overheads. The fixed cash costs comprise direct labor, supervision (see appendix 1), maintenance, insurance and local rates, local taxes, and interest on working capital. Working capital is the money tied up in stocks of raw materials, product and work in progress, and debts, plus the funds needed to pay salaries, and so on. These costs are dominated by maintenance charges which, other things being equal, are related to plant size and complexity. Hence, plants for heavier feedstocks carry a further penalty only partly compensated for by income credits.

Meanwhile, the variable costs make up about one-half of all costs and are crucial to the process economics. They comprise raw material costs plus the costs of fuel and other utilities to run the plant minus credit for coproducts. The average costs of the various feedstocks and coproducts in 2000 in \$/tonne and ¢/lb are given in Table 2.8. We stress that these represent a single year's average prices and that they fluctuate all the time. This table gives some idea of relative prices at a time of European overcapacity, and the reader should consult more recent sources for up-to-date information (see note at the end of this chapter).

As noted earlier, naphtha is more expensive in the United States than in Europe because of the higher demand for gasoline. The price differential, however, is only about \$15/tonne because, at a higher price, producers will export material westward across the Atlantic. When gaseous feedstocks are available, they are usually cheaper per tonne than naphtha but do not give so many coproducts. Other things being equal, raw material costs are related to the amount of raw material required to produce a tonne of ethylene. This is higher for naphtha than for gaseous feeds and higher still for gas oil, because they produce more coproducts. Correspondingly, there is more coproduct credit. The coproducts sell at a higher price than the raw materials but at a lower price than ethylene. Depending on the relative prices of the various feedstocks and products, the net raw material price may favor liquid rather than gaseous feedstocks as, for example, when there is a propylene shortage. Nonetheless, even when it exists, this saving is sometimes negated by the higher fixed costs and depreciation.

The flexibility to crack gases or liquids, whichever is more economic and more readily available at a given time, is available to companies who have paid more for

TABLE 2.8 Average Feedstock and Coproduct Prices, 2002[a]

	European Contract price ($/tonne)	European Spot price ($/tonne)	US Contract price ($/tonne)	European Contract price (cents/lb)	European Spot price (cents/lb)	US Contract price (cents/lb)
Naphtha	223	220	229	10.1	10	10.4
LPG	206–210	206–210	214–227	42.3–43.1/gal	42.3–43.1/gal	43.9–46.6/gal
Propane	240	240	213	46.0/gal	46.0/gal	40.8/gal
Butane	207	209	222	45.7/gal	46.1/gal	49.0/gal
Gas oil		207	203		9.4	9.2
Fuel oil (3.5% sulfur)		131			5.9	
Ethylene	489	436	496	22.2	19.8	22.5
Propylene (polymer grade)	419	450	434	19.0	20.4	19.7
Butadiene	407	396	475	18.5	18.0	21.5
Pyrolysis gasoline		241			10.9	
Benzene	342	347	360	15.5	15.7	16.3
Toluene	312	317	293 (spot)	14.2	14.4	13.3
Xylenes	324	212	297	14.7	9.6	13.5

Source: Courtesy of Nexant Chemsystems, White Plains, NY.

[a] Gallon to weight conversion factors are in Appendix B.

their plants. Gaseous feedstocks have traditionally been the more economic. These two factors have accounted for the advantage that the United States, with its historically abundant supplies of natural gas and large supply of refinery propylene, has held in world chemical markets. This advantage has been eroded by the rise in US gas prices.

The dominance of the United States has been modified by the entry of Saudi Arabia as a major producer. Ethane is produced there at the wellhead from associated gas and is priced at zero plus the logistic cost of separation and transport, which amounts to about $38/tonne (75 ¢/million Btu). The Saudi Government wants to penetrate world markets and takes the view that the ethane would have to be flared if it were not separated; hence zero wellhead value is acceptable. Indeed, because flaring would cause pollution, one might even maintain that the wellhead value is negative. On the zero-value basis, Saudi ethane cracking is much the most economic and sets free for export quantities of propane plus butane (LPG) not required for fuel (Section 2). On the other hand, the availability of ethane in Saudi Arabia is limited because it comes from associated gas, the quantity of which is linked to production of crude. Subsequent investment has been based increasingly on the use of condensate and propane (see note at the end of this chapter). A 30% discount off the lowest export price was granted on feedstocks other than ethane.

Gas cracking has generally been more economic when propylene was not in short supply. The United States has taken full advantage of this, importing small amounts of Saudi LPG in addition to its own supplies of ethane/propane and LPG from natural gas. Western Europe cannot take as much advantage of imported LPG because only 5 of the 52 steam crackers that existed at the end of 1993 were truly flexible, and the infrastructure for handling LPG does not exist in Europe to the extent that it does in the United States. Alone among European producers, BASF built port facilities at Antwerp, but the rise in LPG prices meant that they never used them. European natural gas from the North Sea contains little ethane and propane, and only the gas from the northernmost fields provides sufficient C_2+ material to be worth cracking. The Mossmoran cracker and a second train at the BP Grangemouth cracker, both in Scotland, are thus the only dedicated gas cracking units in Western Europe (see note at the end of this chapter).

In addition, Europe is dependent on pyrolysis gasoline for about three-quarters of its benzene and toluene (Fig. 2.4), which gas cracking produces in only small amounts. The toluene is used largely for dealkylation and disproportionation to provide more benzene. Europe's situation is echoed in Japan, Taiwan, and South Korea, and is part of the economic structure of their chemical industries. Other Southeast Asian countries are already cracking gases, for example, Malaysia and Thailand, which has a gas cracker alongside two liquid crackers. As yet these have had little impact on the market. The key countries likely to crack gas in the future, however, are those of the Middle East—Iran, Kuwait, Abu Dhabi, and Qatar—all of whom are planning facilities in the next few years following the Saudi example. They will aim to export to Europe, while Canada will also crack gas for export to the United States, and Venezuela will export to Central and South America and the United States.

Ethylene from naphtha is economically marginal. Substantial overcapacity in the early 1990s and early 2000s kept prices depressed and forced the sale of surplus product on the spot market. Capacity utilization dropped from 94% in 1989 to 83% in 1993. A remarkable sequence of accidents and plant breakdowns in 1994 and early 1995 led to shortages and price rises, and capacity utilization rose to 93%. Prices fell again once repairs had been carried out and by 2002 utilization had dropped to 88%. Overcapacity seems endemic. Why and how, therefore, do producers based on usually less economic liquid feedstocks keep going? There are four main reasons.

First, many of the crackers in Europe and Japan as in the United States, are linked into integrated petrochemical complexes. Ethylene is more expensive to ship than to pump over the fence, hence many producers of ethylene derivatives will prefer to draw on their own cracker or a European pipeline to which they are connected rather than to pay for the shipping of ethylene in refrigerated tankers. Nonetheless, the European pipeline network is much shorter than that in the United States. With an effective pipeline network, fewer crackers are needed and, indeed, the United States has fewer crackers than Western Europe. In 1993, only 63% of European ethylene capacity was connected to a pipeline grid, in contrast to 94% in the United States.

Second, as the European plants are already built, their owners insist on operating them so long as cash costs are covered. Huge new capacity in Europe, planned in the 1980s, came on stream at the start of the 1990s. The plants already operating did not provide sufficient cash flow to justify fresh investment, but the new plants were built on a tide of what in retrospect appears to have been unjustified optimism. The BASF cracker, opened in 1994, was the last European cracker to have been built from scratch. The European industry association has tried to encourage reductions in capacity but has been largely unsuccessful. Indeed, there have been extensive expansions and debottlenecking exercises, which are relatively inexpensive, and these have kept capacity ahead of demand. Meanwhile, investment costs in developing countries are usually higher than in Europe.

Third, there is the question of tariffs (see note at the end of this chapter). These are being reduced in the developed world as a result of GATT (General Agreement on Trade and Tariffs) and WTO (World Trade Organization, which replaced GATT in 1995) negotiations, but they remain. Southeast Asia is permitted to protect indigenous manufacturers. In 1995, Chandra Asri started up a 550,000 tonne per year naphtha cracker in Indonesia, built there because polyethylene is heavily protected. The Southeast Asian chemical industry relies for its profitability on a local market allied to high tariffs together with exporting to neighboring China.

Fourth, the price differential between naphtha relative to gaseous feedstocks has been fluctuating. If the world ethylene market was swamped with material based on ethane, some naphtha-based crackers would have to close. There would then be a propylene shortage and prices would rise, making the naphtha-based route economic once more. Similarly the rise in US gas prices in the early 2000s has tilted the balance somewhat towards naphtha.

European producers have survived for the above reasons, but there is no doubt that they have suffered from the new producers around the world and from their misjudgment in building new capacity. ICI, Rhone-Poulenc, and Hoechst decided to leave the heavy chemicals sector. Western Europe's share of total international trade in ethylene derivatives dropped from 31% in 1980 to 13% in 1990, although there has been an improvement since then. Thus the chemical industries in developed countries are under pressure from those in developing countries. This has everything to do with availability and price of feedstocks, location of plant, and tariffs, and nothing to do with the availability of cheap labor, which makes up a tiny proportion of total costs (see note at the end of this chapter).

2.2.1.3 Mechanism of Cracking Catalytic cracking involves carbenium ion intermediates, but steam cracking, which is of greater concern to the chemical industry, is a free radical reaction involving the steps illustrated in Figure 2.6, which assumes that ethane is being cracked. In the initiation step (a) two methyl radicals form. These attack another molecule of ethane (b) to give methane plus an ethyl radical. Propagation proceeds as shown in (c) and (d). Thus far, only ethylene has been produced, and it is indeed the major product of ethane cracking. The termination reaction (e) produces *n*-butane by coupling, and this undergoes cracking to yield small amounts of olefins. Also, if ethylene reacts with an ethyl radical, C_4 olefins can be produced by disproportionation (g) and if it reacts with a methyl radical (h) propylene may result. Note that a corresponding amount of alkane is produced that can undergo further cracking.

When propane is cracked, as in Figure 2.6 (i–l) much more propylene is produced. The reason is that propane can be attacked by a hydrogen atom to yield an isopropyl radical (j), which can only convert to propylene. The initial hydrogen atom can come from propane scission (i), which produces a propyl radical. This is in fact a dominant reaction and explains why ethylene is always the major product as in (l). With higher molecular weight feeds, the long chains fragment readily (m), and the preferred reaction of the resulting free radicals is β-scission (n) to give ethylene and another free radical.

2.2.2 Catalytic Cracking

Catalytic cracking, as its name implies, fragments molecules over a catalyst. It also dehydrogenates some of them. Typical heavy naphtha and gas oil feedstocks give a mixture of products consisting mainly of isoalkanes suitable for gasoline together with *n*- and isoolefins and *n*-alkanes from C_3 upward. Little ethylene but significant amounts of propylene and C_4 monoolefins are produced. Although important to the gasoline industry, catalytic cracking is not a major route to petrochemicals, except to insure an ample supply of propylene and butenes for the United States. They are largely used for alkylate for gasoline (Section 2.2.5).

More propylene is produced by catalytic cracking in the United States than by steam cracking, but it occurs in a more dilute stream and cost is higher. Thus about 55% of refinery propylene is used for chemical production. For the preparation of isopropanol (Section 4.9.3), cumene (Section 4.5), and oligomers (Section 4.2), it is

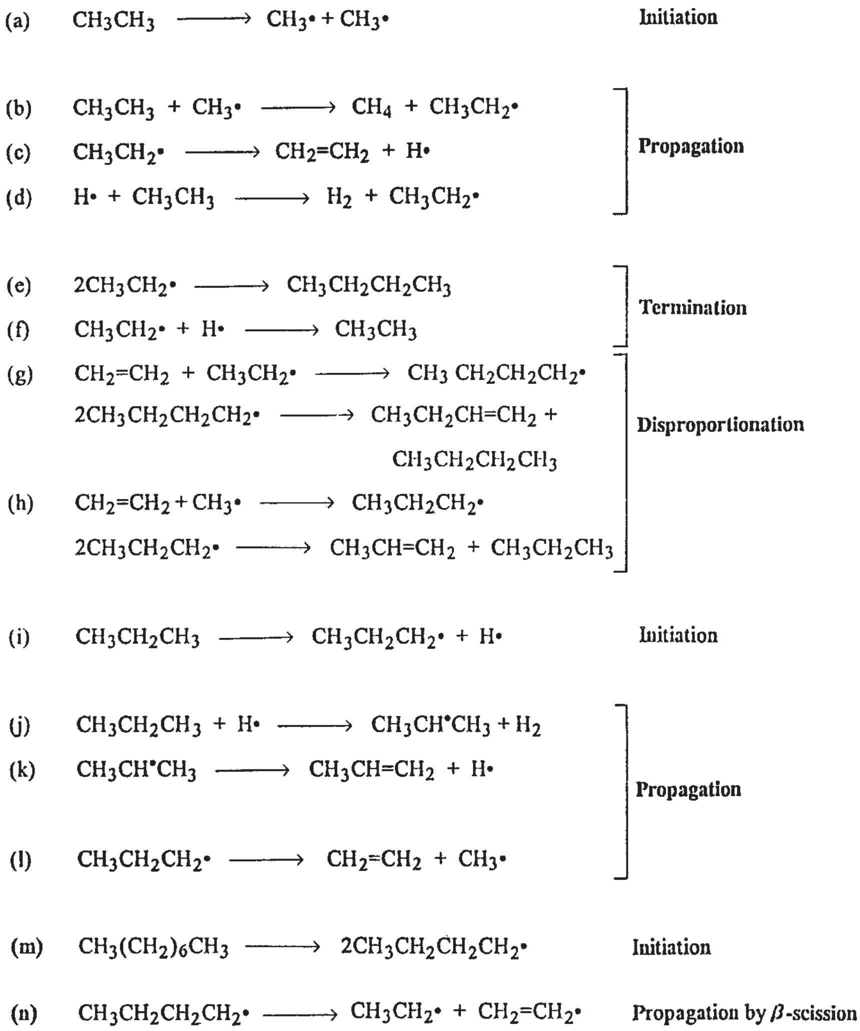


FIGURE 2.6 Mechanism of steam cracking.

possible to use refinery grade propylene without upgrading. Also there are legitimate uses for propylene from catalytic cracking in the refinery itself. As indicated above, the two largest are for alkylation (Section 2.2.5) and directly as fuel. In addition, it is mixed in the refinery with LPG and is also used for polymer gasoline (Section 2.2.4). For the C_4 fraction, alkylation with *n*-butenes and isobutene is a major refinery use. Another use is for direct blending of *n*-butane into gasoline, although legislation in the United States now requires that this be eliminated in the summer because volatile butane contributes to ozone layer destruction. A major use for refinery isobutene and isopentene is their reaction with methanol to produce methyl *tert*-butyl and, on a smaller scale, methyl *tert*-amyl ethers (Section 5.4.4) but this may well decline.

Catalytic cracking received impetus from World War II because military planes required high-octane gasoline. At that time, naturally occurring aluminosilicates, primarily amorphous montmorillonites, were used as catalysts. In the mid-1960s synthetic zeolites were introduced. These too are aluminosilicates but with a well-defined crystalline structure. The Y zeolites, such as a so-called faujasite with a ratio of silicon to aluminum of 1.5:3.0 and a composition of $Na_{56}(AlO_2)_{56}(SiO_2)_{136}$ are used (Section 16.9). Synthetic zeolites are characterized by the presence of microscopic pores of consistent diameter, and chemical reactions take place inside these pores. The sites within the zeolite that create reactive species include Brønsted sites, Lewis sites and even superacid sites. It is these that bring about the formation of carbocations, the intermediates that in catalytic cracking lead to the formation of the branched-chain compounds, prized because they have a high octane number.

The Y zeolites are modified with rare earths by an ion exchange process. These impart high thermal stability and additional acidity for promotion of chemical reactions. In the early 1990s, catalytic cracking catalysts were announced that increased the isobutene content of the product so that more was available for methyl *tert*-butyl ether production. It is now commonplace to add the zeolite ZSM-5 to the catalyst to increase propylene yields and inhibit tar formation.

Catalytic cracking is an excellent example of the important contribution catalysts can make to the improvement of selectivity and yield. In the cracking of gas oil, a conversion of 73% can be obtained with a synthetic zeolite as compared to 64% with a natural silica/alumina.

As indicated in Section 2.1, vacuum gas oil is a major feed for catalytic cracking as is atmospheric gas oil. Virtually any petroleum fraction can be cracked, but vacuum gas oil, derived from residual petroleum fractions, has few other uses. Catalytic cracking takes place at a temperature of about 500°C and at atmospheric pressure or slightly above. The reaction is carried out in a fluidized-bed reactor in which the finely divided catalyst is maintained in a fluid state by a stream of steam. Residence time is of the order of 1–3 seconds. The products must be rapidly quenched to prevent their decomposition. Coke deposits on the catalyst reducing its activity. In its fluidized state, the catalyst can be removed continuously from the reactor as though it were a liquid and is sent to another reactor at 630°C, where the coke is burned off in a stream of air. The regenerated catalyst is then recycled to the fluidized bed. A typical product mix from catalytic cracking is shown in Table 2.9.

The search for improved catalysts for catalytic cracking is a vigorous one. The objectives are obvious—to improve yields of branched-chain compounds and to decrease the yield of coke, residue, and olefins, except for those useful for alkylation. Zeolite-like materials such as aluminophosphates are reported to offer certain advantages as are zirconium phosphates. These are not true zeolites, because they have layered rather than crystalline structures, the sites for catalytic reaction being the space between the layers.

TABLE 2.9 Product Mix from Fluidized-Bed Catalytic Cracking of Gas Oil

Compound	Approximate Wt. %
Propylene	3.2
n-Butenes and isobutene (no butadiene)	5.8
Isobutane	3.3
Branched C_5+ compounds (gasoline or cat. cracker naphtha)	36.5
C_{10}+ compounds (gas oil)	15.0
Residue and coke	29.0
Ethylene, ethane, propane, *n*-butane, H_2, H_2S	7.2

Catalytic cracking is an ionic rather than a free radical reaction, but otherwise the mechanism, involving initiation, propagation, and termination, is formally similar to that in Figure 2.6. Why then do the products differ widely? The reason is that, under cracking conditions, free radicals rearrange and fragment at roughly comparable rates, whereas carbocations rearrange much more rapidly than they fragment, and hence rearrangement to branched-chain compounds is the dominant process. This relates to the relative stabilities of free radicals and carbocations. Tertiary free radicals are more stable than secondary radicals, which are more stable than primary, but the differences are quite small. In contrast, the differences between tertiary, secondary and primary carbocations are very large, and such ions have a much greater tendency to rearrange. In the later stages of cracking, furthermore, fragmentation with the expulsion of a small free radical is energetically unfavorable but not markedly so, whereas expulsion of a small unstable ion is energetically highly unfavorable. Thus chain transfer to give alkanes is a much more favorable reaction for small ions than fragmentation. Catalytic cracking therefore gives only alkanes with at least three carbon atoms.

2.2.3 Catalytic Reforming

Catalytic reforming, a process first commercialized in 1950 by Universal Oil Products, converts aliphatic or cycloaliphatic compounds to aromatics. It is carried out with naphtha (Fig. 2.3), the original intention being to raise the octane number of the gasoline fraction. It has also become the major source of aromatics (BTX) in the United States.

Catalytic reforming comprises three basic reactions: dehydrogenation, isomerization, and hydrogenolysis. Dehydrogenation is exemplified by the dehydrocyclization of a paraffin as shown in Figure 2.7 and by the dehydrogenation of an alicyclic compound to an aromatic one. Isomerization is demonstrated by the molecular

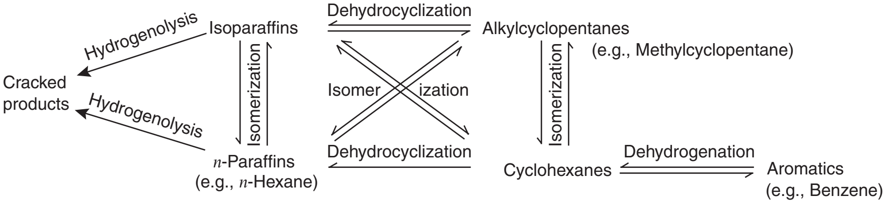


FIGURE 2.7 Catalytic reforming.

rearrangement of methylpentane to cyclohexane. Hydrogenolysis is a hydrocracking bond-breaking reaction that takes place during catalytic reforming, in which heavy molecules are cracked into lighter ones such as propane, isobutane, and *n*-butane.

Most important are the reactions of dehydrogenation and isomerization. For these a dual function catalyst is required, in this instance platinum or rhenium supported on alumina with a chloride adjuvant that helps to achieve and maintain uniform metal dispersion. The catalyst effects two reactions. In the first, compounds are isomerized (Fig. 2.7) and in the second the isomerized products are dehydrogenated. Cyclohexane is transformed to benzene and methylcyclohexane to toluene. Thus the dual function catalyst precludes an equilibrium state by causing the product of an initial reaction (isomerization) to undergo a second reaction (aromatization) as soon as it is formed. The isomerization step is rate determining. Because it is slower than the aromatization step, there is an opportunity for the undesirable hydrogenolysis or hydrocracking reaction to occur. This can be reduced but not eliminated by lower operating pressures. The reaction is carried out at 400–500°C and 25–35 bar. Gas and hydrogen yield is about 15%, the remaining 85% comprising aromatics and unreacted feed.

Catalytic reforming provides toluene and xylenes for unleaded gasoline. These are preferred to benzene because of their higher octane number and lower toxicity. Accordingly, higher molecular weight naphthas are reformed for unleaded gasoline, and a surplus of light naphtha, which yields benzene, started to develop in the mid-1980s. This fraction may be isomerized to branched-chain compounds, which have higher octane numbers and are less polluting than the aromatics. It may also be steam cracked to produce olefins. It cannot be reformed efficiently to benzene because yield is low owing to the facile formation of cracked products.

A typical catalytic reformate contains benzene, toluene, and xylenes in the ratios shown in Table 2.10. Toluene is the major component. The chemical industry, however, requires more benzene than toluene, so there is a mismatch. Little can be done to change the reforming yields since they depend on the composition of the feed. The problem is solved instead by dehydroalkylating toluene to benzene (Section 8.1).

The separation of the components of catalytic reformate is complicated. The gas stream from the reformer is cooled, and products containing five or more carbon atoms condense. Hydrogen and the C_1–C_4 alkanes are taken as a top product. The hydrogen

TABLE 2.10 Catalytic Reformate Production Ratio versus US Chemicals Demand

Reformate	Production Ratio (%)	Chemicals Demand (%)
Benzene	11	45
Toluene	55	22.7[a]
Xylenes	34	32.3

[a] The increase in this figure since the first edition is because of a greater amount of dehydroalkylation and disproportionation.

is usually used to dealkylate toluene (Section 8.1), and the alkanes are burned as fuel. The liquid product is treated with a solvent that preferentially dissolves aromatic compounds. Diethylene glycol/water, *N*-methylpyrrolidone/ethylene glycol, and sulfolane (Section 5.1.4) are used in various processes. Sulfolane appears to be preferred because it produces an aromatic stream with less than 1% non-aromatics. The aromatics appear in the extract, and the C_5 compounds are left in the raffinate. The solvent is distilled off and recycled, and the benzene, toluene, and mixed xylenes are separated on three fractional distillation columns, leaving a high boiling C_9+ aromatics fraction.

Separation of the mixed xylenes is difficult because their boiling points are close. The separation process is described in Section 9. As with benzene and toluene, the isomer distribution as shown in Table 2.11 does not match market requirements. Whereas 74% of *p*-xylene is required, nature provides about 19%. Similarly 5% of *m*-xylene is needed, whereas the C_8 fraction contains about 43%. The imbalance is corrected by isomerizing unwanted *o*- and *m*-xylenes to an equilibrium mixture (Section 9), which must again be separated. A zeolite catalyst, ZSM-5, is most often used. It converts ethylbenzene to benzene, although other catalysts isomerize it to the xylene isomers.

An interesting technology developed by Chevron is *in situ* hydrodealkylation during catalytic reforming, the key being a zeolite catalyst such as ZSM-5 doped with

TABLE 2.11 Equilibrium Composition of C_8 Fraction from Catalytic Reforming

Component	Wt.% in C_8 Fraction	Wt. % in Pyrolysis Gasoline	End Use Requirement (%)
Ethylbenzene	17–22	43–57	0
p-Xylene	17–22	10–12	74
m-Xylene	40–45	23–26	5
o-Xylene	16–20	16–19	21

platinum. The reaction is carried out at 540°C, the temperature necessary for the hydrodealkylation of both the toluene and the xylenes. Benzene and methane are the major products. The process was later modified to make benzene and toluene the major products. The zeolite decreases hydrogenolysis to lower alkanes and may even facilitate the conversion of those alkanes, once formed, to aromatics.

The mechanism of benzene formation in catalytic reforming differs from that of toluene and xylenes. The latter are obtained by dehydrogenation of alkylcyclohexanes, which in turn result from the dehydrogenation of the corresponding alkanes. Some benzene results similarly from the dehydrogenation of cyclohexane, but also catalytic reforming involves the dehydroisomerization of cyclopentanes, which combines dehydrogenation and carbenium ion reactions. A cyclopentyl cation forms, which undergoes ring opening and the subsequent formation of the cracked products shown in Figure 2.6.

2.2.4 Oligomerization

In the refinery, the oligomerization of olefins is termed polymerization because the term oligomer had not been coined when the process was invented. Low molecular weight olefins produced either by steam or catalytic cracking, but usually by the latter, are dimerized and trimerized to branched-chain olefins, suitable for gasoline. They may be used as such or, preferably, hydrogenated. These oligomers are called polymer gasoline or polygas. Their popularity waned with the advent of alkylation (Section 2.2.5), whose products do not require hydrogenation. The removal of lead from gasoline has prompted a renewed interest in polygas.

Oligomerization is carried out with propylene, 1- and 2-butenes, and isobutene, traditionally with a Friedel–Crafts catalyst such as phosphoric, sulfuric, or hydrofluoric acids. More recently, solid catalysts (zeolites or acid ion exchange resins) have been introduced. In the Friedel–Crafts reaction, a low energy content intermediate species forms readily. Because of its stability, it does not polymerize. Ethylene does not oligomerize in this way because its intermediate species, formed only with difficulty and requiring initiators or catalysts, is highly energetic and polymerizes readily. An advantage of the oligomerization process is that dilute olefinic streams (catalytic cracker off-gases) from the refinery can be used.

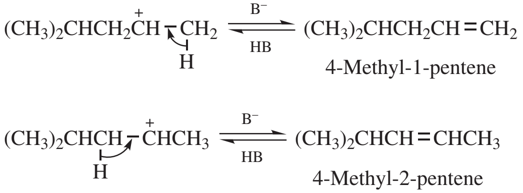
The reaction proceeds by a classical carbenium ion (carbocation) mechanism. In the presence of an acid catalyst (HB), the olefin takes on a proton from the catalyst to yield the carbenium ion.

$$CH_3CH{=}CH_2 + HB \longrightarrow CH_3CH^+CH_3 + B^-$$

This may add to another molecule of olefin in a propagation reaction to yield a new carbenium ion:

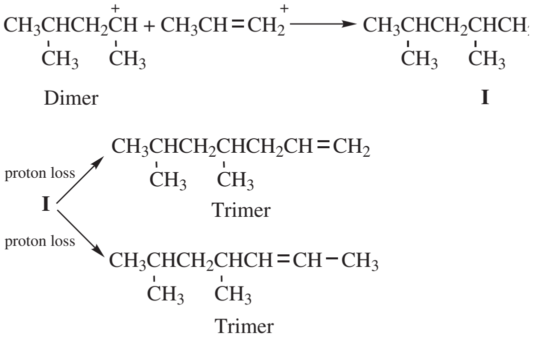
$$CH_3CH^+CH_3 + CH_3CH{=}CH_2 \longrightarrow CH_3CH(CH_3)CH_2CH^+CH_3$$

which can be stabilized or terminated by loss of a proton in one of two ways to form a dimer.

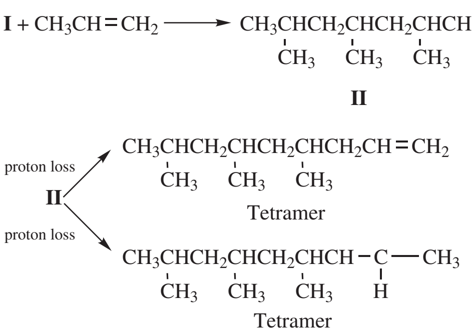


Repetition of the propagation reaction with another molecule of propylene yields isomeric trimers, and the trimeric carbenium ion may add a fourth molecule of propylene to give a mixture of tetramers. Even pentamers and hexamers may form.

Trimerization



Tetramerization

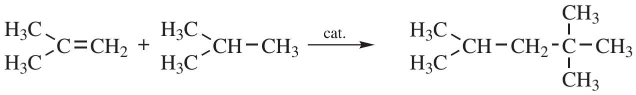


Because the intermediate species are relatively unreactive, polymers cannot be made in this way. Propylene could not be polymerized until the advent of Ziegler–Natta catalysis (Section 4.1).

The branched C_9 and C_{12} olefins have chemical uses that are discussed later (Section 4.2). Ziegler-type catalysts may be used for the oligomerization in processes such as “Dimersol” (Section 4.2).

2.2.5 Alkylation

Polymerization involving two or three molecules of olefins was replaced by the more sophisticated alkylation reaction between 1 mol each of an isoparaffin and an olefin. An olefin such as isobutene is used to alkylate a branched-chain hydrocarbon, usually isobutane, in the presence of Friedel–Crafts catalysts such as sulfuric acid or hydrogen fluoride:



Isobutene Isobutane 2,2,4-Trimethylpentane (isooctane)

2,3,4- and 2,3,3-trimethylpentanes are also formed. The interaction of propylene with isobutane yields a complex mixture including 38% 2,3-dimethylpentane and 19% 2,4-dimethylpentane. In addition, 25% propane results. The remainder is a mixture of branched-chain hydrocarbons with eight carbon atoms. Since the carbenium ion intermediate attacks tertiary carbon atoms, the products are highly branched and have high octane numbers.

The octane number of a fuel is defined in terms of its knocking characteristics relative to *n*-heptane and isooctane (2,2,4-trimethylpentane), which have been arbitrarily assigned octane numbers of 0 and 100, respectively. The octane number of an unknown fuel is the volume percent of isooctane in a blend with *n*-heptane that has the same knocking characteristics as the unknown fuel in a standard engine. Three kinds of octane numbers are recognized. The first is Research Octane Number (RON), which is the octane number measured under relatively mild test conditions. The Motor Octane number (MON) is determined at higher engine speeds and temperature. A third octane number, RON 100°C, is the RON of the fraction of the gasoline distilling below 100°C. This fraction plays a special role in controlling antiknock performance during acceleration.

The olefins for alkylation, as for oligomerization, come primarily from the off-gases from catalytic cracking. The isobutane is produced during catalytic cracking as well as in catalytic reforming. It also occurs in the gas fraction from petroleum distillation, and on-purpose isobutane is made by the isomerization of *n*-butane (Section 2.2.8). Hydrogen fluoride is the preferred catalyst in modern refineries because the process can operate in the liquid phase at temperatures in the range of 50°C. With sulfuric acid, lower temperatures of 0–10°C are required to prevent oxidation of the olefin. Solid acid catalysts, with their nonpolluting features, are being vigorously explored. These not only solve the ecological problems associated with liquid acid catalysts but also require less capital investment, because disposal of spent catalyst is simpler and less catalyst-handling equipment is needed.

2.2.6 Hydrotreating and Coking

Hydrotreating is a term applied to several refinery processes intended to remove impurities from petroleum and/or to reduce the viscosity of very viscous oils or "bottom of the barrel" fractions. Hydrotreating will become increasingly important when heavier more impurity-laden oils enter the refinery, as they are certain to do since the world's reserves contain a high proportion of heavy oil. Light crude oils have a higher hydrogen/carbon ratio than heavy oils. Hydrotreating adds hydrogen to heavy oils so that they can be handled in a refinery like the lighter, more desirable materials. Hydrocracking is today's best established technology for adding hydrogen to heavy fuels, particularly heavy gas oils. It can also be applied to the so-called resid fraction, the residue left when practically everything else in the petroleum barrel is removed.

Hydrocracking is a variant of hydrotreating and also of catalytic cracking. A different catalyst is used, and the cracking reactions take place in an environment of hydrogen at 60–100 bar. Because hydrogen is present, the catalyst does not "coke" as it does in catalytic cracking; a wider range of feedstocks can be tolerated (e.g., heavy distillate can be used); and objectionable sulfur, nitrogen, and oxygen compounds are converted to hydrogen sulfide, ammonia, and water. The products are paraffins, not olefins, and are fairly low in aromatics and very low in sulfur. They are used for low-sulfur jet fuels and diesel fuels, where lack of aromatics and absence of sulfur are desirable.

In addition to hydrocracking, there are several other forms of hydrotreating. The mildest is used to remove sulfur as hydrogen sulfide from gas oil and naphtha with a catalyst comprising cobalt–molybdenum or nickel/molybdenum on alumina at about 300°C and 20–25 bar. Hydrotreating of vacuum gas oil (Section 2.1) is carried out for the same reason but requires a temperature of 350–400°C and a pressure of 35–55 bar. If the feed material is resid, the required temperature may be 450°C and the pressure may vary from 60–120 bar. Hydrotreating is also used for the refining of lubricating oils, primarily to remove waxes by cracking. This is competitive with extraction processes.

Several newer hydrotreating processes were under development in the 1990s but interest seems to have diminished. One, known as Dynacracking, developed by the Hydrocarbon Research Institute, combines hydrocracking with the conversion of a portion of the feed to synthesis gas, that is, carbon monoxide and hydrogen (Section 10.4). In this way, hydrogen is provided for the process. The so-called Aurabon process, developed by UOP, makes use of metals (e.g., vanadium) and sulfur present in the residual oil as catalysts. It uses less hydrogen than standard hydrocracking and removes metals efficiently, which could be a significant advantage in that a deterrent to the use of hydrotreating is the high cost of hydrogen. It is produced in most refineries but in dilute streams and recovery costs are high. New membrane processes for removing hydrogen from gaseous streams may provide a solution to this problem (see note at the end of this chapter). The Clean Air Act has caused a decrease in hydrogen availability in the refinery because it requires a drastic cut in the aromatic content of gasoline. A major source of hydrogen is the catalytic reforming reaction (Section 2.2.3) used to make aromatics. Refineries are supplementing their hydrogen needs by contracting with gas producers to build on-purpose plants on site.

Coking is the reverse of hydrotreating, for in this process the hydrogen is rejected. Thus heavy fractions are heated to produce volatiles that are used in the refinery. The coproduct, which is impure carbon, is known as coke. If it has low sulfur and metal content, it can be used to make anodes for aluminum manufacture. Lower quality cokes can be used as fuel. Coke can also be gasified to carbon monoxide and hydrogen but seldom is (Section 10.4).

Alternate processing involves the extraction of residual oil with light solvents such as propane, butane, or pentane to remove asphalts and to provide a higher grade residual oil for hydrocracking. The asphalts can be used in paving, roofing, as fuels, and for conversion to synthesis gas.

2.2.7 Dehydrogenation

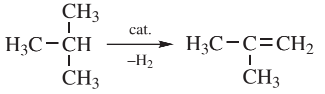
If cracking and reforming are considered dehydrogenations, then dehydrogenation is the most important reaction carried out industrially. In refinery practice, however, the term is restricted to specialized dehydrogenations such as the conversion of ethylbenzene to styrene (Section 3.9) or butenes to butadiene (Section 5).

Butenes have been dehydrogenated to butadiene, particularly in the United States, where ethane and propane are steam-cracked to produce primarily ethylene and propylene and lesser amounts of the C_4 olefins (Sections 2.1, 2.3.2). Most widely used is the Houdry process. The dehydrogenation process, however, had to compete with imported butadiene and, in recent years, the latter has been more economical.

Propane dehydrogenation processes have been available for several decades but have been of little interest because of the large amount of cheap propylene produced by catalytic cracking (Section 2.2.3) in the United States. The possibility of a propylene shortage (Section 2.3.2) and improvements in catalysts have motivated their reexamination. The chemistry is simple, involving catalytic abstraction of hydrogen from propane to give propylene. The major competing reaction is cracking of propane to ethylene and methane which, in turn leads, to hydrogenation of the ethylene to form ethane. Because of thermodynamic limitations the process is operated above 600°C in order to achieve acceptable conversions per pass, but above 700°C cracking is the dominant reaction. The major process conditions are determined by thermodynamic limitations, reaction kinetics, and economics of the conversion–selectivity relationship.

Propane dehydrogenation process technology is offered by several licensors including UOP, ABB Lummus, Linde/BASF, Snamprogetti/Yarsintez, and Krupp Uhde. The processes vary among the licensors in terms of reactor design, pressure, temperature, heating method, catalysts, and catalyst regeneration techniques. Table 4.2 shows all these parameters by licensor. The Lummus process is a variant of the Houdry process (see above). The first propane dehydrogenation plant was built in Thailand. In the early 2000s, there were three propane dehydro plants in Asia, one in Belgium, one in Mexico, and one under construction in Spain.

A recent use for dehydrogenation was to convert isobutane to isobutene for further conversion to methyl *tert*-butyl ether (Section 5.4.4).



$$H_3C-\underset{CH_3}{\overset{CH_3}{CH}} \xrightarrow[-H_2]{\text{cat.}} H_3C-\underset{CH_3}{C}=CH_2$$

Isobutane Isobutene

The dehydrogenation goes readily because a labile tertiary hydrogen is involved. Without this reaction, it would have been virtually impossible to produce enough methyl *tert*-butyl ether for the United States' unleaded gasoline needs.

Several companies have studied the dehydrogenation of ethane to ethylene, which goes with difficulty. The Union Carbide process makes use of an oxidative dehydrogenation at a considerably lower temperature than steam cracking (325°C versus 800°C) at a pressure of about 20 bar. A typical catalyst comprises a combination of molybdenum, vanadium, niobium, antimony, and calcium. It is specific for the oxidative dehydrogenation of ethane, higher hydrocarbons being transformed into carbon dioxide and water. A disadvantage is that acetic acid is a major coproduct. Although this provides an effective way to make acetic acid without investment in equipment to produce synthesis gas (Section 10.4) the process must be run in such a way that the ethylene and acetic acid are produced in quantities that the market can absorb. Since over 10 times as much ethylene (55.4 billion lb in 2000) is used in the United States as acetic acid (4.7 billion lb in 2000), there would be an embarrassing surplus of the latter, although one or two plants could be accommodated.

2.2.8 Isomerization

Isomerization is used to convert straight- to branched-chain compounds. The term may be applied to cracking and reforming reactions but usually these are excluded. In petroleum refining *n*-butane is isomerized to isobutane for alkylation to supplement isobutane from catalytic cracking and petroleum distillation. Isomerization is also used to increase the octane rating of C_5/C_6 alkanes and to convert a mixture of *m*- and *o*-xylenes and ethylbenzene from which the *p*-xylene has been extracted into a random mixture from which more *p*-xylene can be obtained (Section 2.2.3).

The isomerization of C_5/C_6 alkanes for the gasoline pool is of interest. These are available since light naphtha is now used to a lesser extent in catalytic reforming because of the desire to eliminate benzene from gasoline. Although the C_5/C_6 fraction may be isomerized as such, it has been usual to remove the C_5 fraction by distillation. The *n*-pentane and *n*-hexane are isomerized to isopentane and isohexane over a fixed-bed platinum catalyst in a hydrogen atmosphere, although hydrogen consumption is low.

The isomerization of *n*-butane to isobutane is effected by an aluminum chloride catalyst in either the liquid or gas phase at temperatures of around 100°C. Isobutane can be readily dehydrogenated to isobutene and the importance of this reaction has already been described (Section 2.2.7). The dehydrogenation is capital intensive and units are built in areas where infrastructure exists or where low-cost raw materials are available, for example, the US Gulf Coast, Saudi Arabia, Canada, and Malaysia.

2.2.9 Metathesis

Metathesis is said to be one of the most important organic chemical reactions discovered since World War II. It originated as a refinery reaction at Phillips

Petroleum Company in 1964. This technology, the interchange of olefins, while amazing from a theoretical point of view, initially found only niche applications. The main objective was to convert cheap propylene into more valuable ethylene and butene:

$$\underset{\text{Propylene}}{2CH_2{=}CHCH_3} \longrightarrow \underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{2-Butene}}{CH_3CH{=}CHCH_3}$$

The original metathesis reaction was used only in Canada by Shawinigan, the process having been instituted commercially only six and a half years after its discovery. This plant is no longer operating because of change in feedstock availability.

The reaction is reversible, however, and the potential propylene shortage (Section 2.3.2) has motivated a reaction with the same catalysts in which 2-butene and ethylene interchange to yield propylene. The shift of equilibrium to the left is achieved by recycling ethylene to give a high ethylene/butene ratio at the reactor inlet. In this way, it is possible to obtain nearly 100% conversion of butene. The reaction can be carried out with 1-butene as well as *cis*- or *trans*-2-butene provided that another catalyst is added to promote the shift of the double bond from the less thermodynamically stable 1 position to the more stable 2 position.

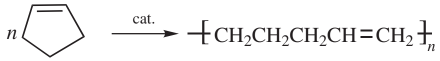
In 1984, Lyondell built a one billion lb/year unit to produce propylene by this reaction, which had been developed by its sister company ARCO. Thus a major use for metathesis developed that was exactly opposite from the use that initially motivated the reaction's invention. Originally, Lyondell even made the 2-butene by dimerization of ethylene, a process also pioneered by Phillips, so that the propylene product was formed entirely from ethylene. Nickel catalysts have been widely studied for this dimerization, and one described in a Phillips' patent comprises nickel oxide supported on silica and alumina. A more sophisticated catalyst later described by Phillips is tri-*n*-butylphosphine nickel dichloride mixed with ethyl aluminum dichloride. With this catalyst the reaction goes at 33°C and 12 bar to give an ethylene conversion of 93%. 2-Butene is also available from the C_4 fraction from raffinate-2 from steam or catalytic cracking (Section 5) and Lyondell switched to it, so that two-thirds of the propylene molecule was then derived from the cheap 2-butene.

In the late 1990s, ABB Lummus bought the licensing rights to the Phillips metathesis technology. It uses tungsten oxide on silica as the catalyst and operates at a temperature of 300–375°C in a fixed-bed reactor. BASF and Fina have jointly built a new world scale steam cracker (2 billion lb/year of ethylene at Port Arthur, TX, and are planning to incorporate a metathesis unit to convert ethylene and butenes to propylene (Section 1.3.4). As the economics of the conversion will vary with market prices for the feedstocks as well as the product propylene, BASF/Fina will have the flexibility to turn the unit on or off depending on market conditions. When run with it on, the new cracker will have the capability of producing 1.6 billion lb/year—almost equal amounts—of both ethylene and propylene. The residual butadiene/isobutene will make this the world's largest butadiene plant.

IFP has developed a metathesis process that uses a rhenium on alumina catalyst operating at a much lower temperature of 25–50°C in a moving bed reactor. Homogeneous catalysts can also be used, comprising complexes of molybdenum or tungsten with alkyl aluminum halides. The homogeneous reaction goes at room temperature as opposed to the high temperature required by heterogeneous catalysts, demonstrating an advantage of homogeneous reactions, but the system is apparently not used industrially. Common to all metathesis processes is the need to purify carefully the feeds of any polar impurities and dienes as these materials will poison the catalyst.

2.2.9.1 Metathesis Outside the Refinery Metathesis reactions can be carried out with most olefins except those with conjugated double bonds or with functional groups near to the double bond. It has been used for the synthesis of various chemicals outside the refinery. The SHOP process is described in Section 3.2.4, but the other syntheses are described here because the original metathesis process was intended for refinery use.

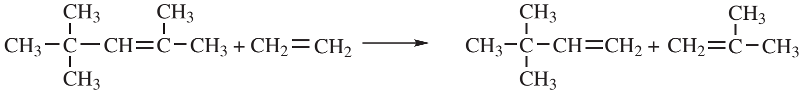
When applied to cyclic compounds, metathesis yields polymers. Thus cyclopentene and cyclooctene undergo metathesis to yield specialty polymers. The one from cyclopentene is called a pentenomer.



Cyclopentene   Pentenomer

If there are nonconjugated double bonds in a cyclic structure, a cross-linked polymer forms. Hercules took advantage of this in the development of a reaction injection molding (RIM) compound comprising dicyclopentadiene and a metathesis catalyst that polymerizes it to a cross-linked structure (Section 6.2). Hercules has subsequently sold the business.

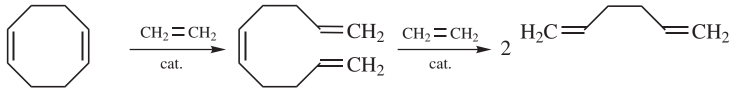
Ethylene will undergo metathesis with a mixture of diisobutene isomers. The isomer that undergoes metathesis is 2,4,4-trimethyl-2-pentene, whose internal double bond reacts most readily. A catalyst is added to isomerize other diisobutenes with terminal double bonds to the desired pentene. 2,2-Dimethyl-1-butene results together with isobutene. The branched-chain product, known also as neohexene, is a precursor for the preparation of a synthetic musk fragrance.



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH=\overset{\displaystyle CH_3}{C}-CH_3+CH_2=CH_2 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-CH=CH_2+CH_2=\overset{\displaystyle CH_3}{C}-CH_3$$

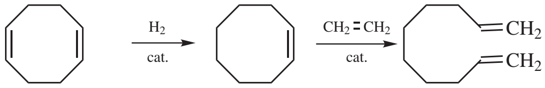
2,4,4-Trimethyl-2-pentene   Neohexene (2,2-dimethyl-1-butene)   Isobutene

Shell has announced the development of a metathesis route to α,ω-dienes. One such compound, 1,5-hexadiene, results from the reaction of ethylene with 1,5-cyclooctadiene, which in turn comes from the dimerization of butadiene (Section 5.1.3.2).



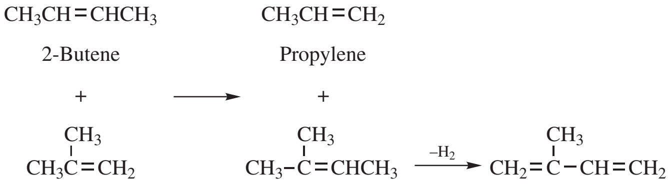
1,5-Cyclooctadiene 1,5,9-Decatriene 1,5-Hexadiene

A related product is 1,9-decadiene made by reacting ethylene with cyclooctene, which is made by selective hydrogenation of 1,5-cyclooctadiene.



1,5-Cyclooctadiene Cyclooctene 1,9-Decadiene

An isoprene precursor results from the metathesis of isobutene and 2-butene (Section 6.1).



$$\begin{array}{ccc} CH_3CH{=}CHCH_3 & & CH_3CH{=}CH_2 \\ \text{2-Butene} & & \text{Propylene} \\ + & \longrightarrow & + \\ CH_3\overset{CH_3}{\overset{|}{C}}{=}CH_2 & & CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CHCH_3 \xrightarrow{-H_2} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \\ \text{Isobutene} & & \text{2-Methyl-2-butene} \qquad\qquad \text{Isoprene} \end{array}$$

None of these three reactions was commercialized.

2.2.9.2 Mechanism of Metathesis

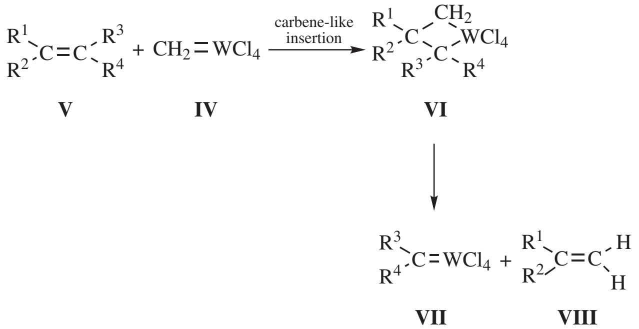
The mechanism of metathesis is intriguing because it differs from other catalytic transformations of olefins. It can be best explained if one assumes a homogeneous catalyst such as tungsten hexachloride in combination with a metal alkyl such as methyllithium. As in all such reactions, a metal complex **III** forms first.

$$WCl_6 + CH_3Li \longrightarrow \underset{\textbf{III}}{CH_3WCl_5} + LiCl$$

This complex reacts with more methyllithium to form a compound with a carbon–tungsten double bond (**IV**). This is a true double bond but it may also be considered as an encumbered carbene, thus reacting like a stabilized carbene.

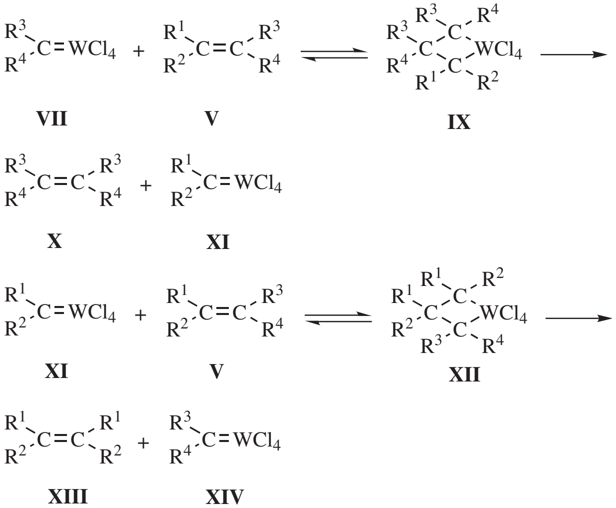
$$CH_3WCl_5 + CH_3Li \longrightarrow \underset{\textbf{IV}}{CH_2{=}WCl_4} + CH_4 + LiCl$$

This catalyst brings about the rearrangement of compound (**V**), an olefin with four different R groups by the following propagation steps. The reaction of (**IV**) and (**V**) provides (**VI**), which in turn dissociates to give (**VII**) and (**VIII**).



V **IV** **VI** **VII** **VIII**

Compound (**VII**), which contains alkyl groups R^3 and R^4, reacts with more of the initial olefin to give (**IX**). This compound in turn dissociates to give (**X**) and (**XI**). Compound (**X**) is considered one of the major products of the metathesis since it contains only two of the four groups present in compound (**V**). The other two are resident in the catalyst complex (**XI**). Accordingly, (**XI**) reacts with the initial olefin (**V**) to give (**XII**), which can dissociate just as (**IX**) did to give (**XIII**) and (**XIV**). Compound (**XIII**), the counterpart of (**VIII**), contains the other two groups present in the initial olefin (**V**). The catalyst complex (**XIV**) can then continue the reaction just as the complex (**XI**) did.



VII **V** **IX** **X** **XI** **XI** **V** **XII** **XIII** **XIV**

The dissociation reactions are mechanistically the inverse of the carbene-like insertion reactions. These reactions are also reversible, but such reversions have no observable consequences. Termination steps are obscure and presumably are brought about by impurities and possibly by dimerization of the catalyst.

2.3 THE REFINERY—A PERSPECTIVE

The petroleum refinery provides feedstocks for the petrochemical industry throughout the world. It underwent basic changes in the 1980s, which it is important for a student of industrial organic chemistry to understand. These changes result from three factors:

- The prediction of a petroleum and natural gas shortage in the 1970s and the reversal of that prediction in the 1980s when crude oil prices, which rose precipitously in the 1980s, collapsed.
- The entry of new players into the petroleum refining and petrochemical arena, most important of which are Western Canada, Saudi Arabia, and Korea, but include many countries in the Middle East and Southeast Asia.
- The advent of unleaded gasoline and related environmental pressures.

2.3.1 The Function of the Refinery and the Potential Petroleum Shortage

A major objective of the US refinery has traditionally been to produce high-octane gasoline. To be sure, the fractions heavier than naphtha (Fig. 2.1) were important for aviation, diesel, boiler and heating fuels, lubricants, and paving materials, but production was driven by the demand for gasoline. Because of need for high octane number, catalytic cracking was developed and always played a far more important role in American refineries than it did in refineries in Europe and Japan that were geared to production of fuel oil, since much less gasoline was needed and cheap coal was not available (Section 2).

The refinery reactions (Sections 2.2.3–2.2.5) of oligomerization, alkylation, and catalytic reforming were all devised to raise octane number as were lead tetraalkyls. The many catalytic crackers in the United States produced large quantities of C_3 and C_4 olefins, and it was these that provided feed for the oligomerization and alkylation reactions. They also proved useful in chemical reactions for cumene (Section 4.5) and isopropanol production (Section 4.9.3). Today they are purified to polymer grade propylene in so-called propane splitters that separate propylene from the major impurity, propane.

Catalytic crackers give C_3 and C_4 olefins in more dilute form than do steam crackers (Section 2.2.1). The dilute streams, which contain propane, are less economic for use by the chemical industry except for production of cumene and isopropanol. In any case, the refinery had first call on the olefins for polymer gasoline (Section 2.2.4) and alkylation (Section 2.2.5) and also for adding to LPG. The remainder could be upgraded for the chemical industry, despite the higher cost. The supply is still large because of the many catalytic crackers. In 2002, the refinery provided 52% of the chemical industry's propylene in the United States.

In Europe, the situation is reversed. Less refinery propylene is produced in catalytic crackers (because there are fewer of them) and more is produced from steam cracking (because much more naphtha is cracked). Catalytic cracking in 2001 provided about 20% of the European chemical industry's 13.4 million tonnes of propylene and this accounted for 80% of the refinery propylene available. About 27% of west European propylene production came from refinery and dehydrogenation sources. Because of Europe's longstanding propylene shortage, an effort was made to obtain more propylene from the refinery, but this amounted to less than 1.4 million tonnes in 2001. The deficit in supply was made up by imports, which amounted to about 0.33 million tonnes.

The rise in gasoline prices in the 1970s motivated the development of smaller, lighter cars with lower gasoline consumption. Also diesel fuel became popular. With lower gasoline production, there was lower production of the middle distillate (gas oil fraction, Fig. 2.2) from which diesel fuel comes. Thus the cost of diesel fuel also increased and, in Europe, Japan, and Southeast Asia, there were threatened shortages.

Shell was motivated to develop a process based on Fischer–Tropsch technology to make diesel fuel, lubricants and wax for candles (Section 12.2) and built a plant in Malaysia.

2.3.2 Unleaded Gasoline and the Clean Air Act

The advent of unleaded gasoline provided a "dislocation" (Section 1.3.9), but the refineries in the United States accommodated to it well. Some oligomerization units (Section 2.2.4) were reactivated to obtain branched-chain, high-octane number olefins. These had been shut down in the 1960s in favor of alkylation (Section 2.2.5), which unleaded gasoline caused to become much more important. Catalytic cracking catalysts were improved so that higher octane products resulted. Refiners raised the octane number of gasoline by including higher amounts of aromatics such as toluene and xylenes made by catalytic reforming (Section 2.3).

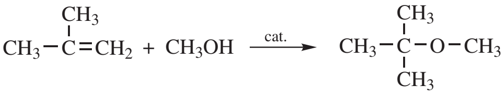
In 1991, a much greater dislocation was provided by the Clean Air Act. It became necessary to reduce benzene content of gasoline from about 3% to 1%. In nine areas in the United States, where pollution exceeded levels specified by the Environmental Protection Agency, aromatics (i.e., toluene and xylenes) content had to be reduced from 36 to 25% by 1995. Ironically this occurred after some refineries had increased their capacity for manufacturing aromatics to maintain octane number.

There are at least three scenarios for achieving the one percent benzene level. Refineries in the early 1990s stripped naphtha to remove the low-boiling C_5–C_6 fraction, to minimize benzene formation in catalytic reforming. The fraction in turn became available for isomerization to branched-chain, higher octane number components (Section 2.2.8) and for cracking to olefins. Carried to the extreme, a benzene shortage for the chemical industry might result. Even so some benzene will always form in catalytic reforming because of *in situ* hydrodealkylation (Section 8.1) of toluene and xylenes.

A second possibility is to remove the benzene by distillation. This would add about 150,000 tonnes of benzene to the current US supply, which would not be disruptive. On the other hand, the decision to extract benzene from gasoline in Western Europe could increase supply by 450,000 tonnes.

A third scenario is for the refinery to produce a reformate with as little benzene as possible for gasoline, and another reformate containing benzene for the chemical industry. Although this seems logical, it might be disruptive for the refinery, which is programmed to carry out continuous reactions without interruption. Nonetheless, the approach is being adopted.

The next problem was how to compensate for the octane number lost by removal of lead compounds and the drastic reduction of aromatics content. The answer was found in oxygenates, compounds that are primarily the province of the chemical industry, and the Clean Air Act specified that the reformulated gasoline had to contain compounds that contributed 2.7% oxygen. The best oxygenate appeared to be MTBE made by reacting isobutene with methanol over an acid catalyst, usually an acidic ion exchange resin.



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + CH_3OH \xrightarrow{\text{cat.}} CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-O-CH_3$$

Isobutene Methanol Methyl *tert*-butyl ether

MTBE content, to contribute this amount of oxygen, must be about 17%, although, at this level, it contributes more octane number than most US gasoline requires.

The sources of isobutene at the time were raffinate-1 from the refinery (Fig. 5.2), off gases from catalytic cracking and the byproduct from propylene oxide production, where it comes from the facile dehydration of the *tert*-butanol coproduct (Section 4.7). There was not enough isobutene in the world from these sources to make the amount of MTBE required, and a further process for its production from *n*-butane was developed (Section 2.2.8). It suddenly became an important chemical, whereas in the past it had always been a cheap byproduct.

From 1995, the United States imported about 9 billion lb/year of MTBE and probably one-half the methanol needed to make MTBE domestically. By 2000, the market had risen to 29.6 billion lb (Section 1.3.9) and production to 20.05 billion lb. West European production was about 6.6 billion lb and world production in 1998 was 40 million lb. The isobutene for United States MTBE production came mainly from *n*-butane via isobutane (53.9%) with smaller amounts from *tert*-butanol dehydration (24.3%), catalytic cracking (12.4%), and steam cracking (9.3%).

It was then realized that MTBE was contaminating groundwater. The point is that most gas stations store their gasoline in underground tanks and, over the years, these deteriorate. Strict regulations exist in the United States and Europe to prevent this, but they are inadequately enforced. Slight damage to tanks is unimportant, because gasoline is hydrophobic, and therefore does not leak readily into damp subsoil nor diffuse through it rapidly. MTBE, however, is sparingly soluble (4.8 g/100 g water) and both leaks and diffuses. Even in tiny concentrations, it has a strong terpene-like odor and gives a bitter taste to water. Like many branched-chain materials, it biodegrades slowly. In the United States, it may well be outlawed in favor of the alternative oxygenate, ethanol. California arbitrarily decided to phase out MTBE by 2002 and other states indicated they would follow suit., but phase out has been delayed. The automobile companies say they have modified their systems and oxygenates are no longer necessary, but the issue is clouded by political factors.

Usage of MTBE in the rest of the world, especially Western Europe, is said still to be increasing. The attitude of European industry, where the ethanol lobby is relatively weak, is that the MTBE problems are not inherent in the product itself, and that even gasoline leakage should be avoided. Europe has a high population density and relatively small watercourses, so the extent of the problem may force retail gasoline outlets to upgrade their sites.

In contrast to Europe, fermentation ethanol has become an important product in the United States because of government subsidies, and it is used in American gasoline despite high volatility. Further replacement of MTBE by fermentation ethanol would be a huge boost to the ethanol producers. If use of ethanol becomes mandatory, there would be the incongruous situation of the Government subsidizing a mandated product.

Ethanol is also used as a motor fuel as such and in combination with hydrocarbon fuels in Brazil. There, however, the alcohol is made by the fermentation of juice from sugar cane, which has a much higher carbohydrate content that does the corn that yields the starch used as a raw material in the United States. Also, the sugar cane juice is obtained simply by crushing the cane and is thus cheap, whereas starch isolation is a relatively expensive and energy-intensive process. Even in Brazil, however, its use is not economic, even though the energy for distilling the alcohol comes partly from burning bagasse, the sugar cane residue.

The use of fermentation alcohol represents a trend back to renewable natural products for commodity chemicals. All the same, it is difficult to think of ethanol as a renewable resource if it generates less energy as a motor fuel than was spent in its production and purification (Section 14.5.5). The deficit, of course, comes from petroleum and natural gas. The possibility of retrofitting methanol plants so that they will produce mixtures of higher alcohols has also been studied but does not appear economical. Ethyl *tert*-butyl ether is acceptable in unleaded gasoline and results from the interaction of ethanol and isopentene. It has the advantage over ethanol of lower volatility.

Methanol has been studied as a neat automotive fuel and as a component in petroleum-based gasoline. Because it separates out in the presence of a small amount of moisture, gasoline containing it must include a cosolvent alcohol. *tert*-Butanol has been used with methanol in a proprietary product known as "Oxinol." It is not, however, as effective as MTBE. Methanol and dimethyl ether derived from it are of particular interest for replacing diesel fuel in trucks and buses. It is available cheaply from many parts of the world where natural gas is in surplus, and huge excesses were in prospect in the early 2000s because of the construction of giant plants. The banning of MTBE would set free further large tonnages.

The final alcohol that has been used in gasoline is isopropanol, which is also an acceptable oxygenate and can be made from refinery propylene. It was marketed in the United Kingdom after World War II under the name "Cleveland Discol."

Still another part of the dislocation due to the Clean Air Act was the decreased supply of hydrogen that occurred in the already hydrogen-deficient refinery when catalytic reforming was drastically reduced because aromatics content was decreased. On-purpose hydrogen had to be manufactured.

2.4 SEPARATION OF NATURAL GAS

In addition to methane, most American natural gases contain recoverable amounts of ethane, propane, butane, and higher alkanes. The latter are called condensate. These are extracted as feedstock for steam crackers. At the wellhead, the gas is at a high pressure (30–100 bar), and propane and higher alkanes may be absorbed in a high-boiling oil at ambient temperature and subsequently purified by low-temperature fractional distillation. Ethane may be absorbed similarly at −50°C. Hydrogen sulfide and carbon dioxide are scrubbed out with aqueous mono- or diethanolamine (Section 3.10.6.4), and water removed with hygroscopic diethylene glycol (Section 3.11.6.1).

Methane is the major component of natural gas and may be "steam-reformed" (Section 10.4) to synthesis gas. Even when most C_2+ compounds are removed, some ethane is retained in natural gas to raise its Btu content to the value demanded for heating gas.

Thus natural gas provides the chemical industry with methane primarily for conversion to synthesis gas (Section 10), ethane and propane for steam cracking to olefins, and butane, which is oxidized to maleic anhydride (Section 11.1.3) and isomerized to isobutane (Section 2.2.8).

NOTES AND REFERENCES

Chemicals from natural gas and petroleum occupy much space in the general books on the chemical industry referred to in Section 0.4.2 and we shall not repeat their titles here. The world oil industry, although not a theme of this book, is of importance to anyone concerned with petrochemicals. An old book on the chemistry of petroleum, which has never really been superseded, is B. T. Brooks, C. T. Boord, S. S. Kurtz, and L. Schmerling, *The Chemistry of the Petroleum Hydrocarbons*, 3 Vols., Reinhold, New York, 1955. A somewhat different treatment is given in A. A. Petrov, *Petroleum Hydrocarbons: Composition, Structure, Ways of Formation of Various Petroleum Hydrocarbons*, Springer, Berlin, 1987.

The best introduction to the oil industry is *Our Industry—Petroleum*, 5th ed., British Petroleum, London, 1970. Two nontechnical books for general reading are A. Sampson, *The Seven Sisters*, Hodder and Stoughton, London, 1975, which recounts the history of the seven great oil companies, and C. Tugendhat and A. Hamilton, *Oil—The Biggest Industry*, 2nd ed., Eyre Methuen, London, 1975. Those looking for a vivid and entertaining history of the oil industry should read *The Prize*, D. Yergin, Simon and Schuster, London, 1991.

Statistics on world oil production and consumption are published annually in the *BP Amoco Statistical Review of World Energy*, BP Amoco, London, coplanca@bp.com, a well presented publication either free or at a nominal price, also available on the Internet at www.bpamoco.com/worldenergy. Figure 2.1 in particular was derived from this source. The Shell Petroleum Company also publishes a useful *Information Handbook*, and a *Chemicals Information Handbook*.

The details of gasoline formulation are described in E. G. Hancock, *The Technology of Gasoline Production*, SCI Critical Reports on Applied Chem., Blackwell, Oxford, 1985.

Section 2 Liquid petroleum gas (LPG), primarily propane and butane, became available cheaply when Saudi Arabia decided to crack only ethane in its first cracker. Large amounts of a propane–butane mixture were placed on the world market and more was available than energy uses required. Thus it was predicted in the early 1990s that the United States, by feeding LPG to its crackers, will use predominantly gas feedstock well into the next decade, a prediction negated by the high gas prices of the early 2000s.

Section 2.1 The catalytic reforming of low-boiling naphtha, which contains predominantly C_6 compounds, is normally accompanied by cracking and the formation of unacceptably large amounts of gases. New catalysts under development in the late 1980s, primarily large pore type L zeolites doped with various metals, made possible the conversion of light naphtha to benzene for chemical use in high yields. (cf. US Patents 4,539,304-5 March 8, 1984 to Chevron.) The figures for the proportion of natural gas from “tight” sands comes from Paul Smolarchuk, *GRID*, Fall 2001, p. 22 and *GTI J.*, Spring 2003, pp. 10–13.

Section 2.2.1 Steam cracking, strictly speaking, is not a refinery reaction. Because it derives feedstock from a refinery, however, steam cracking units are usually closely associated with a refinery.

Historical insight into the development of the cracking process is provided in an article in *CHEMTECH*, March 2, 1976, p. 180. This article reproduces William Burton’s acceptance address for the 1922 Perkin Medal that was awarded him for his research on cracking. Another article describing early work on cracking and the development of the petrochemical industry generally has been published by B. Achillaides, *Chem. Ind.*, April 19, 1975, p. 337. The Burton process for cracking was first, but close on its heels was the Dubbs process. Dubbs was so involved with technology that he named his son Carbon and his daughters, Methyl and Ethyl. Carbon later took on the middle name of Petroleum.

Section 2.2.1.1 For descriptions of gas oil cracking, see a series of articles by S. B. Zdonik in *Hydrocarbon Proc.*, September 1975; December 1975; April 1976. Gas oil cracking is also discussed by M. J. Offen, *Hydrocarbon Proc.*, October 1976, p. 123.

For articles describing the cracking of whole oil see *Eur. Chem. News*, **30**, No. 785 (1977); *Chem. Week*, September 28, 1977, p. 39; December 7, 1977, p. 55.

A discussion of substitute feedstocks by the year 2000 will be found in *Chem. Eng. News*, September 26, 1977, p. 7.

Section 2.2.1.2 The problems of the European industry are discussed in B. G. Reuben and H. A. Wittcoff, *Chem. Ind.*, 577 (2001). A United States perspective is provided by A. M. Thayer, *Chem. Eng. News*, March 13, 2000, pp. 20–24.

Methods of costing are discussed in Appendix A. Further complications arise because of tariffs and transport charges. For example, if South Korea exports propylene to Taiwan, the freight costs are ~$70/tonne. A costing in Taiwan will include propylene at $70/tonne more than a similar costing in South Korea, hence ethylene costs from an identical plant will appear to be about $35/tonne lower. Similarly, a tariff barrier on imported coproducts will raise their value in the importing country and make home-produced ethylene appear cheaper. There is no easy answer to these problems, and the reader should treat all costings with circumspection and demand details of all costing conventions before making judgments.

This section draws on the APPE (Association of Petrochemicals Producers in Europe) *Activity Review 1993–1994*, Brussels: CEFIC, 1994. There was a feature on tariffs in *Eur. Chem. News "Chemscope"* in September 1993.

The question of spot and contract prices is complex and depends on availability. Spot prices are higher than contract at times of shortage and lower at times of surplus. Overcapacity has meant that they have been generally lower in recent times, although 1994 was an exception. The increase in the price of propylene in the early 1990s resulted because in the mid-1980s steam crackers were shut down to bring the supply of ethylene in line with the demand. This decreased the supply of propylene and its price increased. As indicated earlier, the large catalytic cracking facilities in the United States makes ample supplies of refinery propylene available.

It is not strictly true that Mossmoran and BP are the only gas crackers. There is a small facility operated by Atochem at Lacq in the Pyrenees, France, that has been cracking gas from a small high sulfur deposit of natural gas for more than 30 years. It is, however, of little economic significance.

Section 2.2.1.3 For the mechanism of steam cracking see P. A. Wiseman, *J. Chem. Educ.* **54** (154) (1977).

Section 2.2.2 The development of zeolites for cracking catalysts is well described in an article in CHEMTECH by Plank (April 1984, p. 243). A thorough review of the topic is to be found in B. W. Wojciechowski, *Catalytic Cracking—Catalysis, Chemistry and Kinetics*. See also D. de Croocq, *Catalytic Cracking of Heavy Petroleum Fractions*, Inst. Français de Pétrole, Editions Technip, Paris, 1984, and *Advanced Fluid Catalytic Cracking Technology*, K. C. Chuang, G. W. Young, and R. M. Benslay, Eds. AIChemE, 1992.

Section 2.2.3 An excellent description of the development of catalytic reforming has been published by M. J. Sterba and V. Haensel, *Ind. Eng. Chem., Res Dev.* **15**, 2 (1976).

The Chevron technology for *in situ* hydrodealkylation during catalytic reforming reaction is described in US Patent 4,347,394 (August 31, 1982); US Patent 4,434,311 (February 28, 1984) and in UK Patent Appl. 2,114,150A, August 17, 1983.

Section 2.2.5 A review of octane number has been published by J. Benson, *CHEMTECH*, January 1976, p. 16.

Section 2.2.6 Use of hydrocracking on residues from petroleum distillation as well as coal-derived liquids, shale oil, and tar sands is described in an article in *Chem. Week*, February 18, 1976, p. 69.

Membrane processes for hydrogen removal are described by J. Haggin, *Chem. Eng. News.*, June 6 (1988) p. 7. The first industrial hydrogen-separating membranes were Monsanto's Prism separators, made of "skinned" polysulfone and used in the Haber process to recycle hydrogen, so that the wasteful "bleed" to get rid of argon build-up was no longer required. The “skinned” membrane is anisotropic and a thin layer of polymer of small well-defined porosity is supported on a thicker layer of more porous polymer.

Section 2.2.7 Carbide’s process for ethane dehydrogenation is claimed in several patents. A typical one is US Patent 4,524,236, June 18, 1985.

Section 2.2.9 The original metathesis reaction was described by its inventors Banks and Bailey in *Ind. Eng. Chem., Prod. Res, Dev.* **3**, 170 (1964). The ARCO development has been reported in *Chemical Marketing Reporter*, November 18, 1985, p. 36 and also in *J. Molecular Catalysis* **8**, 269 (1980). The conversion of 2-butene and ethylene to propylene is also described in US Patent 3,915,897 (October 28, 1975) to Phillips Petroleum Company.

Metathesis was reviewed in detail in two articles by A. M. Rouhi in *Chem. Eng. News*, December 23, 2002 (Olefin metathesis: big-deal reaction, pp. 29–33, and Olefin metathesis: the early days, pp. 34–38).

Ethylene dimerization is described in US Patent 4,242,531 (December 30, 1980) to Phillips Petroleum Company. A catalyst that gives primarily l-butene on ethylene dimerization is discussed in US Patent 4,487,847 (December 11, 1984) to Phillips Petroleum Company.

Section 2.3.1 Interestingly the need for diesel fuel in South Africa decreased markedly because buses for transporting the predominantly black population gave way to jitneys. Whereas the buses used diesel fuel, the jitneys use gasoline.

Section 2.3.2 An article on the affect of unleaded gasoline on the chemical industry has been authored by H. Wittcoff, *J. Chem. Educ.* 64, 773 (1987).

Details of European production facilities and the problems with MTBE are discussed by the European Fuel Oxygenates Association on their web site, www.efoa.org.

CHAPTER 3

CHEMICALS AND POLYMERS FROM ETHYLENE

We have described how the petroleum refinery, the steam crackers, and the catalytic reformers provide six of the seven raw materials on which the petrochemical industry is based. The seventh, methane, comes from natural gas. We can now examine the extensive chemistry associated with each of these building blocks. We start with ethylene not only because it has the simplest structure but also because it is the most important in terms of tonnage.

In 2002 the United States produced 53 billion lb of ethylene. This in turn (Section 1.5) was converted to about 200 billion lb of chemicals and polymers, a figure that includes the intermediate products and the ethylene itself. Since the total US annual production of organic chemicals and polymers was about 550 billion lb, one can gauge the importance of ethylene as a raw material. By 2010, it is predicted that US ethylene production will be over 65 billion lb and that global production will be 160 billion lb. United States ethylene, propylene, and benzene production over a 50-year period is shown in Figure 3.1.

About 80% of all the ethylene produced is destined to end up as thermoplastic polymers. Ethylene is itself a monomer for low-, high-, and linear low-density polyethylenes as well as for ethylene oligomers. It is the raw material for other important monomers including vinyl chloride, vinyl acetate, styrene, and ethylene glycol. Some of these monomers also have nonpolymer uses. Thus ethylene glycol is the main component of antifreeze. Ethanol, another ethylene-based chemical, is a versatile solvent.

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff, Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

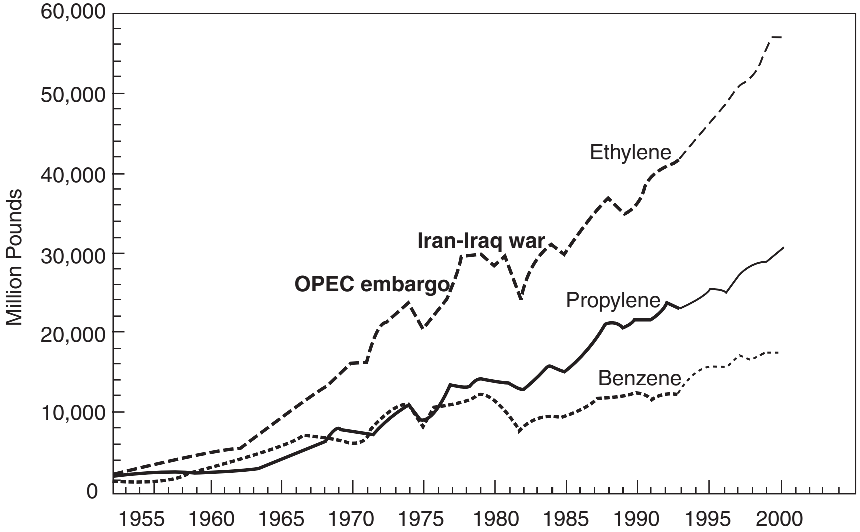


FIGURE 3.1 United States ethylene, propylene, and benzene production, 1953–2002.

Ethylene chemistry is the most mature in the petrochemical industry and is discussed in Section 3.10. The major chemicals and polymers from ethylene are shown in Figure 3.2. The figure is deceptively simple since many of the reactions are multistep, and the intermediates have uses in their own right. Even so, the chart demonstrates a basic tenet of industrial organic chemistry, namely, that most of the tonnage of the industry derives from relatively few materials. The major chemistry of ethylene can be divided into three categories—polymerization and oligomerization, four oxidation reactions practically unknown in textbook organic chemistry, and two reactions termed "classical" because they are typical of textbook chemistry. Some of the smaller volume chemicals and polymers from ethylene are listed in Table 3.1 with references to where they are discussed. Figure 3.3 shows the end-use breakdown in the United States and Western Europe.

The price of ethylene from 1970 to 2002 in current and constant 2001 dollars is shown in Figure 3.4. For a 14-year period, from 1960 to 1974, the price was almost constant. The OPEC embargo of 1974 caused the price to more than double. Inflation contributed to a steady increase with a precipitous rise in 1980 because of the Iranian crisis. Overcapacity, maturity, and weakening oil prices caused the price to decrease in 1985 and 1986. By 1988, price increased markedly due in part to increased petrochemical demand but, more important, to industry restructuring, which eliminated marginal suppliers as well as effective producers who felt that capital redeployment would lead to greater profit. Actually, on a constant dollar basis, the price of 18 ¢/lb for ethylene in 1987 is equivalent to 4.7 ¢ in 1960 and 28.2 ¢ in 2001. Figure 3.4 also shows the price of propylene that has consistently been about 20% lower than the price of ethylene. This ratio is shown in the lower part of the figure. Propylene's price relationship to ethylene was maintained until 1986 when the price

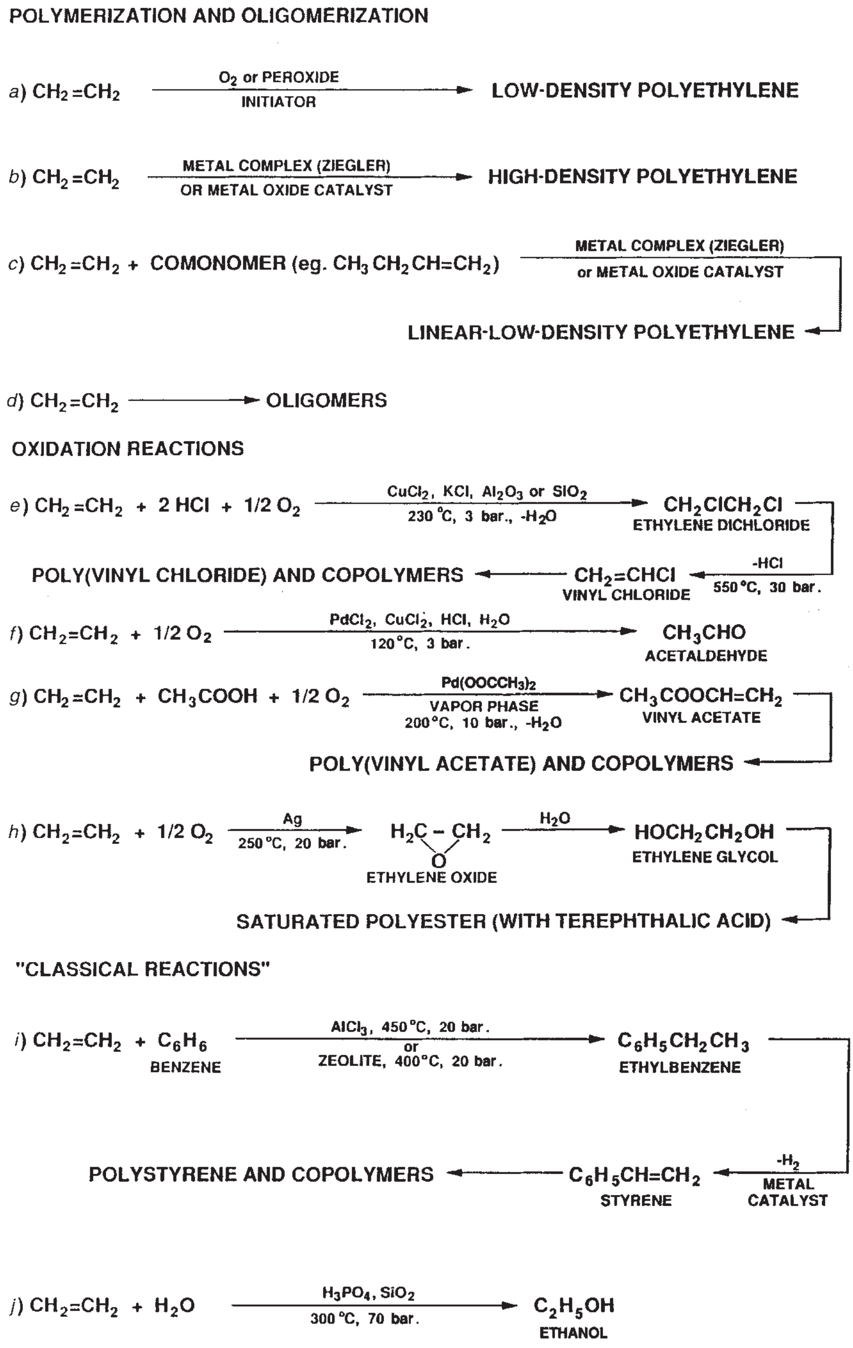


FIGURE 3.2 Major chemicals and polymers from ethylene.

TABLE 3.1 Some Lesser Volume Chemicals and Polymers from Ethylene
(Numbers in parentheses show where the chemicals are discussed)

Polymers	Chemicals	
Very high molecular weight polyethylene (3.11.12)	Propionaldehyde (3.11.1)	Trichloroethylene (3.11.7)
Very low density polyethylene (3.2.6)	Propionic acid (3.11.1)	Perchloroethylene (3.11.7)
Chlorosulfonated polyethylene (3.2.1)	*n*-Propanol (3.11.1)	Ethylene glycol oligomers (3.11.6.1)
Ethylene–vinyl acetate (3.2.2)	Ethyl chloride (3.11.2)	Glycol ethers and esters (3.11.6.2)
Ethylene–vinyl alcohol (3.2.2)	Ethyl bromide (3.11.2)	Ethylene carbonate (3.11.6.3)
Ethylene–ethyl acrylate (3.2.2)	Chemicals from acetaldehyde (3.11.3)	Aminoethyl alcohols (3.11.6.4)
Ethylene–methyl methacrylate (3.2.2)	Metal complexes (3.11.4)	1,3-Propanediol (3.11.6.6)
Ethylene–butyl acrylate (3.2.2)	Ethylene diamine and related compounds (3.11.5)	Vinyl fluoride (3.11.8)
Ethylene–acrylic acid ionomer (3.2.3)	Ethylamines (3.11.7)	Vinylidene fluoride (3.11.8)
Polyethylene–nylon blends (3.2.4)	Ethylenimine (3.11.6.5)	Ethylene dibromide (3.11.9)
Ethylene–propylene elastomers (3.2.5)	Vinylidene chloride (3.11.7)	Vinyl esters and ethers (3.11.11)

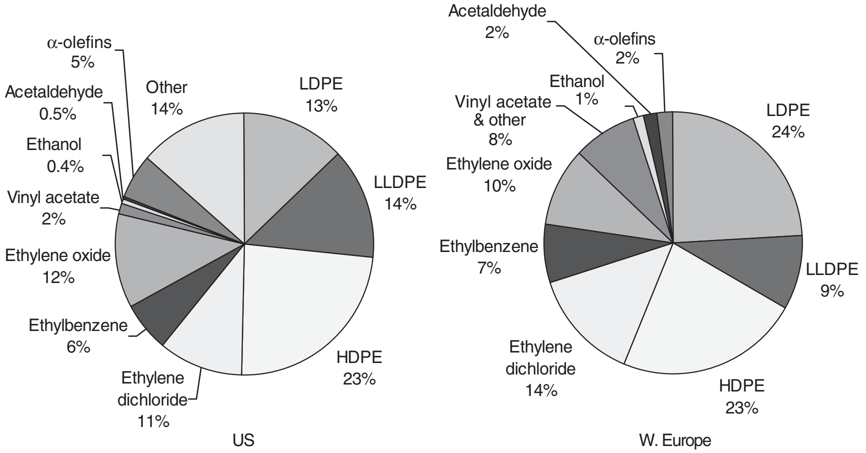


FIGURE 3.3 Chemicals from ethylene United States (2000) *versus* Western Europe (1999).

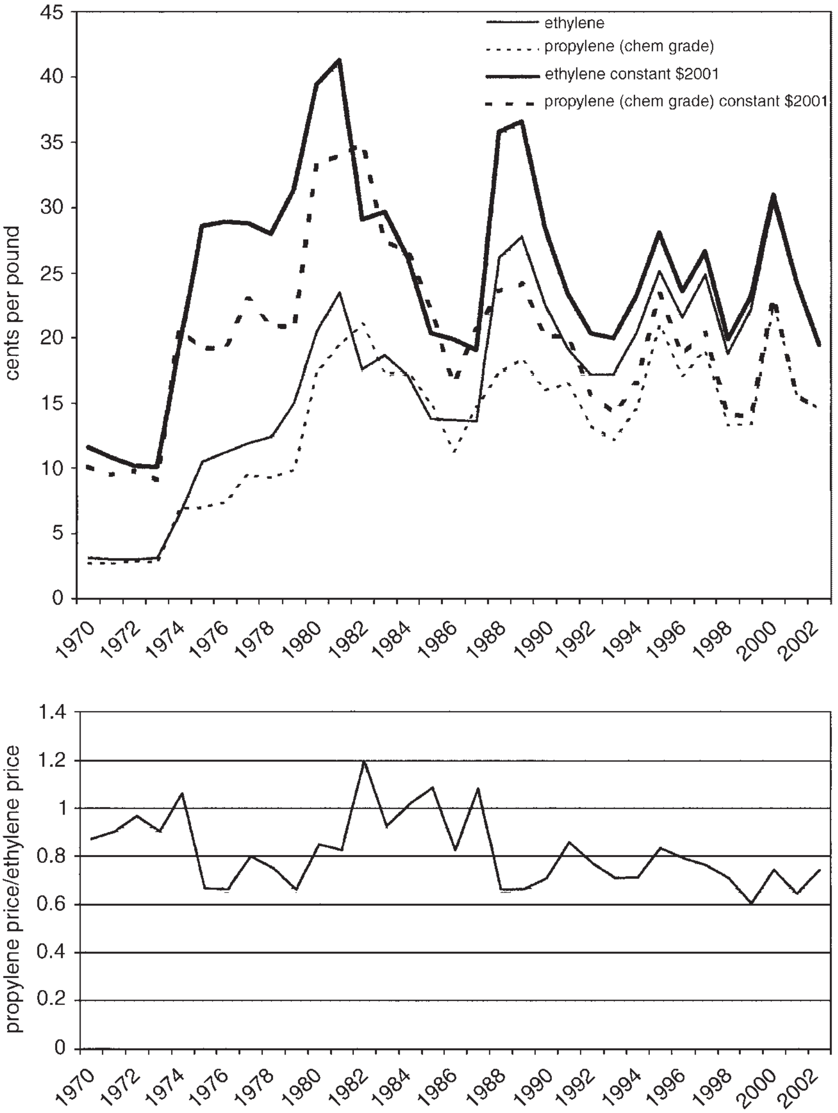


FIGURE 3.4 Average prices for ethylene and propylene and the ratio of their prices, United States 1970–2002.

of the two products became equal. At that point, propylene usage was growing faster than that of ethylene. Also, there was a slight shortage of propylene, particularly in Europe, for reasons discussed earlier (Section 2.3.2). The traditional price relationship resumed in the late 1980s and was maintained into the early 2000s when rapid propylene growth again led to a shortage. In the United States, this was not a problem because propylene was available from catalytic cracking. The shortage was more acute in Southeast Asia and Western Europe. To counteract it, a pipeline is under construction in northwest Europe that will distribute almost one billion lb of propylene, most of it imported from North and South America. It is expected onstream in 2005.

3.1 ETHYLENE POLYMERS

Polyethylene is cheap and is the largest volume polymer. Consumption in the United States in 2002 was about 28 billion lb, 46% of which was accounted for by high-density polyethylene (HDPE) and the remaining 54% by low-density and linear low-density polyethylenes (LDPE and LLDPE). These are the three important forms of polyethylene.

3.1.1 Discovery of Low- and High-Density Polyethylenes

The discovery of LDPE in 1932 was serendipitous. Fawcett and Gibson at ICI in Runcorn, England were studying chemical reactions at high pressures, hoping to make synthetic rubber from ethylene and benzaldehyde. ICI had decided to study high-temperature chemistry to see if they could make basic advances that would get them on a par with IG Farben in Germany. Du Pont decided to investigate polymers for similar reasons. ICI discovered LDPE and Du Pont discovered nylon. ICI's discovery hinged on a leaking autoclave. It had been pumped up to reaction pressure and allowed to stand over the weekend prior to the performing the reaction. Pressure was lost during this period because of an ethylene leak, and more ethylene was added to the reactor which, at this stage, contained traces of oxygen from the air that replaced the leaking ethylene. The pressure of the autoclave was raised to 2000 bar and the temperature increased to 200°C. Subsequently, when cooled to room temperature, the reactor turned out to be full of a white powder, and the benzaldehyde was intact. After many more experiments, it was realized that oxygen was serving as an initiator for the polymerization of the ethylene.

The conventional wisdom of the 1930s dictated that polyethylene could not be made, because it was not possible to put sufficient energy into the ethylene molecule to achieve the transition state. This is, however, quite possible with pressures in the range of 2000 bar and a temperature of 200°C in the presence of a free radical initiator such as oxygen or various peroxides. The polymerization is carried out in the gas phase, high pressures favoring the propagation reaction, which is in part a function of ethylene concentration. Termination, on the other hand, is independent of ethylene concentration.

The discovery of HDPE was similarly serendipitous. Investigators at Standard Oil of Indiana and Phillips Petroleum, seeking to oligomerize ethylene to gasoline-size molecules, were surprised to obtain instead a stiff form of polyethylene. Whereas LDPE finds its greatest use in the manufacture of film, the stiffer linear high-density material enjoys its major applications in the manufacture of bottles by blow molding and in structural parts by injection molding.

The first linear polyethylene was probably made in 1950 at Standard Oil of Indiana by Zletz who observed that a molybdenum oxide catalyst on silica at mild temperatures and pressures did not give oligomers but rather HDPE. Soon thereafter, Banks and Hogan at Phillips Petroleum obtained similar results with a catalyst comprising chromium oxide supported on silica or alumina. Phillips developed and licensed its process aggressively; hula hoops amazingly provided the first application for the new product.

In 1954, Karl Ziegler announced his discovery. He was successfully studying ethylene oligomerization reactions (Section 3.3.2) based on aluminum alkyls. A metal salt impurity in the reaction mixture led serendipitously to the formation of high molecular weight linear polyethylene. From this evolved the famous Ziegler catalyst, typical of which is a combination of aluminum triethyl with titanium tetrachloride. The Ziegler process attracted great theoretical as well as practical interest because it can be applied to propylene (Section 4.5.1) and to practically any unsaturated compound, unlike the metal oxide processes, which are effective, for practical purposes, only with ethylene (see note at the end of this chapter). The Ziegler process accounts for 60% of the HDPE produced in both the United States and Western Europe. The latest development is the use of metallocenes or single site catalysts. These are described in Section 15.3.12.

3.1.2 Low-Density Polyethylene

Low-density polyethylene may be manufactured batchwise in an autoclave or, more commonly, in a tubular reactor that makes possible continuous processing and easier heat removal. Batch-produced product is useful for paper or cardboard extrusion coating, where its highly branched structure is advantageous. The somewhat less branched continuously produced product is useful for film. About 35% of the ethylene is allowed to react in the continuous process and the remaining 65% is recycled. This is termed 35% conversion per pass and is necessary to eliminate excess branching. With HDPE, branching is not a problem and conversion may be 100%. The properties of LDPE and HDPE are listed in Table 3.2.

The branched structure of LDPE profoundly affects its properties. Because of steric hindrance from the branching, the polymer chains cannot get as close together as they can in HDPE. Hence, the crystallinity is of the order of 55% as compared to 85–95% for HDPE. The crystalline melting point, softening point, and tensile strength of LDPE are all a function of the branched structure and are considerably lower than the corresponding values for HDPE. On the other hand, the softer LDPE shows higher elongation at break and higher impact strength than does the rigid HDPE. It is also translucent rather than opaque because of its lower crystallinity. Opacity occurs because the amorphous and crystalline portions of the polymer transmit light at different rates, that is they have different refractive indexes. Light is scattered at the crystal boundaries because of the change in refractive index (Section 15.5.1). The difference in densities, which characterizes the two polymers, is of the order of 0.3–0.4 g cm^{-3}. The density of LDPE may be as low as 0.915 g cm^{-3} and of HDPE as high as 0.965 g cm^{-3}.

TABLE 3.2 Properties of Polyethylenes

Property	LDPE	HDPE	LLDPE
Initiator or catalyst	Oxygen or organic peroxide	Ziegler or Phillips catalyst	Ziegler or Phillips catalyst
Reaction temperature	200–300°C	As low as 60°C	As low as 60°C
Pressure (bar)	1300–2600	1–300	1–300
Structure	Branched	Linear	Linear with short branches
Approximate crystallinity	55%	85–95%	55%
Comonomer	None	1-Butene[a]	1-Butene, 1-Hexene or 1-Octene
Tensile strength (psi)	1200–2000	3000–5500	2000–2500
Tensile strength (tonnes m^{-2})	850–1400	2100–3900	1400–1800
Elongation at break (%)	500	10–1000	500
Density (g cm^{-3})	0.915–0.925	0.945–0.965	0.915–0.925

[a] One percent as compared with 6–8% for LLDPE.

3.1.3 High-Density Polyethylene

Most HDPE is actually a copolymer containing up to 1% of 1-butene or less commonly 1-hexene. The comonomer is required, particularly when metal oxide catalysts are used, to avoid formation of molecular weights so high that the polymer becomes intractable. The copolymer also has improved low temperature properties.

The production of HDPE is much less energy intensive than that of LDPE. Reaction temperatures can be as low as 60°C and pressures as low as 1 bar. Nonetheless, temperatures of 130–270°C and pressures of 10–160 bar are used commercially. Conversion per pass approaches 100%.

High-density polyethylene is manufactured in solution, slurry, or fluidized-bed processes. In the slurry process, the catalyst is dispersed in a solvent such as hexane, and the ethylene is polymerized batchwise in a series of reactors. The gas phase, fluidized-bed processes were devised first by Union Carbide and subsequently by BP and BASF. Small HDPE particles are fluidized by gaseous ethylene and comonomer (e.g., 1-butene) at 85–105°C and 20 bar. Catalyst is continuously sprayed into the reactor. The ethylene and comonomer copolymerize around the preformed polymer particles. At the same time, the gaseous ethylene removes the heat of reaction.

The initial particles grow to an average diameter of 500 microns over a period of three to five hours, during which time only about 2–3% of the ethylene polymerizes. The unconverted reactants are recycled. Polyethylene, once prepared, is melted, mixed with stabilizers and other additives, and extruded to form spaghetti-like rods, which are then cut into small pellets. The extrusion is an energy-intensive operation. An objective of the fluidized bed process (Carbide's Unipol process), not achieved initially, was to obtain the polymer as a powder with uniform-sized particles that could be used as such for molding and extrusion. Further development has apparently made this possible, although the value of the powder is questionable, because its low-bulk density increases shipping costs. But, serendipitously, the gas-phase process has proved to be an economical way to prepare both high- and linear low-density polyethylenes. It has been licensed extensively and is the most important process in use today.

3.1.4 Linear Low-Density Polyethylene

Linear low-density polyethylene (LLDPE) is the successful result of a desire to prepare LDPE by the less energy-intensive conditions used for high-density polyethylene. High-density polyethylene copolymers with high comonomer content have been known for many years. Their density was less than that of HDPE, their crystallinity was lower, and the properties that depended on crystallinity were altered. Considerable time elapsed before it was recognized that a copolymer of HDPE, in which crystallinity had been reduced to about 55% (the crystallinity of LDPE, see Table 3.1) and its density to about 0.925, had many of the characteristics of LDPE. Thus a copolymer of ethylene and 6–8 wt% 1-butene—several times as much comonomer as is used for HDPE—resembles LDPE. Like the other polyethylenes, it may be manufactured by solution, slurry, or fluidized-bed processes.

The serendipity leading to several of the polyethylenes and the fact that copolymers of the above type were known before they were recognized as economically useful emphasizes the importance not only of discovery but of its recognition. As Louis Pasteur remarked, “where observation is concerned, chance favors only the prepared mind.”

Linear low-density polyethylene, like LDPE, has branching that inhibits close approach of polymer molecules and decreases crystallinity. The branching in LDPE is irregular and, if the LDPE is prepared by the autoclave process, there are secondary branches on the primary ones. The LLDPE has regular branching because of the pendant C_2 groups provided by the 1-butene comonomer. This uniformity makes possible closer association of the polymer molecules in the crystalline portion, for which reason LLDPE has a higher tensile strength than LDPE, allowing the use of thinner or lower gauge films.

Its growth in the United States was rapid at first and almost completely at the expense of LDPE. Growth was facilitated because LLDPE could be processed in HDPE equipment. Subsequently, new uses for it were found in stretch wrap film, injection molding, and rotomolding—applications for which LDPE is not suitable. The cost advantage provided for LLDPE manufacture by lower energy use is in large part counterbalanced by the cost of the more expensive monomer, 1-butene, which became one of the fastest growing chemicals of the mid-1980s. Newer processes for LLDPE make use of 1-hexene, 1-octene and, to a much lesser extent, 4-methyl-1-pentene (a propylene dimer, Section 4.6) as comonomers.

1-Butene for LLDPE may be obtained either by dimerization (Section 3.3.1) or oligomerization (Sections 3.3.2, 3.3.3) of ethylene or by isolation from the C_4 olefin stream from steam or catalytic cracking (Section 5). In fact, practically all of it in the United States and Western Europe is obtained from the latter source, which underscores the point that refinery processes usually are more economical than processes in chemical plants. Saudi Arabia makes 1-butene by dimerization of ethylene (Section 3.3.1) since refinery 1-butene is not available. 1-Hexene and 1-octene are obtained solely by ethylene oligomerization and 4-methyl-1-pentene by propylene dimerization (Section 4.2). Growth has been particularly rapid for the copolymer containing 1-hexene.

3.1.5 Very High Molecular Weight Polyethylene

Very high molecular weight polyethylene with a density of 0.941 g cm^{-3} or higher is not used widely because it is difficult to process. It is made under HDPE conditions without comonomer and is used primarily for plastic ropes. A growing application is for the preparation of high-strength polyethylene fibers. Tensile strength in polymeric fibers may be increased by drawing, a process that causes the polymer molecules to crystallize or to align themselves so closely that physical forces of attraction between polymer molecules come into play. However, physical stretching does not cause uncoiling of small portions of molecules that are "tangled" because of folds and crossovers. It has been found that polymer molecules uncoil in very dilute solution if the solvent has high solvating power and the polymer is nonpolar. DSM has developed a process in which a dilute hydrocarbon solution of very high molecular weight polyethylene at 120°C is cooled to give a gel that is extruded into gel-like fibers. The solvent is removed and replaced with dichloromethane, which effects more unraveling. The second solvent is then removed and the dry gel oriented or drawn to provide a fiber, whose trade name is Dyneema, and whose tensile strength is 15 times as great as that of steel on a weight for weight basis and 40% greater than Aramid fibers (Section 9.3.4). Dyneema is sold in the US by Allied-Signal under the name Spectra. An obvious disadvantage of polyethylene fibers is their low melting point as compared with Aramids. On the other hand, they absorb less water. Cloth from these fibers is used in body armor, ropes, cables, nets, and sporting goods.

Very high molecular weight polyethylene is also used for the bottoms of skis. These must be abrasion resistant, hydrophobic, and absorb wax well. Polytetrafluoroethylene (Section 10.2.3) would be ideal but is subject to creep. The cheaper skis use polyethylene with a molecular weight of about 500,000 and a density of 0.95 g cm^{-3}. The molecular weight is just low enough for the bottoms to be extruded from the melt. Racing skis use polyethylene with a molecular weight of about 3.5 million and a density of about 0.94 g cm^{-3}. They are formed by sintering the polymer into a block and then slicing it. This gives them a slightly porous structure leading to higher wax absorption and abrasion resistance. Sintering does not always produce uniform materials and various additives may improve this. Graphite or carbon black are often added, which make the bases more conductive and decrease the effect of static electricity on snow adhesion (see note at the end of this chapter).

3.2 ETHYLENE COPOLYMERS

3.2.1 Chlorosulfonated Polyethylene

Ethylene is found in many other copolymers in addition to HDPE and LLDPE, but all of them are sold in comparatively low volumes. One of the earliest is chlorosulfonated low density polyethylene, known as “Hypalon.” It is an elastomer formed by chlorosulfonation of polyethylene with sulfur dioxide and chlorine leading to insertion of SO_2Cl and Cl groups into the chain. For the various grades of Hypalon, LDPE, LLDPE, and HDPE may be used. This is a rare example of polymer modification by a chemical reaction in which the polymer is one of the reactants. The polymer can be cross-linked through the sulfonyl chloride group (which has destroyed the polymer’s crystallinity and made it rubbery) with inorganic oxides such as lead oxide or with di- or polyamines. This elastomer is prized because of its ozone and oxidation resistance. It finds use in gaskets, wire and cable installation, roof coatings, white side-wall tires, and coated fabrics.

3.2.2 Ethylene-Vinyl Acetate

The most important ethylene copolymer after HDPE and LLDPE is ethylene-vinyl acetate (EVA). Its consumption was approximately 960 million lb in 2000, which is about 64% of all ethylene copolymers excluding HDPE and LLDPE. Ethylene-vinyl acetate is a random copolymer. Depending on the proportion of vinyl acetate, it may be either hard or rubbery.

The hard form requires less than 50% of vinyl acetate. Like most copolymers, it has a lower density than the homopolymer and is useful in agricultural films because it demonstrates better heat retention, toughness, and greater transparency, trapping more infrared light than does LDPE. Its biggest use is for adhesives, particularly hot melts, where the adhesive is applied as a solvent-free melt and bonds almost instantaneously on cooling. It is used as a coating often blended with waxes, polyolefins, and elastomers. An interesting medical application is as a semipermeable film for drugs administered in sustained release dosage forms. A drug such as trinitroglycerol is placed in a reservoir covered with the semipermeable film, which in turn is placed next to the skin. The drug enters the body since the skin too is semipermeable, and it makes its way into the bloodstream at a controlled rate via the semipermeable capillaries.

If more than 50% vinyl acetate is present, a rubbery polymer results, which in the form of a latex is useful for water-based paints along with other homo- or copolymers of vinyl acetate, acrylates, and methacrylates. The ethylene lowers the cost of the polymer and contributes much-prized water resistance.

Related copolymers include ethylene-ethyl acrylate, ethylene-methyl methacrylate, and ethylene-butyl acrylate. Each of these has properties that fit it for specific uses. For example, ethylene-ethyl acrylate is used mainly as a cable coating. Ethylene-butyl acrylate provides a tough film with excellent low-temperature properties, fitting it for the packaging of frozen foods.

Ethylene-vinyl alcohol is a copolymer prepared by conversion of the ester groups of ethylene-vinyl acetate to alcohol groups by ester interchange with methanol. Its films are good oxygen barriers and, because of its high polarity, it has good resistance to oils and greases. The copolymer was developed in Japan; U.S. manufacture started in 1986. Laminates may be made by coextrusion of EVA copolymer with other polymers such as polyethylene, polypropylene, or polyesters such as poly(ethylene terephthalate) (PET). Ethylene-vinyl alcohol/PET and ethylene-poly(vinylidene chloride)/PET laminates are less permeable to oxygen and carbon dioxide than PET alone and are being used for small beer bottles in the international market (Section 9.3.3).

3.2.3 Ionomers

Ethylene-acrylic acid and ethylene-methacrylic acid are examples of random copolymers. They are useful as such and also in the preparation of ionomers. Ionomers comprise a class of copolymers of which Du Pont's "Surlyn" is typical. An ionomer contains ionic groups such as pendant carboxyl groups. These react with both divalent and monovalent metal ions such as Zn^{2+} and Na^{+} to cross-link the polymer chains by the formation of carboxylates. The monovalent ion is effective because of the formation of ion aggregates through coulombic forces. The hygroscopic aggregates attract water even in a medium as nonpolar as an ethylene-containing polymer. The water serves to stabilize the aggregate and makes possible the reversal of salt formation on heating.

The virtue of an ionomer is that it has some of the stiff, tough properties of a cross-linked resin at room temperature. On heating, the ionic bonds or ion aggregates are disrupted, and the polymer becomes thermoplastic and processible. Major uses for ionomers include ski boots, tough, flexible hosing, and the coating of golf balls, where toughness is a major requirement. Very tough forms of ionomers have been proposed for body panels and bumpers of automobiles. It is also used for specialty packaging.

3.2.4 Copolymer from "Incompatible" Polymer Blends

Polar polymers such as nylon are incompatible with nonpolar polymers such as polyethylene for the same reasons that polar and nonpolar liquids are immiscible. They can, however, be combined in an imaginative process, which uses a third polymer. The technique is exemplified by Du Pont's "Selar."

Selar is a blend of nylon and ethylene plus a graft copolymer of ethylene and acrylic or methacrylic acid. The copolymer serves as a "nail" to hold the incompatible polyethylene and nylon together. Its polar portion, the pendant carboxyl groups, associate with the nylon and may even react chemically with amine end groups. The polyethylene backbone of the copolymer, on the other hand, associates with the polyethylene homopolymer. These physical bonds are sufficiently strong to prevent phase separation, and accordingly the nylon, which is the lesser component, "plates out" in the polyethylene matrix when the molten mixture is cooled. The nylon platelets overlap providing a barrier that makes the blend suitable for structures where good oil resistance is required. One use is for the fabrication of automotive fuel tanks. Figure 3.5 illustrates this important concept for combining incompatible polymers.

3.2.5 Ethylene–Propylene Elastomers

Ethylene–propylene copolymers containing 20–80% ethylene are noncrystalline elastomers, which can be cross-linked with peroxide. They are known as EP rubbers. Alternatively a diene may be included such as *trans*-1,4-hexadiene (Section 5.1.2),

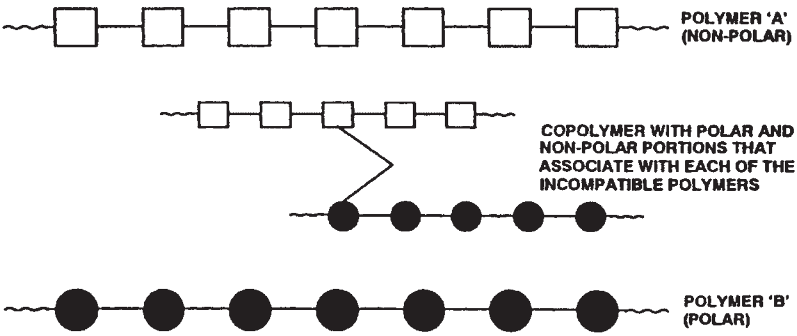


FIGURE 3.5 A chemical "nail" holds two incompatible polymers together.

ethylidene norbornene (Section 5.1.2), or dicyclopentadiene (Section 6.3), each of which contains one active double bond to copolymerize with the ethylene and propylene and one less reactive pendant double bond for cross-linking of the rubber with conventional sulfur-based vulcanizing agents. They are known as ethylene-propylene-diene monomer rubbers (EPDM). The polymerization is carried out with a Ziegler catalyst. Because only enough double bonds are present to permit cross-linking, the polymer is particularly stable and resistant to oxidation. These elastomers find specialty uses where long service life is required, particularly for roofing. They are also used in automobiles for gasketing, belts, hose, wire and cable coating and under-the-hood applications where high-temperature resistance is required. They may be used to reinforce other polymers.

3.2.6 Ultra-Low-Density Polyethylene

Ultra-low-density polyethylene is useful in applications normally reserved for ethylene copolymers such as EVA. The designation "very low density" applies if the density is below 0.915 $g\,cm^{-3}$. A product with a density as low as 0.890 $g\,cm^{-3}$ was announced by Union Carbide in the 1980s. The material is suitable for "noiseless" film of the type needed in adult diapers and other applications where low stiffness coupled with reasonable strength is required. The very low density is achieved in part by copolymerization of ethylene with up to 10% of one of the α-olefins used for the preparation of LLDPE. Metallocene catalysis (Section 15.3.12) also makes possible synthesis of very low density polyethylene.

3.2.7 Photodegradable Copolymers

Photodegradable polymers are one answer to the problem of plastic litter. In the United States only 7% by weight of the contents of waste dumps is plastics, but that still amounts to 20% by volume. Forty percent of the litter along roadsides is plastics, and this visibility, abetted by consumer concern, has motivated the development of photodegradable plastics. These were already in use in the early 1990s for yokes for "six-pack" beverage bottles in those states where legislation required it. There is evidence that animals are trapped by the holes in these yokes.

Some grocery bags today are made from a photodegradable version of HDPE. Photodegradability is achieved by copolymerization of about 1% of carbon monoxide to give ketone groups in the polymer chain. These are degraded by ultraviolet light below 350 nanometers. The effect is enhanced by addition of an ultraviolet light absorber.

Shell and BP each developed but subsequently dropped a product containing ethylene, propylene, and carbon monoxide. It was an alternating copolymer of structure $-\!\!\!\!+CH_2CH_2COCH_2(CH_3)CH_2CO-\!\!\!\!+_m$. The ketone group contributed the photodegradability. The homogeneous copolymerization is carried out with a catalyst comprising a palladium salt of trifluoroacetic or *p*-toluenesulfonic acid with a bidentate ligand identified in the patent literature as 2,2′-bipyridine, 1,10-phenanthroline, or 1,3-bis(diphenylphosphino)propane.

In the early 2000s, a polylactate from lactic acid, which is said to be compostable, was under development in a Dow Chemical–Cargill joint venture (Section 14.1). Developmental quantities became available in 2002. The lactic acid is made by fermentation of glucose (Section 14.1). Thus the raw material is replaceable and the product biodegradable, both seen as environmental benefits. Polylactic acid has been known for over a century but was never commercialized in the absence of a cost effective production technology.

3.3 OLIGOMERIZATION

Ethylene oligomerizes with difficulty because the free radical intermediate, once formed, is highly energetic and polymerizes rapidly to give high molecular weight polymers. Thus it was not until the advent of Ziegler technology that ethylene oligomerization became feasible. Conversely, ionic intermediates from propylene and butenes form readily. Since they are much less energetic, they oligomerize, but do not polymerize.

3.3.1 Dimerization

Ethylene may be dimerized either to 1-butene or to the more thermodynamically stable 2-butene. The incentive for the development of dimerization processes was the possibility of dehydrogenating the resulting butenes to butadiene just as refinery butenes are dehydrogenated (Section 2.2.7). Although this was never done commercially with the dimerization products, ethylene dimerization was used in Lyondell's process for producing propylene via metathesis from ethylene and 2-butene. Lyondell's source of butenes for this metathesis reaction is probably raffinate-2 (Section 2.2.8).

Dimerization to 1-butene has been commercialized in Saudi Arabia to obtain this chemical for use in LLDPE since in that country there are limited amounts of refinery butenes. Another possibility is the production of 1-butene *in situ* before or during ethylene polymerization to provide the comonomer needed for LLDPE (Section 3.1.4). This has never been commercialized.

Catalysts for ethylene dimerization are primarily combinations of nickel compounds and an alkylaluminum. This catalyst resulted from a chance observation by

Ziegler that nickel from reactor corrosion produced 1-butene rather than ethylene oligomers in the presence of alkylaluminum compounds. Cobalt salts and titanium complexes are also effective. A catalyst that converts ethylene primarily to 1-butene comprises bis(1,5-cyclooctadiene) nickel, triphenylphosphine, and *p*-toluenesulfonic acid. A catalyst for 1-butene preparation proposed by the Institut Français du Pétrole (IFP) comprises triethylaluminum with a complex of tetra *n*-butyl titanate and tetrahydrofuran. A catalyst useful for the formation of 2-butene comprises tri-*n*-butylphosphine nickel dichloride and ethylaluminum dichloride. A simpler catalyst is a mixture of nickel oxide, silica, and alumina. 1-Butene is manufactured in Saudi Arabia from ethylene in a process devised jointly with IFP (Section 3.14).

3.3.2 Ziegler Oligomerization of Ethylene

Related to Ziegler polymerization is the oligomerization of ethylene as shown in Figure 3.6. Triethylaluminum reacts with ethylene to form a trialkylaluminum at 100°C and 100 bar. An aluminum alkoxide results from the interaction of the trialkylaluminum with oxygen. It can be hydrolyzed to straight-chain fatty alcohols with an even number of carbon atoms from C_4 to C_{24}. Alternatively, the trialkylaluminum may be heated to 280–300°C and 50 bar in the presence of ethylene to give linear α-olefins. Both groups of compounds are useful in the manufacture of biodegradable detergents, but the alcohols are much more widely used. The α-olefins are converted to alcohols with one additional carbon atom by use of the oxo reaction (Section 4.12). The C_{10} α-olefins may in turn be oligomerized to trimers to obtain compositions valuable as synthetic lubricants, and the C_{18} compounds, may be sulfonated to obtain both industrial grade and specialty surfactants useful in cosmetics. The C_6 and C_8 olefins are useful as comonomers for LLDPE (Section 3.1.4).

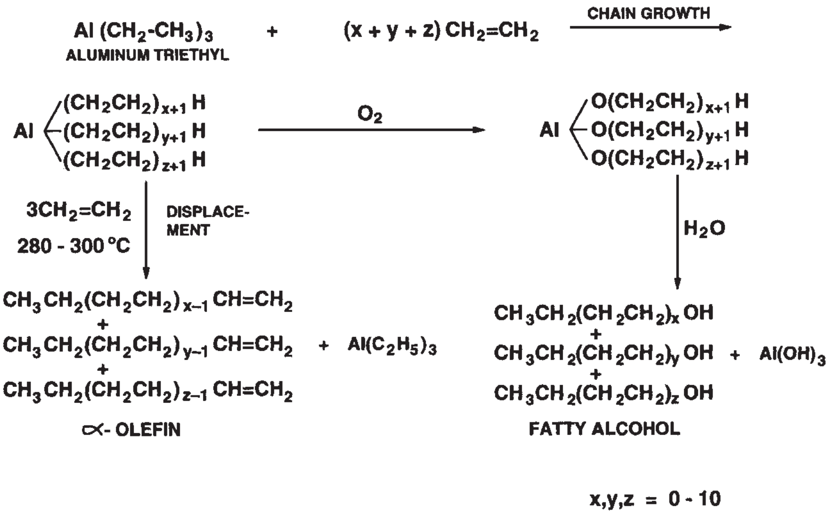


FIGURE 3.6 Ethylene oligomerization (Ziegler).

This technology was adopted by several companies. The major problem with the process is an unfavorable molecular weight distribution of the products, which ranges from C_4 to C_{24}. Conoco (spun-off as Vista, now owned by Sasol) produced the alcohols whereas Ethyl (now BP) and Gulf (now Chevron Phillips Chemical) produced α-olefins. The most desirable materials for surfactants contain 12–14 carbon atoms. A process developed by the Ethyl Corp. recycles α-olefins to the chain growth step so that transalkylation takes place. This gives a higher concentration of C_{12}–C_{18} compounds and fewer of the lower molecular weight materials, although it introduces some branching. The displacement is effected by raising the temperature to 300°C. The alkylaluminums with chain lengths from 12 to 18 are replaced by the lower molecular weight olefins that form at the high temperature. This provides alkylaluminums with chain lengths of 4–12 and free C_{12}–C_{18} α-olefins. In other words, the displacement reaction shown in Figure 3.6 is allowed to take place *in situ* rather than as a separate step, using C_4–C_{12} α-olefins to displace the alkyl chains rather than ethylene. High pressure favors chain growth since it reduces the number of molecules. Displacement, on the other hand, as indicated above, is favored by high temperature. The effectiveness of the transalkylation reaction is indicated by the fact that C_{12}–C_{14} α-olefin production is increased from 10–18% to 20–35%.

The equations in Figure 3.6 show that the reaction requires stoichiometric quantities of triethylaluminum. However, it is possible to carry it out with catalytic amounts if the conditions are such that ethylene continually displaces the growing chains on the catalyst. β-Hydrogen abstraction from the growing alkyl chain regenerates an Al—H bond that can start growth of a new alkyl chain. When alcohols are made, stoichiometric amounts of $Al(OH)_3$ are formed. This may be converted to a high-value catalyst support.

α-Olefin technology may now be licensed from either UOP or Axens (formerly IFP). The UOP process, Linear-1 (trademarked), was developed jointly with Union Carbide. It employs a homogeneous nickel-based catalyst system. While many ligand combinations were tested, it appears that 2-diphenylphosphino-1-naphthalene sulfonic acid is used. UOP claims that, by making simple adjustments to the operating parameters, the output can be varied between 45 and 75 wt% C_4 to C_8 linear α-olefins. The Axens process, AlphaSelect (trademarked), is based on a proprietary soluble catalyst system. Varying the catalyst and cocatalysts ratio allows different α-olefin distributions.

3.3.3 Other Ethylene Oligomerization Technologies

Other processes for the oligomerization of ethylene have been devised. Esso's process depends on a catalyst combination comprising an alkylaluminum chloride and titanium tetrachloride. The reaction is carried out in an organic solvent and the molecular weight of the α-olefins produced increases as the reaction temperature is raised. Nonpolar solvents also favor higher molecular weights.

The chromium-catalyzed trimerization of ethylene to 1-hexene is a remarkable reaction devised by Phillips Petroleum. In the early 2000s, they announced plans to produce 1-hexene in Qatar as a comonomer for LLDPE. The proposed mechanism is shown in Figure 3.7. The original chromium complex, designated as "Cr," specifying the actual

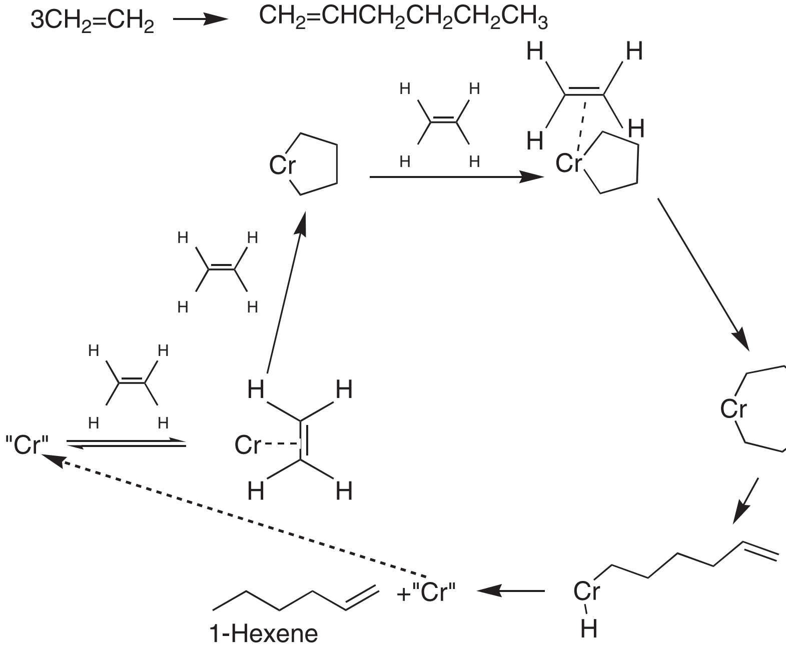


FIGURE 3.7 Trimerization of ethylene to 1-hexene.

proprietary ligand system, binds first one and then a second ethylene molecule to give a five-membered chromium-containing ring. Five-membered rings are thermodynamically relatively stable, and this one remains intact long enough to bond to another ethylene molecule to give a complex that rearranges to a seven-membered ring. Seven-membered rings are relatively unstable and this one decomposes via ring opening and reductive elimination to give 1-hexene and the original chromium starting complex.

Recent competition in the α-olefins market has come from Sasol in South Africa (Section 12.2), whose economical process is based on byproducts from the Fischer–Tropsch conversion of coal to petroleum-like liquids.

3.3.4 The Shell Higher Olefins Process (SHOP)

Shell devised an oligomerization process, which is integral to their SHOP process, based on a nickel chloride catalyst with ligands comprising diphenylphosphinoacetic acid and triphenylphosphine. Sodium borohydride is present to reduce the nickel salt to a nickel hydride catalyst, and a glycol such as 1,4-butanediol serves as a solvent for the reactants but not the products.

The oligomerization takes place at about 100°C and 40 bar in the presence of excess ethylene. The mixture of α-olefins that forms has chain lengths varying from C_4 to C_{40}. The distribution includes 40.5% of C_{10}–C_{18} α-olefins, 41% C_4–C_8 compounds, and 18.5% of C_{20} and higher materials. The α-olefin distribution is similar to that obtained in a Ziegler process carried out without transalkylation. The mechanism of α-olefin formation, like the one for the alkylaluminum reaction, involves β-hydrogen abstraction as shown in Section 3.3.2. The product α-olefins precipitate because they are not soluble in the 1,4-butanediol.

The SHOP process is one of the most ingenious in the chemical industry. Its initial objective was the preparation of linear or almost linear α-olefins and fatty alcohols with the most suitable chain lengths for surfactants, that is, C_{11}–C_{15}. The natural products—coconut and palm kernel oils, from which fatty alcohols may be prepared (Section 13.6)—provide C_{12} and C_{14} chain lengths, but a carbon more or less is also acceptable. The SHOP process comprises a combination of four reactions, each of which was already known, at least in concept, although some required modification. Thus it is an excellent example of that form of creativity that involves the reordering of old knowledge to achieve a new end result.

As shown in Figure 3.8, the first step in the process is the oligomerization of ethylene as described in Section 3.3.3. A spread of chain lengths is obtained with a "bell-shaped" statistical distribution. The processes can be engineered so that the peak of the distribution is at C_{10}–C_{14} and these α-olefins comprise about 30% of the reaction mixture, which means that approximately 70% of unwanted chain lengths is produced.

From the C_4–C_{40} mixture of α-olefins, C_{10}–C_{14} products are separated by distillation (Step 2, Fig. 3.8). Any other chain length may also be removed by fractionation should a market exist for it. The C_{10}–C_{14} α-olefins are hydroformylated (Step 3, Fig. 3.8) to C_{11}–C_{15} alcohols. Linear hydroformylation normally requires a rhodium catalyst (Section 4.8), which is best recovered by distilling the product to leave the expensive rhodium in the vessel.

Shell's products have too high molecular weights to allow for rhodium recovery in this way. More important, the rhodium catalyst does not shift the double bond to the α-position as is required later in the process. Accordingly, Shell uses a dicobalt octacarbonyl catalyst with ligands such as tributylphosphine. This catalyst has the even more important advantage of making possible the linear hydroformylation of internal olefins, as will be seen later. From the C_{10}–C_{14} α-olefins, linear alcohols result with chain lengths of 11–15 carbon atoms.

In the fourth step (Fig. 3.8), the C_4–C_{10} and the C_{16}–C_{40} α-olefins are isomerized to internal olefins using heterogeneous catalysts such as magnesium oxide granules. Isomerization takes place at 80–140°C and 4–20 bar. Internal double bonds are distributed randomly throughout the olefin molecules.

The next step (Step 5 in Fig. 3.8) involves metathesis (Section 2.2.8) of the short and long-chain internal olefins to provide new internal olefins with a broad distribution of chain lengths, some of which are in the desired C_{10}–C_{14} range. The example shows a metathesis reaction between a C_4 and a C_{20} internal olefin to yield two molecules of a C_{12} internal olefin. The desired chain lengths are removed by distillation, 10–15% being obtained (Step 6 in Fig. 3.8). These internal olefins are again subjected to linear hydroformylation as shown in Step 7, using the above-described cobalt octacarbonyl catalyst, which causes the migration of the double bond to the α-position. The intermediate aldehydes, which are produced by hydroformylation, are hydrogenated *in situ*.

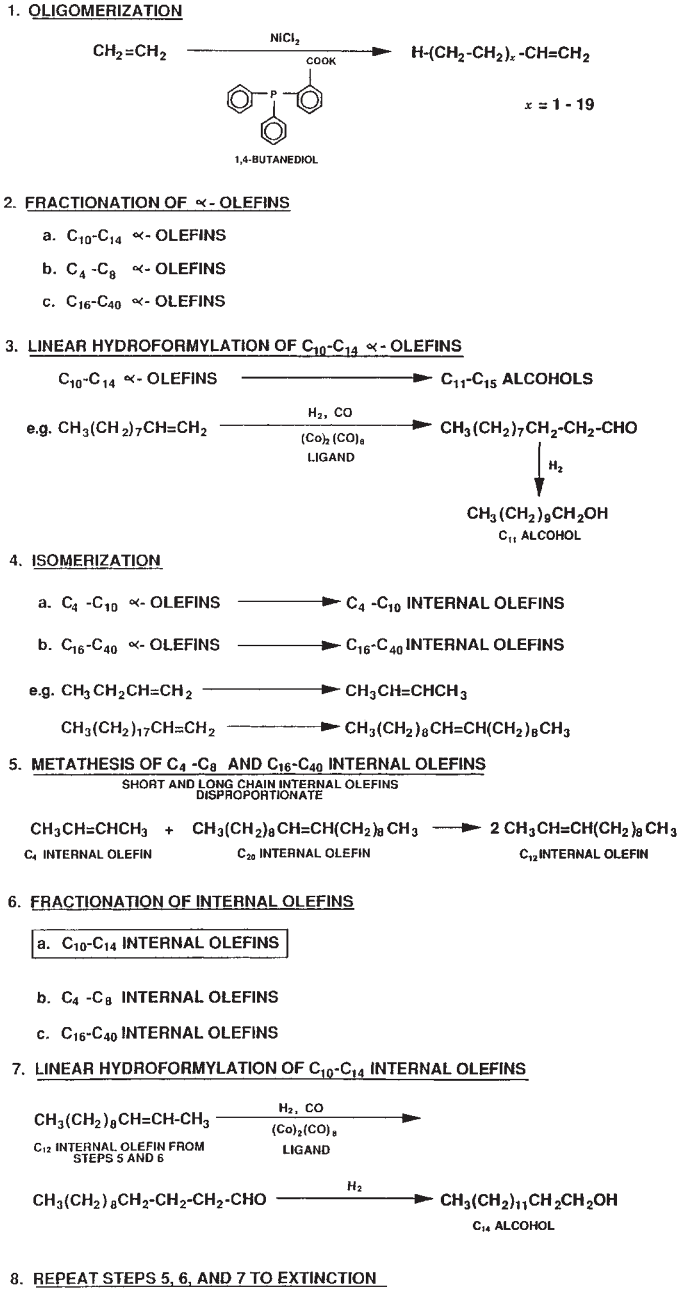


FIGURE 3.8 Shell higher olefins process (SHOP).

Step 6 provides further quantities of C_4–C_8 and C_{16}–C_{40} internal olefins and these again are subjected to metathesis. Thus Steps 5–7 are repeated to extinction. High yields are obtained in each step.

The process is versatile. Thus C_6 and C_8 olefins may be removed for sale to LLDPE manufacturers (Section 3.1.4) and the C_{10} olefin may be isolated for use in synthetic lubricants. In this case, only the C_4 olefin is used in the metathesis reaction, and if necessary more can be obtained from steam or catalytic cracking (Sections 2.2.1, 2.2.2). The internal olefins may be sold for the alkylation of benzene (Section 7.4) for surfactants.

3.4 VINYL CHLORIDE

Vinyl chloride is the monomer for poly(vinyl chloride) (PVC). Originally it was made by addition of hydrogen chloride to acetylene:

$$CH{\equiv}CH + HCl \longrightarrow CH_2{=}CHCl$$

Ethylene-based vinyl chloride was first made by production of ethylene dichloride from ethylene and chlorine which, when heated in contact with pumice or charcoal, yielded vinyl chloride and 1 mol of HCl

$$CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2ClCH_2Cl \longrightarrow CH_2{=}CHCl + HCl$$

The byproduct presented a problem, for hydrogen chloride is corrosive and difficult to ship. Unless it can be used on site, its value is small. Disposal presents economic and environmental problems. Furthermore, half the chlorine (produced by electrolysis, which requires expensive electrical energy) was wasted.

One solution was to react the byproduct hydrogen chloride with acetylene in a second plant. In this way, the chlorine was saved but, as the price gap between ethylene and acetylene widened, the process (the so-called integrated chlorine economy) became less attractive and a wholly ethylene-based process became desirable.

The first approach involved resurrection of a Victorian process. In 1858, Deacon had shown that hydrogen chloride can be oxidized to chlorine by air over bricks soaked in copper chloride. It was the first heterogeneous catalytic process to be operated.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

Shell investigated the reaction and improved the catalyst. The snag was that the hydrogen chloride had to be isolated and oxidized and the chlorine separated and recycled. Before the process could be instituted, a related process was developed called oxychlorination. No one, except Du Pont briefly, used the modernized Deacon process; its value lies in the fact that it led to oxychlorination. Oxychlorination is typical of modern petrochemical processes whose aim is to pass a simple feedstock through a hot tube over an appropriate catalyst, with the desired chemical emerging at the end. Of course, the secret lies in the “appropriate” catalyst.

In oxychlorination, the Deacon chemistry was incorporated into a one-step reaction in which 1 mol of ethylene, 2 mol of hydrogen chloride and air are passed over a copper chloride–potassium chloride catalyst to give ethylene dichloride. This is mixed with the ethylene dichloride from the chlorination process and cracked to vinyl chloride and byproduct hydrogen chloride, which is returned to the oxychlorination process (Fig. 3.2*e*). Unless there is a separate source of byproduct hydrogen chloride, the chlorination and oxychlorination plants are integrated and half of ethylene dichloride production is made by chlorination and half by oxychlorination. The two reactions are necessary since each provides 1 mol of hydrogen chloride. Together, this gives the 2 mol that oxychlorination requires.

This was the dominant process for many years, but a more modern approach is to make use of the hydrogen chloride produced in isocyanate manufacture (Sections 7.3.1, 8.3) to supplement supplies from the chlorination step of the integrated process. The reaction of a diamine with phosgene and its subsequent cracking to a diisocyanate (the most important route to isocyanates) generates four molecules of hydrogen chloride:

$$H_2N-R-NH_2 + 2COCl_2 \longrightarrow OCN-R-NCO + 4HCl$$

If the hydrogen chloride was not used for oxychlorination, it would present a disposal problem. It is corrosive and cannot be stored or shipped by conventional means. It can, however, be transmitted by pipeline to a vinyl chloride unit, and every isocyanate manufacturer does this. The volume of vinyl chloride produced is so large (16.92 billion lb in the United States in 2000, of which 8.46 billion lb would result from oxychlorination) that only a proportion of hydrogen chloride needs are filled by this byproduct. United States 2000 production of 4,4′-diphenylmethane diisocyanate (MDI) was 1.39 billion lb, which would give rise to about the same quantity of hydrogen chloride. Production of toluene diisocyanate was about 1 billion lb giving rise to about 1.5 billion lb of hydrogen chloride. Together these supply about 30% of oxychlorination requirements.

The direct chlorination of ethylene is generally carried out in the liquid phase with the product ethylene dichloride as the reaction medium and with dissolved $FeCl_3$, $CuCl_2$, or $SbCl_3$ as catalyst at 40–70°C and 4–5 bar.

Oxychlorination is a gas-phase reaction taking place at about 225°C and 2–4 bar with a cupric chloride catalyst supported on alumina or silica together with potassium chloride, whose chloride ion serves as an activator. The cupric chloride is the chlorinating agent. It chlorinates the ethylene and is itself reduced to cuprous chloride. Oxygen regenerates the cuprous chloride by converting it to a double salt of cupric oxide and cupric chloride. The double salt in turn reacts with the hydrogen chloride to give cupric chloride and water.

$$CH_2{=}CH_2 + 2CuCl_2 \longrightarrow CH_2ClCH_2Cl + 2CuCl$$

$$4CuCl + O_2 \longrightarrow CuO{\cdot}CuCl_2$$

$$CuO{\cdot}CuCl_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$

Because the reaction is highly exothermic, a fluidized-bed reactor, which has much better heat transfer capability than a fixed bed, may be used. The chemical industry provides many examples of the use of fluidized beds for heat transfer as in acrylonitrile production (Section 4.4), catalytic cracking (Sec 2.2.2), and recently vinyl acetate production (Section 3.6).

Vinyl chloride manufacture consumes about 20% of the chlorine produced in the United States. An objective of the chemical industry has been to devise routes to vinyl chloride and other C_2 compounds from ethane rather than ethylene. Several processes have been devised but had not been commercialized by 2004. ICI developed a vapor-phase oxychlorination of ethane, which yielded vinyl chloride, water, and hydrogen chloride. The catalyst comprised metallic silver with salts of manganese or lanthanum impregnated on an Offretite zeolite. Although conversions above 95% could be achieved, the selectivity to vinyl chloride was only about 50%. Other products included ethylene dichloride and ethylene. The latter could be oxychlorinated in a separate operation. In the mid-1990s, European Vinyl Corporation (EVC, now INEOS) announced they had developed a cost-effective process. The advantage of their technology was that the catalyst system was active at relatively low temperatures (~400°C), which contrasts with most previous efforts, which required higher operating temperatures and led to severe corrosion problems. EVC have built a 1000 ton/year pilot plant in Wilhelmshaven, Germany, and plan to construct a 300,000 tonne/year full commercial facility. The chemistry will be discussed in Section 11.2.1.

Another research aim for vinyl chloride production is to develop a process in which the overall reaction can be accomplished without isolation of the ethylene dichloride intermediate. The reaction conditions for the two steps, particularly temperatures, differ so widely, however, that satisfactory yields may not prove possible. Another possibility is the intermolecular dehydrogenation of ethylene and hydrogen chloride in the presence of a reactant for the hydrogen produced. This reaction is thermodynamically feasible but elusive.

The major use for vinyl chloride is the manufacture of polymers or copolymers (Chapter 15). It is also a starting material for vinylidene chloride, trichloroethylene, and tetrachloroethylene (Section 3.11.7). Ethylene dichloride, vinyl chloride's precursor, finds some application as a solvent, but use of most chlorine compounds in chemical processing is decreasing because of their persistence in the body. They are lipophilic and are not destroyed or excreted but are stored in body fat. Vinyl chloride itself is toxic, causing angiosarcoma, a rare type of liver cancer. Accordingly, its concentration in ambient air during manufacture must be strictly limited.

3.5 ACETALDEHYDE

Acetaldehyde is one of the few industrial chemicals whose production has shrunk in the past 15 years. Its decline has been paralleled only by acetylene (Section 10.3) and more recently by US petrochemical ethanol (Section 3.9). In the

United States in 1969, 1.65 billion lb of acetaldehyde was manufactured. By the late 1980s, this had decreased to an estimated 650 million lb and growth was not foreseen.

Acetaldehyde was manufactured by an ingenious process, the Wacker reaction. Its demise was caused by the discovery of equally ingenious processes for the preparation of the two chemicals for which it served as precursor, *n*-butanol (Section 4.12) and, more important, acetic acid (Section 10.5.2.2). These three processes are examples of shutdown economics (see Appendix 1). *n*-Butanol is no longer made by the old process, but a little acetaldehyde is still oxidized to acetic acid in Europe. The plants still operate because the cash cost of operating them is lower than the total cost of the newer processes.

Acetaldehyde was originally made by the hydration of acetylene over an oxidation–reduction catalyst, mercurous–mercuric sulfate buffered by ferric sulfate. Vinyl alcohol is assumed to form momentarily and to rearrange to acetaldehyde at atmospheric pressure and 95°C.

$$\underset{\text{Acetylene}}{CH\equiv CH} + H_2O \longrightarrow \underset{\text{Vinyl alcohol}}{[CH_2{=}CHOH]} \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO}$$

Ethylene became much cheaper than acetylene in the early 1960s and the above route was displaced by the oxidation of ethylene-based ethanol at 450°C and 3 bar with air over a silver gauze catalyst.

$$\underset{\text{Ethanol}}{2CH_3CH_2OH} + O_2 \longrightarrow \underset{\text{Acetaldehyde}}{2CH_3CHO} + 2H_2O$$

Alternatively, the ethanol may be dehydrogenated over a chromium oxide activated copper catalyst at 270–300°C. This is a more attractive process if a use exists for the byproduct hydrogen. By 1974, only 15% of acetaldehyde was made from acetylene.

These routes in turn gave way to the Wacker process described by Parshall as "a triumph of common sense." It is based on the observation that ethylene is oxidized by palladium chloride to acetaldehyde. As indicated, stoichiometric quantities of palladium chloride are required.

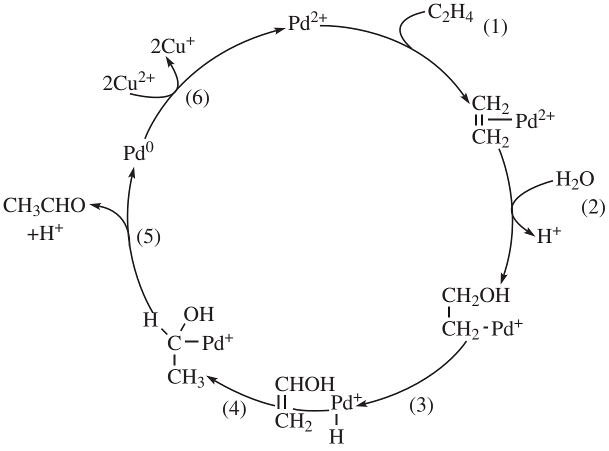
$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + PdCl_2 + H_2O \longrightarrow \underset{\text{Acetaldehyde}}{CH_3CHO} + Pd^0 + 2HCl$$

In the 1950s, chemists at Wacker Chemie in Germany converted the palladium salt from a stoichiometric to a catalytic component by including cupric chloride, oxygen, and hydrogen chloride in the reaction mixture. Each atom of palladium, when formed, is then oxidized back to palladium chloride. The cuprous chloride is converted back to cupric chloride by oxygen:

$$Pd^0 + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

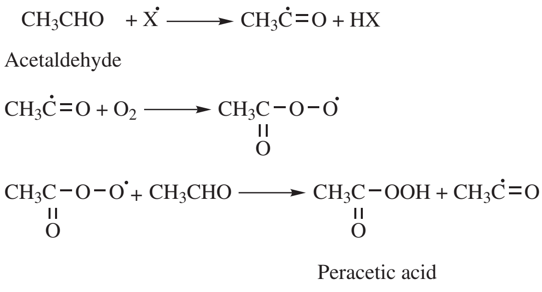
$$4CuCl + 4HCl + O_2 \longrightarrow 4CuCl_2 + H_2O$$

The mechanism proposed by Parshall (see notes at the end of this chapter) is shown in the following cycle:



There is general agreement about the formation of the π-complex (Step 1). Step (2) is the OH addition. There is controversy as to how this step takes place. Thereafter the mechanism is straightforward, with hydrogen abstraction by the palladium (Step 3) followed by rearrangement (Step 4) and acetaldehyde formation (Step 5). The palladium chloride–copper chloride mixture is analogous to the oxychlorination system (Section 3.4).

n-Butanol (Section 4.12) was originally made from acetaldehyde by an aldol condensation (Section 3.11.3). Today it is made from propylene (Section 4.12) by hydroformylation. Acetic acid was made by oxidation of acetaldehyde with either air or oxygen over a manganese or cobalt acetate catalyst at 60°C. The oxidation takes place by a radical mechanism in which peracetic acid is the intermediate.

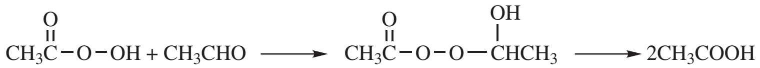


$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \dot{X} \longrightarrow CH_3\dot{C}=O + HX$$

$$CH_3\dot{C}=O + O_2 \longrightarrow CH_3\underset{\underset{O}{\|}}{C}-O-\dot{O}$$

$$CH_3\underset{\underset{O}{\|}}{C}-O-\dot{O} + CH_3CHO \longrightarrow \underset{\text{Peracetic acid}}{CH_3\underset{\underset{O}{\|}}{C}-OOH} + CH_3\dot{C}=O$$

The peracetic acid in turn reacts preferentially with acetaldehyde to give α-hydroxyethylperacetate, which decomposes through a cyclic transition state to 2 mol of acetic acid. The reaction goes without a catalyst at room temperature and 25–40 bar in a solvent such as ethyl acetate.



$$CH_3\overset{O}{\overset{\|}{C}}-O-OH + CH_3CHO \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-O-O-\overset{OH}{\overset{|}{C}}HCH_3 \longrightarrow 2CH_3COOH$$

α-Hydroxyethyl peracetate Acetic acid

Cheap naphtha in Europe in the 1950s motivated the development of the primary flash distillate route to acetic acid (Section 10.5.2.2). This process is still in use in Europe because it gives valuable byproducts including formic acid and propionic acid. *n*-Butane is oxidized in a related process in the United States giving methyl ethyl ketone, propionic acid, and formic acid byproducts. Cheap methanol in the 1970s similarly led to the development of methanol carbonylation (Section 10.5.2.2), a process whose economics are so good that it shut down every US manufacturer using the acetaldehyde route.

In spite of the apparently unbeatable economics of methanol carbonylation, Showa Denko in Japan developed a one-step vapor-phase process for acetic acid production by direct oxidation of ethylene and, in 1997, they constructed a 100,000 tonne/year plant (Section 10.5.2.2). The reaction is based on a supported palladium catalyst and takes place in a fixed-bed reactor at about 150–160°C and 9 bar. The gases fed to the reactor are ethylene, oxygen, steam, and nitrogen. Selectivity to acetic acid based on ethylene is reported to be about 86–88% with ethylene conversion per pass of 7–8%.

Lesser volume processes based on acetaldehyde are described in Section 3.11.3.

3.6 VINYL ACETATE

Like acetaldehyde, vinyl acetate was originally made from acetylene, except that acetic acid rather than water was added across the triple bond. The catalyst comprised zinc acetate on charcoal with sodium acetate and the reaction proceeded at about 200°C.

$$CH{\equiv}CH + CH_3COOH \longrightarrow CH_3COOCH{=}CH_2$$

Acetylene Vinyl acetate

The modification of the Wacker reaction (Section 3.5) by substitution of acetic acid for water in the presence of potassium acetate yields vinyl acetate. Two processes were developed, one a homogeneous liquid-phase reaction with a palladium chloride–cupric chloride catalyst, and the other a heterogeneous gas-phase reaction with a $PdCl_2$—$CuCl_2$, $PdCl_2$—Al_2O_3, or palladium-on-carbon catalyst onto which a trickle of potassium acetate solution flows. Fixed- and fluidized-bed variants of the heterogeneous processes are in use.

$$\underset{}{CH_2{=}CH_2} + PdCl_2 + \underset{\text{Sodium acetate}}{2CH_3COONa} \longrightarrow \underset{\text{Vinyl acetate}}{CH_3COOCH{=}CH_2} + 2NaCl + Pd^0 + CH_3COOH$$

The Pd^0 is regenerated by the $CuCl_2$ in the catalyst analogously to the conversion of Pd^0 to $PdCl_2$ in the acetaldehyde reaction (Section 3.5) except that the Cu^+ ion is converted to Cu^{2+} with air. No HCl is present since, together with the acetic acid, it is formidably corrosive.

The liquid-phase process ran into severe corrosion problems from this combination. These might have been overcome, but there were also serious mass-transfer problems because foaming in the reactor prevented sufficient ethylene from dissolving quickly enough, and thus the plant was closed.

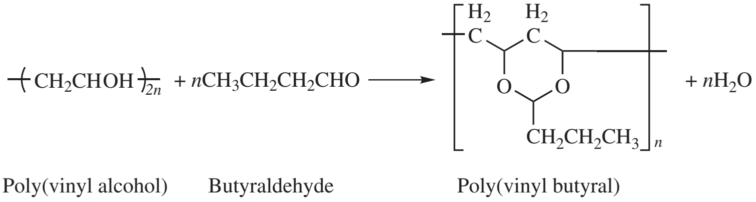
Although the liquid-phase process never really worked, it is of interest because the water produced in the reaction leads to byproduct acetaldehyde. This can be oxidized to acetic acid, which can be returned to the reactor. The system can be varied so that acetaldehyde is produced in just the right quantity to provide, on oxidation, the correct amount of acetic acid. In most two-for-one reactions (two products, in this instance acetaldehyde and vinyl acetate, from one set of equipment) the ratio of the products cannot be varied [cf. phenol–acetone production (Section 4.9)] and accordingly a market must exist for the products in the ratio in which they are produced. Here the ratio may be varied by controlling the concentration of water. This same flexibility has been demonstrated in a new process that produces both acetic acid and acetic anhydride (Section 10.5.2.3), and in a process for making ethylene glycol and dimethyl carbonate (Section 3.7.1).

The heterogeneous gas-phase process is now generally used. The sodium acetate trickle is necessary because the acetate, essential to the catalyst's performance, migrates continually. Byproducts include acetaldehyde, as might be expected, together with methyl and ethyl acetates. The conventional design for the heterogeneous gas-phase vinyl acetate process employs a tubular fixed reactor. Ethylene conversion per pass is typically about 10% and selectivity to vinyl acetate is about 94–95%, based on ethylene. In the mid-1990s, BP announced development of a fluidized bed process. In principle, this offers several advantages: improved mixing of catalyst, promoters, and feedstock; continuous removal of deactivated catalyst and addition of replacement catalyst; isothermal operation; lower capital investment and the potential to scale-up to sizes not possible with tubular reactors.

An uncommercialized process for preparing vinyl acetate from methanol is described in Section 10.5.2.4.

Vinyl acetate's major use is for conversion to poly(vinyl acetate), the basis of many adhesives and water-based emulsion paints. Some poly(vinyl acetate) is converted to poly(vinyl alcohol) by saponification or more often by transesterification with methanol to give methyl acetate as a coproduct. Ethanol may also be used, giving ethyl acetate byproduct. Poly(vinyl alcohol) reacted with formaldehyde is widely used in Japan as the basis of Vinylon fibers, which found their most spectacular use in the manufacture of the durable Mao uniform in Communist China.

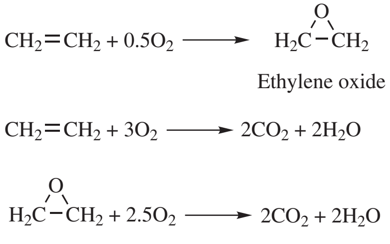
On reaction with butyraldehyde (Section 4.12), poly(vinyl alcohol) gives poly(vinyl butyral):



It forms the inner layer in safety glass, which is a sandwich of two sheets of glass held together by a layer of poly(vinyl butyral). The refractive index of poly(vinyl butyral) is the same as that of glass, hence its presence is unnoticeable, but its “stickiness” prevents the glass from shattering under impact.

3.7 ETHYLENE OXIDE

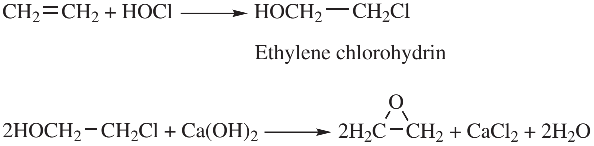
The most important ethylene-based chemical that is not primarily a polymer precursor is ethylene oxide. It is made (Figure 3.2*h*) by direct reaction of ethylene and oxygen over a silver catalyst (Section 16.1.1). The reaction is exothermic, and the simultaneous even more exothermic oxidation of both ethylene and ethylene oxide leads to the byproducts carbon dioxide and water.



Ethylene oxide technology provides an excellent example of yield improvement through incremental advances in catalyst technology. High selectivity is important because approximately 75% of the cost of ethylene oxide derives from the raw material, ethylene. Initially, selectivity with a silver catalyst supported on alumina was of the order of 65–70%. Because of improved catalysts, selectivities now average about 82% over the length of catalyst life and, at the start of a run, the very latest silver catalysts give over 90% selectivity. Shell Development, Union Carbide (now Dow Chemical), and Halcon/Scientific Design have numerous patents describing improved catalysts. One of Shell’s patents discloses the addition of minute amounts of potassium, rubidium, or cesium ions to a silver catalyst to increase yields. Apparently the concentration of the added ions is critical.

The reaction is carried out at 15 bar and 250°C. A few parts per million of ethylene dichloride are frequently included in the reaction mixture to inhibit oxidation of ethylene to carbon dioxide and water. The ethylene dichloride decomposes to give chlorine atoms, which adsorb preferentially on the silver surface on the sites where oxygen would otherwise chemisorb to catalyze the combustion reaction.

The direct addition of oxygen to a double bond, discovered in the 1930s by Union Carbide, provides a striking example of the power of catalysis. The original process for ethylene oxide production, now obsolete, involved addition of hypochlorous acid to ethylene to give ethylene chlorohydrin, which with calcium hydroxide underwent a dehydrohalogenation to provide ethylene oxide and calcium chloride.



$$CH_2{=}CH_2 + HOCl \longrightarrow HOCH_2{-}CH_2Cl$$

Ethylene chlorohydrin

$$2HOCH_2{-}CH_2Cl + Ca(OH)_2 \longrightarrow 2H_2C\overset{O}{-}CH_2 + CaCl_2 + 2H_2O$$

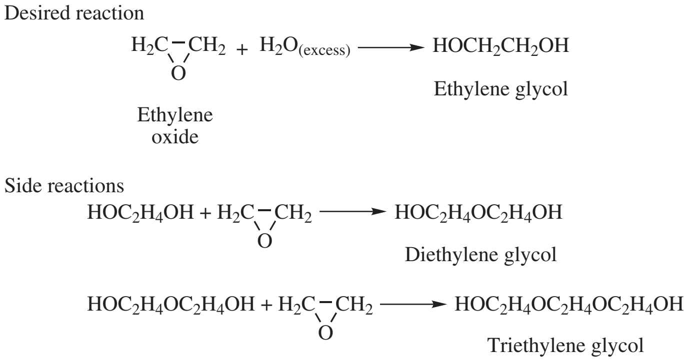
The process was wasteful of chlorine and, although yields were high, dilute solutions were necessary. The calcium chloride, whose weight was three times greater than that of the product, provided disposal problems. Also, since HOCl forms in an equilibrium reaction ($Cl_2 + H_2O \leftrightharpoons HCl + HOCl$) ethylene dichloride was a byproduct as was chloroethyl ether, $ClCH_2CH_2OCH_2CH_2Cl$.

In 2002, about 61% of US ethylene oxide was hydrolyzed to ethylene glycol (Section 3.7.1). Other major uses include reaction with alkylphenols, fatty alcohols, (Sections 3.3.2, 13.6), fatty amides and amines (Section 13.2), and anhydrosorbitol to yield nonionic surfactants. The ethoxylated alkylphenols are the most important. Hydroxyl-terminated polymers of ethylene oxide and propylene oxide are useful as isocyanate coreactants for urethanes. Ethylene oxide reacts with ammonia to provide aminoethyl alcohols (Section 3.11.6.4), and may be converted to poly(ethylene glycols) (Section 3.11.6.1).

Ethylene oxide reacts with starch and cellulose to provide hydroxyethyl derivatives (Sections 14.2, 14.3). The former is a more readily dispersible form of starch, which finds application in both food formulation and paper manufacture. The latter is a thickener for water-based paints and a protective colloid for water dispersions.

3.7.1 Ethylene Glycol

Ethylene glycol is prepared either by the acid catalyzed or more often by the uncatalyzed hydration of ethylene oxide (Fig. 3.2*h*). A huge excess of water is used (18–24 mol of water per mole of ethylene oxide) to prevent the formation of di-, tri-, and higher ethylene glycols. Even with high water/ethylene oxide ratios, mono-, di-, and triglycols are obtained in a weight ratio of about 91:8.6:0.4.



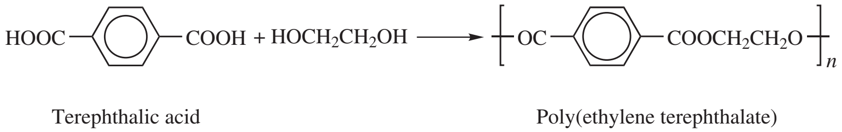
$$H_2C\overset{O}{-}CH_2 + H_2O_{(excess)} \longrightarrow HOCH_2CH_2OH$$

$$HOC_2H_4OH + H_2C\overset{O}{-}CH_2 \longrightarrow HOC_2H_4OC_2H_4OH$$

$$HOC_2H_4OC_2H_4OH + H_2C\overset{O}{-}CH_2 \longrightarrow HOC_2H_4OC_2H_4OC_2H_4OH$$

The reaction of ethylene oxide with glycols may form oligomers of ethylene oxide, and they may be prepared in this way "on purpose," if needed, by the side reactions shown.

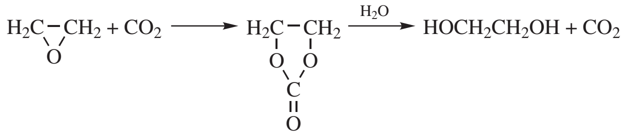
Purification of the ethylene glycol is complex requiring repeated fractional distillations to remove the water and to separate the glycol from its oligomers. High purity is necessary for the preparation of polyester resins, one of ethylene glycol's two major uses. About 68% of ethylene glycol production is reacted with purified terephthalic acid or sometimes with dimethyl terephthalate to produce poly(ethylene terephthalate) (Sections 9.3.3, 15.1).



The polymer may be spun into textile fibers; Dacron or Terylene are well-known brand names. It can also be made into strong biaxially oriented films known as "Mylar." In the 1990s, it found an important and rapidly growing application as a plastic for the fabrication of soft-drink bottles.

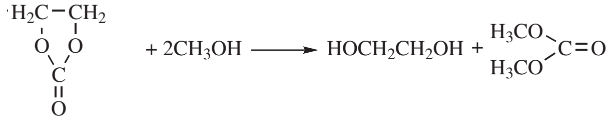
Ethylene glycol's other major use, a nonpolymer one, is as antifreeze in automobile radiators. In 2001, the United States used about 30% of its ethylene glycol for antifreeze; in Western Europe the figure was about 20%. Uses for di- and triethylene glycol are described in Section 3.11.6.1.

A process for converting ethylene oxide to ethylene glycol in high selectivity is described in Union Carbide (now Dow) and Texaco (now Huntsman) patents. It involves the reaction of ethylene oxide with carbon dioxide at 190°C and 13 bar to give ethylene carbonate (Section 3.11.6.3), which in turn reacts with water at the same pressure but at 170°C to give ethylene glycol and carbon dioxide. The first step is catalyzed by tetraethylammonium bromide and potassium iodide.



Ethylene
carbonate

The process eliminates large excesses of water as well as the possibility for the formation of di-, tri-, and higher ethylene glycols. Union Carbide started to commercialize this process in a Canadian ethylene oxide–ethylene glycol plant. The winters in Canada are so cold, however, that the ethylene carbonate froze and plugged the process lines, so that the approach had to be abandoned. A related approach is to react the ethylene carbonate with methanol to give a mixture of ethylene glycol and dimethyl carbonate, which can be separated by distillation.



Ethylene carbonate Ethylene glycol Dimethyl carbonate

Dimethyl carbonate was originally prepared from methanol and the highly toxic phosgene. The above route eliminates the hazard as does another route involving the oxidative carbonylation of methanol.

$$\underset{\text{Methanol}}{2CH_3OH} + 0.5O_2 + CO \longrightarrow \underset{\text{Dimethyl carbonate}}{(CH_3O)_2C{=}O} + H_2O$$

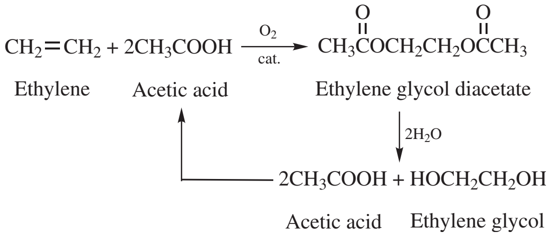
The reaction of carbon dioxide with diepoxides leads to carbonate polymers, which have not been commercialized but which are of interest because of their biodegradability. The use of dimethyl carbonate in a non-phosgene route to polycarbonates is described in Section 7.1.2.2.

Still another means for reducing oligomer formation is described in a Carbide patent. The ethylene oxide hydrolysis is carried out with a vanadate or molybdate catalyst attached to an ion exchange resin. Only 2.5 mol of water are used per mol of ethylene oxide, and 100% selectivity to ethylene glycol at 100% conversion is claimed. The route has not been commercialized presumably because of the difficulty of removing traces of catalyst from the final product.

3.7.2 Proposed Non-Ethylene Oxide Processes for Ethylene Glycol Production

Even with improved catalysts, yields of ethylene oxide from ethylene epoxidation are on average only about 82%. Hence, other processes for ethylene glycol were sought. If an economic one were to be found, the 2002 market for ethylene oxide would be cut by 40%, since at least that proportion is converted to glycol in Europe. In the United States, the figure is 61%.

In one proposed reaction, ethylene, acetic acid, and oxygen combine to give ethylene glycol diacetate. These are the reactants that give vinyl acetate in the Wacker process, but the proportion of acetic acid is greater, and a different catalyst, tellurium oxide with an alkyl halide, is used. Two ethylenic hydrogen atoms instead of one are substituted. The diacetate can be hydrolyzed to ethylene glycol and the acetic acid recycled so that the overall reaction involves only ethylene, air, and water.



$$CH_2{=}CH_2 + 2CH_3COOH \xrightarrow[\text{cat.}]{O_2} CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_2O\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{2H_2O} 2CH_3COOH + HOCH_2CH_2OH$$

An 800 million lb/year plant was built in the late 1970s but corrosion problems not unlike those associated with the original liquid-phase vinyl acetate plant (Section 3.6) proved its downfall.

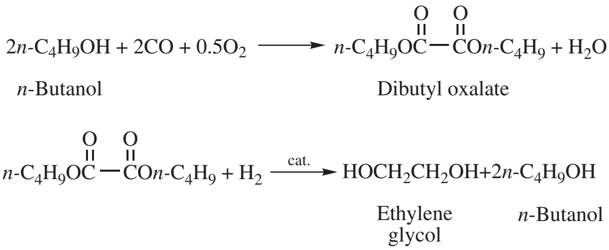
Although corrosion-resistant materials could undoubtedly be found to withstand the chemistry of this process, there has been no attempt to revive it, but Mitsubishi is using the same chemistry successfully for the manufacture of 1,4-butanediol (Section 5.1) from butadiene. Because of the greater reactivity of the conjugated double-bond system, a catalyst comprising palladium and tellurium without halide can be used so that the environment is less corrosive.

Carbide has pioneered a process for ethylene glycol based on the direct combination of carbon monoxide and hydrogen:

$$2CO + 3H_2 \longrightarrow HOCH_2CH_2OH$$

Carbide investigated many catalysts including rhodium carbonyl cluster catalysts, which require temperatures of 240°C and pressures of 1000–3000 bar. In other studies, a ruthenium carbonyl complex and an organosilicon compound such as trimethylethoxysilane were used at 400°C and 1000 bar. Selectivity to ethylene glycol is 60–65% and methanol is the major coproduct. Methyl formate, other esters, 1,2-propanediol, glycerol, and water are also formed.

This poor selectivity led Carbide to join forces with Ube Industries in Japan to develop a process based on the hydrogenolysis of oxalate esters, compounds that Ube had investigated extensively as described in Section 10.6.1. Selectivity is usually improved when reactions are carried out stepwise. Thus in the first step di-*n*-butyl oxalate results, which on hydrogenolysis yields ethylene glycol and butanol for recycling.



$$2n\text{-}C_4H_9OH + 2CO + 0.5O_2 \longrightarrow n\text{-}C_4H_9O\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}On\text{-}C_4H_9 + H_2O$$

n-Butanol Dibutyl oxalate

$$n\text{-}C_4H_9O\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}On\text{-}C_4H_9 + H_2 \xrightarrow{\text{cat.}} HOCH_2CH_2OH + 2n\text{-}C_4H_9OH$$

Ethylene glycol *n*-Butanol

The second step is similar to one used by Du Pont until 1968 in which formaldehyde was carbonylated in the presence of water to give glycolic acid at 200°C and 700 bar. The esterification of the acid with methanol provided methyl glycolate which, on hydrogenolysis, yielded ethylene glycol and methanol for recycling.

$$HCHO + CO + H_2O \longrightarrow HOCH_2COOH$$

Glycolic acid

$$HOCH_2COOH + CH_3OH \longrightarrow HOCH_2COOCH_3 + H_2O$$

Methyl glycolate

$$HOCH_2COOCH_3 + 2H_2 \longrightarrow HOCH_2CH_2OH + CH_3OH$$

Ethylene glycol

The carbonylation takes place at 200°C and 70–100 bar at high selectivity, as does the esterification reaction. The hydrogenolysis occurs at 200°C and 30 bar with an appropriate catalyst. The released methanol is recycled so that the overall reaction is

$$2H_2 + HCHO + CO \longrightarrow HOCH_2CH_2OH$$

An improvement in the process involves the use of HF in the carbonylation step. Coupled with the development of more active catalysts for the hydrogenolysis (Section 10.3), this could make the Du Pont process attractive should coal-based synthesis gas become a major feedstock.

A Monsanto process for ethylene glycol is based on the hydroformylation of formaldehyde in the presence of a homogeneous rhodium catalyst. The ligand is tri(*p*-trifluoromethylphenyl)phosphine together with triethylamine. Glycol aldehyde results, which on hydrogenation yields ethylene glycol.

$$HCHO + CO + H_2 \longrightarrow HOCH_2CHO \xrightarrow{H_2} HOCH_2CH_2OH$$

Glycol aldehyde

A free radical-induced chain reaction between methanol and formaldehyde provides the basis for an interesting process in which free radicals from di-*tert*-butyl peroxide convert methanol to a hydroxymethyl radical. This radical attacks formaldehyde to provide an ethylene glycol radical, which attacks another molecule of methanol to provide ethylene glycol and a hydroxymethyl radical for further propagation.

$$CH_3OH + \dot{X} \longrightarrow \dot{C}H_2OH + HX$$

$$\dot{C}H_2OH + HCHO \longrightarrow HOCH_2CH_2\dot{O}$$

$$HOCH_2CH_2\dot{O} \xrightarrow{CH_3OH} \underset{\text{Ethylene glycol}}{HOCH_2CH_2OH} + \dot{C}H_2OH$$

Unfortunately, the chains in the process are too short, and many of the hydroxymethyl radicals couple to provide ethylene glycol and terminate the chain reaction. Thus consumption of the peroxide initiator is unacceptably high.

$$2\dot{C}H_2OH \longrightarrow HOCH_2CH_2OH$$

Another approach involves the electrohydrodimerization of formaldehyde. The problem, as in all electrochemical reactions, is to obtain adequate current efficiencies.

$$2HCHO + 2H^+ + 2e^- \longrightarrow HOCH_2CH_2OH$$

Improved catalysts for ethylene oxide production and the difficulties involved in the direct routes have prevented the commercialization of any of the routes to ethylene glycol that do not go via ethylene oxide, despite the apparent possibility of higher overall yields based on ethylene and the large growth in glycol demand stemming from the explosion of poly(ethylene terephthalate) consumption for bottles.

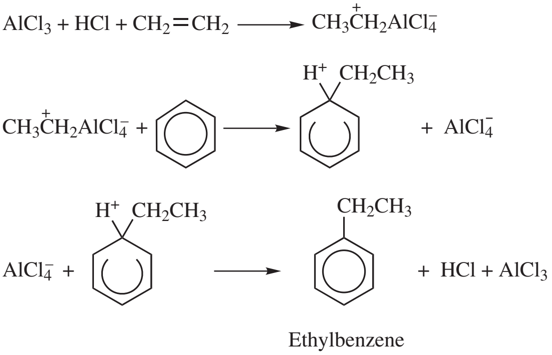
3.8 STYRENE

After polyethylene and poly(vinyl chloride), the third large tonnage polymer to be made from ethylene is polystyrene. Its monomer, styrene, was used initially not in polystyrene but in a copolymer with butadiene that served as a substitute for natural rubber. Germany had started commercial production of Buna S rubber in 1938 and during World War II was totally dependent on it. With the capture by Japan of the rubber producing areas of Southeast Asia, the United States too was forced into a crash program for synthetic rubber development. The Buna S-type (GR-S) rubber was the result of an admirable coordinated effort between many academic, industrial, and government laboratories. If either side in the war had lacked synthetic rubber, its war effort might have collapsed.

Synthetic rubbers now account for about 62% of world consumption. Styrene–butadiene (SBR) rubber, the descendant of Buna S and GR-S, is the preferred material for automobile tires together with lesser amounts of polybutadiene rubber, butyl rubber, and natural rubber (Section 5.1) and accounts for some 60% of world synthetic rubber production. Styrene is widely used in copolymers as well as in homopolymers and rubber-modified styrene polymers.

Styrene provides an example of a "classical" reaction for ethylene. The major process for styrene manufacture involves a Friedel–Crafts reaction between benzene and ethylene to form ethylbenzene. Some ethylbenzene is also produced during catalytic reforming (Section 2.2.3) and can be removed from the C_8 fraction by so-called superfractionation. Dehydrogenation to styrene in the presence of steam and a catalyst provides styrene and hydrogen. (Fig. 3.2*i*). An alternate process for styrene, to be described later (Section 4.7), gives propylene oxide as a coproduct. It is used commercially by Lyondell, Repsol, and ELLBA, a joint venture between Shell and BASF.

The Friedel–Crafts alkylation was initially carried out at 85–95°C at atmospheric pressure in the liquid phase with aluminum chloride and a small amount of HCl. In one process, boron trifluoride is used. The mechanism is well-established



Yields are high, but small amounts of di- and polyethylbenzenes result, because the alkylaryl complex is more reactive than the hydrogen aryl complex and can continue to add ethyl groups. The di- and polyethylbenzenes are recycled and transalkylated with excess benzene to give ethylbenzene. The aluminum chloride catalyst originally used is corrosive and hard to dispose of. An improvement was the development of zeolite ZSM-5 as a catalyst in a continuous vapor-phase reaction that can operate at a temperature of 400°C at 18 bar. The higher temperature makes heat recovery easier, and the product is obtained in 99.5% selectivity with 98% ethylene conversion.

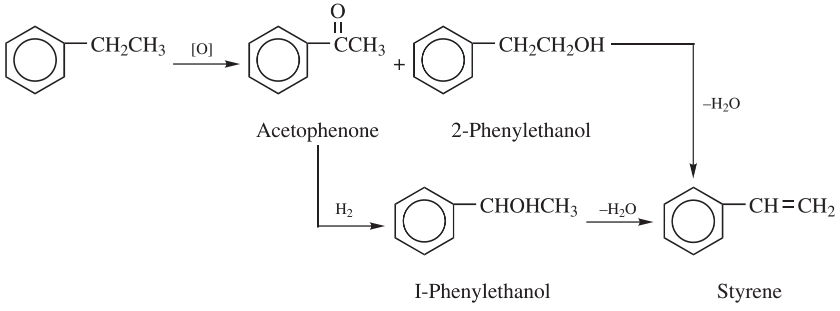
The dehydrogenation is endothermic and requires a high temperature (550–600°C) and low pressure. As in steam cracking (Section 2.2.1), superheated steam is added to inhibit coking and reduce the partial pressure of the reactants. The catalyst is highly selective. Its major component, present usually to the extent of more than 50%, comprises the oxides of iron, cobalt, manganese, chromium, or zirconium. If iron oxide is used, another oxide is added as a stabilizer to keep the iron in the ferric state. Alkaline metal oxides, particularly potassium and rubidium oxides, are effective. A third ingredient is a carbon formation inhibitor, which may also be the oxide of potassium or rubidium. An oxide of copper, silver, cadmium, thorium, or vanadium is added as a secondary promoter to increase the effectiveness of the primary active ingredient. A "cement" such as calcium aluminate aids pellet formation. Organic substances such as methylcellulose may be included to introduce porosity when they burn off during the calcining of the catalyst.

The oxidative dehydrogenation of ethylbenzene was never considered practical because both ethylbenzene and styrene are oxygen-sensitive. In the mid-1980s, UOP described a new catalyst, to be used in combination with present catalysts. It preferentially oxidizes to water the hydrogen produced from the ethylbenzene in a separate step, thus not affecting the other components of the reaction mixture. It comprises platinum, tin, and lithium on alumina. Since water formation is exothermic, the heat generated reduces the superheated steam input necessary in the current process. This development was commercialized in the late 1990s.

Dow has proposed a route to styrene by oxydehydrogenation of 4-vinylcyclohexene prepared by butadiene dimerization (Section 5.1.3.1). The dimerization is performed in the gas phase at 100°C and 25 bar over a proprietary catalyst consisting of copper-loaded Y-zeolite. The second step is oxydehydrogenation of vinylcyclohexene to styrene. This reaction is catalyzed by mixed-metallic oxides in the vapor phase at about 400°C and 2.4 bar.

A variant of this process, developed by DSM, converts the vinylcyclohexene to ethylbenzene, and the dehydrogenation can then be carried out in a conventional plant. The DSM process employs liquid-phase butadiene dimerization to 4-vinylcyclohexene catalyzed by iron dinitrosyl chloride–zinc complex [$Fe(NO_2)Cl/Zn$], while the dehydrogenation to ethylbenzene is catalyzed by palladium on magnesium oxide. Final conversion of ethylbenzene to styrene can be carried out with conventional dehydrogenation catalysts. Other proposed routes are the conversion of toluene to stilbene followed by metathesis with ethylene (Section 8.4), and the ZSM-5-catalyzed alkylation of toluene with methanol (Section 8.4). The literature contains references to the production of styrene directly from benzene and ethylene in the presence of oxidants for the liberated hydrogen. Apparently, none of these routes can compete economically with the conventional route and, as of the early 2000s, there were no plans for commercialization.

An obsolete process for styrene production involved oxidation of ethylbenzene to acetophenone and 2-phenylethanol, followed by hydrogenation of the acetophenone to 1-phenylethanol, which dehydrates easily to styrene.



p-Methylstyrene was at one time proposed as an alternative monomer to styrene. It is made by the ZSM-5-catalyzed alkylation of toluene with ethylene. This zeolite catalyst is *para*-orienting providing high selectivity to *p*-methylbenzene. Dehydrogenation of the ethyl group provides *p*-methylstyrene. Since toluene is cheaper than benzene, *p*-methylstyrene should enjoy an economic advantage. In fact, the initial lower scale of production and escalating toluene prices in the mid- and late-1980s eliminated this advantage and the product was not commercialized.

Styrene's major use is for the manufacture of polystyrene, almost half of which is used for disposables such as packaging, and plastic cups and cutlery. The remainder goes into radio and TV cabinets, toys, door liners and trays for refrigerators, housings for small appliances such as clocks, housewares, furniture components, and in construction for window moldings, window shutters, and pipes. The longer lasting applications such as radio cabinets require so-called high-impact styrene (HIPS), made by polymerizing styrene in the presence of polybutadiene elastomer. A fast growing use is for audio and video cassettes and for support materials for magnetic tapes.

The second largest use for styrene is for elastomers including styrene–butadiene rubbers and latexes. An important application is in so-called thermoplastic rubbers, typical of which is a block polymer of polystyrene–polybutadiene–polystyrene (Section 5.1).

The third largest use is in styrene copolymers of which the most important is acrylonitrile–butadiene–styrene (ABS), an engineering polymer widely used for computer and calculator cases, telephones, and related applications. The acrylonitrile provides strength, the butadiene flexibility and impact resistance, and the styrene gloss and hardness. Styrene is also found in styrene–acrylonitrile (SAN) and styrene–maleic anhydride copolymers. Both are glass-like and are useful for cosmetics bottles with decorative shapes.

The fourth most important use for styrene is as a reactive solvent for unsaturated polyesters, which, after curing, become copolymers of styrene and the polyester (Section 9.1.1).

3.9 ETHANOL

Ethanol was first produced from ethylene in 1930. Ethylene was reacted with sulfuric acid to provide ethyl sulfate and diethyl sulfate, both of which were hydrolyzed to ethanol. Sulfuric acid was recycled. Diethyl ether is a byproduct and indeed the reaction can be run selectively to provide it (Section 3.11.10).

$$CH_2{=}CH_2 + H_2SO_4 \longrightarrow \underset{\text{Ethyl sulfate}}{CH_3CH_2OSO_3H} + \underset{\text{Diethyl sulfate}}{(CH_3CH_3O)\ SO_2}$$

$$CH_3CH_2OSO_3H + H_2O \longrightarrow CH_3CH_2OH + H_2SO_4$$

$$(CH_3CH_2O)_2SO_2 + 2H_2O \longrightarrow 2CH_3CH_2OH + H_2SO_4$$

The above process was replaced by direct hydration in which water is added to ethylene over a phosphoric acid catalyst on silica or celite.

$$CH_2{=}CH_2 + H_2O \xrightleftharpoons{\text{cat.}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

Selectivity to ethanol is of the order of 92–98%. There is a problem, however, in that high temperatures are required to give acceptable rates of reaction but, as in the classic Haber process (Section 10.5.1), the higher temperatures favor the ethylene–water side of the equilibrium. Under optimum conditions, conversion per pass may be as low as 4%, although 20% has been reported. This means that large amounts of ethylene must be recycled.

Typical reaction conditions for the direct hydration are 300°C and 69 bar. The crude ethanol is purified by distillation to produce an azeotrope with water containing 95.6 volume percent ethanol. Absolute or 100% ethanol is usually prepared by azeotropic distillation. Benzene is added and the mixture distilled. The ternary azeotrope that distills carries the benzene and water with it, leaving anhydrous alcohol as the bottom product. Another method uses countercurrent extraction with glycerol or ethylene glycol. The added component hydrogen bonds to the water and allows anhydrous alcohol to be obtained from the top of the column. Less energy-intensive methods for obtaining anhydrous ethanol provide an active area of research. Membrane technology has apparently held promise for at least two decades, but its development is slow.

Until about 1950, ethylene was expensive and was obtained from fermentation ethanol by dehydration—the reverse of the above processes. With the advent of cheap ethylene from steam cracking, the petrochemical route to ethanol became more economical than fermentation. By the early 1970s, scarcely any industrial ethanol was made by fermentation in the United States, although there was a legal requirement in most countries that potable ethanol be made in the traditional way.

In the United States in the 1980s, this trend was reversed when government subsidies were introduced to facilitate the production of ethanol by fermentation of corn starch. The product went into automotive fuel known as gasohol. Fermentation ethanol is not economical without subsidies; and whether it provides a positive energy balance considering the energy required to grow the corn, isolate the starch from it, and distill the resulting ethanol is controversial. If petroleum or natural gas is required to make up the energy deficit, fermentation ethanol cannot be considered a renewable energy source (see note at the end of this chapter). Fermentation alcohol is discussed in Chapter 14 and Section 2.3.3. The fact remains that production of fermentation alcohol in the US has boomed. Between October 2001 and January 2004, ten new plants came onstream, producing about 315 million gallons ethanol, three have expanded, giving another 50 million gallons and twelve are under construction promising another 275 million gallons. Industrial demand for synthetic plus fermentation alcohol is about 270 million gallons and fuel, food and beverage demand (all fermentation) is about 1800 million gallons. This could triple by 2012 if legislation favors ethanol as the oxygenate in gasoline.

The development of gasohol has motivated the development of other routes to ethanol, the most important of which is methanol homologation, as yet uncommercialized (Section 10.6.1).

Ethanol was once the basis for acetaldehyde and acetic acid production (Section 3.5) and this still may be practiced to a small extent in India and Brazil. In these countries, ethylene was also prepared by the dehydration of ethanol as late as the mid-1980s. In addition to gasohol, ethanol has humble uses for ethyl ester formation. Ethyl acetate is made by esterification of acetic acid with ethanol, from acetaldehyde (Section 3.11.3), or by the direct addition of ethylene to acetic acid. BP started a 220,000 tonne/year plant in 2001 to operate the last of these processes, known as AVADA. Ethylene and acetic acid react in the presence of a heteropolyacid catalyst to give ethyl acetate at a claimed high selectivity and 99.97% purity. This is the world's largest ethyl acetate plant and is motivated by its increasing use as a more "acceptable" solvent than hydrocarbons.

$$CH_2{=}CH_2 + CH_3COOH \longrightarrow \underset{\text{Ethyl acetate}}{CH_3COOCH_2CH_3}$$

In some countries, where ethanol is expensive or there is surplus acetaldehyde capacity, ethyl acetate is made by a Tishchenko reaction (Section 3.11.3). Sasol in South Africa was said to be investigating such a process in the early 2000s. Ethanol is a solvent for surface coatings, cleaning preparations, and cosmetics. Industrial ethanol is aerobically fermented to white vinegar (dilute acetic acid) of the type used for pickling. Gourmet vinegars—wine vinegar, cider vinegar, and so on, made by fermentation of alcoholic beverages—are also available. Ten percent of industrial ethanol production was used for vinegar in the United States in 2001.

3.10 MAJOR CHEMICALS FROM ETHYLENE—A SUMMARY

Sections 3.1–3.8 described the "major" chemicals from ethylene, that is, chemicals that are produced in the United States at a level of more than about 1 billion lb/year. These chemicals and their production volumes for 1977, 1993, and 2000 are shown in Table 3.3 together with growth rates over this period. The sixth column gives the quantity of ethylene required to give the product, if it is made directly from ethylene. Thus figures for ethylbenzene and ethylene dichloride are given, but not for styrene and vinyl chloride, which are made from them. Only one polymer family, polyethylenes, is included in Table 3.3 since these are made directly from ethylene. Styrene, vinyl chloride, ethylene glycol, and vinyl acetate are all important monomers for polymers. Indeed, this is the most important use for all the chemicals except ethanol and ethylene oxide. The latter is mainly converted to ethylene glycol, for use in polymers and antifreeze, but the polymer application is now dominant.

Four chemicals (acetic acid, acetic anhydride, acetaldehyde, and ethanol) lost volume precipitously between 1977 and 1993 insofar as they were based on ethylene. The first three of these were displaced by processes for acetic acid production, especially methanol carbonylation (Section 10.5.2.2), which did not involve ethylene. Acetic acid from ethylene-based acetaldehyde was formerly acetaldehyde's most important use. Acetic anhydride may be made from acetic acid via intermediate production of ketene or by a carbonylation route from methyl acetate (Section 10.5.2.3). Accordingly it is no longer ethylene based.

TABLE 3.3 Production of Chemicals from Ethylene: United States and Western Europe (1977–2000)

Polymer or Chemical	1977	1993	2000	Average Annual Increase 1993–2000 (%)	Ethylene Consumption[a] (Million lb)	United States End-use Pattern (%)	Western European End-use Pattern (%)
		(Million lb)					
Ethylene	24,650	41,250	55,364	4.3			
Polyethylenes	8,000	21,956	29,494	4.3			
LDPE		7,226	7,575	0.7	7,575	13.7	24.1
LLDPE		4,841	7,951	7.3	7,951	14.4	9.3
HDPE		9,941	13,968	5.0	13,968	25.2	22.6
Ethylene dichloride	10,480	17,950	21,850	2.8	6,180	11.2	13.9
Ethylbenzene	7,300	11,760	13,156	1.6	3,489	6.3	7.3
Ethylene oxide	4,420	5,680	8,526	6.0	6,782	12.2	9.7
Vinyl acetate	1,600	2,830	3,300	2.2	921	1.7	8.0
Ethanol[b]	1,300	210	180	−2.2	201	0.4	1.5
Acetaldehyde	970	385	420	1.3	267	0.5	1.6
α-Olefins	820	1,952	3,150	7.1	3,150	5.7	2.0
Other						14.5	

[a] This figure is the ethylene required to give the 2000 production. Yields are assumed to be 100% except for ethylene oxide where 80% is assumed.

[b] Consumption of industrial ethanol is considerably higher because of imports from Saudi Arabia.

Source: *Chem. Eng. News; Guide to the Business of Chemistry* (cited in Section 0.4.5).

Ethanol was formerly a raw material for acetic acid too, because it was oxidized to acetaldehyde prior to the advent of the Wacker process, but that application had disappeared long before 1977. However, ethanol production in the United States has plummeted more recently (Section 1.5) because of imports from Saudi Arabia.

Another chemical showing low growth in Table 3.3 is ethylene glycol. Sixty percent of US ethylene glycol goes into poly(ethylene terephthalate). Thus one reason for the low growth is the depressed poly(ethylene terephthalate) fiber market in developed countries. The bottle market, although growing at 9%/year, has only a quarter of the global market so far and is not making up for the low fiber growth, except in the United States where, in 2002, 5 billion lb was used for bottles and 4.4 billion lb was used for fiber. Growth in East Asia overall, on the other hand, has been strong. In 1996 consumption of the precursor terephthalic acid was 21 billion lb and is expected to rise to 36 billion lb by 2005. In 2000, Asia Pacific had 37% of world capacity for PET production as compared to 25% in 1990. The profitability of the Asian plants has been low, however, because of overcapacity.

Ethylene glycol in antifreeze is growing only slowly because sealed radiator formulations last longer. Also, a small amount has been replaced by which, although less effective as an antifreeze, is not toxic to household pets who might lick up spilled material. This marketing initiative was probably an attempt to expand propylene glycol business. However, other compounding ingredients in antifreeze are toxic, especially anticorrosives. Finally, the methyl and ethyl glycol ethers from ethylene oxide (Section 3.11.6.2) were found to be teratogenic and were banned.

A relative newcomer to the list of major chemicals is α-olefins, some of which are converted to fatty alcohols (Section 3.3). Fatty alcohols as ethoxylates or sulfates are increasingly used in surfactants for detergents because of their greater biodegradability. α-Olefins are comonomers in linear low- and high-density polyethylene production. 1-Decene finds a growing use because its trimer is a synthetic lubricant. C_{12}–C_{18} α-olefins are converted to C_{13}–C_{19} alcohols by hydroformylation (Section 4.8) for use in surfactants, and C_6–C_8 α-olefins yield C_7–C_9 alcohols for plasticizers (Section 9.1.1).

Much of the growth in ethylene consumption came from the polyethylenes, which continue to find new applications. The LDPE usage is declining as it is being replaced by LLDPE. A market for LDPE will continue because in some applications it is used in combination with LLDPE to give easier molding and extrusion and because it is essential for extrusion coating of paper board for milk and juice cartons.

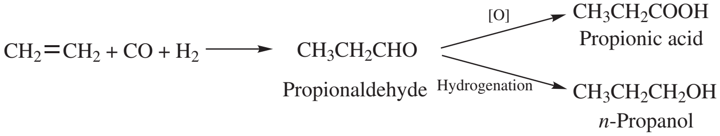
The sixth column of Table 3.3 shows the amount of ethylene going into each of the end-uses. The requirements of these major end-uses account for 90% of ethylene consumption even on the basis of the assumed 100% yields. That leaves about 10% to go into the myriad lesser volume chemicals, which will be discussed in the remainder of this chapter

3.11 LESSER VOLUME CHEMICALS FROM ETHYLENE

This section deals with chemicals from ethylene that are produced in volumes of less than 1 billion lb/year in the United States. The chemicals are listed in Table 3.1.

3.11.1 Hydroformylation—Propionaldehyde, Propionic Acid, and *n*-Propanol

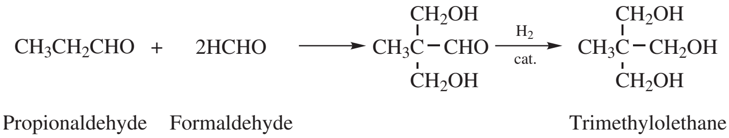
The oxo- or hydroformylation reaction with ethylene produces propionaldehyde, which in turn can be oxidized to propionic acid or reduced to *n*-propanol.



$$CH_2{=}CH_2 + CO + H_2 \longrightarrow CH_3CH_2CHO \begin{cases} \xrightarrow{[O]} CH_3CH_2COOH \\ \xrightarrow{\text{Hydrogenation}} CH_3CH_2CH_2OH \end{cases}$$

Hydroformylation, which is discussed in Section 4.12, was carried out initially with a dicobalt octacarbonyl, $(Co)_2(CO)_8$, catalyst at temperatures of about 150°C and 250–300 bar. A breakthrough was the discovery that rhodium chloride with ligands such as triphenylphosphine allowed the reaction to take place at temperatures of around 100°C and 10–25 bar. Hydrogenation of the aldehyde to the alcohol takes place with a nickel catalyst at 2–3 bar at about 115°C in the gas phase. In the liquid phase, higher pressures are required.

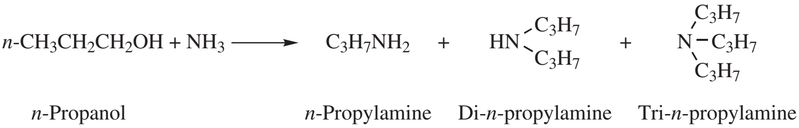
Propionaldehyde reacts with formaldehyde to provide trimethylolethane.



$$CH_3CH_2CHO + 2HCHO \longrightarrow CH_3\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}{-}CHO \xrightarrow[\text{cat.}]{H_2} CH_3\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}{-}CH_2OH$$

The formaldehyde condenses with the two active hydrogens to give a dimethylolaldehyde. The aldehyde group may then be reduced *in situ* by another mole of formaldehyde, which is itself oxidized to formic acid. Alternatively, the dimethylolaldehyde may be isolated and reduced catalytically. The same chemistry, the so-called Tollens reaction, is used to synthesize pentaerythritol (Section 3.11.3) and trimethylolpropane (Section 10.5.2.1). Trimethylolethane is used for alkyd resins and urethanes (Section 7.3.1).

n-Propanol reacts with ammonia to form mono-, di-, and tripropylamines:



$$n\text{-}CH_3CH_2CH_2OH + NH_3 \longrightarrow C_3H_7NH_2 + HN(C_3H_7)_2 + N(C_3H_7)_3$$

One of *n*-propanol's important uses is as a solvent, particularly for flexographic inks used with natural rubber rolls that would be attacked by more powerful solvents. Natural rubber rolls are necessary because printing on plastic film requires high flexibility and low hysteresis losses. *n*-Propanol also finds small use in the production of propyl esters such as propyl acetate.

Propionic acid may be made by the oxidation of propionaldehyde. The liquid-phase reaction is catalyzed by a cobalt salt at 100°C and 6–7 bar.

An alternative process involves the carbonylation of ethylene by a so-called Koch reaction, which is carried out with a nickel carbonyl catalyst in the liquid phase at 200–250 bar and 300°C. Nickel carbonyl is poisonous and in this reaction it is formed *in situ*.

$$CH_2{=}CH_2 + CO + H_2O \longrightarrow \underset{\text{Propionic acid}}{CH_3CH_2COOH}$$

A low-pressure process for carbonylation of ethylene in the presence of water, which has not been commercialized, makes use of a nickel–molybdenum carbonyl catalyst with iodide and phosphoric acid promoters at about 200°C and 10–30 bar.

The route to acetic acid by oxidation of naphtha (Section 11.2.1) gives propionic acid as a byproduct. In the United Kingdom, such a plant is kept in operation because of the value of the byproducts. A proposed propionic acid synthesis involves the homologation of acetic acid with CO and H_2 at 220°C and 270 bar. Butyric and valeric acids form as minor coproducts. The reaction is homogeneous and is catalyzed by ruthenium or rhodium with ligands such as acetylacetonate, with an iodide promoter or cocatalyst.

$$CH_3COOH + CO + 2H_2 \longrightarrow C_2H_5COOH + H_2O$$

The major use of propionic acid is as a feed and grain preservative. An important use, particularly for the calcium or sodium salts, is as a food preservative especially in baked goods. A minor use is for the preparation of cellulose propionate via propionic anhydride.

3.11.2 Ethyl Halides

Ethyl chloride and ethyl bromide can be made by the addition of the corresponding hydrogen halides to ethylene. The reaction between ethylene and hydrogen chloride takes place either in the liquid or the gas phase at moderate temperatures and pressures with halide catalysts such as $AlCl_3$. A second process involves the chlorination of ethane, which, unlike methane (Section 10.2), gives 80% ethyl chloride before the dichloro compound starts to form. The chlorination of ethane generates ethyl chloride and hydrogen chloride, which can then be added to ethylene to provide more ethyl chloride in an integrated process.

$$C_2H_6 + Cl_2 \longrightarrow C_2H_5Cl + HCl$$

$$CH_2{=}CH_2 + HCl \longrightarrow C_2H_5Cl$$

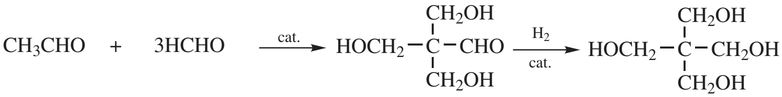
The chlorination reaction takes place at 400°C. Since chlorine will not add to an olefin (Section 4.14.1) at this high temperature, the ethylene and ethane may be in the same reaction mixture, the chlorination of the ethane taking place in the presence of the essentially inert ethylene.

A route to ethyl chloride from ethanol and hydrogen chloride is obsolete because ethanol is more expensive than either ethane or ethylene.

Ethyl chloride consumption in the United States in 1974 was 662 million lb. By 1991, this had dropped by 80%. Its major use was in the manufacture of lead tetraethyl, an octane improver for gasoline. The tetraethyl was combined with lead tetramethyl to control volatility. Both of these were almost completely phased out from the United States by 1991. Ethyl chloride is still used to etherify cellulose to ethyl cellulose. Small quantities are consumed as solvents, refrigerants, and topical anesthetics. Ethyl bromide is a low volume specialty chemical which, like its chlorine analogue, can be made either by the addition of HBr to ethylene or by the bromination of ethane.

3.11.3 Acetaldehyde Chemistry

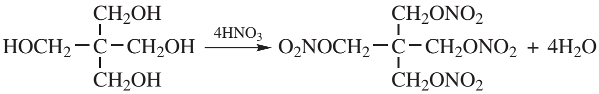
Acetaldehyde has been discussed previously (Section 3.5) as a derivative of ethylene whose consumption has declined because its major uses have disappeared. Nonetheless, in 2001, 400 million lb were produced in the United States. There are many lower volume chemicals still requiring acetaldehyde. Acetaldehyde with formaldehyde in the presence of alkali yields pentaerythritol:



$$CH_3CHO + 3HCHO \xrightarrow{\text{cat.}} HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CHO \xrightarrow[\text{cat.}]{H_2} HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

Acetaldehyde Formaldehyde Pentaerythritol

In pentaerythritol, as in trimethylolethane formation, the aldehyde group of the trimethylolacetaldehyde may be reduced by 1 mol of formaldehyde, which oxidizes to 1 mol of formic acid in a crossed Cannizzaro reaction. Calcium hydroxide is frequently used as a catalyst. Alternatively, the aldehyde may be isolated and reduced catalytically. Pentaerythritol production in 2001 was 150 million lb and, in 2002, 136 million lb. Sixty percent goes into alkyd resins, 16% mixed with neopentyl glycol in esters (Sections 4.12.1 and 10.5.2.1) for lubricants, and 11% into rosin and tall oil esters. The tetranitrate is an explosive and is also a vasodilator for the treatment of *angina pectoris*, as is the more widely used glyceryl trinitrate, but it consumes only 4% of production.



$$HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH \xrightarrow{4HNO_3} O_2NOCH_2-\overset{\displaystyle CH_2ONO_2}{\underset{\displaystyle CH_2ONO_2}{C}}-CH_2ONO_2 + 4H_2O$$

Pentaerythritol tetranitrate

Acetaldehyde undergoes the aldol condensation with an alkaline catalyst. Mild hydrogenation to avoid dehydration leads to 1,3-butanediol, which is of historical interest because on double dehydration it yields butadiene. This reaction was important during World War II when the monomer was needed with styrene for synthetic rubber.

$$2CH_3CHO \longrightarrow \underset{\text{Acetaldol}}{CH_3CHOHCH_2CHO} \xrightarrow[\text{cat.}]{H_2}$$

$$\underset{\text{1,3-Butanediol}}{CH_3CHOHCH_2CH_2OH} \xrightarrow{-2H_2O} \underset{\text{Butadiene}}{CH_2{=}CH{-}CH{=}CH_2}$$

Dehydration of acetaldol in the presence of acetic acid gives crotonaldehyde, which can be oxidized to crotonic acid. The oxidation is a mild one, carried out at room temperature and slightly above atmospheric pressure. Crotonic acid is a speciality monomer for use in copolymers where pendant carboxyl groups are required.

$$CH_3CHOHCH_2CHO \xrightarrow{-H_2O} \underset{\text{Crotonaldehyde}}{CH_3{-}CH{=}CH{-}CHO} \xrightarrow{[O]} \underset{\text{Crotonic acid}}{CH_3{-}CH{=}CHCOOH}$$

Mild hydrogenation of crotonaldehyde yields *n*-butyraldehyde. More extensive hydrogenation attacks both the double bond and the aldehyde group to give *n*-butanol. Today, that route is obsolete and *n*-butanol comes from the hydroformylation of propylene (Section 4.12).

$$\underset{\text{Crotonaldehyde}}{CH_2CH{=}CH{-}CHO} \xrightarrow[\text{cat.}]{H_2} \underset{n\text{-Butyraldehyde}}{C_3H_7CHO} \xrightarrow[\text{cat.}]{H_2} \underset{n\text{-Butanol}}{C_3H_7CH_2OH}$$

Crotonaldehyde, in a curious reaction with ethanol, gives butadiene and acetaldehyde.

$$\underset{\text{Crotonaldehyde}}{CH_3CH{=}CHCHO} + \underset{\text{Ethanol}}{CH_3CH_2OH} \longrightarrow \underset{\text{Butadiene}}{CH_2{=}CHCH{=}CH_2} + \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O$$

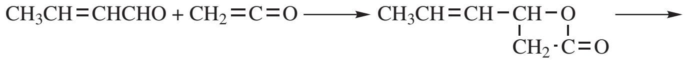
The latter can be recycled and converted to more crotonaldehyde. This synthesis of butadiene is still in use in India and in the People's Republic of China, although it will no doubt be phased out as petrochemical C_4 fractions become available.

Sorbic acid, 2,4-hexadienoic acid, in which both double bonds are *trans*, was originally made by two processes, one of which involves an aldol condensation between acetaldehyde and crotonaldehyde. The resulting sorbic aldehyde was then mildly oxidized to sorbic acid.

$$\underset{\text{Crotonaldehyde}}{CH_3CH{=}CHCHO} + \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{-H_2O} \underset{\text{Sorbaldehyde}}{CH_3CH{=}CH{-}CH{=}CH{-}CHO} \xrightarrow{[O]}$$

$$\underset{\text{Sorbic Acid}}{CH_3CH{=}CH{-}CH{=}CHCOOH}$$

Selectivities are low since several aldol condensations can take place. In today's more sophisticated process, crotonaldehyde is reacted with ketene to give a β-lactone intermediate, which is hydrolyzed and dehydrated to sorbic acid.



$$CH_3CH{=}CHCHO + CH_2{=}C{=}O \longrightarrow CH_3CH{=}CH{-}\underset{CH_2\cdot C{=}O}{CH{-}O} \longrightarrow$$

β-Lactone

$$CH_3CH{=}CH{-}CH{=}CHCOOH$$

Sorbic acid

It is also possible to form an intermediate polyester by the self-polymerization of the lactone. It too will hydrolyze to sorbic acid. Ketene results from the pyrolysis of either acetone or acetic acid (Section 10.5.2.3).

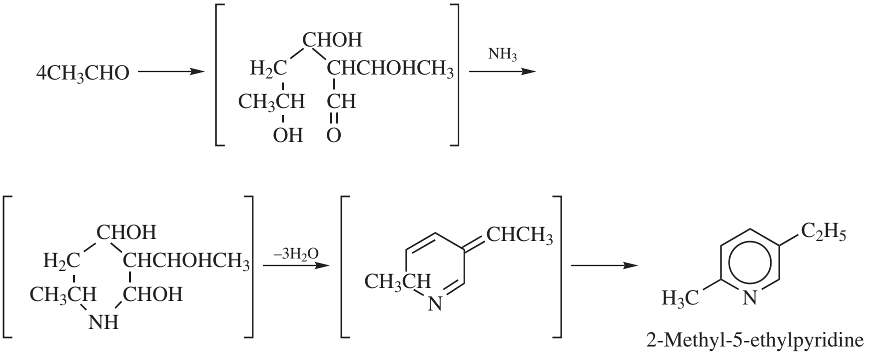
Sorbic acid and its calcium and potassium salts (Section 3.11.1) are used like calcium propionate as preservatives for foods, especially baked goods.

Acetaldehyde is a source of ethyl acetate by way of the Tishchenko reaction (Section 3.9). The catalyst is aluminum ethoxide.

$$2CH_3CHO \xrightarrow{\text{cat.}} CH_3COOCH_2CH_3$$

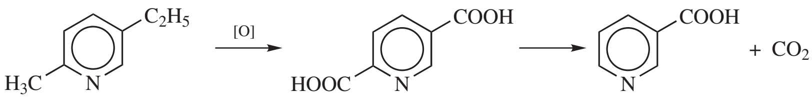
Ethyl acetate

Pyridine and some of its derivatives are still isolated from coal tar (Section 12.1), but synthetic pyridines from acetaldehyde have achieved importance. Ammonium acetate catalyzes the reaction of acetaldehyde and ammonia to 2-methyl-5-ethylpyridine by way of aldol condensations between four molecules of the aldehyde, followed by ring closure with ammonia. Triple dehydration brings about aromatization. The reaction takes place at high temperatures and pressures.



2-Methyl-5-ethylpyridine

Oxidation of 2-methyl-5-ethylpyridine with nitric acid gives nicotinic acid by way of the decarboxylation of the intermediate dicarboxylic acid.

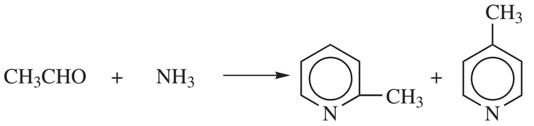


2-Methyl-5-ethylpyridine

Nicotinic acid

Nicotinic acid and its amide are both termed vitamin B_6. They lower lipid levels in the blood but their use is limited by side effects. They have a long established but more doubtful pharmaceutical use as peripheral vasodilators.

The reaction of acetaldehyde and formaldehyde in the presence of ammonia and a catalyst yields a mixture of pyridine and 3-picoline. Acetaldehyde and ammonia in a 3:1 ratio, when passed over various dehydration–dehydrogenation catalysts (e.g., PbO or CuO on alumina; ThO_2 on ZnO; or CdO on silica-alumina) give equimolar quantities of 2- and 4-picolines. 2-Picoline is a component of a coccidiostat; 4-picoline is a precursor of the antituberculosis drug isoniazid. Pyridines generally are of value as intermediates for herbicides, pesticides, and pharmaceuticals.



Acetaldehyde Ammonia 2-Picoline 4-Picoline

The chlorination of acetaldehyde yields trichloroacetaldehyde or chloral. In practice, ethanol is chlorinated and is oxidized to the aldehyde *in situ*. In the presence of the HCl that forms, the trichloroacetaldehyde reacts with more ethanol to give the acetal.

$$\mathrm{CH_3CH_2OH + 4Cl_2 \longrightarrow 5HCl + [CCl_3CHO] \xrightarrow{2C_2H_5OH} CCl_3CH\begin{matrix}OC_2H_5\\ OC_2H_5\end{matrix} + H_2O}$$

Diethylacetal of trichloroacetaldehyde

The reaction of the acetal with sulfuric acid provides the desired trichloroacetaldehyde and ethyl hydrogen sulfate.

$$\mathrm{CCl_3CH\begin{matrix}OC_2H_5\\ OC_2H_5\end{matrix} + 2H_2SO_4 \longrightarrow CCl_3CHO + 2C_2H_5OSO_3H + 2H_2O}$$

Trichloro acetaldehyde

The hydrate of chloral is stable and in the past has been used as a soporific known in the vernacular as “knock-out” drops. The major use for trichloroacetaldehyde has been in DDT manufacture (Section 7.6).

Peracetic acid (more appropriately peroxyacetic acid) is an intermediate in the oxidation of acetaldehyde to acetic acid (Section 3.5). If the oxidation is carried out at temperatures no higher than 40°C and at about 35 bar, the peracetic acid can be isolated.

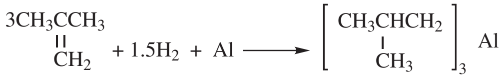
$$CH_3CHO + O_2 \longrightarrow CH_3\underset{\displaystyle O}{\underset{\|}{C}}-OOH$$

Peracetic acid

The alternative route to peracetic acid is the reaction of acetic acid with expensive hydrogen peroxide. Peracetic acid is used for several industrially important epoxidation reactions including the epoxidation of soybean oil (Section 13.7), α-olefins, and certain diunsaturates such as vinylcyclohexene (butadiene dimer, Section 5.1.3.1), which give reactive intermediates for the formation of materials resembling epoxy resins.

3.11.4 Metal Complexes

Triethylaluminum is important for the production of Ziegler alcohols and α-olefins (Section 3.3.2). Its combination with titanium salts provides the Ziegler–Natta catalyst (Sections 3.1, 4.5). Triisobutylaluminum is an alternative. The process for preparing triethylaluminum is more complex than that for its higher analogues. Triisobutylaluminum results from the interaction of isobutane with hydrogen and aluminum at 150°C and 200 bar.



$$3CH_3\underset{\displaystyle CH_2}{\underset{\|}{C}}CH_3 + 1.5H_2 + Al \longrightarrow \left[CH_3\underset{\displaystyle CH_3}{\underset{|}{C}H}CH_2\right]_3 Al$$

Isobutene Triisobutylaluminum

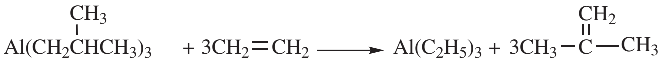
Triethylaluminum, on the other hand, cannot be made directly from ethylene, hydrogen, and aluminum, because so high a temperature is required that the triethylaluminum formed reacts with more ethylene to give a mixture of higher alkyl aluminums. Thus it is necessary to react preformed triethylaluminum with aluminum powder and hydrogen to produce diethylaluminum hydride, which then reacts with more ethylene to yield more triethylaluminum than was used initially. Alternatively, both steps can be combined by simultaneous addition of hydrogen and ethylene to a mixture of triethylaluminum and aluminum powder.

$$4Al(C_2H_5)_3 + 2Al + 3H_2 \xrightarrow{120^\circ C} 6AlH(C_2H_5)_2$$

Triethylaluminum Diethylaluminum hydride

$$AlH(C_2H_5)_2 + C_2H_4 \xrightarrow{70^\circ C} Al(C_2H_5)_3$$

The exchange reaction between triisobutylaluminum and ethylene also gives triethylaluminum. Isobutene is recycled.



$$Al(CH_2\overset{\displaystyle CH_3}{\overset{|}{C}H}CH_3)_3 + 3CH_2{=}CH_2 \longrightarrow Al(C_2H_5)_3 + 3CH_3-\overset{\displaystyle CH_2}{\overset{\|}{C}}-CH_3$$

Triisobutylaluminum Isobutene

3.11.5 Ethylenediamine and Related Compounds

The reaction of ethylene dichloride (Section 3.3) with ammonia provides ethylenediamine and higher homologues including diethylenetriamine, triethylenetetramine, and tetraethylenepentamine. The compounds form as hydrochlorides and are transformed to free bases with sodium hydroxide. The structures of the bases are shown in the equation. The reaction is carried out in the liquid phase with molar excesses of ammonia as great as 30:1 on a molar basis to minimize the formation of higher homologues. If the latter are required, less ammonia is used.

$$\mathrm{ClCH_2CH_2Cl + 2NH_3} \longrightarrow \underset{\text{Ethylenediamine dihydrochloride}}{\mathrm{NH_2CH_2CH_2NH_2.2HCl}} + \underset{\text{Diethylenetriamine}}{\mathrm{NH_2CH_2CH_2NHCH_2CH_2NH_2}} +$$

$$\underset{\text{Triethylenetetramine}}{\mathrm{NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2}} + \underset{\text{Tetraethylenepentamine}}{\mathrm{NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2}}$$

The above reaction gives vinyl chloride and organic-contaminated ammonium chloride as byproducts, formed by the dehydrohalogenation of ethylene dichloride:

$$\underset{\text{Ethylene dichloride}}{\mathrm{ClCH_2CH_2Cl + NH_3}} \longrightarrow \underset{\text{Vinyl chloride}}{\mathrm{CH_2{=}CHCl}} + \mathrm{NH_4Cl}$$

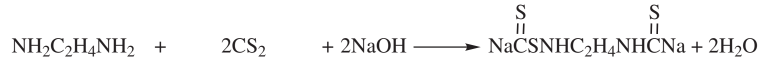
These present environmental problems. Accordingly, a process now more widely used has been devised for the production of ethyleneamines from ethanolamines (Section 3.11.6.4) and ammonia. Piperazine, aminoethylpiperazine, and hydroxyethylpiperazine are byproducts.

$$\underset{\text{Ethanolamine}}{\mathrm{HOC_2H_4NH_2}} + \mathrm{H_2 + NH_3} \longrightarrow \text{Di- and polyamines shown in the above equation plus}$$

Piperazine Aminoethylpiperazine Hydroxyethylpiperazine

The reaction, a reductive amination, is carried out at high pressure in the vapor phase in the presence of hydrogen, with an amination catalyst such as nickel, cobalt, or copper. These polyamines are used as cross-linking agents for epoxy resins (Section 4.14.1) and for the preparation of low molecular weight fatty polyamide resins by reaction with so-called dimer acids (Section 13.3).

The reaction of ethylenediamine with carbon disulfide and sodium hydroxide gives the sodium salt of a bis(dithiocarbonate), an important fungicide, "Dithane."



$$NH_2C_2H_4NH_2 + 2CS_2 + 2NaOH \longrightarrow Na\overset{S}{\overset{\|}{C}}SNHC_2H_4NH\overset{S}{\overset{\|}{C}}Na + 2H_2O$$

Ethylene diamine Carbon disulfide Dithane

The reaction of ethylenediamine with formaldehyde and sodium cyanide in alcohol solution gives the sodium salt of ethylenediaminetetraacetic acid (EDTA), an important chelating agent.

$$H_2NCH_2CH_2NH_2 + 4HCHO + 4NaCN + 4H_2O \xrightarrow[80^{\circ}C]{NaOH}$$

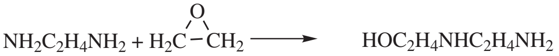
Formaldehyde Sodium cyanide

$$(NaOOCCH_2)_2NCH_2CH_2N(CH_2COONa)_2 + 4NH_3$$

Disodium salt of EDTA

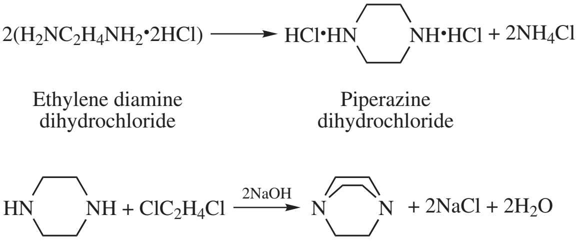
An alternative route involves the reaction of ethylenediamine with sodium chloroacetate. The product is a chelating agent both for alkaline earth and heavy metal ions.

Ethylenediamine reacts with ethylene oxide to provide hydroxyethylaminoethylamine, a textile finishing agent and an epoxy resin curing agent.



Ethylene oxide Hydroxyethylaminoethylamine

Piperazine dihydrochloride forms from the condensation of 2 mol of ethylenediamine dihydrochloride. Reaction of piperazine with ethylene dichloride yields triethylenediamine or DABCO, the acronym of its chemical name 1,4-diazabicylo-(2,2,2)-octane. Triethylenediamine is an important catalyst for the interaction of isocyanates with polyols in urethane technology.



Ethylene diamine dihydrochloride

Piperazine dihydrochloride

"DABCO"

3.11.6 Ethylene Oxide and Ethylene Glycol Derivatives

3.11.6.1 Oligomers Ethylene oxide oligomers—diethylene glycol and triethylene glycol—form during the hydrolysis of ethylene oxide to ethylene glycol (Section 3.8.1). If more of the oligomers are desired, less water is used for the hydrolysis, but normally more than enough byproduct diethylene glycol is available. Additional triethylene glycol is produced by the reaction of ethylene oxide with ethylene glycol or diethylene glycol (Section 3.7.1).

Di- and triethylene glycols are used in the manufacture of unsaturated polyesters (Section 9.3.4) to which they impart resilience and toughness. The ether linkages, however, increase water sensitivity. They are also used as solvents in polyurethane formulations and as the basis for textile chemicals, which serve as lubricants, softeners, finishers, and dye assistants. They have been used for the extraction of aromatic hydrocarbons from aliphatic/aromatic mixtures such as catalytic reformate (Section 2.2.3) but sulfolane (Section 5.1.4) has largely replaced them. The glycols are useful for dehydration of natural gas, in the manufacture of plasticizers and surfactants, as tobacco humectants, and at a concentration no greater than 5% as antifreeze components. Triethylene glycol serves as a coalescing agent in water base paints to fuse solid particles of the vehicle into a film. The oligomeric polyethylene glycols are water soluble, waxy solids, useful in cosmetic formulations and as ion coordination catalysts.

It is possible to obtain high molecular weight polyethylene glycols by the polymerization of ethylene oxide with an iron catalyst. These have not found extensive use. One of their interesting applications is to reduce the viscosity of water by decreasing its hydrogen bonding. Lower viscosity water enables it to flow through pipes more easily particularly in fire fighting systems.

3.11.6.2 Glycol Ethers and Esters Ethylene oxide reacts with alcohols to provide glycol ethers, the most important of which was ethylene glycol monoethyl ether (Cellosolve, Oxitol), the reaction product of ethanol and ethylene oxide. Oligomers, for the most part of little value, also form despite the use of large excesses of ethanol.

$$H_2C\overset{O}{-}CH_2 + C_2H_5OH \longrightarrow C_2H_5OCH_2CH_2OH$$

Ethanol Ethylene glycol monoethyl ether

The glycol ethers may be esterified with acetic acid to give ethylene glycol ether acetates or further etherified by conversion of the hydroxyl to a sodium salt, which in turn will react with methyl chloride to give 1-methoxy-2-ethoxyethane.

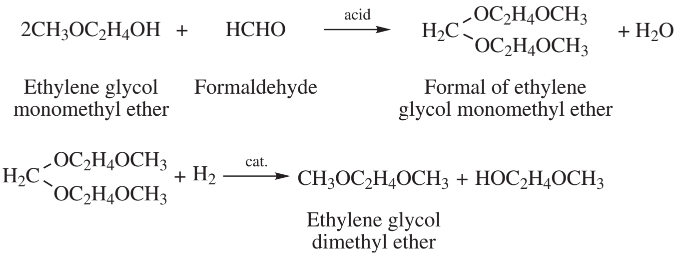
$$C_2H_5OCH_2CH_2OH \xrightarrow[-H_2O]{NaOH} C_2H_5OCH_2CH_2ONa \xrightarrow[-NaCl]{CH_3Cl} C_2H_5OCH_2CH_2OCH_3$$

1-Methoxy-2-ethoxyethane

Other commercial glycol ethers are based on methanol and butanols. The range is large; Many of the commercially important compounds are shown in Table 3.4, together with their chemical and trade names and structures. The consumer products in which they appear are also shown. The production figures are for 1994–1995 and give some indication of the market size in the mid-1990s. More recent figures do not appear to be available, perhaps because of the problems mentioned in the next paragraph. The total market for ethylene glycol based ethers and esters in 2001 was 323,000 tonnes in the United States and Brazil, 323,000 tonnes in Western Europe and 71,800 tonnes in Japan.

The ethylene glycol monomethyl and monoethyl ethers and their acetates, however, have been found to harm the reproductive and development process in mammals. Accordingly, very low emission levels in industry have been specified, and the compounds have not been used in consumer products for over 20 years. The question of their being banned generally has been debated for many years, but as late as 2002 there had been no legislation. To some extent, they are being replaced by related materials either with longer alkyl chains or based on propylene oxide (Section 4.11), which may not be quite as good solvents because of their branched structure.

The glycol ethers and esters are largely used as solvents for protective coatings and in smaller volumes as solvents for printing inks, liquid cleaners, dyestuffs, and cosmetics. They are jet fuel deicing agents and brake fluids. Ethylene glycol monobutyl ether is particularly useful in water-borne coatings. Ethylene glycol dimethyl ether is used as an aprotic solvent (Section 4.8). A synthesis that decreases raw material costs by eliminating the need for sodium hydroxide and chlorine involves formation of the formal of the ether, which on hydrogenolysis yields one mole of the dimethyl ether and one mole of the starting material for recycle.

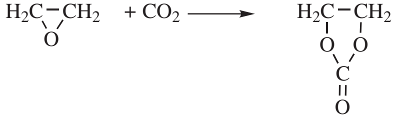


$$2CH_3OC_2H_4OH + HCHO \xrightarrow{\text{acid}} H_2C\begin{cases}OC_2H_4OCH_3\\OC_2H_4OCH_3\end{cases} + H_2O$$

$$H_2C\begin{cases}OC_2H_4OCH_3\\OC_2H_4OCH_3\end{cases} + H_2 \xrightarrow{\text{cat.}} CH_3OC_2H_4OCH_3 + HOC_2H_4OCH_3$$

3.11.6.3 Ethylene Carbonate

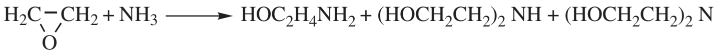
Ethylene carbonate can be prepared by reaction of ethylene oxide and carbon dioxide with basic catalysts such as sodium hydroxide, and tertiary amines or quaternary ammonium compounds. The reaction is one of the few apart from the Kolbe synthesis, methanol formation (Section 10.4.2), and urea production (Section 10.5.1) in which carbon dioxide participates. The product is a high-boiling, aprotic solvent useful in the synthesis of rubber chemicals and textile agents. Its use as an intermediate in ethylene glycol and dimethyl carbonate formation has been described (Section 3.7.1).



Ethylene oxide Ethylene carbonate

3.11.6.4 Aminoethyl Alcohols (Ethanolamines) and Derivatives

The interaction of ethylene oxide with ammonia provides ethanolamine, diethanolamine, and triethanolamine. The reaction is carried out with aqueous ammonia at about 100°C and 100 bar. If a high selectivity to ethanolamine is desired, excess ammonia is used. The formation of the di- and tri-products is favored because the rate of reaction of ammonia with ethanolamine is greater than with ethylene oxide.



$$H_2C{-}CH_2 + NH_3 \longrightarrow HOC_2H_4NH_2 + (HOCH_2CH_2)_2\,NH + (HOCH_2CH_2)_2\,N$$

Ethanolamine Diethanolamine Triethanolamine

A clever process has been devised by Nippon Shokubai, which uses a Zeolite catalyst to enhance ethanolamine and diethanolamine yields, which are currently demanded by the market. This is similar to toluene disproportionation, which provides a high yield of *p*-xylene (Section 8.1).

Ethanolamines are used for the removal of acid gases from gaseous streams. Ethanolamine absorbs carbon dioxide and hydrogen sulfide, but diethanolamine is required to absorb carbonyl sulfide. Being weakly basic, the ethanolamines form loose compounds with acid gases, but these are decomposed by steam stripping and the ethanolamines regenerated for recycle.

The reaction of fatty acid methyl esters such as methyl laurate with ethanolamine provides a fatty ethanolamide, widely used as a foam stabilizer in detergent formulations.

$$CH_3(CH_2)_{10}COOCH_3 + NH_2C_2H_4OH \xrightarrow{\text{cat.}} CH_3(CH_2)_{10}COONHC_2H_4OH + CH_3OH$$

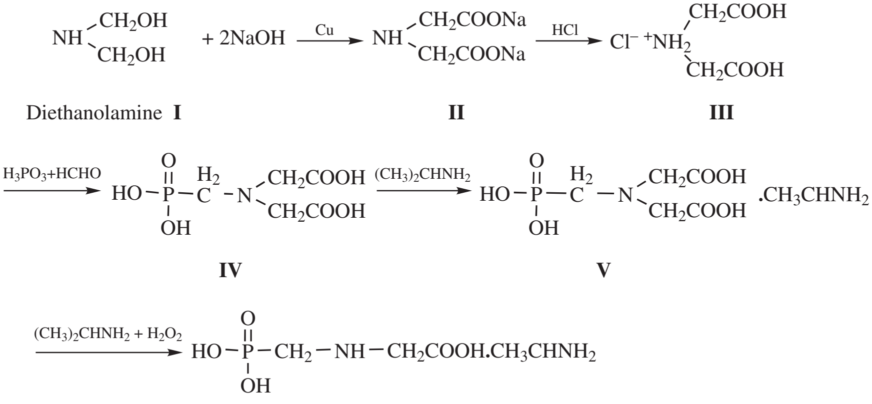
Methyl laurate Ethanolamine *N*-Hydroxyethyllauramide

Diethanolamine (DEA) demand is rising. It is required for the synthesis of the herbicide, glyphosate, better known as Round-Up (Section 17.3.10) used as its isopropylamine salt. Treatment of DEA (**I**) with sodium hydroxide and copper gives the disodium iminodiacetate (**II**). Acidification gives the amine hydrochloride (**III**). Treatment with phosphonic acid and formaldehyde inserts the phosphonomethyl moiety to give (**IV**) and further treatment with isopropylamine and then isopropylamine and hydrogen peroxide or oxygen and a catalyst gives the isopropylamine salt of glyphosate.

TABLE 3.4 Commercially Important Ethylene Glycol Ethers and Esters

Trivial Name	Chemical Name	Trade Names	Formula ($R = \text{—}OCH_2CH_2\text{—}$)	Direct Consumer End-Uses	US Production (million lb, 1994–1995)
		Ethylene Glycol ethers			
Ethylene glycol monomethyl ether	2-Methoxyethanol	Methyl Cellosolve Glycol ether EM	$HROCH_3$	None	15
Ethylene glycol monoethyl ether	2-Ethoxyethanol	Cellosolve Glycol ether EE	$HROC_2H_5$	None	32
Ethylene glycol monopropyl ether	2-Propoxyethanol		$HROC_3H_7$	Paints/coatings, cleaners, solvents	<15
Ethylene glycol monobutyl ether	2-*n*-Butoxyethanol	Eastman EB Butyl Cellosolve Dowanol EB Butyl oxitol EB	$HROC_4H_9$	Paints/coatings, cleaners, solvents, polishes	408.5
Ethylene glycol monohexyl ether	2-Hexoxyethanol	Hexyl Cellosolve	$HROC_6H_{13}$	Cleaners	<10
Ethylene glycol monophenyl ether	2-Phenoxyethanol	Dowanol EPH	$HROC_6H_5$	Paints/coatings, cleaners, dyes	<20
Diethylene glycol monomethyl ether	2-(2-Methoxyethoxy) ethanol	Eastman DM Methyl carbitol Dowanol DM Glycol ether DM	$HRROCH_3$	Paints/coatings, solvents	69.5
Diethylene glycol monoethyl ether	2-(2-Ethoxyethoxy)ethanol	Eastman DE Carbitol low gravity Glycol ether DE	$HRROC_2H_5$	Hair colorant, floor polish, paints/coatings, cleaners, solvents	33
Diethylene glycol monopropyl ether	2-(2-Propoxyethoxy)ethanol	Eastman DP	$HRROC_3H_7$	Floor polish, brake fluids	<5

Diethylene glycol monobutyl ether	2-(2-Butoxyethoxy)ethanol	Eastman DB Butyl Carbitol Dowanol DB	$HRROC_4H_9$	Paints/coatings, cleaners, solvents, brake fluids	101.5
Diethylene glycol monohexyl ether	2-(2-Hexoxyethoxy)ethanol	*n*-Hexyl Carbitol	$HRROC_6H_{13}$	Cleaners	<5
Triethylene glycol monomethyl ether	2-[2-(2-Methoxyethoxy) ethoxy]ethanol	Methoxytriglycol Glycol ether TM	$HRRROCH_3$	Brake fluids	19.8
Triethylene glycol monoethyl ether	2-[2-(2-Ethoxyethoxy) ethoxy]ethanol	Ethoxytriglycol Eastman DTE Glycol ether TE	$HRRROC_2H_5$	Brake fluids	2.2
Triethylene glycol monopropyl ether	2-[2-(2-Propoxyethoxy) ethoxy]ethanol	Eastman DTP	$HRRROC_3H_7$	Brake fluids	<5
Triethylene glycol monobutyl ether	2-[2-(2-*n*-Butoxyethoxy) ethoxy]ethanol	Butoxytriglycol Eastman DTB Glycol ether DTP	$HRRROC_4H_9$	Brake fluids	38.9
		Ethylene Glycol Ether Acetates			
Ethylene glycol monoethyl ether acetate	2-Ethoxyethyl acetate	Glycol ether EE acetate	$CH_3COROCH_3$	Solvents	<30
Ethylene glycol monobutyl ether acetate	2-*n*-Butoxyethyl acetate	Eastman EB acetate Butyl Cellosolve acetate Glycol ether EB acetate	$CH_3COROC_4H_9$	Paints/coatings, solvents	15.6
Diethylene glycol monoethyl ether acetate	2-(2-Ethoxyethoxy)ethyl acetate	Eastman DE acetate	$CH_3CORROC_2H_5$	Paints/coatings, solvents	<5
Diethylene glycol monobutyl ether acetate	2-(2-*n*-Butoxyethoxy)ethyl acetate	Eastman DB acetate Glycol ether DB acetate Butyl Carbitol acetate	$CH_3CORROC_4H_9$	Paints/coatings, solvents	9.9



Diethanolamine **I**

II

III

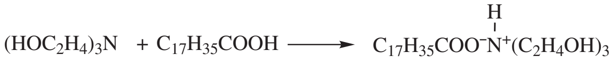
IV

V

Glyphosate isopropylamine salt **VI**

Monsanto has devised a “green” route to the iminodiacetate (**II**) described in Section 17.3.10.

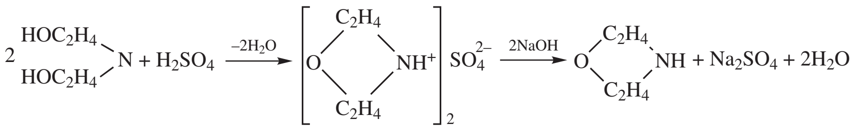
Two other major herbicides 2,4-D (2,4-dichlorophenoxyacetic acid) and 2,4-DP (2,4-dichlorophenoxypropionic acid) are both marketed as diethanolamine salts. Triethanolamine’s major application is in the formation of a quaternary salt with fatty acids to provide a surfactant useful in dry cleaning and cosmetic formulations.



$$(HOC_2H_4)_3N + C_{17}H_{35}COOH \longrightarrow C_{17}H_{35}COO^-\overset{H}{\overset{|}{N}}{}^+(C_2H_4OH)_3$$

Triethanolamine Stearic acid tris(Hydroxyethylammonium) stearate

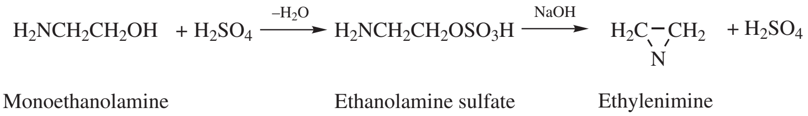
Morpholine results from the dehydration of diethanolamine with sulfuric acid to form a sulfate, which on treatment with alkali provides the free base.



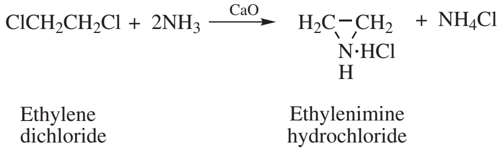
Morpholine sulfate

Morpholine

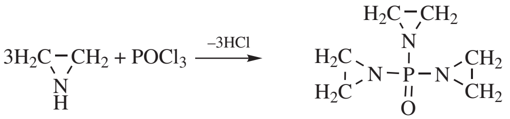
3.11.6.5 Ethylenimine Ethylenimine can be made either from ethanolamine or ethylene dichloride. The aminoalcohol is esterified with sulfuric acid and the resulting compound treated with a stoichiometric amount of sodium hydroxide to generate the imine.



Ethylene dichloride with ammonia in the presence of lime also yields ethylenimine.

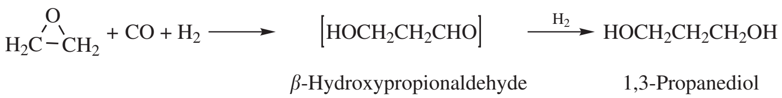


There is a large body of chemistry associated with ethylenimine most of which is beyond the scope of this volume. Most important is its polymerization to poly(ethylenimine), a cationic flocculent useful for the purification of waste waters, particularly water from paper manufacture. Reaction with phosphoryl trichloride, $POCl_3$, provides tris(1-aziridinyl phosphine oxide) a reactive intermediate for use in imparting fire resistance and crease proofing for textiles. Ethylenimine and some of its derivatives are toxic and ecologically harmful.



tris(1-Aziridinyl phosphine oxide)

3.11.6.6 1,3-Propanediol It was known as early as the 1940s that polyester made from 1,3-propanediol and terephthalic acid or dimethyl terephthalate had unexpectedly good resilience and wear properties in comparison with its two and four carbon analogues, poly(ethylene terephthalate) and poly(butylene terephthalate). It had the potential to combine the stain resistance inherent in polyesters with the resilience and wear resistance of nylon. This phenomenon is sometimes termed the "odd carbon effect." The unique blend of properties in poly(trimethylene terephthalate) should find application in fibers for carpets and apparel. This finding lay dormant for more than 50 years as there was no low cost way to make 1,3-propanediol. In the mid-1990s, however, Shell developed catalysts that could combine syngas (mixtures of hydrogen and carbon monoxide) with ethylene oxide to give 1,3-propanediol in high yield. The chemistry goes through intermediate formation of β-hydroxypropionaldehyde. Shell has indicated they can carry out this reaction in one or two steps.



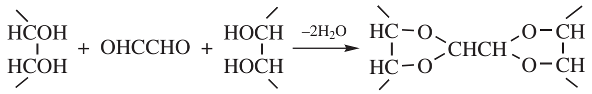
In 1999, Shell constructed a 160 million lb/year 1,3-propanediol plant in Geismar, Louisiana. A 200 million lb/year poly(trimethylene terephthalate) plant is being built jointly by Shell and Societé Générale de Financement du Quebec (SGF) near Montreal with start-up scheduled for 2003. Du Pont is not abandoning this market to Shell and has purchased old acrolein-based technology from Degussa to supply developmental quantities of 1,3-propanediol (see Section 4.14.4). Du Pont's real objective, however, is to develop a glucose-based biotech route to this monomer (Section 14.2).

3.11.6.7 Ethylene Glycol Derivatives The gas-phase oxidation of ethylene glycol at 300°C yields glyoxal. Catalysts are silver or copper inhibited with halide additives to prevent total oxidation of the glycol. Alternatively, acetaldehyde can be oxidized with nitric acid less selectively to give glyoxal and a number of byproducts including glyoxylic acid, OHCCOOH.

$$\mathrm{HOCH_2CH_2OH} \xrightarrow[\text{nitric acid}]{\text{cat or}} \mathrm{OHCCHO}$$

Ethylene glycol Glyoxal

Glyoxylic acid is the major product when the oxidation is carried out at a higher temperature. It was at one time important in the synthesis of ethylene glycol (Section 3.7.1). Since anhydrous glyoxal polymerizes readily, it is sold as a hydrate. In textile finishing, it functions as a shrink-proofing agent by cross-linking the cellulose chains of cotton through the formation of cyclic acetals with adjacent hydroxyl groups.

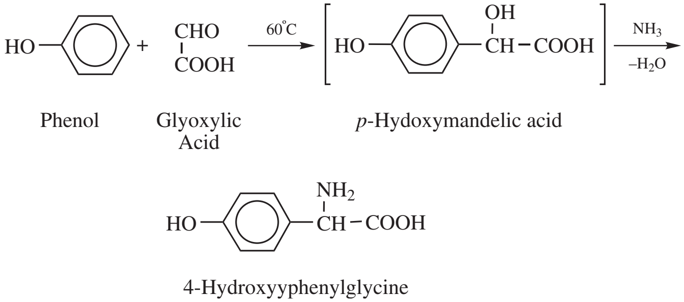


Adjacent hydroxyls of cellulose

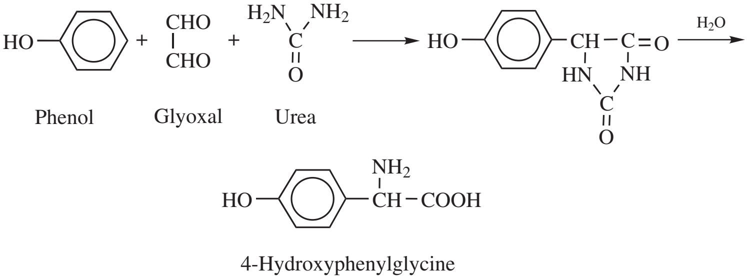
Cyclic acetal

The ability of glyoxal to react with cellulose also means that it lends wet strength to paper and increases its absorbency. It insolubilizes starch and protein and has been used as a reducing agent in the process of silvering mirrors. It reacts with amino groups, and hence insolubilizes casein and animal glues. It is used to immobilize enzymes by bonding both to them and a substrate such as glass. Glyoxal mixed with formaldehyde is the basis for embalming fluid.

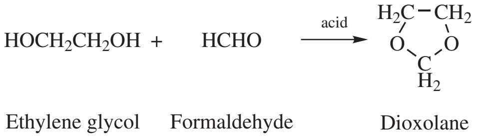
Glyoxal and glyoxylic acid are both used in the synthesis of 4-hydroxyphenylglycine, the side-chain precursor in the manufacture of ampicillin. In one process—a modified Mannich reaction—phenol in aqueous ammonia reacts with glyoxylic acid to give 4-hydroxyphenylglycine, presumably via the intermediate *p*-hydroxymandelic acid.



In the second method, phenol, glyoxal, and urea react to give a hydroxyphenylhydantoin that is hydrolyzed by water to 4-hydroxyphenylglycine.

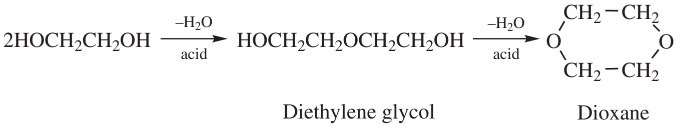


Dioxolane is related to ethylene carbonate (Section 3.11.6.3) and is the acetal from the acid-catalyzed reaction of ethylene glycol and formaldehyde.



It is a comonomer in the formation of polyacetal polymers for which the major monomer is formaldehyde. It is also a strong aprotic solvent. Being an acetal, it is unstable in strong acid.

Another ethylene glycol derivative is 1,4-dioxane, which results from the dehydration of ethylene glycol with dilute sulfuric acid. Presumably, diethylene glycol forms as an intermediate and cyclizes to dioxane, since diethylene glycol may also be used as the starting material.

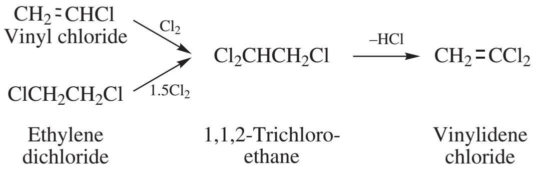


Ethylene oxide, ethylene chlorohydrin, or 2,2-dichlorodiethyl ether (prepared by treating ethylene chlorohydrin with sulfuric acid) all condense to form 1,4-dioxane. Dioxane's major use is as a solvent, but care must be exercised because it readily forms explosive peroxides.

Ethylene glycol can be nitrated to form ethylene glycol dinitrate, useful as a freeze inhibitor for explosives.

$$HOCH_2CH_2 + 2HNO_3 \longrightarrow \underset{\text{Ethylene glycol dinitrate}}{O_2NOCH_2CH_2ONO_2}$$

3.11.7 Vinyl Chloride and Ethylene Dichloride Derivatives Vinyl chloride is the basis for other chlorinated compounds. Vinylidene chloride (1,1-dichloroethylene) results from the chlorination of vinyl chloride followed by dehydrohalogenation. The intermediate 1,1,2-trichloroethane can also be made by chlorinating ethylene dichloride:



Vinylidene chloride is the basis for "Saran," which is a copolymer of 85% vinylidene chloride with 15% vinyl chloride. The polymer has high tensile strength, which makes possible the formation of thin films whose electrostatic properties cause it to cling and assume the shape of the products, primarily food, which it protects. Poly(vinylidene chloride) films are clear because they are biaxially oriented, that is, they are stretched in two directions simultaneously. The polymer is also used as a coating for nitrocellulose and polypropylene films to impart air and water impermeability.

The direct chlorination of ethylene dichloride gives a mixture of trichloroethylene and tetrachloroethylene in addition to 1,1,2-trichloroethane, mentioned above.

$$ClCH_2CH_2Cl + Cl_2 \longrightarrow \underset{\text{Trichloroethylene}}{Cl_2C{=}CHCl} + \underset{\text{Tetrachloroethylene}}{Cl_2C{=}CCl_2} + HCl$$

To avoid waste of the quantities of hydrogen chloride byproduct (the above equation is not balanced), oxychlorination can be used as it is in vinyl chloride manufacture (Section 3.4). The mechanism of the process, however, is somewhat different, since it makes use of ethylene dichloride and chlorine in the presence of oxygen with a cupric chloride catalyst. In the vinyl chloride process, cupric chloride is used as a source of chlorine. In this process, chlorine, oxygen, and ethylene dichloride react to provide tri- and tetrachloroethylene and water. The hydrogen chloride that forms presumably oxidizes immediately to chlorine for further chlorination.

The traditional synthesis of tri- and tetrachloroethylene started with acetylene (Section10.3). The route is still used in Europe.

$$CH{\equiv}CH + Cl_2 \longrightarrow CHCl_2CHCl_2 \xrightarrow{-HCl} Cl_2C{=}CHCl \xrightarrow{Cl_2}$$

Trichloroethylene

$$CHCl_2CCl_3 \xrightarrow{-HCl} Cl_2C{=}CCl_2$$

Tetrachloroethylene

Trichloroethylene is used as a solvent and as a degreasing agent in metal working. In 2001, 235 million lb were consumed. Tetrachloroethylene, also called perchloroethylene, is used to extract fats and oils, and is the major solvent used in dry cleaning. Both solvents, however, are in jeopardy because of toxicity and ecological problems, and consumption has decreased. In Western Europe between 1996 and 2001, for example, demand for trichloroethylene dropped from 223 to 139 million lb and for perchloroethylene from 187 to 143 million lb. A substitute for perchloroethylene in dry cleaning is liquid carbon dioxide. It is environmentally friendly, but only about 1% of the dry cleaners in the United States currently use it because the equipment is more expensive. ICI and Linde have an agreement to develop a proprietary carbon dioxide based solvent containing boosters—probably fluorine or silicone-based surfactants.

3.11.8 Vinyl Fluoride and Vinylidene Fluoride Vinyl fluoride can be prepared either from acetylene (Section 10.9) or from vinyl chloride. In the latter process, vinyl chloride is treated with HF with a mercury salt or metallic fluoride catalyst to give an addition product, which on dehydrohalogenation yields vinyl fluoride.

$$CH{\equiv}CH + HF \longrightarrow CH_2{=}CHF$$

Vinyl fluoride

$$CH_2{=}CHCl + HF \xrightarrow{cat.} CH_3CHClF \xrightarrow{-HCl} CH_2{=}CHF$$

The noncatalyzed addition of HF to vinyl chloride proceeds at mild temperatures and pressures. Dehydrochlorination at 500–600°C with copper powder, Cu—Ni catalyst, or in special steel tubes yields vinyl fluoride. A byproduct, 1,1-difluoroethane, can be converted to additional vinyl fluoride by dehydrofluorination. Vinyl fluoride's major use is for free radical polymerization to poly(vinyl fluoride) with peroxide initiation. Films of this polymer have excellent resistance to weathering, ultraviolet light, chemicals, and solvents.

Vinylidene fluoride results from the dehydrochlorination of 1,1,1-chlorodifluoroethane.

$$\underset{\text{Chlorodifluoroethane}}{ClF_2CCH_3} \xrightarrow{-HCl} \underset{\text{Vinylidene fluoride}}{CF_2{=}CH_2}$$

Either alkali or heat is used. The precursor results from the addition of 2 mol of HF to acetylene followed by dehydrofluorination.

$$CH{\equiv}CH \xrightarrow{HF} [CH_2{=}CHF] \xrightarrow{HF} CH_3CHF_2 \xrightarrow{HF} CH_2{=}CHF$$

Vinylidene fluoride undergoes free radical polymerization to poly(vinylidene fluoride) which, unlike polytetrafluoroethylene (Teflon), may be molded by conventional techniques. It is useful for the preparation of high-temperature wire insulation and heat-shrinkable tubing. As an emulsion, it is used to coat metal for building panels.

Tetrafluoroethylene is not produced from ethylene but from methyl chloride and is described in Section 10.2.

3.11.9 Ethylene Dibromide

Ethylene dibromide results from direct addition of bromine to ethylene.

$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

This reaction at one time provided the major outlet for bromine. Ethylene dibromide was used as a lead scavenger in leaded gasoline. The lead tetraethyl that served as an octane improver would otherwise have been oxidized to nonvolatile lead oxide, which would have accumulated in the engine. Addition of ethylene dibromide meant that lead bromide was formed, which was volatile enough to be swept out of the cylinders. This application became obsolete in the United States in the early 1990s. Ethylene dibromide is also a fumigant for soil and grain, but its use was prohibited in the United States in 1984 because of toxicity problems. Declining consumption has meant that a phase-transfer catalytic route to ethylene dibromide was never commercialized (Section 16.10).

Dehydrobromination of ethylene dibromide yields vinyl bromide, used in small quantities in the formulation of fire retardants for carpet textiles.

$$CH_2BrCH_2Br \xrightarrow{cat.} \underset{\text{Vinyl bromide}}{CH_2{=}CHBr} + HBr$$

Reaction of ethylene dibromide with sodium cyanide gives succinonitrile, an aprotic solvent.

$$CH_2BrCH_2Br + 2NaCN \longrightarrow CH_2CNCH_2CN + 2HBr$$

A better synthesis, if hydrogen cyanide is available, involves the addition of that compound to the active double bond in acrylonitrile. Triethylamine serves as catalyst.

$$\underset{\text{Acrylonitrile}}{CH_2{=}CHCN} + HCN \longrightarrow \underset{\text{Succinonitrile}}{CH_2CNCH_2CN}$$

Hydrogenation of succinonitrile gives 1,4-diaminobutane:

$$CH_2CNCH_2CN \xrightarrow{H_2/\text{cat.}} \underset{\text{1,4-Diaminobutane}}{H_2NCH_2CH_2CH_2CH_2NH_2}$$

1,4-Diaminobutane reacts with adipic acid to give nylon 4,6, a development product that came on the market in the mid-1980s. Nylon 4,6 has more amide groups than nylon 6,6 (Section 7.2.1.1) per equivalent of molecular weight. Accordingly, there is more opportunity for hydrogen bonding, which leads to greater tensile strength and higher melting point. On the other hand, the greater concentration of amide groups provides greater moisture sensitivity.

3.11.10 Ethanol Derivatives Ethyl ether is prepared from ethanol by reaction with sulfuric acid (Section 3.8) to form ethyl hydrogen sulfate, which is transformed to diethyl ether by heating with more alcohol at 140–150°C, a temperature slightly below that at which it decomposes to ethylene. Ethyl ether is an important laboratory solvent and was at one time used as an anesthetic.

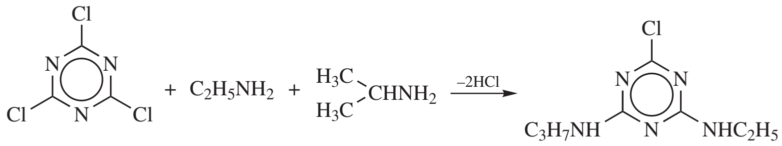
$$\underset{\text{Ethanol}}{C_2H_5OH} + H_2SO_4 \xrightarrow{-H_2O} \underset{\text{Ethyl hydrogen sulfate}}{C_2H_5OSO_3H} \xrightarrow{C_2H_5OH.}$$

$$\underset{\text{Ethyl ether}}{C_2H_5OC_2H_5} + H_2SO_4$$

Ethylamines result when ethanol and ammonia are passed over a dehydration catalyst such as alumina or a mixture of silica and alumina. Amines and water are removed and unreacted ammonia and ethanol recycled. The ratio of ammonia to alcohol is varied from 2:1 to 6:1 depending on the mix of amines required.

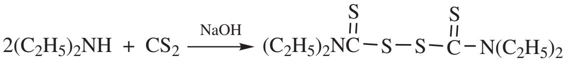
$$C_2H_5OH + NH_3 \xrightarrow{\text{cat.}} \underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\text{Diethylamine}}{(C_2H_5)_2NH} + \underset{\text{Triethylamine}}{(C_2H_5)_3N}$$

The ethylamines are used at a much lower level than the methylamines. Ethylamine finds its largest use in the preparation of herbicides by reaction with cyanuric chloride and isopropylamine. An ethylaminoisopropylamino-substituted chlorotriazine results, which is the herbicide atrazine.



Cyanuric chloride Ethylamine Isopropylamine Atrazine

Diethylamine with carbon disulfide and sodium hydroxide gives tetraethyl thiuram disulfide or disulfiram:



$$2(C_2H_5)_2NH + CS_2 \xrightarrow{NaOH} (C_2H_5)_2N\overset{\overset{S}{\|}}{C}-S-S-\overset{\overset{S}{\|}}{C}-N(C_2H_5)_2$$

Disulfiram

This compound is a rubber cure accelerator but is better known as “Antabuse,” a pharmaceutical used in the treatment of alcoholism.

Triethylamine forms a salt with phosphoric acid, which is a corrosion inhibitor.

3.11.11 Vinyl Esters and Ethers One synthesis for ethyl acetate involves the direct addition of acetic acid to ethylene (Section 3.9):

$$CH_2{=}CH_2 + CH_3COOH \xrightarrow{cat.} CH_3COOC_2H_5$$

Ethyl acetate

Analogously, vinyl esters of higher acids are prepared by their addition to acetylene. Vinyl ethers result from the interaction of alcohols and acetylene.

$$CH{\equiv}CH + RCOOH \xrightarrow{cat.} RCOOCH{=}CH_2$$

Vinyl ester

$$CH{\equiv}CH + ROH \xrightarrow{cat.} ROCH{=}CH_2$$

Vinyl ether

Vinyl esters may also be prepared by an exchange reaction in which an acid higher than acetic reacts with vinyl acetate in the presence of a catalyst. The vinyl acetate process is a transesterification and is catalyzed by mercuric acetate with sulfuric acid, or by palladium chloride with lithium chloride.

$$CH_3COOCH{=}CH_2 + RCOOH \xrightarrow{cat.} RCOOCH{=}CH_2 + CH_3COOH$$

Vinyl acetate Vinyl ester Acetic acid

$(R{=}C_3$ or higher$)$

Vinyl esters of fatty acids are used primarily as comonomers to impart flexibility to polymers based on vinyl chloride.

NOTES AND REFERENCES

Ethylene is central to the petrochemical industry, hence discussion of it features in all the books on the industry listed in the general bibliography. The classic work is *Ethylene and its Industrial Derivatives*, S. A. Miller, Ed., Benn, London, 1969, but it does not appear to have been either updated or superseded, except, possibly by *Ethylene: Keystone to the Petrochemical Industry*, L. Kniel, Dekker, New York, 1980. A relatively simple book from the University of York (UK) Science Education Group is *Ethene: Industry's most important Chemical*, M. F. Uttley, 1986.

Early 1990s thinking about ethylene technology and economics is to be found in *Ethylene Producers Conference Proceedings, Volumes 1 & 2*, AIChemE, 1992, 1994. (The Ethylene Producers have a conference every year; it is now conducted in association with the AIChemE spring meetings.) For a discussion of recent commercially employed ethylene production technologies and cost of production economics see Nexant Chemsystems PERP report 00/01-4, Ethylene/Propylene (June, 2001).

The northwest Europe propylene pipeline is described by N. Alperowicz, *Chem. Week*, September 24, 2003.

Section 3.1.1 The investigators at both Standard Oil of Indiana and Phillips Petroleum tried to make polypropylene with their catalysts. Both obtained insignificant yields. But these experiments, carefully recorded, made Phillips the victor in a patent lawsuit with many contenders.

Section 3.1.5 High strength polyethylene fibers are the subject of Allied Corporation's US Patent 4 413 110 (November 1, 1983).

Ski manufacture is a classic example of adding value to a few kilograms of polymers. Our interest was roused by D. L. Lind and S. P. Sanders, *The Physics of Skiing*, American Institute of Physics, Woodbury, NY, 1997. We were also grateful to have received from the manufacturer, *The K2 Skibook: Some information on the technical aspects of skis*, K2 Corporation, Vashon, WA, but this is not generally available.

Section 3.2.2 Ethylene–vinyl alcohol copolymer resins with particularly good barrier properties are described in *Chem. Week*, April 17, 1985, p. 13.

Section 3.2.4 Newer information on nylon–polyethylene mixtures made compatible by copolymers with polar and nonpolar functional groups is found in US Patent 5,859,137 (January 12, 1999) issued to Du Pont. This patent describes the inclusion of unsaturated dibasic acids, primarily fumaric acid, with or without acrylic or methacrylic acid.

Section 3.2.6 Carbide's development of ultra low density polyethylene is described in European Patent Appl. 0,120,503 (October 3, 1984).

Section 3.2.7 Many patents granted to Shell Research describe ethylene– carbon monoxide copolymers. Typical is US Patent 4 880 909 (November 14, 1989). There is some discussion of photodegradable polymers in *Chem. Brit*. October 2002, p. 9.

Section 3.3.1 The catalyst for 2-butene formation, tri-*n*-butylphosphine nickel dichloride mixed with ethylaluminum dichloride, is described in US Patent 4,242,531 (December 30, 1980) issued to Phillips Petroleum Company.

The nickel oxide catalyst for 2-butene formation is described in US Patent 3,341,620 (September 12, 1967) issued to Phillips Petroleum Company. A catalyst for preparing 1-butene is described in US Patent 4,487,847 (December 11, 1984) issued to Phillips Petroleum Company. The Institut Français du Pétrole catalyst for 1-butene preparation is described in European Patent Appl. 0135 441 A1 (March 27, 1985).

Section 3.3.3 The Shell oligomerization process is described in US Patent 4,020,121 April 26, 1977) issued to Shell Oil.

Phillips has issued many patents related to selective trimerization of ethylene to 1-hexane. Some of these are listed here: US Patent 5,523,507 (June 4, 1996), US Patent 5470,926 (November 28, 1995), US Patent 5,451,645 (September 19, 1995), US Patent 5,438,027 (August 1, 1995) all assigned to Phillips. See also A. Brownstein, *Eur. Chem. News* 2–8 October 2000, pp. 29–30.

Section 3.3.4 The isomerization step in the SHOP process is described by R. A. Nieuwenhuis, *Pétrole et Techniques,* No. 268, January, 1980, p. 46. The SHOP process has been described in detail in B. G. Reuben and H. A. Wittcoff *J. Chem. Educ.* **65**, 605 (1988).

Section 3.4 The ICI developments are described in British Patent Appl. 2,095,242A and 2,095,245A (September 29, 1982). Previous work in this area is described in a Lummus patent (US Patent 3,557,229, January 19, 1971).

Key patents covering EVC's ethane to VCM process are WO 95/07249 (March 16, 1995), WO 95/07250 (March 16, 1995), WO 95/07251 (March 16, 1995), and WO 95/07252 (March 16, 1995) all to EVC Technology AG.

Section 3.5 G. W. Parshall's statement about the Wacker reaction is found in his excellent book *Homogeneous Catalysis*, John Wiley & Sons, inc., New York, 1980, p. 102.

Showa Denko's process for the direct oxidation of ethylene to acetic acid is described in US Patent 5, 405,996 (April 11, 1995) to Show Denko.

Acetaldehyde's demise has been discussed by H. A. Wittcoff, *J. Chem. Educ.*, **60**(12), 1045 (December 1983).

Section 3.6 BPs fluidized-bed reactor process for making vinyl acetate is described in US Patent 6,180,821 (January 30, 2001) and US Patent 5,817,866 (October 6, 1998) both to BP Chemicals Ltd.

Section 3.7 Patents describing improved catalysis for ethylene oxide production include European Patent Appl. 0,076,504 (April 10, 1982) to Union Carbide, British Patent 1,512,625 (June 1, 1978) to Shell, US Patent 4,125,480 (November 14, 1978) to Shell and West German Offen, 2,809,835 (September 14, 1978) to Halcon.

Section 3.7.1 Union Carbide's process for converting ethylene oxide to ethylene glycol via the carbonate is described in five British Patents 2,011,400; 2,011,401; 2,011,402; 2,010,685, and 2,010,694.

The conversion of ethylene oxide to ethylene glycol in high selectivity with a vanadate or molybdate catalyst is described in International Patent Appl. WO85/04393 (October 10, 1985) to Union Carbide.

Section 3.7.2 Typical of the many patents describing Carbide's process for ethylene glycol via the direct combination of CO and H_2 is US Patent 4,360,600 (November 23, 1982). The Ube modification is described in many patents, typical of which are US Patent 4,229,589 (October 21, 1980), US Patent 4,229,591 (October 21, 1980) and Japanese Patent 8,242,656 (March 10, 1982).

The free radical induced chain reaction between methanol and formaldehyde has been described by M. Oyama, *J. Org. Chem.* **30**, 2429 (1965). It is further developed in US Patent 4,337,371 (June 29, 1982) to Redox Technologies.

The electrohydrodimerization technology is described in US Patents 4,478,694 (October 23, 1984) and 4,270,992 (June 2, 1981).

Catalysts that effect hydrogenolysis at mild conditions are described in International Patents W086/03189 (June 5, 1986) and WO82/03854 (November 11, 1982).

The process for preparing ethylene glycol from synthesis gas has been discussed by Dombek, *J. Chem. Educ.* **63**, 210 (1986).

Section 3.8 UOPs catalyst, which makes possible the oxidative dehydrogenation of styrene, is the subject of US Patent 4,565,898 (January 21, 1986). The use of ZSM-5 for ethylbenzene production is described in US Patent 3,751,506 (August 7, 1973) to Mobil Oil Company and in US Patent 4,107,224 (August 15, 1978) to Mobil.

Catalyst formulation for ethylbenzene dehydrogenation is disclosed in numerous patents typical of which are US Patents 2,414,585 (January 21, 1947) to Shell, US Patent 2,461,147 (February 8, 1949) to Shell, US Patent 2,603,610 (July 15, 1952) to Dow, US Patent 3,205,179 (September 7, 1965) to Dow, US Patent 4,143,083 (March 6, 1979) to Shell, and World patent WO 8,300,687 (August 17, 1981) to Shell.

Work on the production of styrene by the coupling of benzene and ethylene is described in two publications by R. S. Shire of Phillips Petroleum Co.: *J. Chem Soc, Chem. Commun.*, 1510 (1971) and *J. Cataly.* **26**, 112 (1972). This oxidative coupling with a Pd^{2+} catalyst takes place with oxygen at a total benzene plus oxygen pressure of 20 bar at 80°C. Selectivity is 95% but conversion is only 2.3% based on ethylene.

The Dow approach for making styrene via butadiene cyclodimerization is described in US Patent 5,276,257 (January 4, 1994) to Dow Chemical.

Section 3.9 The details of ethanol production and demand appeared in *Chem. Mkt. Rep.*, January 20, 2003, p. 27. The use of fermentation alcohol as an automotive fuel has been discussed in *Chem. Eng. News,* November 5 1984, p. 25. Although Brazil's program aimed at replacing petroleum-based fuel for automobiles with ethanol was successful technically, its economics were poor in light of the low petroleum costs of the late 1980s. Collar, the president elected in 1989, campaigned on a platform that included phase-out of the alcohol program. In fact, market interactions helped him, for the world price of sugar cane increased and many refiners chose to convert sugar cane juice to sugar rather than alcohol. By so doing, they created an alcohol fuel shortage, which caused Brazil to import alcohol to fuel its 1 million cars that could not operate on petroleum-based fuel. The Iraqi invasion of Kuwait caused a stunning reversal of both Collar's campaign platform and the manufacture of sugar, because it caused the price of crude petroleum to increase to a point that the economics of Brazil's alcohol fuel program became more reasonable. Gasohol is widely used in Brazil today, but cars that are dependant only on ethanol have almost been phased out. There is a vigorous debate between Professor D. Pimentel of Cornell University and the U.S. Dept. of Agriculture about the energy contribution of ethanol to gasoline. Pimentel (D. Pimentel, in *Encyclopedia of Physical Science and Technology*, 3rd ed., Vol. 2, Academic Press, San Diego, pp. 159–171) maintains that fuel bioethanol yields 41% less energy than is required to grow and harvest the corn. Shapouri (H. Shapouri et al., US Department of Agriculture, Economic Research Service, Office of Energy. Agricultural Economic Report No. 721) maintains that the ethanol contributes 24% more energy than is required to produce it. Obviously each contender makes different assumptions, which it is not our intention to evaluate here. However, there is no question but that expensive corn-based ethanol must be government subsidized if it is to be used in gasoline). If the fuel oxygen mandate is continued and if ethanol replaces MTBE, then the Government is mandating a subsidized product. This does not make much sense.

The BP ethyl acetate process is described in *Eur. Chem. News* 10–16 December, 2001, p. 27.

Section 3.10 Most of the figures for Table 3.2 are taken from *Chem. Eng. News*, July 4, 1994, and Wittcoff and Reuben, Part I, *op. cit.* The published ethanol figure is probably in error and has been replaced with one from databases maintained by Nexant/Chemsystems, White Plains, New York.

Section 3.11.1 The homologation of acetic acid has been described by J. F. Knifton, *J. Chem Soc, Chem. Commun.* 1981, p. 41, and *Hydrocarbon Processing*, December 1981, p. 113.

The low-pressure process for ethylene carbonylation is described in British Patent Application 2,099,430 (December 8, 1982) issued to Halcon.

Section 3.11.3 The pentaerythritol market was outlined in *Chem. Mkt. Rep.*, May 12, 2003, p. 31.

Section 3.11.6.2 The toxicity of glycol ethers and their derivatives is discussed in *Chem. Week*, June 4, 1986, p. 10.

Section 3.11.6.4 The Nippon Shokubai process is mentioned in *Eur. Chem. News,* 9–15 April 2001, p. 43.

Section 3.11.6.6 Patents involving the production of hydroxyphenylglycine from glyoxal and glyoxylic acid include British Patents 1,576,678 to Tanabe Seiyaku, 2,012,756 to Ajinomoto, US Patent 4,175,206 to Tanabe Seiyaku, and European Patents 241,81 8,514; Japan. Patent 7,941,876; German Patent 21,515,210 all to Beecham.

By analogy with ethylene and butylene, the polyester based on propanediol should be called poly(propylene terephthalate). The reason that Shell prefers poly(trimethylene terephthalate) is that polypropylene, in the carpet business, implies "cheap." Shell did not want any confusion on this point so they came up with poly(trimethylene terephthalate).

Section 3.11.7 Chlorinated solvent sales data are taken from *Chem. Brit.*, March 2003, p. 14. The ICI-Linde joint project is described in *Chem. Eng. News*, September 2, 2002, p. 12.

Section 3.11.9 The bromine situation at the end of the 1990s was reviewed by B. G. Reuben, An Industry under threat? *Chem. Ind.*, 547 (1999). The addition of HCN to acrylonitrile is described in Canadian Patent 1,135,72 (November 16,1982) to Stamicarbon BV. Section 3.11.12.

CHAPTER 4

CHEMICALS AND POLYMERS FROM PROPYLENE

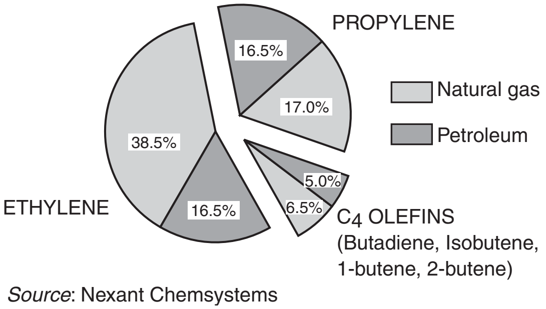
After ethylene, the most important olefin is propylene. In 2001, the United States produced about 42 billion lb of propylene, about 49% as a coproduct of ethylene production in the steam cracking of ethane, propane and higher alkanes (Section 2.2.1) and 51% as a byproduct of catalytic cracking and of other refinery processes (Section 2.2.2). About 32.8 billion lb was used for chemicals. Much of the remainder was reacted with isobutane to give alkylates for gasoline (Section 2.2.5) or, to a lesser extent, oligomerized to polygas (Section 2.2.4). In this respect, propylene differs from ethylene, which has no nonchemical or fuel uses.

Figure 4.1 shows the ratio in which the three major olefins were used in the early 1990s in the United States for chemical applications and indicates also the proportion of each that came from natural gas and petroleum. This division is not thought to have changed much since then. In 2001, ethylene claimed 58% of the total consumption of olefins, propylene 36.5%, and the butenes and butadiene 5.5%.

Most natural gas contains about 2.5 times as much ethane as propane. On the other hand, catalytic cracking (Section 2.2.2) of higher petroleum fractions, which gives negligible amounts of ethylene (see note at the end of this chapter), is a source of propylene, although it is more dilute and thus more expensive to isolate than the propylene from steam cracking. The steam cracking of ethane, propane, butane, naphtha, or gas oil inevitably gives propylene as one of the coproducts, although the cracking of ethane yields so little it is usually not isolated (see note at the end of this chapter). The amount depends on the feed (the higher the molecular weight the more is produced) and on severity of cracking. For naphtha and gas oil it varies from 0.9 to 0.4 mol

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9



Source: Nexant Chemsystems

FIGURE 4.1 Source of C_2, C_3 and C_4 olefins: United States early 1990s.

propylene per mol of ethylene as the cracking becomes more severe. A typical figure is about 0.5. This means that high-severity (high-temperature) cracking leads to a product rich in ethylene. Low-severity cracking increases propylene content. Table 4.1 gives the yield of propylene and the propylene/ethylene ratio as a function of feedstock type and cracking severity.

For many years propylene was ethylene's ugly sister, a byproduct that was sold at a fraction above its fuel value or else was burned. This availability, coupled with propylene's greater reactivity, stimulated chemists' creativity, and many ingenious chemical uses were developed. Propylene's price is usually lower than that of ethylene, although a shortage in Europe in the 1990s has at times erased this differential. By the mid-1990s, propylene's price was again lower than ethylene's, but in the early 2000s the propylene price rose again as a result of its higher growth rate and possible shortages (see Fig. 3.4 and note at the end of this chapter).

4.1 ON-PURPOSE PROPYLENE PRODUCTION TECHNOLOGIES AND PROPANE DEHYDROGENATION

Owing to the strong global demand for polypropylene, there is concern that the supply of propylene from its traditional sources—steam cracking and refinery-based

TABLE 4.1 Overall Typical Propylene Yield from Representative Cracker Feedstocks

Feedstock	Severity	Weight % of Feed	Propylene/Ethylene Weight Ratio
Ethane	High	1.5	0.019
Propane	High	13.7	0.304
n-Butane	High	15.9	0.376
Light naphtha	High	14.9	0.433
	Moderate	16.4	0.500
	Low	17.8	0.570
Full-range naphtha	Moderate	15.7	0.512
Gas oil	Moderate	15.6	0.632

fluid catalytic cracking units—will not be enough to keep pace with demand. Consequently, much effort has been expended on improving propane dehydrogenation technology and in developing new so-called on-purpose routes to propylene. Propane dehydrogenation process technology is discussed in Section 2.2.7. Table 4.2 gives details of the processes by licensor.

4.2 PROPYLENE VIA DEEP CATALYTIC CRACKING

Deep catalytic cracking (DCC) is a catalytic cracking process for producing light olefins from heavy feedstocks such as vacuum gas oil. It was developed by the Research Institute for Petroleum Processing (RIPP) and Sinopec International, both located in the People's Republic of China. DCC uses fluid catalytic cracking principles combined with a proprietary catalyst to produce up to 20% propylene and other light olefins from vacuum gas oil (VGO) and correspondingly less gasoline. The RIPP has worked on the development of a zeolite catalyst for DCC for over 10 years. Four plants were operating in China in 2000, with three more under construction. The first application outside China was a plant built by TPI in Rayong, Thailand in 1997. Stone & Webster have the licensing rights to DCC outside of China.

4.3 PROPYLENE VIA OLEFIN METATHESIS

As described in Section 2.2.9, Phillips Petroleum Company discovered olefin metathesis in 1964. This technology, the interchange of olefins, while quite amazing from a theoretical point of view, has found only some niche applications. In the mid-1980s, Lyondell was the first company to use metathesis chemistry to make one of the major building block chemicals, propylene. Lyondell (purchasers of ARCO) achieved this by effecting the metathesis of ethylene and 2-butene. Originally, Lyondell even made the 2-butene by dimerizing ethylene thus giving propylene totally composed of what were formerly ethylene molecules. Lyondell is believed no longer to dimerize ethylene to make 2-butene but instead to use the butenes from raffinate-II. Operating in this fashion has an advantage in that two-thirds of the propylene molecule is derived from lower valued butene-2. Whether the equilibrium lies to the right or the left is determined by the operating conditions:

$$\mathrm{CH_3CH{=}CHCH_3 + CH_2{=}CH_2 \rightleftharpoons 2CH_2{=}CHCH_3}$$

Recently, ABB Lummus bought the licensing rights to the Phillips metathesis technology. In 2002, BASF and Fina completed a new world scale steam cracker in Louisiana and are planning to incorporate ABB Lummus' olefin metathesis process for converting ethylene and butenes to propylene. As the economics of this conversion will vary with market prices for the feedstocks as well as product

TABLE 4.2 Propane Dehydrogenation Process Characteristics

Licensor	UOP	Lummus	Linde–BASF	Snamprogetti–Yarsintez	Krupp Uhde
Process	Oleflex	Catofin	PDH	FBD	STAR
Catalyst	Platinum on alumina	Chromia–alumina	Chromia–alumina	Chromia–alumina with alkaline promoter	Platinum + tin on zinc aluminate
Pressure (bar)	1.38 at last reactor	0.13–0.68	1.4–2.1	1.2–1.5	2.1–4.2
Temperature (°C)	600–700	540–700	540	530–600	565–595
Partial pressure control	Hydrogen recycle	Vacuum	n.a.	n.a.	Steam
Heat method	Furnace reheat	Cyclic, coke burn-off	Fixed-bed multitube fired heater	Coke burn-off in regenerator, supplemental fuel	Fixed-bed multitube fired heater
Regeneration method	CCR	Cyclic	Cyclic (*in situ*)	Fluid bed	Cyclic (*in situ*)

n.a. = not available.

propylene, BASF/Fina will have the flexibility to turn this unit on or off depending on market conditions. When run with the metathesis unit on, the new BASF/Fina cracker will have the capability of producing almost equal amounts of ethylene and propylene.

The ABB Lummus metathesis process uses tungsten oxide on silica as the catalyst and operates at a temperature of 300–375°C in a fixed-bed reactor. Axens (formerly IFP) has developed a similar metathesis process. However, the Axens process uses a rhenium on alumina catalyst that operates at a much lower temperature of 25–50°C in a moving bed reactor. Common to all metathesis processes is the need to remove from the feeds any polar impurities and dienes that poison the catalyst.

4.4 PROPYLENE VIA SELECTIVE C_4/C_5 CRACKING

Selective C_4/C_5 cracking is similar to Phillip's original olefin metathesis reaction, in that lower value olefins are upgraded to more valuable products. However, unlike olefin metathesis, there is no need to use ethylene as one of the reactants. In fact small amounts of ethylene are produced. The chemistry is based on cracking C_4 and C_5 olefins over specially formulated shape selective zeolite catalysts. The feed stream for selective C_4/C_5 cracking can come from a steam cracker, raffinate-I or raffinate-II, fluid catalytic cracking (FCC) C_4 streams, or C_5 streams from steam cracker pyrolysis gasoline. The only pretreatment needed is selective hydrogenation of all dienes. In addition to making relatively high amounts of propylene, selective C_4/C_5 cracking gives small amounts of light gases, some ethylene, and C_6 and heavier components suitable for gasoline. Kellogg Brown & Root are currently licensing their version of this technology called Superflex, which was originally developed by Arco Chemical. ExxonMobil's version of this type of process is called Mobil Olefin Interconversion (MOI) process, while Lurgi's version is called Propylur.

4.5 MAIN POLYMERS AND CHEMICALS FROM PROPYLENE

The main polymers and chemicals made from propylene are shown in Figure 4.2. The three types of reactions that ethylene undergoes—polymerization and oligomerization, oxidation, and "classical" reactions—apply here also. The unconventional chemistry in which one of ethylene's hydrogen atoms is replaced by chlorine, hydroxyl and acetoxy to give vinyl chloride, acetaldehyde, and vinyl acetate is not repeated with propylene. Instead, propylene undergoes some unconventional chemistry of its own based on the stability of the vinyl moiety and the reactivity of the allylic-hydrogen-containing methyl group. This active methyl can be oxidized directly to acrolein, allyl alcohol, acrylic acid and, with ammonia, to acrylonitrile.

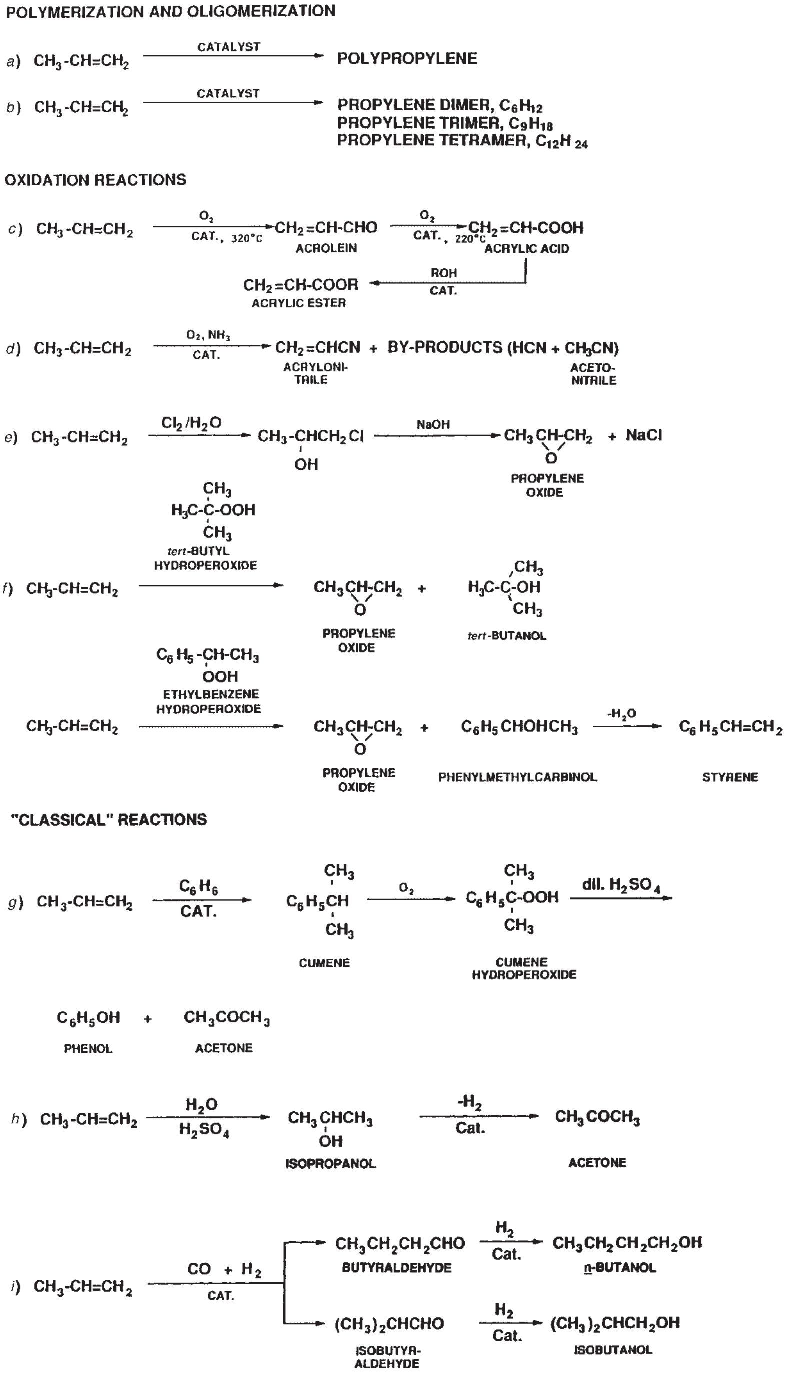


FIGURE 4.2 Chemistry of propylene.

A breakdown of the various end uses for propylene is given in Section 4.13. The largest end-use by far is polypropylene followed by acrylonitrile, propylene oxide and cumene.

4.5.1 Propylene Polymers and Copolymers

Polypropylene is the biggest consumer of propylene. It is made with Ziegler–Natta catalysts (Section 3.1.1), typical of which is one developed by Himont and Mitsui Petrochemical based on titanium tetrachloride with a Lewis base complex and a support of magnesium or manganese chloride. The Lewis base blocks nonstereospecific sites on the catalyst. A cocatalyst is used, which is a combination of an alkylaluminum such as triethylaluminum with a Lewis base.

Polypropylene development provides a superb example of process improvement. As indicated in Section 1.5, polypropylene can exist in two crystalline forms, isotactic and syndiotactic, as well as in the amorphous or atactic form. Initially 1.2 lb of monomer were consumed per pound of isotactic polymer produced. Today, only about 1.3% excess monomer is required. Modern catalysts will produce up to 75,000 lb of polymer per pound of catalyst as compared to 1000–2000 lb initially. This very high yield means that de-ashing or catalyst removal is not necessary. Similarly, an isotactic polymer level of 97% is achieved, which makes unnecessary the removal of atactic material. The catalyst controls molecular weight distribution, important where a narrow weight distribution is required. The simplification of a polypropylene plant made possible by a modern catalyst as compared to the plant required by a first generation catalyst is shown in Figure 4.3. Significant engineering advancements have been made in the polypropylene process technology in addition to catalyst advances. Single line process extrusion capacity is now up to 770 million lb/ year.

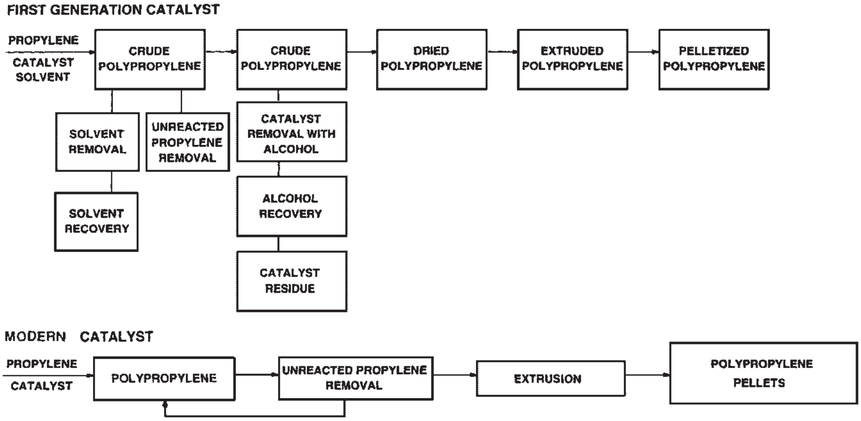


FIGURE 4.3 The modern catalyst simplifies the polypropylene plant.

With a Ziegler catalyst, polymerization takes place at 40–80°C. Polypropylene has been produced by slurry, solution, bulk, and vapor-phase or fluid-bed processes. In the slurry process, the catalyst is dispersed in an inert diluent such as hexane or heptane. The isotactic polymer that forms is insoluble in the hydrocarbon but the atactic material is soluble. Thus an *in situ* separation is effected.

In the solution process, the isotactic polymer is soluble in the solvent. This process has fallen into disuse because of the expense of solvent losses and the difficulty of removing all the solvent from the polymer. The bulk process makes use of pressures that maintain the propylene in liquid form. Atactic product is insoluble in liquid propylene, whereas the stereospecific polymer is soluble. The vapor-phase or fluid-bed process resembles one originally developed for polyethylene production (Section 3.1.3). This process became more popular in the 1990s. While bulk plants still comprise over half of all operating polypropylene plants, vapor-phase plants increased their share from about 15% in 1990 to almost 30% by 2000.

There are fewer copolymers of propylene than there are of ethylene. Ethylene–propylene random copolymer elastomers have already been mentioned (Section 3.2.5). Also important is a block copolymer, comprising a polypropylene block and an ethylene–propylene copolymer block. This is made by first polymerizing propylene and then adding ethylene and more propylene, with the same catalyst as in the first step. The fresh material forms a random copolymer block that grafts onto the original polypropylene block. The copolymer block plasticizes the polypropylene, making it less brittle and improving its impact strength, which is poor at low temperatures. About 40% of polypropylene production is the copolymer. The homopolymer is used largely for fibers, although it may be molded if low-temperature embrittlement is not a problem. Random copolymers of propylene with ethylene or 1-butene have poorer low-temperature impact strengths because they are highly crystalline and therefore stiff. The block copolymer has lower crystallinity and greater flexibility, which gives it better low temperature properties.

Copolymers of propylene with olefins other than ethylene and with monomers such as vinyl chloride and styrene have been explored as possible replacements for expensive resins such as ABS (Section 5.1.1) and nylon.

The application of metallocene catalysts to polypropylene has lagged behind their application to polyethylene. Metallocene polypropylene has narrower molecular weight distribution, higher isotacticity, lower extractables, and slightly lower melt temperatures than conventional grades. It can be manufactured in conventional polypropylene plants, but the polymers are not a “drop-in” in end-use applications because the narrow molecular weight distribution leads to poorer processability. Second generation metallocene catalysts are expected to rectify this. Meanwhile, metallocene polypropylene had less than one percent of the total polypropylene market in 2000, as the high cost of manufacture is inhibiting market penetration.

Metallocene catalysts also enable the production of syndiotactic polypropylene, which cannot be made with Ziegler–Natta catalysts. It has lower crystallinity and a lower melting point than conventional polypropylene but has high clarity and good impact strength. Atofina and Mitsui operate small syndiotactic polypropylene plants. Market penetration has been low, indicating the difficulty of introducing a new product into a mature polymer market

Polypropylene's major use is for injection molded products such as housings and parts for small and large domestic appliances, furniture, and office equipment. In automotive applications, it is used for battery cases, interior trim, and air ducts. Injection molded packaging includes tubs for margarine (also made by thermoforming), medicine bottles, and syringes. Reusable household food containers are made from copolymers. Polypropylene is used to make long-lived currency that resists counterfeiting. In the early 2000s, about ten countries had at least one denomination of currency made from polypropylene. Polypropylene has a sufficiently high modulus (stiffness) and sufficiently low extensibility to be used for textile fibers and even for surgical sutures. It is found in clothing, particularly for sports, and as filament yarn in carpeting, upholstery, and automobile seats. An important application is in carpet backing. Polypropylene cloth can replace canvas in luggage and shoes. Thick polypropylene mats, either woven or nonwoven, are useful in stabilizing soil. They have found increasing use in road building to replace the rocks or aggregate normally combined with asphalt. Polypropylene film and sheet have greater strength and better high-temperature properties than those from polyethylene, and oriented film can be used as a shrink wrap. Polypropylene fiber is useful as an asbestos replacement when high-temperature resistance is not required.

4.6 OLIGOMERIZATION

The oligomerization of propylene to highly branched olefin dimers, trimers, and tetramers (Fig. 4.2*b*), takes place in the presence of Friedel–Crafts catalysts such as sulfuric or phosphoric acids. A gasoline fraction (polygas) results (Section 2.2.4) from which the highly branched compounds can be isolated by fractional distillation, if desired. These oligomers were used for gasoline despite the double bonds that lead to tar formation in engines. The double bond, however, can be hydrogenated to give an aviation fuel, used in World War II notably for the British Spitfire. By the 1950s, they had largely been replaced by alkylate (Section 2.2.5). Zeolites and pillared clays (Sections 13.3, 16.9) have been investigated as catalysts for oligomerization but have not found commercial application. The feed for oligomerization is usually catalytic cracker off-gases and includes not only propylene but the butenes, which are preferred because they form even more highly branched compounds with higher octane numbers. This technology practically fell into disuse with the development of alkylation (Section 2.2.5). It has been revived to a small degree because the oligomers are useful in unleaded gasoline. It may become more important in the mid-2000s if redundant MTBE plants start to convert their isobutene to branched octenes (Section 5.2.1).

A newer process, called "Dimersol," developed by the Institut Français du Pétrole, produces branched oligomers from propylene or propylene–ethylene blends using a nickel complex catalyst activated by an organometallic compound such as tri-*n*-propylaluminum. With *n*-butenes alone, or mixed with propylene, more nearly linear molecules result for petrochemical use such as conversion to oxo alcohols (Section 4.12) for plasticizers.

The important oligomers for chemical use are branched dodecene (propylene tetramer) and branched nonene (propylene trimer), octene (butenes dimer), heptene (dimer of propylene and butenes), diisobutene (dimer of isobutene), and hexene (propylene dimer). Propylene tetramer formerly was used for the alkylation of benzene to make a branched-chain dodecylbenzene that was subsequently sulfonated to provide a nonbiodegradable surfactant. This application is now insignificant in the United States as more biodegradable detergents such as linear alkylbenzene sulfonates (Section 7.4) have replaced them. Phenol may be alkylated with propylene trimer or tetramer to give nonylphenol and dodecylphenol, respectively. Both are used in lubricating oil additives. They react with ethylene oxide to give nonionic detergents.

Propylene trimer and tetramer and butenes dimer undergo the oxo reaction (Section 4.12) and the aldehydes can be hydrogenated to isodecanol, tridecanol, and nonanol, respectively. Their major use is as their phthalates, which are PVC plasticizers.

2-Methyl-1-pentene is a dimer of propylene produced with the aid of a tri-*n*-propylaluminum catalyst. It is the basis for an isoprene synthesis that was never commercialized (Section 6.2). Another dimer, 4-methyl-1-pentene, was developed by ICI as a monomer for a specialty polymer which, despite its crystallinity, is transparent, because the refractive indices of the crystalline and noncrystalline portions are the same. Therefore, light is not reflected at crystal boundaries. The catalyst for the dimerization is a combination of sodium and potassium carbonate. The process was sold to Mitsui who has manufactured the polymer. The monomer has a new lease on life because of its use as a comonomer in LLDPE (Section 3.1.4).

4.7 ACRYLIC ACID

At the beginning of this chapter, we mentioned that propylene underwent some unconventional chemistry based on the stability of its vinyl moiety and the reactivity of its methyl group. This methyl group may be oxidized to a carboxyl group just as the methyl group of toluene may be oxidized to give benzoic acid. Similarly, the methyl groups of both toluene and propylene can be chlorinated and subjected to ammoxidation. The mechanisms that cause these reactions to take place with the two molecules are different, and perhaps this is the reason why the similarity was not recognized earlier. The chlorination and conversion to an alcohol are discussed in Section 4.14.1, and the ammoxidation reaction in Section 4.8. The oxidation to an aldehyde and an acid is described here.

The oxidation of propylene gives acrolein first and then acrylic acid. There are several other routes to acrylic acid and its esters shown in Figure 4.4, all but one of which has, at one time or another, been commercial.

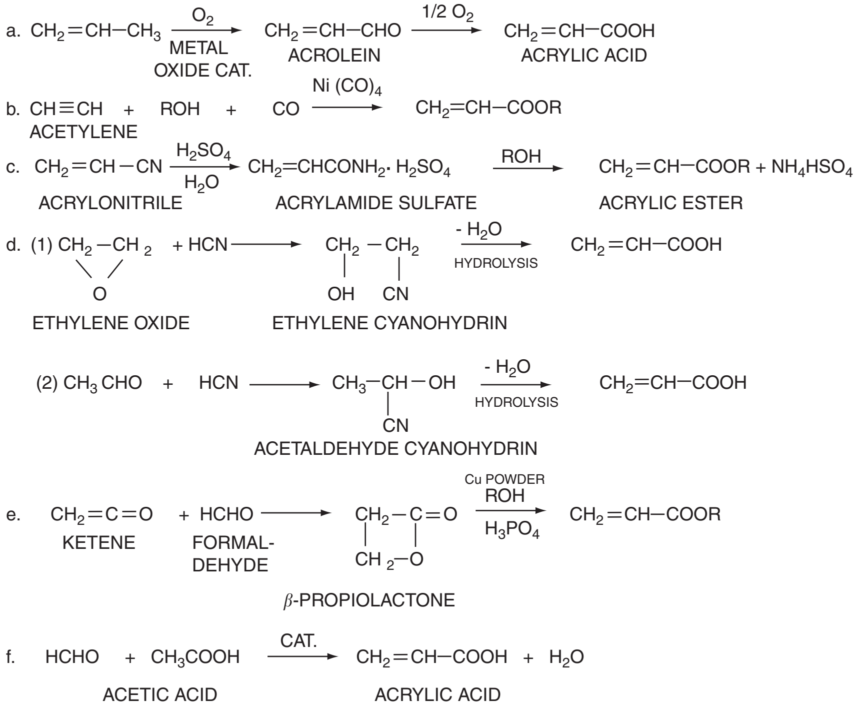


FIGURE 4.4 Acrylic acid: possible production methods.

Acrylonitrile hydrolysis (Reaction *c* in Figure 4.4) is an obvious route. It is economic if small amounts of acrylic acid are required and is still used by some acrylonitrile producers to make acrylic acid for captive use. Another route involves the reaction of hydrogen cyanide with ethylene oxide to give ethylene cyanohydrin, which may be simultaneously dehydrated and hydrolyzed with sulfuric acid [Fig. *d*(1)]. This process was last used in 1971. A third method involves the treatment of acetaldehyde with hydrocyanic acid to give a different cyanohydrin, which may be similarly dehydrated and hydrolyzed [Fig. *d*(2)]. This process too is obsolete.

Reaction 4.4*e* starts with ketene from the pyrolysis of acetic acid (Section 10.5.2.3). It reacts with formaldehyde to give β-propiolactone which, on reaction with an alcohol, gives an acrylate ester directly. The high toxicity and the carcinogenicity of the lactone made this route unattractive.

Reaction 4.4*b* is a relic of the great days of acetylene chemistry. Acetylene is reacted with an alcohol and carbon monoxide in the presence of a nickel carbonyl catalyst to give an alkyl acrylate directly. The process, now obsolete, accounted for almost one-half of the total acrylic acid and ester production in the United States in 1976. It was still used in the United States in the early 1980s, and was one of the last acetylene-based reactions to give way to modern chemistry.

Figure 4.4*f* shows a proposed process in which formaldehyde reacts with acetic acid to give acrylic acid, presumably by way of a hydroxymethyl intermediate. The process, although not commercialized, is of interest because it provides a route to acrylic acid from synthesis gas (Section 10.4) since acetic acid is made from carbon monoxide and methanol, which in turn are made from synthesis gas. Similarly, formaldehyde is made by the oxidation of methanol. The vapor-phase reaction is carried out with a vanadium orthophosphate catalyst. Conversion is as high as 100% at approximately 60% selectivity. Formaldehyde is used in a similar way in a new process for methyl methacrylate (Section 4.10.1).

Propylene oxidation (Fig. 4.4*a*) is now the preferred route. The two-step process yields acrolein as an intermediate that can be isolated if desired (Section 4.14.4). Optimum catalyst and temperatures are different for each of the two steps, the first step requiring a much higher temperature than the second. Molybdenum-based catalysts predominate and a typical catalyst for the first stage of the two-step conversion is $Fe_4BiW_2Mo_{10}Si_{1.35}K_{0.6}$. With this catalyst at 320°C, propylene conversion is 97% and acrolein selectivity is 85%. In addition, however, there is a 6% selectivity to acrylic acid making the useful selectivity 91%. These results are typical of what can be achieved with modern sophisticated catalysts. In the second stage, a catalyst may be used comprising $Mo_{12}V_{4.6}Cu_{2.2}Cr_6W_{2.4}$. The catalyst is supported on alumina and at 220°C a 98% molar yield of acrylic acid is obtained.

Figure 4.5 shows a proposed mechanism for the conversion of propylene to acrolein. The catalyst (**I**), a bismuth molybdate, abstracts a hydrogen from propylene (**II**) and π-bonds the resulting radical (**III**). The formation of a carbon–oxygen bond (**IV**) and a hydride shift (**V**) leads to the formation of acrolein (**VI**) and a reduced form of the catalyst (**VII**). The catalyst is regenerated by reaction with oxygen as shown at the bottom of the figure.

The two major developers and licensors of the modern two-stage acrylic acid process are Japanese companies, Nippon Shokubai and Mitsubishi Chemical. Some licensees have further refined the catalyst systems, notably BASF, in order to improve operating characteristics. These improvements are proprietary and acrylic acid catalyst know-how is closely held, but all major producers are thought to obtain similar yields. The first stage oxidation reactor is a fixed-bed tubular reactor with tubes that are about 5 m long and 2–3 cm in diameter. The catalyst is packed into the tubes in three zones. The catalyst concentration increases as the reactants pass down the tube creating a uniform reaction rate throughout the reactor. The reactors are cooled with molten salt that is circulated around the tubes. The second stage reactor is similar but with a different catalyst. The crude acrylic acid is quenched by absorption in water and isolated by solvent extraction. So-called “semipurified” acrylic acid is obtained in an initial distillation and this is suitable for making acrylic esters. Glacial acrylic acid is obtained by a second distillation. Acrylic acid is corrosive, and corrosion-resistant materials are required in the distillation tower and all downstream handling equipment. Probably stainless steel is used for the piping and titanium clad mild steel for the columns. Purification by crystallization is believed to be used by a few producers.

The world production of acrylic acid in 2002 was about 5.1 billion lb, with BASF (27%) and Rohm & Haas (21%) the major producers. United States consumption was

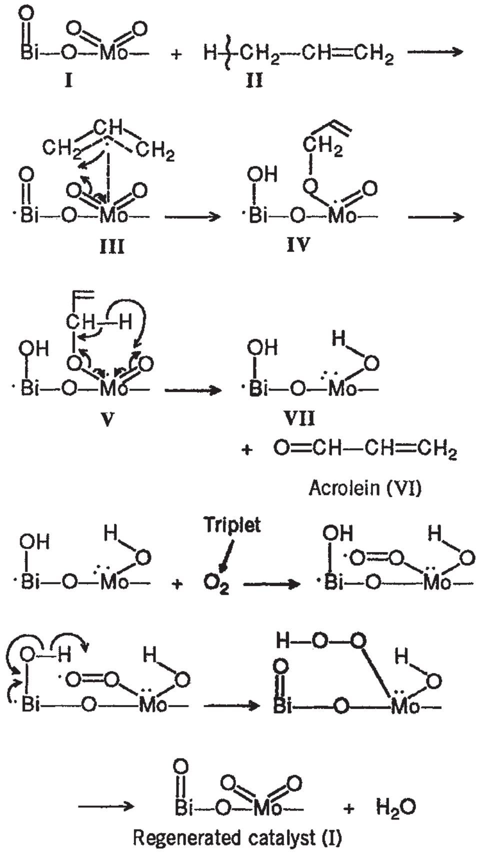


FIGURE 4.5 Mechanism of acrolein formation.

about 43% of the world production with Western Europe consuming 30% and Japan 16%. Glacial acrylic acid is needed for making superabsorbent polymers (see below). This is a growth area and, in 2002, enjoyed 47% of the acrylics market. Fifty-three percent was converted to an important range of esters—methyl, ethyl, butyl, and 2-ethylhexyl acrylates. Butyl acrylate was the dominant ester with about half of the bulk acrylate market, and methyl acrylate had 11%.

Usually, acrylate esters are polymerized with comonomers including methyl methacrylate and/or vinyl acetate. The butyl and 2-ethylhexyl–vinyl acetate copolymers, in the form of emulsions, are used in water-based paints, sometimes with other copolymers. This market accounts for about 30% of the use of all acrylates. They are also used in solvent-based coatings and, as copolymers with methacrylates, for product finishes such as thermosetting automotive topcoats. For this application, the acrylates are combined with melamine (Section 10.5.1). Acrylic coatings are prized for their decorative quality and their film durability, particularly out of doors, where their resistance to ultraviolet light is of benefit. Acrylic emulsions are also found in textile chemicals and adhesives, which are the second and third largest uses, as well as in paper coatings, binders for nonwoven fabrics, polishes, and leather coatings. Ethyl acrylate is important in leather treatment and methyl acrylate has found application as a comonomer in acrylic fiber production (Section 4.8.1) Thermoplastic acrylate coatings have been prized for automobile topcoats. They contain much more solvent than the thermosets, however, and have been phased out because of the contribution of the solvents to air pollution.

A two-package coating based on hydroxyl-containing acrylic copolymers (made with hydroxyethyl acrylate as one of the monomers) may be cross-linked with diisocyanates to give a hard thermoset polymer, which cures at room or slightly elevated temperatures. It is the preferred vehicle for coatings for automobile refinishing.

A growing application for acrylic monomers is in ultraviolet-cured coatings and printing inks. Typical monomers are pentaerythritol tetraacrylate and its oligomers, which are applied to a substrate such as plywood for subsequent polymerization into a film by ultraviolet light. The films must be clear, since pigments absorb UV rays, and they can be applied only to a horizontal surface. Printing inks based on acrylic monomer and oligomers can be cured by UV light because their low-volume pigmentation does not seriously interfere with curing. Heavily pigmented coatings can be cured by electron beams, but the equipment is expensive and the process requires safety precautions.

Two applications for acrylic acid were developed in the mid-1980s, which motivated expansion of acrylic acid production. One is the use of polyacrylic acid (prepared by the peroxide-induced free radical polymerization of acrylic acid) or an acrylic acid–maleic anhydride copolymer as a builder in detergents to replace phosphates for chelating of calcium and magnesium ions. They serve also as dispersing aids and inhibit soil redeposition.

The second use is as a water-absorbing agent for application in disposable diapers and personal care products. The polymers are termed superabsorbent because they can absorb over a thousand times their weight of water. A typical formulation comprises a copolymer of acrylic acid, sodium acrylate, and a small quantity of a cross-linking agent such as trimethylolpropane triacrylate. Cross-linking is necessary in order to impart salt stability to the gels. Another type of water absorber, irreverently termed "superslurper," is made from a starch graft polymer in which acrylonitrile is grafted onto starch to give long chains. Thereafter, the nitrile groups are partially hydrolyzed to amide and carboxyl groups. Here too a small amount of a cross-linking agent—a polyfunctional acrylate or methacrylate—must be used to achieve stability of the gel in the presence of salts. Starch graft polymers may also be prepared with acrylamide and acrylic acid rather than acrylonitrile.

4.8 ACRYLONITRILE

Closely related to the direct oxidation of propylene to acrolein and acrylic acid is oxidation in the presence of ammonia to give acrylonitrile (Fig. 4.2*d*). It is the second largest volume derivative of propylene. The process, developed by Sohio in the United States and by Distillers Company in Great Britain, is known as ammoxidation. It excited much attention when discovered in the late 1950s, for there was no previous example of the formation of a C—N bond in this way. BP Chemicals acquired Sohio and Distillers Company, Chemical Division, in the late 1960s and is a leading producer of acrylonitrile. Over 90% of all acrylonitrile is produced by the Sohio process.

In the early 1960s, ammoxidation displaced various processes for acrylonitrile production such as the addition of hydrogen cyanide to acetylene, the interaction of ethylene oxide with hydrogen cyanide followed by dehydration, and the reaction of propylene with nitric oxide. A bismuth phosphomolybdate catalyst was initially used in the United States, which was replaced by uranium bismuthate based on depleted uranium. In turn, uranium bismuthate has been superseded by proprietary catalysts used in the vapor phase, which have increased the yield of acrylonitrile and boosted reactor throughput.

The catalysts are described in an extensive patent literature. Most of them reduce byproduct acetonitrile production almost to zero, but byproduct hydrogen cyanide is still produced. A typical catalyst contains silica-supported oxides of selenium, iron, and tellurium in ratios corresponding to $OSe_{1.0}FeO_{0.83}TeO_{0.68}O_x$. This catalyst gives 100% conversion of propylene with 86.9% selectivity to acrylonitrile and 2.1% selectivity to HCN. It makes operation possible at the relatively low temperature of 320°C with a contact time of 2–5 seconds. It is interesting that this catalyst contains neither bismuth, molybdenum, or phosphorus. Still another catalyst, which requires a higher temperature of 420°C, comprises iron, antimony, molybdenum, vanadium, tellurium, and copper, supported on silica. It gives an overall acrylonitrile yield of 85% and a hydrogen cyanide yield of 3% with no acetonitrile. The ammoxidation reaction is highly exothermic and is carried out in a fluidized bed to ensure effective heat exchange and temperature control.

The fact that the methyl group of propylene can be oxidized preferentially to give acrolein indicates that not all the hydrogens of propylene are equivalent. The methyl hydrogens are allylic and hence reactive; the allyl radical $CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CH_2$, on the other hand, is relatively stable (see note at the end of this chapter). It is the recognition of this difference that makes the oxidation and ammoxidation processes feasible.

The mechanism for the formation of acrylonitrile from propylene is similar to the one previously proposed for acrolein formation (Fig. 4.5) and is shown in Figure 4.6. The mechanism is illustrated for the original Sohio catalyst, an oxidized bismuth molybdenum species, which reacts with ammonia to give the imminium compound (**VIII**). This bonds with an allyl radical resulting from the abstraction of a hydrogen from propylene (**II**) to give (**IX**). As indicated in (**X**) a double hydride shift occurs to liberate a mol of ammonia and to give the species (**XI**). This species is oxidized to give (**XII**), which forms (**XIII**) by a hydride shift. Compound (**XIII**) undergoes the transformation shown in (**XIV**) to give the desired product, acrylonitrile (**XV**), and the catalyst species (**XVI**), which with oxygen regenerates the initial catalyst

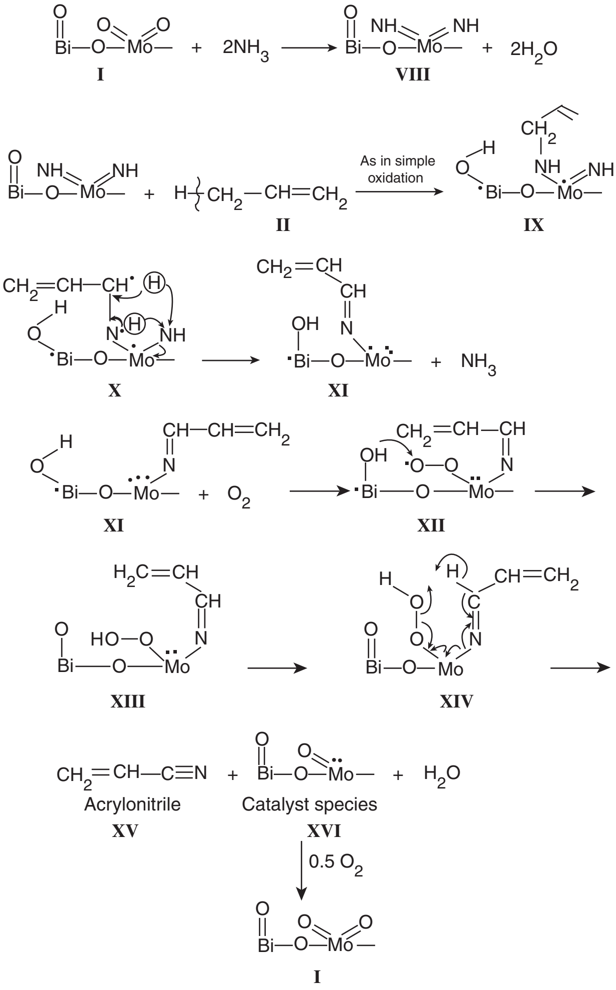


FIGURE 4.6 Mechanism of acrylonitrile formation.

species (**I**). In the early years of the process, there was the problem of disposal of the acetonitrile and highly toxic hydrogen cyanide byproduct, used by the Germans in their death camps.

Hydrogen cyanide is used in the major process for methyl methacrylate synthesis (Section 4.10.1), by Du Pont for hexamethylenediamine (Section 5.1.2) and for other products such as amino acids (DL-methionine) and chelating agents, but only small uses were found for the acetonitrile. One suggestion was reaction with methane to give acrylonitrile:

$$CH_3CN + CH_4 + O_2 \xrightarrow{\text{cat.}} CH_2{=}CHCN + 2H_2O$$

The catalyst comprises potassium or calcium halides on quartz. Molybdenum and bismuth oxides individually or combined on quartz or other supports are also proposed. The process was never commercialized because the amount of acetonitrile byproduct was reduced by catalyst development.

Some acetonitrile is used as an aprotic solvent, particularly for the separation of butadiene from other C_4 olefins (Section 5). Modern catalysts are so efficient in decreasing acetonitrile production that in the early 1990s there was actually a shortage of acetonitrile for use as an aprotic solvent.

On the horizon is a process based on the ammoxidation of propane rather than propylene (Section 11.2.1). This is formally analogous to the oxidation of butane to maleic anhydride (Section 5.4.2) with the simultaneous introduction of a double bond and functional groups into a saturated hydrocarbon. BP has indicated that its next world scale acrylonitrile plant may be propane based. However, commercialization of this new technology has been delayed because of global overcapacity for acrylonitrile in the early 2000s. In addition to BP, patent information indicates that Asahi Chemical and Mitsubishi Chemical, both in Japan, have developed effective propane ammoxidation catalysts (Section 11.2.1).

4.8.1 Uses of Acrylonitrile

Acrylonitrile is used primarily to make polymers. Its most important application is for the production of polyacrylonitrile for textile fibers. Because polyacrylonitrile is not thermally stable, it must be spun from solution as cellulose acetate is. The problem is that acrylonitrile polymerizes to a very high molecular weight, hence the polymer is only slightly soluble in ordinary solvents, despite the fact that it is thermoplastic. Spinning was made possible by the discovery of so-called aprotic solvents such as *N,N*-dimethylformamide and *N,N*-dimethylacetamide. Polyacrylonitrile is also soluble in aqueous solutions of inorganic salts and acids such as sodium thiocyanate solution and, to a lesser degree, nitric acid and zinc chloride. These are used competitively with the aprotic solvents. The problem of spinning polyacrylonitrile thus gave rise to the science of aprotic solvents, which find application today in extractive distillation (Fig. 5.2) and in the synthesis of aromatic polymers whose monomers are insoluble in more usual solvents.

Acrylic fibers are also made more tractable by inclusion of 10–15% of comonomers such as methyl acrylate or vinyl acetate. *p*-Vinylbenzenesulfonic acid is also incorporated into the copolymer to make the fiber dyeable with basic dyes. Familiar trade names of acrylic fiber are Orlon, Acrilan, and Courtelle.

Another important copolymer made from acrylonitrile is acrylonitrile–butadiene–styrene resin (ABS) (Section 3.8). ABS is the most widely used engineering (i.e., metal-replacing) plastic, and US consumption in 2002 reached 1.4 billion lb. It is a two-phase polymer system, with the elastomeric butadiene–acrylonitrile copolymer dispersed in a rigid styrene–acrylonitrile matrix. Because light reflects at the phase boundaries, it is opaque.

Butadiene–acrylonitrile rubber was developed in Germany prior to World War II and is still used today. The acrylonitrile imparts valuable oil and abrasion resistance.

High acrylonitrile-containing polymers have good barrier properties to carbon dioxide and oxygen. They are clear and have good extensibility, which makes them useful for the fabrication of bottles. Monsanto developed such a resin based on a copolymer of acrylonitrile and styrene. The development was banned from food packaging by the Food and Drug Administration because of the slight possibility that some undetectable levels of free acrylonitrile might remain in the resin. This was proved to be unlikely, but Monsanto never re-established the project and the market for bottles for carbonated beverages was taken over by poly(ethylene terephthalate) (Section 9.3.3) Styrene–acrylonitrile remains a useful copolymer but sells only on the scale of about 120–130 million lb/year. Other acrylonitrile formulations contain styrene, methyl methacrylate, and styrene–butadiene rubber. Barrier resins based on acrylonitrile were available for nonfood packaging and were approved for food use in the early 2000s.

The electrohydrodimerization of acrylonitrile provides a significant route to adiponitrile, which in turn can be hydrogenated to hexamethylenediamine for nylon 6,6 production. It's economics are less favorable than hydrocyanation of butadiene (Section 5.1.2). What is presumed to be a catalytic route for the dimerization of acrylonitrile was developed by ICI and was scheduled for commercialization in the early 1990s, but ICI instead left the nylon business and subsequently most other petrochemicals as well.

Acrylonitrile production grew slowly in the period 1980–1993, and domestic United States demand rose by only 3.7%/year in the subsequent decade. The market for acrylic fibers shrank from 671 million lb in 1984 to 433 million lb in 1993 and 339 million lb in 2000 because of fashion changes. Acrylonitrile consumption has only been maintained by growth in ABS resins, hexamethylene diamine, and acrylamide. In the decade 1990–2000, acrylonitrile grew at 2.7%/year, ABS at 3%/year, and fibers—a smaller end-use—shrank at 3.9%/year.

4.9 CUMENE, CUMENE HYDROPEROXIDE, AND PHENOL

Cumene (isopropylbenzene) is the precursor of phenol and acetone. It results from the acid-catalyzed alkylation of benzene with propylene as shown in Figure 4.2*g*. It is a continuous reaction similar to ethylbenzene production (Section 3.8), where benzene is alkylated with ethylene. Both liquid- and gas-phase alkylations are possible. Almost any Friedel–Crafts catalyst can be used. The conventional process, gas-phase alkylation, is still the most popular, with aluminum chloride, phosphoric acid, or even boron trifluoride catalysts at 200–350°C and 10–15 bar. The molar ratio of benzene to propylene is 8–10:1. Either chemical grade (92 wt%) or refinery grade propylene is suitable. Refinery grade propylene from catalytic cracking is typically about 70% by weight (Section 2.2.2) with the remainder mostly propane. Cumene yields are 96–97% based on benzene and 91–92% based on propylene. Selectivity to cumene is 92–94% based on propylene, and an excess of benzene is used to depress the formation of di- and triisopropylbenzene as well as a small amount of *n*-propylbenzene.

Solid acid catalysts, such as the zeolite ZSM-5, which are more ecologically acceptable, were introduced in the early 1990s and their use has grown rapidly. They offer several advantages over phosphoric acid or aluminum chloride. They are able to bring about the alkylation at lower temperatures and pressures and reduce the formation of polyalkylbenzenes and olefin oligomers, thus leading to overall yields of 98%. In addition, the higher selectivity allows the ratio of benzene to propylene to be reduced from 8–10:1 to 4–5:1. This doubles the capacity of an existing cumene reactor with virtually no additional capital expenditure, although downstream separation capacity inevitably must be increased. In addition to the savings on operating and capital costs, zeolite catalysts can be regenerated by the burning off of deposits of high molecular weight hydrocarbons. This eliminates the disposal problems associated with phosphoric acid and aluminum chloride. The cumene processes may also incorporate a transalkylation reactor to convert any di- and triisopropylbenzene to cumene by reaction with benzene.

Alkylation of benzene with propylene to give cumene was first carried out in refinery polygas units (Section 2.2.4). Cumene was an important octane improver in aviation gasoline in World War II (Section 2.2.4). Its production was fostered because polygas units became available when that product was replaced by alkylate (Section 2.2.5). Conversely, oligomerization can be carried out in units built specifically for cumene production.

Virtually all cumene is converted to phenol and acetone, which is the classical two-for-one reaction in which two products are manufactured in one plant. Cumene is thus the basis for an extensive value chain shown in Figure 4.7. Phenol will be discussed in detail in Section 7.1.

Cumene reacts with oxygen from the air in the presence of aqueous alkali at 130°C and pH 6–8 to give cumene hydroperoxide at a concentration of about 25 wt% (Fig. 4.2*g*). An emulsifying agent is often added to facilitate contact between the

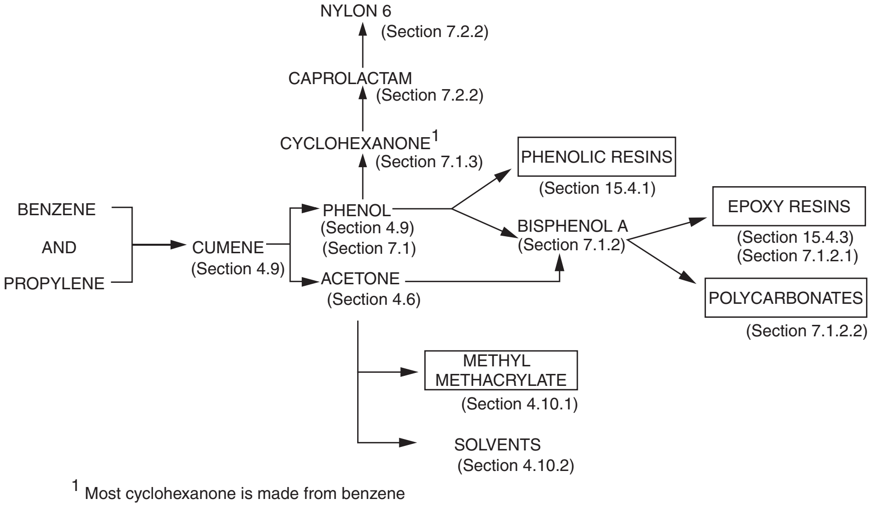


FIGURE 4.7 The cumene value chain.

cumene and aqueous phases. Sodium carbonate is added to maintain the pH. Metallic catalysts such as cobalt, copper, or manganese with promoters, may be used, but usually are not, because they facilitate oxidation of the cumene itself to carbon dioxide.

As might be expected, the reaction is sensitive to acids such as formic and acetic, which decompose the cumene hydroperoxide. These are only slowly neutralized by the alkali present, which is in the aqueous rather than the organic phase, but they are also volatilized in the oxygen stream. Other possible impurities in the cumene such as sulfur compounds, phenol, or aniline may also attack the hydroperoxide.

Surplus cumene is distilled off for recycle. The concentrated cumene hydroperoxide (75–85 wt%) is cleaved to phenol and acetone without further purification by treatment with 10% sulfuric acid at about 50°C in the liquid phase. The mechanism for the decomposition is shown in Figure 4.8. Byproducts are dimethylphenylcarbinol, α-methylstyrene, and acetophenone, as well as diacetone alcohol, which forms from the self-condensation of acetone. The stoichiometry demands that 0.6 tons of acetone form for every ton of phenol. The α-methylstyrene in most cases is hydrogenated back to cumene and recycled.

In 2003, Sumitomo Chemical commercialized a new process for making propylene oxide based on oxidation of propylene with cumene hydroperoxide. The cumyl alcohol (dimethylbenzyl alcohol) byproduct undergoes dehydration and hydrogenation in one or two steps to reconstitute the starting cumene. This approach to propylene oxide is much less capital intensive than the propylene oxide–styrene monomer or propylene oxide–*tert*-butanol coproduct processes (Section 4.11).

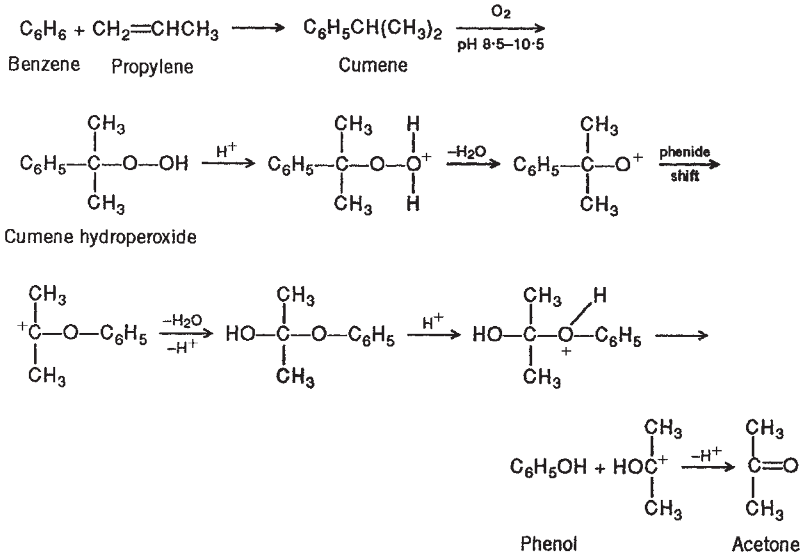


FIGURE 4.8 Mechanism of the cumene–phenol process.

4.10 ACETONE AND ISOPROPANOL

The cumene–phenol process is the major source of acetone. This two-for-one reaction suffers from the same problem as all such reactions in that it is seldom that the marketplace requires both products in the ratio in which they are produced. Historically, there has been a shortfall of acetone, and it would have been uneconomic to satisfy acetone demand by the accumulation of unsaleable phenol. Hence, an alternative route to acetone was required.

The alternative route already existed. It was the first petrochemical reaction, having been pioneered by Exxon, and is shown in Figure 4.2*h*. Absorption of propylene in concentrated sulfuric acid gives isopropyl sulfate, which is hydrolyzed to isopropanol. This has a number of uses, primarily as a solvent, but some of it is air-oxidized or dehydrogenated to acetone.

$$CH_3CHOHCH_3 \longrightarrow CH_3COCH_3 + H_2 \text{ (dehydrogenation)}$$

$$CH_3CHOHCH_3 + 0.5O_2 \longrightarrow CH_3COCH_3 + H_2O \text{ (oxidative dehydrogenation)}$$

The dehydrogenation process is preferred and employs a zinc oxide catalyst at 300–400°C and 3 bar or a copper or brass catalyst at 500°C. Conversions per pass are over 90% and an overall yield of 96% results. The oxidative dehydrogenation takes place in the presence of air at 400–600°C over a silver or copper catalyst. Low pressures, a temperature of 550°C, and a zinc oxide catalyst are employed. The dehydrogenation is endothermic and lack of a use for the byproduct hydrogen may make the oxidative route, which is exothermic, worthwhile.

During the 1980s, acetone from isopropanol accounted on average for about 8% of acetone production in the United States. By 1990, this had fallen to 4.5%. It disappeared completely in the late 1990s because more phenol was needed for bisphenol A (Section 7.1.2) and for polycarbonate (Section 7.1.2.2), and less acetone for solvent use. Shell and Exxon have both exited this business.

Mitsui Chemical has developed a process in which the acetone byproduct from phenol production is hydrogenated to isopropanol, which in turn is dehydrated to propylene for recycle to the cumene alkylation unit. Mitsui has the ability to turn this unit on or off depending on the market conditions for acetone.

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{H_2} \underset{\text{Isopropanol}}{CH_3CHOHCH_3} \xrightarrow{-H_2O} \underset{\text{Propylene}}{CH_3CH{=}CH_2}$$

A variant of the Wacker process (Section 3.5) is used in Japan to obtain acetone from propylene. Propylene reacts with oxygen in the presence of catalytic amounts of palladium chloride and a stoichiometric amount of cupric chloride, which is reduced to cuprous chloride. The latter is then reoxidized to cupric chloride in a separate reactor. In the original Wacker process, both the $CuCl_2$ and $PdCl_2$ were used in catalytic amounts, the CuCl being reoxidized to $CuCl_2$ *in situ*.

$$CH_2{=}CHCH_3 + \tfrac{1}{2}O_2 \longrightarrow CH_3COCH_3$$

A Shell process, not in use, involves the oxidation of isopropanol to acetone and hydrogen peroxide in a two-for-one process.

$$\underset{\text{Isopropanol}}{CH_3CHOHCH_3} + O_2 \longrightarrow \underset{\text{Acetone}}{CH_3COCH_3} + \underset{\text{Hydrogen}}{H_2O_2}$$

The three major chemical (i.e., nonsolvent) uses for acetone are for the preparation of methyl methacrylate (Section 4.10.1), methyl isobutyl ketone (Section 4.10.2), and bisphenol A (Section 7.1.2).

4.10.1 Methyl Methacrylate

The classical route to methyl methacrylate starts with the sodium hydroxide-catalyzed condensation of acetone and hydrocyanic acid to give acetone cyanohydrin, as shown in Figure 4.9*a*. Dehydration and hydrolysis of the nitrile group followed by esterification provides methyl methacrylate. The conversion of acetone cyanohydrin to methacrylamide sulfate via acetone cyanohydrin sulfate is carried out with 98% sulfuric acid at temperatures as high as 140°C. The amide reacts with methanol at 80°C to yield methyl methacrylate. Overall molar yield based on acetone has been raised in recent years from 75 to 92%, an indication of the intense process development to which old processes are frequently subjected. The corresponding overall plant yields for methanol and HCN are about 92 and 89%.

A major problem with this process is the production of about 1.5 tonnes of ammonium bisulfate byproduct per tonne of methyl methacrylate by the reactions shown in Figure 4.9*a*. This byproduct problem was never satisfactorily solved over a period of 50 years, but ICI brought a process for byproduct treatment on stream in the early 1990s and Mitsubishi Gas Chemical has an entirely new process (see below). Another problem is that about 21% of US hydrogen cyanide production is a byproduct from acrylonitrile manufacture (Section 4.8). New acrylonitrile processes generate decreased amounts of hydrogen cyanide, which means that new, dedicated, and for this process uneconomical, hydrogen cyanide facilities (Section 10.1) may be required. These two problems, particularly acute in Japan where hydrogen cyanide is in short supply, have motivated the development of alternative processes.

The ICI process, developed jointly with Air Liquide, is called the SAROX process and involves high-temperature pyrolysis of the ammonium bisulfate in the presence of air or oxygen. The bisulfate decomposes to ammonia and sulfur trioxide which, at the temperature of operation, dissociates partly to sulfur dioxide and oxygen. The ammonia is oxidized by air to nitrogen and water, and the reaction stream is sent to a sulfuric acid plant where it is reconverted to sulfuric acid, which is recycled. Overall conversion and recovery of the sulfur content of "spent acid" as sulfuric acid is about 90%.

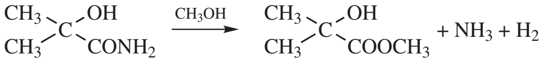
The Mitsubishi Gas Chemical Co. process for methyl methacrylate manufacture demonstrates a high level of ingenuity and was announced in 1989. It solves the two defects that characterize the acetone cyanohydrin process—the need to generate hydrocyanic acid and the production of unwanted ammonium bisulfate. It is noteworthy that the solution to these problems did not come from methyl methacrylate's major suppliers but from a Japanese company.

In this process, acetone cyanohydrin, produced conventionally from acetone and hydrocyanic acid, is partially hydrolyzed to α-hydroxyisobutyramide (Fig. 4.9*b*). An ester–amide interchange with methyl formate produces methyl α-hydroxyisobutyrate. Thus, the carboxyl function has been inserted in the molecule without ammonium bisulfate production. Formamide is the coproduct. Dehydration of the butyrate provides the desired methyl methacrylate. Hydrocyanic acid is regenerated for reuse by dehydrating the formamide

$$HCONH_2 \longrightarrow HCN + H_2O$$

The dehydration is performed in the gas phase, catalyzed by iron with magnesium, calcium, zinc, or manganese promoters at about 400°C, or by α-alumina at 450–540°C at reduced pressure. The need for a dedicated plant for hydrocyanic acid production is thus obviated. Make-up hydrocyanic acid can be generated from formamide made by reacting methyl formate with ammonia. The methyl formate required for this use, as well as for the exchange reaction, is made by the carbonylation of methanol with a basic catalyst. Thus, the overall reaction for the MGC process consumes only acetone, methanol, and carbon monoxide, with the CO replacing HCN as the source of the fourth carbon atom needed to convert acetone to methyl methacrylate.

By early 1990, the Mitsubishi Gas Chemical Co. was operating a pilot plant for this process and a full scale plant was built in 1997 at Niigata, Japan. Recent patents granted to MGC reveal some improvements to two of the reaction stages. In particular, instead of the α-hydroxyisobutyramide undergoing an ester–amide interchange with methyl formate, the amide is reacted with methanol with simultaneous removal of the evolved ammonia to give methyl α-isobutyrate.



$$(CH_3)_2C(OH)CONH_2 \xrightarrow{CH_3OH} (CH_3)_2C(OH)COOCH_3 + NH_3 + H_2$$

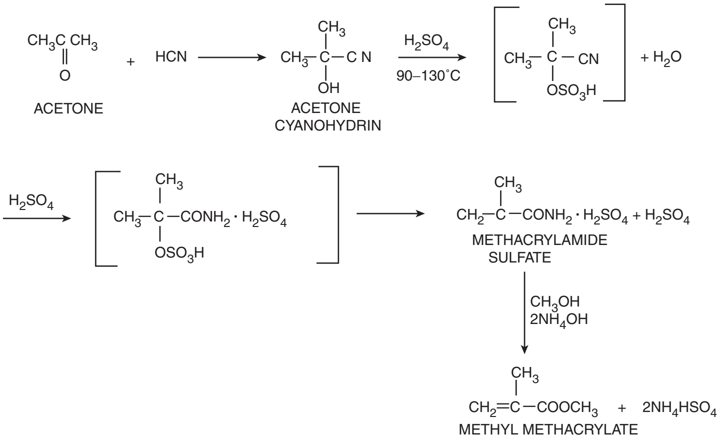
Hydroxyisobutyramide

Methyl α-Hydroxy-
isobutyrate

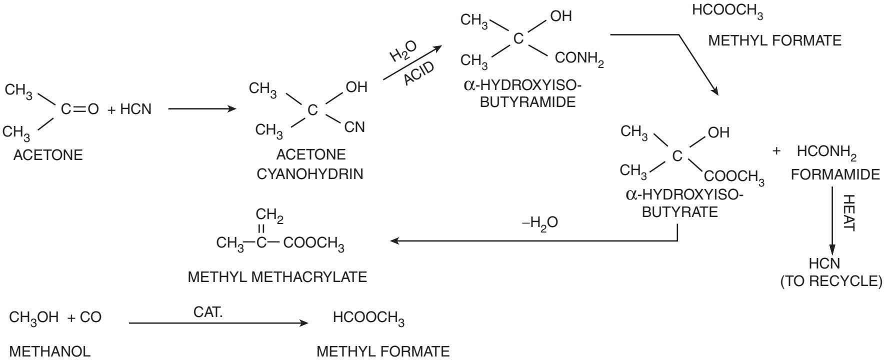
Dehydration gives methyl methacrylate. The other improvement relates to regeneration of HCN. The ammonia byproduct is reacted with methanol and oxygen over a ferric–molybdenum oxide catalyst. Thus, the overall process converts acetone, methanol, and oxygen to methyl methacrylate.

Unfortunately, this creative process has too many steps, which makes it less economical than isobutene oxidation (Fig. 4.9*d*) in the United States. This will be especially true if methyl *tert*-butyl ether (MTBE) usage decreases markedly in the United States, making large quantities of isobutene available (Section 5.2.1).

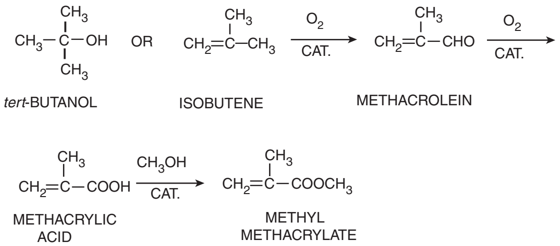
A summary of other processes follows. In the Mitsubishi Rayon Process in use in Japan (Fig. 4.9*c*) *tert*-butanol or isobutene is oxidized to methacrylic acid, via methacrolein, which is not isolated. If *tert*-butanol is used, the reaction probably proceeds via its dehydration to isobutene. Catalysts are similar to those described for the oxidation of propylene to acrolein and acrylic acid (Section 4.7) and are based on molybdenum and bismuth. A typical catalyst for the first stage to methacrolein comprises molybdenum, bismuth, iron, and lithium in a molar ratio of 1:1:0.3:0.1. The (*a*) CONVENTIONAL ROUTE



(*b*) MITSUBISHI GAS CHEMICAL ROUTE



(*c*) C_4 OXIDATION (SEVERAL JAPANESE COMPANIES)



(*d*) C_4 AMMOXIDATION (ASAHI GLASS CO.)

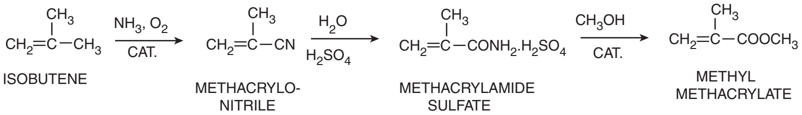
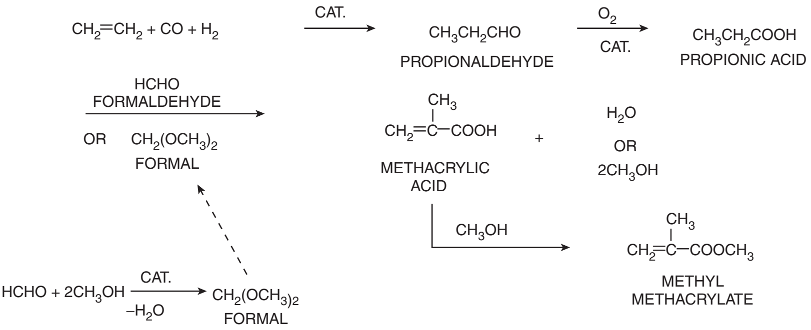
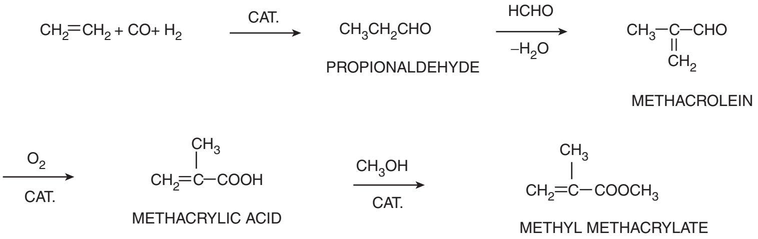


FIGURE 4.9 Methyl methacrylate syntheses.

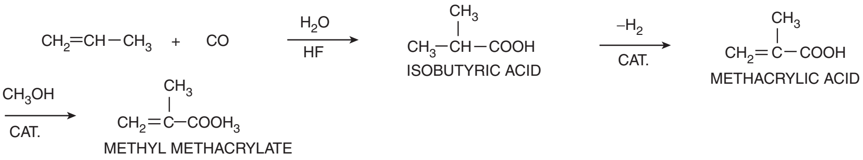
(*e*) ETHYLENE - BASED (DEVELOPMENTAL, INEOS)



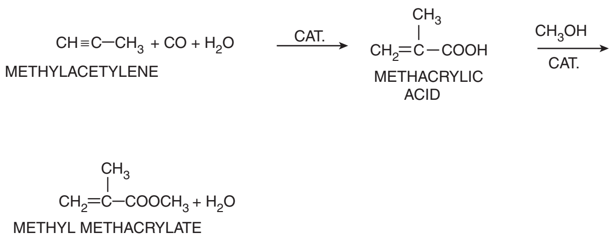
(*f*) ETHYLENE-BASED (BASF)



(*g*) PROPYLENE-BASED (DEVELOPMENTAL, ATOCHEM)



(*h*) METHYLACETYLENE-BASED (DEVELOPMENTAL, SHELL)



(*i*) ETHYLENE-BASED (ICI/INEOS)

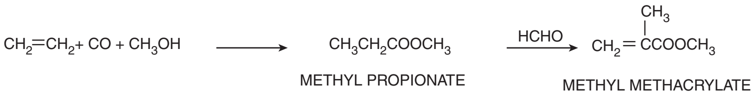


FIGURE 4.9 (*Continued*)

second stage of the oxidation may be carried out with a vanadium phosphomolybdate catalyst with cesium and strontium. A typical composition is $Mo_{12}P_2VCs_2SrO_{.0.5}$. Japan Catalytic in a joint venture with Sumitomo oxidizes isobutene directly.

In much the same way that propylene undergoes ammoxidation to acrylonitrile, Asahi Chemical in Japan ammoxidized isobutene to methacrylonitrile in a converted acrylonitrile plant (Fig. 4.9*d*). Thereafter, the process uses conventional chemistry. This is a multistage process and generates ammonium bisulfate in the hydrolysis of the nitrile to the amide. While this approach was apparently economic, because it was carried out in depreciated equipment, it was closed down in the late 1990s.

Asahi Chemical has devised a two-step process ("Direct Metha" Process) to methyl methacrylate that involves oxidation of isobutene to methacrolein followed by simultaneous oxidation and esterification to methyl methacrylate. This is similar to Figure 4.9*c*, but with the two final processes merged. The economics appear excellent, and such two-step processes will probably be the major ones in the future. Mitsubishi Rayon announced a similar process in the early 2000s.

A synthesis announced as a commercial process by BASF (Fig. 4.9*f*) in the late 1980s is based on the hydroformylation of ethylene to propionaldehyde (Sections 3.11.1, 4.12). Reaction of propionaldehyde with formaldehyde yields methacrolein. Oxidation of the methacrolein gives methacrylic acid which, following esterification with methanol, finally affords methyl methacrylate. Methyl propionate may be used instead of propionaldehyde.

A newer but related process was developed by INEOS, who bought ICI's methacrylate business. Figure 4.9*e* shows the production of propionic acid, which is then treated with formaldehyde or formal to give methacrylic acid. Although the process appears cumbersome, it must be recognized that only the intermediate step of inserting the methylene group, which also was used in a proposed acrylic acid process (Section 4.7), is new. Whereas formaldehyde may be used directly, the formal, produced from formaldehyde and methanol, will be more compatible and may lead to higher selectivities. On the other hand, the methanol generated in the condensation must be recovered. In these ethylene-based processes, three of the five carbon atoms are derived from syngas, either directly or indirectly, and their economics depend on the economics of syngas production.

Another ICI/INEOS ethylene-based route employs the reaction of methyl propionate with formaldehyde to give methyl methacrylate and water. The methyl propionate is presumably made by reaction of ethylene, carbon monoxide, and methanol (Fig. 4.9*i*). A similar approach has been used by a group of companies working together including Research Triangle Institute, Bechtel, and Eastman Chemical.

A process under development by a number of companies, particularly Atochem, involves propylene carbonylation in the presence of liquid hydrofluoric acid. (Fig. 4.9*g*), to yield isobutyric acid. Oxidative dehydrogenation to methacrylic acid takes place in the presence of aluminum-modified iron phosphate. Esterification with methanol yields methyl methacrylate.

Shell developed a process shown in Figure 4.9*h* and sold it to ICI who sold it to INEOS. It starts with propyne (methylacetylene) or a mixture of propyne with allene $CH_2{=}C{=}CH_2$, the latter being in equilibrium with propyne under the reaction conditions.

$$CH_3C{\equiv}CH \rightleftharpoons CH_2{=}C{=}CH_2$$

Propyne Allene

Propyne and allene are produced during steam cracking (Section 2.2.1) in small quantities and can be recovered by solvent extraction, although they are usually selectively hydrogenated to propylene. Since they are produced in small quantities, isolation of sufficient material to feed a plant could be a problem. In the Shell/INEOS process (Fig. 4.9*h*), however, the mixture is reacted with carbon monoxide and water in the presence of a catalyst comprising palladium acetate, triphenylphosphine, and benzenephosphonic acid. Methacrylic acid results, which is esterified to methyl methacrylate. Alternatively, the carbonylation can be carried out in the presence of methanol rather than water to yield the ester directly. The process is closely related to an obsolete process for acrylic acid production (Section 4.3) from acetylene, which used a conventional nickel carbonyl catalyst.

The target of derivatizing alkanes led to yet another route to methyl methacrylate starting with isobutane. It was actively under investigation in the late 1990s and early 2000s. This approach has the obvious appeal of a low-cost feedstock but suffers from the tremendous difficulty of developing catalysts with sufficient selectivity. More about alkane derivitization is described in Chapter 11.

Another proposed methyl methacrylate process that yields propylene oxide as a coproduct is described in Section 4.11. Despite all these interesting new processes, most of the world's methyl methacrylate was still produced in 2002 by the acetone cyanohydrin route. However, it involves problems of ammonium bisulfate disposal and safety issues associated with the handling of large quantities of HCN. If isobutene becomes cheaply and abundantly available because of the phase out of MTBE, it is likely that the Japanese isobutene oxidation route will grow.

Most methyl methacrylate is polymerized to poly(methyl methacrylate) from which is made acrylic sheet for use in glazing, lighting, signs, and sanitary items such as bathtubs made by thermoforming. Glazing, in which the transparent poly(methyl methacrylate) replaces glass, is by far the largest market. Molding resins and surface coatings provide the other two large applications. Methyl methacrylate is used with other acrylic monomers to make emulsions for water-based paint (Sections 4.3, 3.6). Combined with melamine resin (Section 10.5.1.1) it is the vehicle for the paint used both as the pigmented topcoat for automobiles as well as the clear coat that completes the finish. It also replaces styrene in certain specialty unsaturated polyester compositions (Section 9.1.1). If fears of styrene toxicity in polyester resins turn out to be well founded, methyl methacrylate consumption will increase. Methyl methacrylate has a high refractive index and critical angle, and hence is capable of conducting light around bends. This is the basis for its growing use in fiber optics and light pipes.

4.10.2 Methyl Isobutyl Ketone and Other Acetone Derivatives

Further products from acetone are shown in Figure 4.10. Practically all the materials are solvents, mostly for the paint industry. The most important, as previously indicated, is methyl isobutyl ketone. The aldol condensation of acetone to diacetone alcohol is base

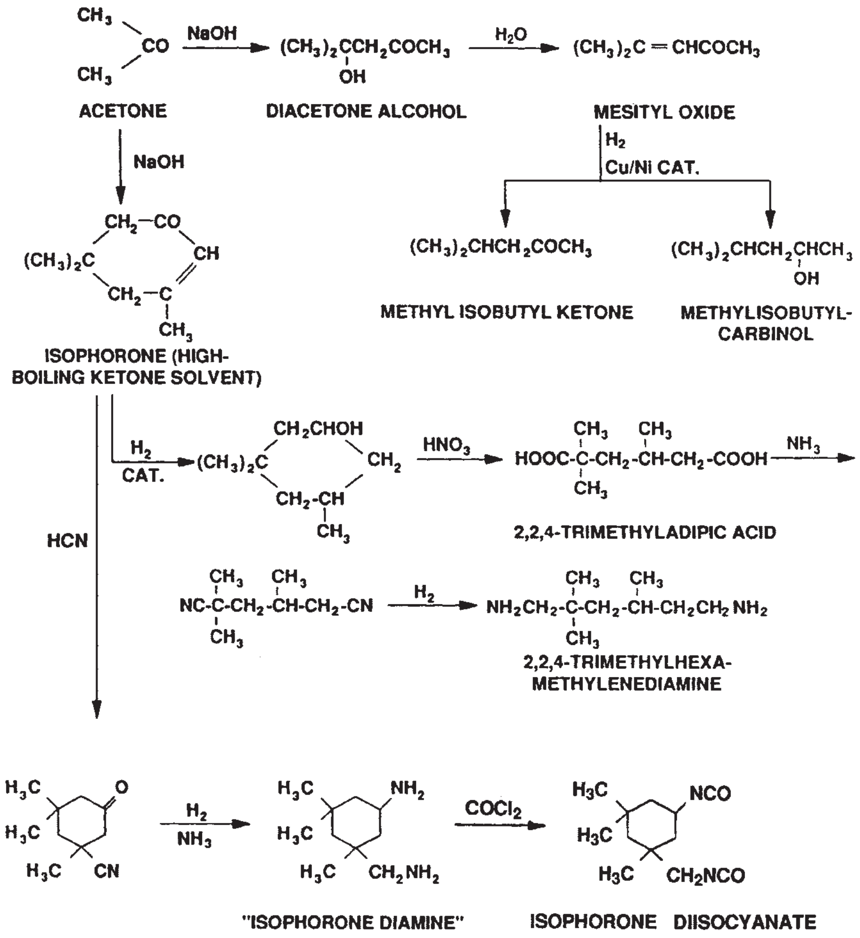


FIGURE 4.10 Acetone reactions.

catalyzed and carried out in the liquid phase. Dehydration takes place at about 100°C in the presence of sulfuric and phosphoric acids to yield mesityl oxide. Hydrogenation of mesityl oxide to methyl isobutyl ketone must be accomplished without involving the carbonyl group. Actually the hydrogenation is carried out with copper and nickel catalysts at 150–200°C and up to 10 bar to give a combination of methyl isobutyl ketone and methylisobutylcarbinol, which can be separated by distillation.

Isophorone, a high-boiling ketone solvent, results from the base-catalyzed trimerization of acetone (Fig. 4.10). Hydrocyanic acid will add across its double bond to give a nitrile, and reductive amination with ammonia and hydrogen gives "isophorone diamine." Like the toluene diamines, treatment with phosgene gives a diisocyanate—isophororone diisocyanate or IPDI—which is used in a light stable polyurethane resin.

Hydrogenation of isophorone reduces the double bond and converts the ketone group to an alcohol. Nitric acid oxidation provides 2,2,4-trimethyladipic acid, which may be converted to a dinitrile with ammonia. Further hydrogenation yields

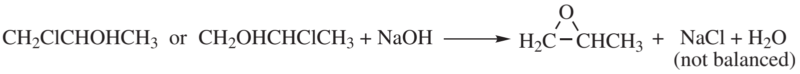
2,2,4-trimethylhexamethylenediamine. Both these diamines, but particularly isophorone diamine, are useful as curing agents for epoxy resins.

4.11 PROPYLENE OXIDE

Propylene oxide (Fig. 4.2*e* and *f*) was made traditionally by reaction of propylene with hypochlorous acid, generated *in situ* from chlorine and water, followed by dehydrochlorination with calcium or sodium hydroxide.

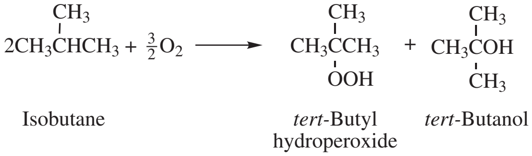
$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

$$CH_2{=}CHCH_3 + HOCl \longrightarrow CH_2ClCHOHCH_3\ (90\%) + CH_2OHCHClCH_3\ (10\%)$$

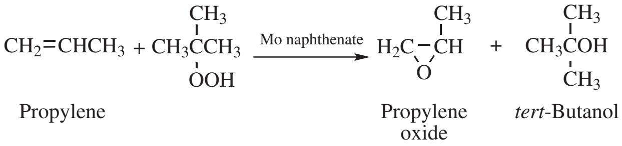


The same process was at one time used for ethylene oxide, with calcium hydroxide generally preferred to sodium hydroxide in the final stage. Many of these plants were converted to propylene oxide production when the direct oxidation route (Section 3.7) to ethylene oxide appeared. The process for propylene oxide with sodium hydroxide is still used by Dow in the United States. Several European and Japanese companies use the calcium hydroxide process. Dow has a highly integrated plant with a chlorine–caustic soda unit to provide chlorine for the chlorohydrin reactor and sodium hydroxide for the dehydrochlorination. In addition, the brine produced by the dehydrochlorination can be reprocessed into caustic and chlorine, although Dow probably does not do this. The reaction takes place in dilute solution and 4.0–4.5% propylene chlorohydrins (the α-isomer predominates) are produced in a molar yield of 94% with 4.7% of 1,2-dichloropropane and 1.7% of chloroisopropyl ether. In the dehydrochlorination, the yield of propylene oxide is 96%.

The process is wasteful of chlorine (or electricity in the integrated plant) and much research was devoted to discovering a direct oxidation route. The first process to be commercialized involved oxidation of isobutane to *tert*-butyl hydroperoxide, which then oxidized propylene to propylene oxide.



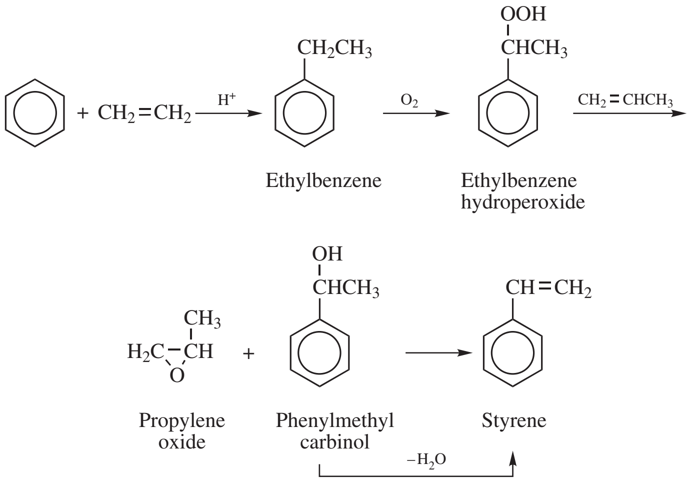
$$2CH_3\overset{CH_3}{\overset{|}{C}}HCH_3 + \tfrac{3}{2}O_2 \longrightarrow CH_3\underset{OOH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_3 + CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}OH$$



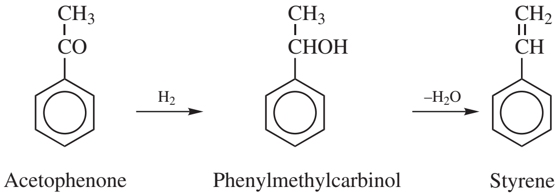
tert-Butanol is a byproduct in both the formation of the peroxide and the epoxidation step. Approximately 2.2 mol of *tert*-butanol/mol of propylene oxide are produced. The reaction provides a second route to *tert*-butanol, the first being the *in situ* hydration of the isobutene in the C_4 fraction from steam or catalytic cracking (Section 5). This low-melting (mp 25.6°C) white solid can be oxidized to methyl methacrylate as is done in Japan (Section 4.10.1). It aroused interest as an octane improver in nonleaded gasoline, where it may be used in combination with methanol. However, MTBE (Section 5.2.1) was felt at the time to be superior, although this view has now changed (Section 2.3.2). Accordingly, in the late 1980s, Arco Chemical, who pioneered the two-for-one reaction with Scientific Design for propylene oxide and *tert*-butanol, started to dehydrate *tert*-butanol to isobutene for conversion to methyl *tert*-butyl ether and quickly became the largest single U.S. producer of this gasoline additive.

Pure oxygen is required for the isobutane hydroperoxidation. The uncatalyzed liquid-phase reaction proceeds at 120–140°C and 34 bar. Acetone forms as a minor byproduct. Water is necessary in the reaction mixture to inhibit oxidation of isobutane to ketones, aldehydes, and acids. The subsequent epoxidation is carried out at 135°C and about 50 bar to keep the reactants in the liquid phase and requires a molybdenum naphthenate catalyst.

A second two-for-one process for propylene oxide, also introduced by Lyondell (formerly Arco), provides styrene as a coproduct. Between 2.2 and 2.5 lb of styrene are generated for each pound of propylene oxide. Thus the first plant produced 1 billion lb of styrene and 400 million lb of propylene oxide. Benzene and ethylene give ethylbenzene, which is converted to ethylbenzene hydroperoxide with air. This epoxidizes propylene to propylene oxide, yielding coproduct phenylmethylcarbinol, whose dehydration provides styrene (Section 3.8).



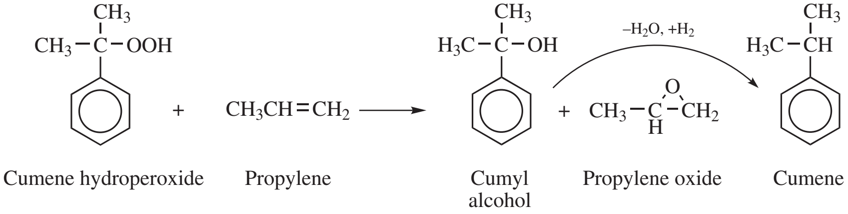
Because of the problems of isolating and recovering styrene, capital investment for this process is about twice as much as that for the propylene oxide–*tert*-butanol process. The process is similar to the oxidation of cumene to cumene hydroperoxide (Section 4.9) and isobutane to *tert*-butyl hydroperoxide. Magnesium carbonate is added to adjust the pH to 7 to reduce the decomposition of the hydroperoxide. Selectivity of about 65% is possible only at a low conversion of 15–17%. Above that concentration, byproducts including phenylmethylcarbinol and acetophenone increase appreciably. Meanwhile, acetophenone can be converted to styrene by hydrogenation to phenylmethylcarbinol and subsequent dehydration.



The epoxidation stage is also similar to the production of *tert*-butyl hydroperoxide, a molybdenum naphthenate catalyst playing an important role. However, this requires milder conditions of 100–130°C in the liquid phase under ambient pressure. Selectivity of propylene to propylene oxide is about 91%. Byproducts include dimers of propylene, whose formation can be inhibited by antioxidants. The vapor-phase dehydration of phenylmethylcarbinol to styrene takes place over a catalyst at 200–280°C. Titania and alumina are typical catalysts.

A Shell variation of the Arco Lyondell route to propylene oxide and styrene involves a heterogeneous system for the epoxidation, with catalysts such as vanadium, tungsten, molybdenum, or titanium supported on silica and treated with a sylylating agent. Two plants using this technology are in operation, one in Europe and another in Singapore, both operated by a joint venture of Shell and BASF called ELLBA. By 2002, 20% of styrene globally was made by the coproduct process.

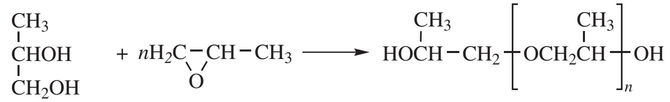
As described in Section 4.5, Sumitomo Chemical in 2003 commercialized a new coproduct-free route to propylene oxide. While details of the new technology have not been revealed, patents issued to Sumitomo indicate that it is based on cumene hydroperoxide as the oxidant. Cumene hydroperoxide is the precursor of phenol and acetone, and thus its manufacture and handling are well known. With the development of a proprietary catalyst by Sumitomo, cumene hydroperoxide epoxidizes propylene to propylene oxide in excellent yield giving cumyl alcohol (dimethylbenzyl alcohol) as a byproduct. The patents give examples that show that cumyl alcohol can undergo simultaneous dehydration and dehydrogenation to cumene, which can be recycled to the beginning of the reaction.



In the United States in the early 2000s, about 48% of propylene oxide production was via the chlorohydrin method, with sodium hydroxide for the dehydrochlorination, and the remaining 52% by the coproduct processes.

4.11.1 Propylene Oxide Applications

Whereas 60% of ethylene oxide is hydrolyzed to ethylene glycol, only about one third of the propylene oxide produced is converted to propylene glycol. The major use, and the reason for the increased consumption of propylene oxide in the past 30 years, is its oligomerization to poly(propylene glycols) for polyurethanes (Sections 7.3.1, 8.3). The oligomerization is initiated by active hydrogen compounds. To provide the hydroxyl end groups necessary for interaction with isocyanates, propylene glycol may be used as the initiator.

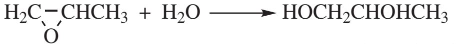


$$\mathrm{CH_3\text{-}CHOH\text{-}CH_2OH} + n\,\mathrm{H_2C\underset{O}{-}CH-CH_3} \longrightarrow \mathrm{HO\overset{CH_3}{CH}-CH_2}\left[\mathrm{OCH_2\overset{CH_3}{CH}}\right]_n\mathrm{OH}$$

1,2-Propylene glycol — Propylene oxide — Difunctional polyether polyol $n = 7\text{–}35$

The polymerization proceeds head-to-tail to give mainly secondary hydroxyl end groups. The polyols and polyethers react with diisocyanates, especially MDI, PMDI, and toluene diisocyanate (Sections 7.3.1, 8.3), to give polyurethane resins. If a more highly cross-linked polymer is desired, as is frequently the case, a triol can be prepared by the interaction of glycerol or trimethylolpropane with 3 mol of propylene oxide. If more active hydroxyl groups are required, reaction with ethylene oxide provides primary hydroxyethyl groups.

The second largest application of propylene oxide is its reaction with water to give 1,2-propylene glycol.

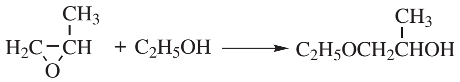


$$\mathrm{H_2C\underset{O}{-}CHCH_3} + \mathrm{H_2O} \longrightarrow \mathrm{HOCH_2CHOHCH_3}$$

1,2-Propylene glycol

In practice, a large excess of water is used to inhibit the formation of oligomers. If the amount of water is decreased, dipropylene and tripropylene glycols form and indeed poly(propylene glycols) with molecular weights of several thousands can be made. Because propylene glycol, unlike ethylene glycol, is not toxic it can be used in cosmetics. The largest use, however, is in the manufacture of unsaturated polyesters (Section 9.1.1). The poly(propylene glycols) can also be manufactured by reacting propylene oxide with propylene glycol. Copolymers of ethylene oxide and propylene oxide are nonionic surfactants.

Useful solvents result when propylene oxide reacts with alcohols to form glycol ethers.



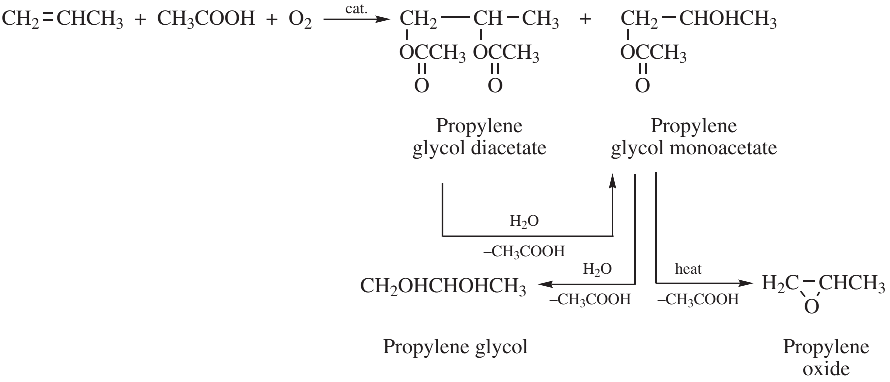
$$\mathrm{H_2C\underset{O}{-}\overset{CH_3}{CH}} + \mathrm{C_2H_5OH} \longrightarrow \mathrm{C_2H_5OCH_2\overset{CH_3}{C}HOH}$$

Propylene oxide — Ethanol — Propylene glycol monoethyl ether

This is analogous to the reaction of ethylene oxide with alcohols (Section 3.11.6.2). To some extent, they are replacing the ethylene oxide-based products, some of which are toxic to humans (see Section 3.11.6.2 and note at the end of this chapter), and hence environmentally undesirable. Because the propylene oxide-based glycol ethers have a branched methyl group, they are probably not as good solvents as the ethylene oxide-based products. Even so, increased demand is expected as the corresponding ethylene oxide-based products are phased out. In 2001, production of glycol ethers based on propylene oxide in the United States plus Brazil was 138,000 tonnes, in Western Europe 203,000 tonnes, and in Japan 22,000 tonnes.

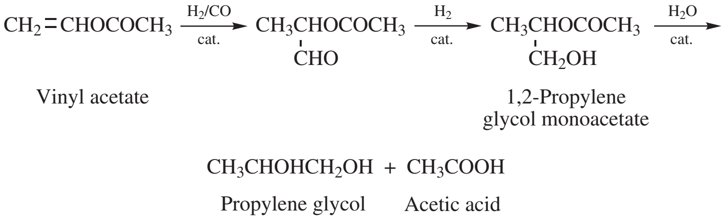
4.11.2 Projected Propylene Oxide–Propylene Glycol Processes

Much work has been done on potential processes for propylene oxide and the corresponding glycol, some of which do not produce coproducts. One of the most interesting involves the direct acetoxylation of propylene to a mixture of propylene glycol mono- and diacetates. The reaction takes place at 180°C and 80 bar over a tellurium oxide-iodine catalyst at 20% propylene conversion. Byproducts include propylene glycol, acetone, carbon dioxide, and water. The diacetoxy compound is hydrolyzed to the monoacetoxy compound, the acetyl group on the secondary hydroxyl being removed preferentially. The liquid-phase hydrolysis is catalyzed by acetic acid at 230°C and 70 bar. The monoacetoxy compound may then be hydrolyzed further to propylene glycol, or cracked catalytically to propylene oxide and acetic acid.



At 380°C and 0.13 bar, selectivity to propylene oxide is about 83% at 42% conversion. Cracking may also be carried out in the liquid phase with a tetrahydrothiophene-1,1-dioxide catalyst to obtain selectivities as high as 93% at 20–30% conversion. Major byproducts are acetone and propionaldehyde, which form by the decomposition of the monoacetates. The reaction system is highly corrosive, and a related process (Section 3.7.2) failed because of corrosion problems.

Another related process involves the hydroformylation of vinyl acetate to α-acetoxypropionaldehyde, which can be reduced to 1,2-propylene glycol monoacetate, which on hydrolysis gives propylene glycol. This circumvents the need for propylene oxide as a starting material.



$$CH_2{=}CHOCOCH_3 \xrightarrow[\text{cat.}]{H_2/CO} \underset{\displaystyle CHO}{CH_3CHOCOCH_3} \xrightarrow[\text{cat.}]{H_2} \underset{\displaystyle CH_2OH}{CH_3CHOCOCH_3} \xrightarrow[\text{cat.}]{H_2O} CH_3CHOHCH_2OH + CH_3COOH$$

Vinyl acetate; 1,2-Propylene glycol monoacetate; Propylene glycol; Acetic acid

4.11.3 Other Novel Syntheses of Propylene Oxide

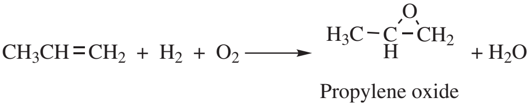
Processes developed to various degrees for propylene oxide production include

1. Direct oxidation.
2. Use of peracids or hydrogen peroxide.
3. Electrochemical processes.
4. Biotechnological approaches.

4.11.3.1 Direct Oxidation A key difference between ethylene and propylene is the fact that propylene contains "allylic hydrogens" that are sensitive to oxidation, hence the success of such propylene oxidation processes as acrylic acid and acrylonitrile. Ethylene, having no allylic hydrogens, undergoes silver-catalyzed epoxidation with oxygen fairly robustly (>80% selectivity). In contrast, the analogous direct oxidation of propylene has not proved commercially feasible. Propylene reacts with oxygen in the presence of silver with low selectivity to give numerous byproducts together with carbon dioxide and water from combustion processes.

Typical of United States work in this area is that of Union Carbide and Phillips who have developed noncatalytic liquid-phase processes in organic solvents such as acetonitrile and methyl formate at 150–225°C and 5–14 bar. Selectivities of 55–65% were achieved at propylene conversions of less than 25%. Work in the late 1990s by Arco Chemical with silver catalysts has shown selectivities up to 59% at propylene conversions of 4.5%. However, in order to achieve this relatively high selectivity, low pressures, and accordingly low throughputs were necessary.

A related approach is to react propylene with a mixture of oxygen and hydrogen gases over gold and titanium catalysts. Use of mixtures of oxygen and hydrogen to epoxidize propylene is termed hydro-oxidation. Lyondell, Nippon Shokubai and Dow Chemical are active in this area.

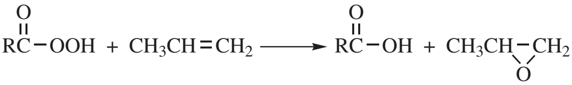


$$CH_3CH{=}CH_2 + H_2 + O_2 \longrightarrow H_3C{-}\underset{H}{C}{-}CH_2\ (\text{O bridging C and }CH_2) + H_2O$$

Propylene oxide

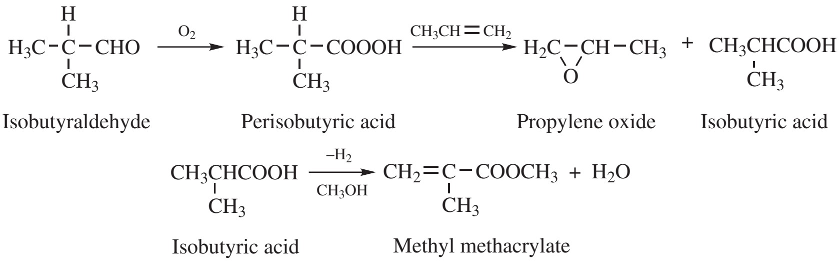
It is likely that this reaction proceeds through some sort of peroxy intermediate. While patents indicate that high selectivities are possible, conversions per pass are less than 3% at best and typically often less than 1%, far too low for commercial exploitation.

4.11.3.2 Use of Peracids or Hydrogen Peroxide The use of peracids provides an elegant way of transferring oxygen to the double bond of propylene. The peracid is converted correspondingly to the parent carboxylic acid.



$$\mathrm{R\overset{\overset{\Large O}{\|}}{C}{-}OOH + CH_3CH{=}CH_2 \longrightarrow R\overset{\overset{\Large O}{\|}}{C}{-}OH + CH_3\underset{\diagdown\, O\, \diagup}{CH{-}CH_2}}$$

These processes are related to the previously described hydroperoxide processes. A process involving the coproduction of propylene oxide and methyl methacrylate has been suggested. It starts with isobutyraldehyde, which is converted to perisobutyric acid. This in turn oxidizes propylene to propylene oxide and gives isobutyric acid, which can be esterified and dehydrogenated to methyl methacrylate.

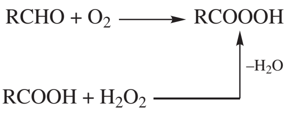


$$\mathrm{H_3C{-}\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}CHO \xrightarrow{O_2} H_3C{-}\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}COOOH \xrightarrow{CH_3CH=CH_2} \underset{\diagdown\, O\, \diagup}{H_2C{-}CH}{-}CH_3 + CH_3\underset{\underset{CH_3}{|}}{C}HCOOH}$$

$$\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}HCOOH \xrightarrow[CH_3OH]{-H_2} CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}COOCH_3 + H_2O}$$

Isobutyric acid is an intermediate in one of the propylene-based routes to methyl methacrylate (Section 4.10.1). Isobutyraldehyde is an undesired byproduct in the cobalt-catalyzed hydroformylation of propylenes (Section 4.12). Lack of demand, except from Eastman and BASF, who convert it to neopentyl glycol (Section 4.12.1) motivated the development of the elegant rhodium-based catalyst system (Section 4.12) that provides high yields of *n*-butyraldehyde.

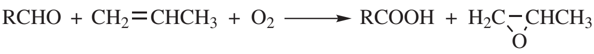
In addition to perisobutyric acid, the peracids of formic, acetic, and propionic acids can be used to make propylene oxide. The peracid can be prepared either by oxidizing the corresponding aldehyde or by reacting the corresponding carboxylic acid with hydrogen peroxide.



$$\mathrm{RCHO + O_2 \longrightarrow RCOOOH}$$

$$\mathrm{RCOOH + H_2O_2 \xrightarrow{-H_2O} RCOOOH}$$

In a single step process, the percarboxylic acid is formed *in situ* by the oxidation of the aldehyde in the presence of propylene. The percarboxylic acid that forms epoxidizes the propylene immediately. In a two-step process, the percarboxylic acid is isolated and used to epoxidize propylene in a second step.

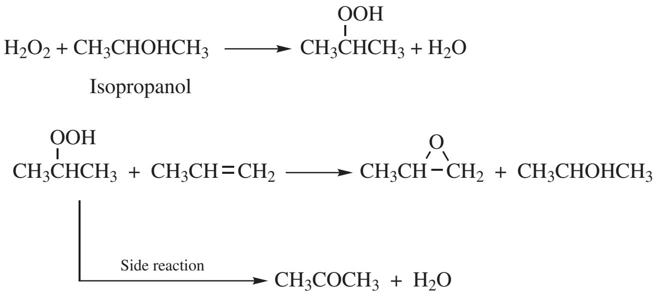


$$\mathrm{RCHO + CH_2{=}CHCH_3 + O_2 \longrightarrow RCOOH + \underset{\diagdown\, O\, \diagup}{H_2C{-}CH}CH_3}$$

Although results are excellent, the processes are not economical because of the high cost of hydrogen peroxide. If the peracid is prepared from an aldehyde, economics are better but not on a par with the previously described hydroperoxide processes.

Hydrogen peroxide can also be used directly to epoxidize propylene to propylene oxide. This reaction has great appeal because of its simplicity; the only coproduct is water. Titanium–silicalite has been found to be an extraordinarily selective catalyst for this reaction, affording selectivities greater than 95%. The major byproduct is propylene glycol, formed from the reaction of propylene oxide with byproduct water. The problem with this approach, as with the previous one, is that hydrogen peroxide is too expensive. In spite of this, both Dow and BASF are said to be working on the project, and BASF has been operating a pilot plant since 2000. Solvay is reportedly developing technology that will allow so-called "mega-scale" hydrogen peroxide plants that will reduce the cost of hydrogen peroxide manufacture and improve the economics of hydrogen peroxide-based propylene oxide routes.

As another possible way of reducing costs, companies have explored so-called *in situ* hydrogen peroxide processes. In this approach, the epoxidation reaction is coupled with a process that generates hydrogen peroxide. Reaction of oxygen with certain alcohols, such as isopropanol or methylbenzyl alcohol, gives hydrogen peroxide and the corresponding ketone, for example, acetone from isopropanol or acetophenone from methylbenzyl alcohol. The oxidate produced contains about 5–7% hydrogen peroxide, and it is combined with propylene and fed to the epoxidation reactors. The acetone or acetophenone is separated and hydrogenated back to the starting alcohols for recycle.



$$H_2O_2 + \underset{\text{Isopropanol}}{CH_3CHOHCH_3} \longrightarrow CH_3\overset{OOH}{C}HCH_3 + H_2O$$

$$CH_3\overset{OOH}{C}HCH_3 + CH_3CH{=}CH_2 \longrightarrow CH_3\overset{O}{CH{-}CH_2} + CH_3CHOHCH_3$$

$$CH_3\overset{OOH}{C}HCH_3 \xrightarrow{\text{Side reaction}} CH_3COCH_3 + H_2O$$

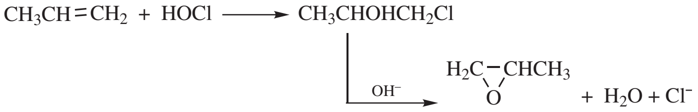
Degussa, BASF, and the Dailin Institute of Chemical Physics separately made announcements in 2001 about progress in hydrogen peroxide-based process technology. While details of their advancements have not been disclosed, it is likely that the processes use *in situ* hydrogen peroxide. Solvay and Degussa are, after all, Western Europe's two largest hydrogen peroxide producers.

4.11.3.3 Electrochemical Processes The electrochemical processes suffer from high energy cost. Typically, brine is electrolyzed in the presence of propylene. The overall reaction is simple, although many reactions are involved. At the anode, chloride ions are discharged to give chlorine, which reacts with water to form hypochlorous acid.

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

$$Cl_2 + H_2O \longrightarrow H^+ + Cl^- + HOCl$$

The reaction of the hypochlorous acid with propylene provides a chlorohydrin that is dehydrochlorinated by hydroxyl ions from the caustic produced at the cathode.



Protons are reduced to hydrogen at the cathode. Their removal increases the basicity of the solution and provides the "caustic" solution to dehydrochlorinate the chlorohydrin:

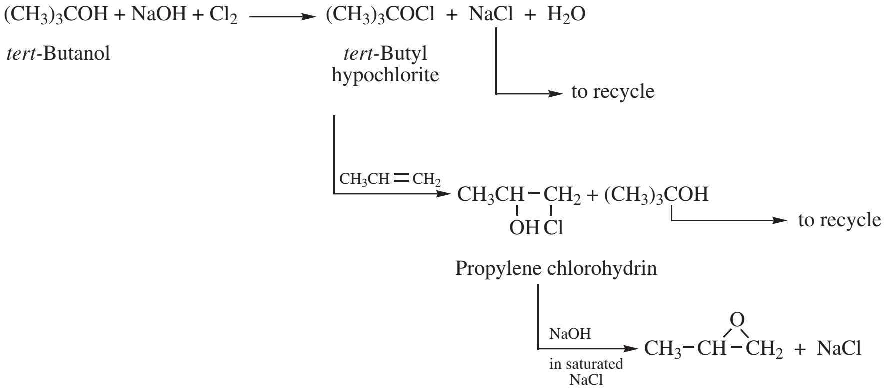
$$2H^+ + 2e^- \longrightarrow H_2$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

The sodium ion is a "spectator" throughout.

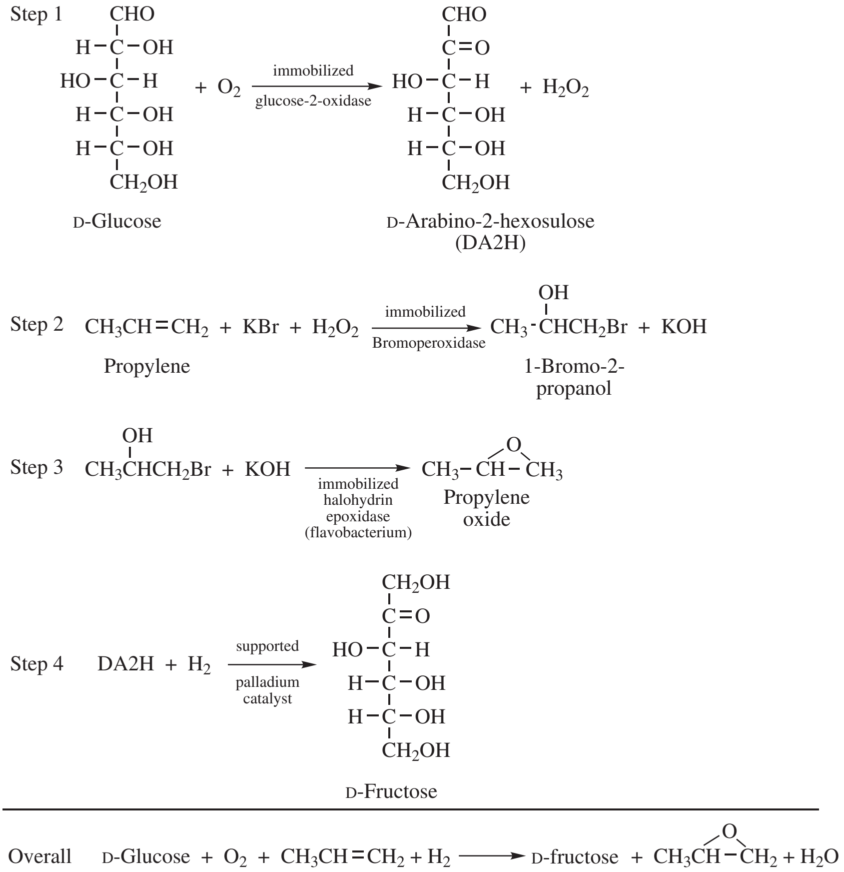
Dichloropropane and propylene glycol are byproducts, the first from the direct addition of chlorine to propylene and the second by the hydrolysis of propylene oxide. Propylene chlorohydrin and chloroisopropyl ether are also possible byproducts.

A problem with the original chlorohydrin process is the disposal of the calcium or sodium chloride that results from the dehydrochlorination. As indicated, in a totally integrated process, the sodium chloride can be used as brine for the generation of chlorine. A proposed Lummus process uses a concentrated brine in both the epoxidation and neutralization steps, which can readily be recycled to the electrolysis unit. In the first step chlorine, sodium hydroxide from the caustic cell liquor, and *tert*-butanol are combined to give *tert*-butyl hypochlorite and sodium chloride. The brine, which does not dissolve the *tert*-butyl hypochlorite, can be recycled to the electrolysis unit, and the hypochlorite can be used to convert the propylene to the chlorohydrin and regenerate *tert*-butanol.



The two products are removed and separated by distillation, and the water is recycled to the hydrochlorination step, where it is saturated with the NaCl produced. The dehydrochlorination is also performed in almost saturated brine, which can be recycled to electrolysis. In this way, there is never need to dispose of salt.

4.11.3.4 Biotechnological Approaches Biotechnological processes have been proposed for propylene oxide production, although they are not practical at the present state of development, and there is no chance of their competing with straightforward chemical processing. A four-step process devised by Cetus starts with the production of hydrogen peroxide in the enzyme-catalyzed conversion of D-glucose to D-arabino-2-hexosulose. The latter can be hydrogenated to D-fructose, which may become one of the products of the reaction. The hydrogen peroxide converts propylene to the bromohydrin with potassium bromide in an enzyme-catalyzed reaction. The bromohydrin can then be dehydrohalogenated either chemically or enzymatically to propylene oxide.



The key to this imaginative process was the discovery of a peroxidase that forms the bromohydrin.

An Exxon process is based on a microorganism, which consumes methane and can oxidize propylene to propylene oxide. Methylotrophic organisms, however, can only function with a coenzyme that undergoes a redox cycle with a readily oxidizable material such as methanol, which oxidizes to formaldehyde. The fragile enzyme and coenzyme are resident in a monocellular microorganism, and the cell rather than the enzymes can be used. Even so, the scale-up of such a process presents formidable problems.

These ingenious but currently uncommercialized processes are described to emphasize that choice of R&D projects is one of the serious problems facing chemical companies today. It has always been a problem, but viability of projects was more obvious in the 1950s and 1960s than in the 1990s and 2000s. The search for the “no-go” factor, and the attempt to resolve it before expensive development is undertaken, is the key to any project evaluation. As modern biotechnology becomes more and more sophisticated, these currently “impractical” processes may well presage the future.

4.12 *n*-BUTYRALDEHYDE AND ISOBUTYRALDEHYDE

n-Butyraldehyde was originally prepared by the aldol condensation of two molecules of acetaldehyde to yield acetaldol and then crotonaldehyde. Hydrogenation of crotonaldehyde provided a mixture of *n*-butyraldehyde and *n*-butanol in a ratio of 70:30 (Section 3.11.3).

The route has been replaced by reaction of propylene (Fig. 4.2*i*) with carbon monoxide and hydrogen (Section 10.4) at 130–175°C and 250 bar over a cobalt carbonyl catalyst to give a mixture of between 3 and 4 mol of *n*-butyraldehyde to 1 mol of isobutyraldehyde. This reaction is called the oxo process or hydroformylation and was invented during World War II by Otto Roelen at Ruhrchemie. The mechanism is shown in Figure 4.11. The cobalt interacts with the olefin to give a π-bonded complex, after which there is a rearrangement in which the propylene inserts itself into the Co—H bond. The manner of the insertion determines whether the final compound will be linear or branched. The two possibilities are shown in the figure.

With a cobalt catalyst, an appreciable amount of branched product forms. If this rearrangement could be influenced so that a branched structure could not form, the yield of linear product would be increased. Collaboration between Union Carbide, Davy McKee, and Johnson Matthey resulted in the adaptation of the so-called Wilkinson catalyst, triphenylphosphine and rhodium chloride, to a homogeneous hydroformylation, in which the ratio of linear-to-branched compounds is 10:1. The mechanism of this linear hydroformylation is shown in Figure 4.12. The reaction takes place at mild temperatures of 100°C and pressures of 10–20 bar. The mild conditions are made possible by the phosphine ligands (represented as L), which increase the activity of the catalyst. It can be seen that the decomposition of the complex (**XIX**) primarily to the linear (anti-Markovnikov) product results because of the steric requirements of the bulky ligands.

Linear hydroformylation is also an important part of the SHOP (Section 3.3.4) process. However, because of the need in this process to hydroformylate internal

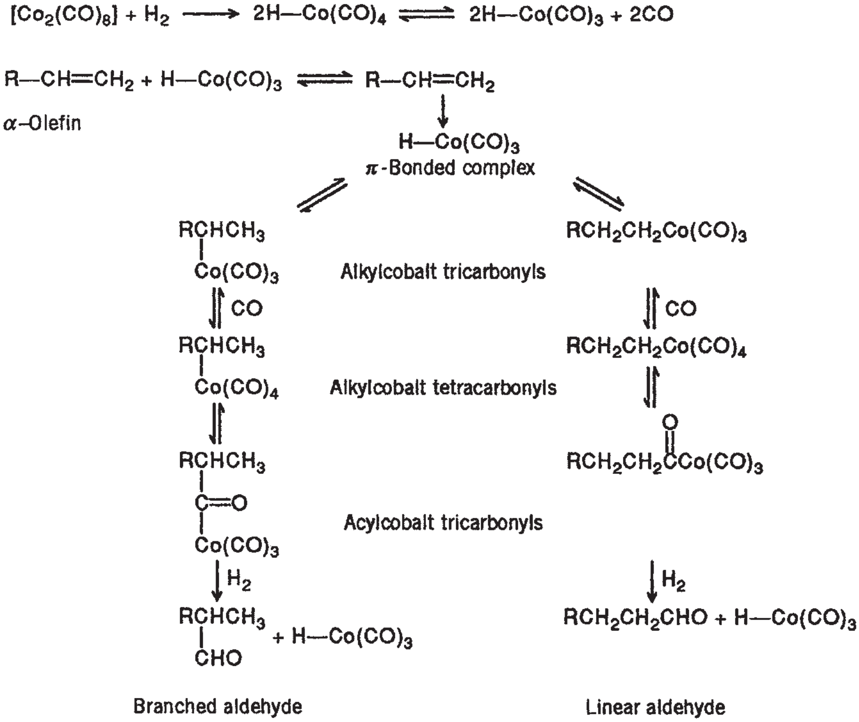


FIGURE 4.11 Hydroformylation–olefin insertion.

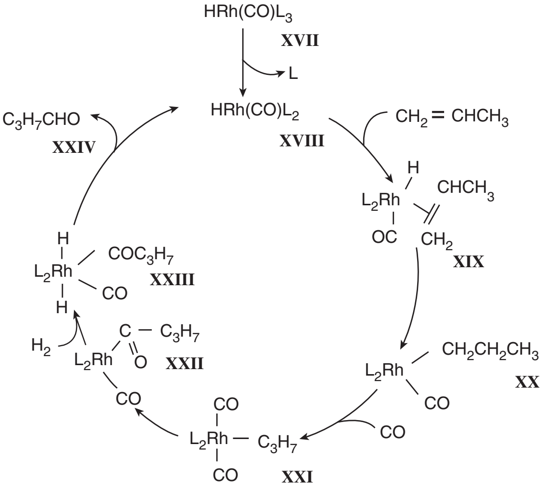
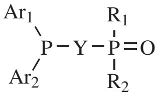


FIGURE 4.12 Linear hydroformylation.

olefins with the concomitant shifting of a double bond to the terminal position, a cobalt rather than a rhodium catalyst is used with the ligands that promote linearity. This catalyst is somewhat less effective, giving a ratio of normal to iso products of 5.7–6.0 to 1 and requiring a temperature of 150–190°C at 40 bar.

Newer ligands described by Union Carbide are diphosphine monoxides of the general structure



where the two aryl groups may be the same or different, and R_1 and R_2 may be aromatic or aliphatic. Y is $(CH_2)_n$. In one example, $Ar_1 = Ar_2 = R_1 = R_2$ and $Y = CH_2$. The ligands give a linear/branched ratio as high as 33.8/1.

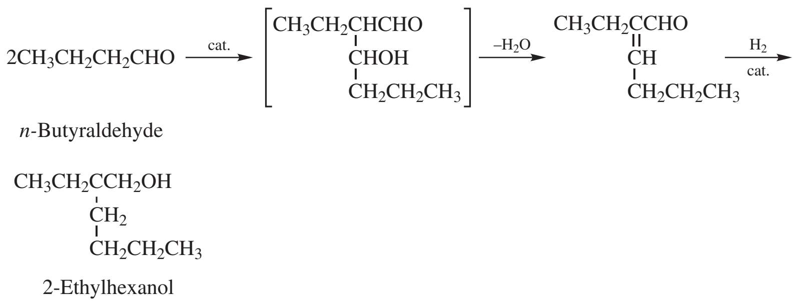
Even newer ligands developed by Carbide and Kvaerner Process Technology (formerly Davy McKee) are bisorganophosphites (see note at end of this chapter). These ligands have a marked stabilizing effect on the catalyst and significantly increase the rate of reaction and linear/branched (*n*/*i*) selectivity. The *n*/*i* selectivities of over 30/1 are achieved using bisphosphite modified rhodium catalysts. They are so active that over 98% propylene conversion per pass is enjoyed, allowing a so-called "single-pass" process to be used, which simplifies operation and reduces capital cost. In addition, these catalyst systems make possible the hydroformylation under mild conditions of less reactive olefins such as 2-butene, isobutene, and vinyl acetate.

Rhodium is expensive, and efficient catalyst recovery is therefore key to the success of the process. Two approaches are noteworthy. In the first, described in a Union Carbide patent, reaction is carried out in a high boiling solvent comprising butyraldehyde aldol condensate, primarily trimers, and tetramers. After reaction, the products can be distilled off, leaving the nonvolatile rhodium complex in the solvent. The second approach, developed primarily by Rhone Poulenc and Ruhrchemie, involves sulfonated or carboxylated arylphosphine catalysts. After reaction, the organic phase in which the reaction was carried out is treated with alkali. The catalyst is converted to an alkali sulfonate or carboxylate, which dissolves in the aqueous layer. Phase separation makes possible catalyst recovery. Another way to cope with the expense of rhodium is to make the catalyst so active that only an insignificant amount is used per pound of product. Today's oxo technology has made important strides in this direction.

4.12.1 Uses for Butyraldehyde and Isobutyraldehyde

The reason a high linear/branched ratio is desired is because the major use of the aldehydes is for hydrogenation to the corresponding alcohols, which are used as solvents either as such or more often in the form of their acetates. *n*-Butanol, because of its linearity, solvates better than the branched isobutanol and is accordingly preferred, particularly for solvents for surface coatings. It is prepared by hydrogenation of *n*-butyraldehyde in the gas phase with a nickel or copper catalyst or in the liquid phase with a nickel catalyst. The gas phase requires mild pressures and a temperature of 115–120°C with a nickel catalyst or a temperature of 160°C with a copper catalyst. With a nickel catalyst in the liquid phase, a temperature of 115°C and a pressure of 80 bar are required.

n-Butyraldehyde will undergo the aldol condensation, in the presence of either sodium hydroxide or a basic ion exchange resin, to provide an intermediate that loses water spontaneously to give an unsaturated aldehyde in quantitative yield. Hydrogenation gives the important plasticizer alcohol, 2-ethylhexanol.

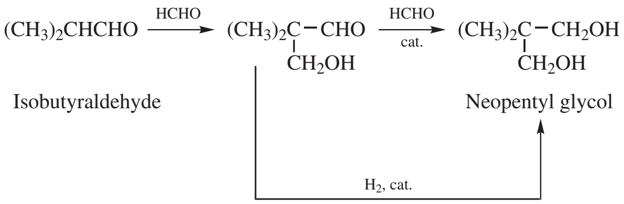


$$2CH_3CH_2CH_2CHO \xrightarrow{cat.} \left[\begin{array}{c} CH_3CH_2\underset{|}{C}HCHO \\ CHOH \\ | \\ CH_2CH_2CH_3 \end{array}\right] \xrightarrow{-H_2O} \begin{array}{c} CH_3CH_2\underset{\|}{C}CHO \\ CH \\ | \\ CH_2CH_2CH_3 \end{array} \xrightarrow[cat.]{H_2} \begin{array}{c} CH_3CH_2\underset{|}{C}CH_2OH \\ CH_2 \\ | \\ CH_2CH_2CH_3 \end{array}$$

n-Butyraldehyde

2-Ethylhexanol

Because isobutyraldehyde was the surplus coproduct in the classical oxo process, uses were devised for it other than hydrogenation to isobutanol. Conversion to neopentyl glycol (2,2-dimethyl-1,3-propanediol) is the most important. In the most commonly used neopentyl glycol process, isobutyraldehyde reacts with 1 mol of formaldehyde to yield hydroxypivaldehyde which, after reduction with hydrogen, gives neopentyl glycol. An alternative, less commonly practiced process, is to react isobutyraldehyde with 2 mol of formaldehyde. This approach combines condensation and reduction in one step to yield neopentyl glycol and coproduct formic acid. Neopentyl glycol is used largely in polyester synthesis to enhance alkali resistance of the cured product as, for example, for polyesters for powder coating. Its preparation is analogous to that of pentaerythritol (Section 3.11.3).



$$(CH_3)_2CHCHO \xrightarrow{HCHO} (CH_3)_2\underset{\underset{CH_2OH}{|}}{C}-CHO \xrightarrow[cat.]{HCHO} (CH_3)_2\underset{\underset{CH_2OH}{|}}{C}-CH_2OH$$

Isobutyraldehyde

Neopentyl glycol

4.12.2 Other Oxo Products

Oxo alcohols are used for solvents, surfactants, and PVC plasticizers. The solvent alcohols, *n*-propanol (Section 3.11.1), butanol, and isobutanol (Section 4.12) have already been discussed. A good example of oxo alcohols for surfactants are those produced by the SHOP process (Section 3.3.4) in which hydroformylation is a major step. Plasticizers are usually esters of phthalic anhydride or less often adipic acid with aliphatic alcohols. Added to PVC during compounding, they lend softness and flexibility to the polymer. 2-Ethylhexanol is still the most important plasticizer alcohol in the United States, but its use is not growing because of possible toxicity problems. Straight-chain alcohols (Sections 2.2.4, 4.6) solvate better so that they have better softening power and compatibility. 2-Ethylhexanol holds its position because of its lower price. Higher molecular weight alcohols are important because their phthalates have better high temperature properties and lower volatility. This helps the “fogged windshield” problem and decreases the rate of embrittlement of plasticized articles because of volatile loss of plasticizer. Perhaps most important, the plasticizer business is static because PVC in automobile seating is being replaced by nylon.

The C_6–C_{12} olefins for hydroformylation to the plasticizer alcohols as well as C_{10}–C_{20} olefins for alcohols for nonbiodegradable surfactants come largely from propylene and butene oligomerization (Section 4.6). The most important plasticizer-range alcohols are isodecanol (from propylene trimer) and isononanol (from diisobutylene). Isooctanol (from propylene and butylene) and tridecanol from butylene trimer or propylene tetramer) are less widely used. In the United Kingdom, “Alfanol,” a mixture of C_7–C_9 alcohols, is important for plasticizers. It is obtained by application of the oxo process to an olefin mixture from the cracking of a petroleum fraction known as slack wax.

A smaller volume use for hydroformylation involves the conversion of 1-octene to pelargonaldehyde. Oxidation of the aldehyde yields pelargonic acid. Reaction with pentaerythritol gives the tetra ester (Section 3.11.3) useful as a component of synthetic lubricants. The oxo catalyst comprises rhodium chloride with triphenylphosphine with or without ferrocene ligand modifiers. The reaction takes place at 5 bar and 100°C. Conversion of 95% of the α-olefin is obtained at a selectivity to the normal aldehyde of 87%. The oxidation is catalyzed by cobalt pelargonate at about 8 bar and 100°C. At 75% conversion of the aldehyde, 96% selectivity to the acid is obtained.

$$\underset{\text{1-Octene}}{CH_3(CH_2)_5CH{=}CH_2} \xrightarrow{CO/H_2} \underset{\text{Pelargonic aldehyde}}{CH_3(CH_2)_7CHO} \xrightarrow{O_2} \underset{\text{Pelargonic acid}}{CH_3(CH_2)_7COOH}$$

4.13 MAJOR CHEMICALS FROM PROPYLENE—A PERSPECTIVE

Sections 4.5–4.12 described the major chemicals (US production > 1 million lb/year) from propylene and their derivatives. These major chemicals and their production volumes in 1977, 1993, and 2001, their growth rates and the amount of propylene used in their production are indicated in Table 4.3. The end-use pattern for Western Europe is also given, and it is similar to the US figures. As with ethylene, we have included only one polymer, polypropylene, since it is the only one made directly from propylene and is the largest and fastest growing consumer of this product.

TABLE 4.3 Production of Chemicals from Propylene (1977–2001)

	1977	1993	2001	Average Annual Increase 1993–2001	Propylene Consumption[a]	United States End-Use Pattern	Western European End-Use Pattern
Polymer or Chemical		(Million 1b)		(%)	(Million lb)	(%)	(%)
Propylene	12,560	22,400	31,700				(29,785 million lb)
Polypropylene	2,747	8,614	15,740	7.8	16,211	51.1	53.3
Cumene	2,640	4,490	8,200	7.8	3,280	10.3	7
Phenol[c]	2,380	3,720[b]	4,850	3.4			
Propylene oxide	1,900	3,300	4,230	3.2	3,342	10.5	10.4
Acrylonitrile	1,640	2,510	3,350	3.7	3,685	11.6	8.6
Acetone	2,140	2,460	3,210	3.4			
Oxo alcohols	1,240	2,150					8.2
including n-Butanol	809	1,328	1,830	5.6	1,410	4.5	
2-Ethylhexanol	389	688	880[d]	4.2			
Acrylate esters	n.a.[e]	1,322[f]	1,556	2.1			
Bisphenol A	555	1,286	1,970	5.5			
Isopropanol	1,870	1,236	1,450	2.0	1,233	3.9	2.6
Acrylic acid	n.a.[e]	1,199[b]	1,930	6.1	1,238	3.9	
Methyl methacrylate	592	1,088	1,510	5.4			
Propylene glycol	473	885	1,140	3.2			
Other					1,294	4.1	9.9

Source: Chem. Eng. News; *Guide to the Business of Chemistry.*

[a] This figure is the propylene required to give the 2001 production. Yields are estimated by Nexant/Chem. Systems.

[b] 1992.

[c] Phenol is really a benzene derivative. Although coproduced with acetone, it contains none of the propylene moiety.

[d] 1999.

[e] Not available = n.a.

[f] 1992 figure. Included 318 million lb *n*-butyl acrylate, 337 million lb ethyl acrylate and 172 million lb 2-ethylhexyl acrylate.

The second largest volume chemical from propylene is cumene, the progenitor of phenol (Section 7.1) and acetone. Acetone is used as a solvent, but its important chemical use is as a starting material for methyl methacrylate, which in turn is polymerized to poly(methyl methacrylate) and related copolymers. Competitive routes based on C_2 and C_4 olefins for methyl methacrylate exist and the figures here represent total methyl methacrylate production. Acetone and phenol are the starting materials for bisphenol A, which in turn is combined with another propylene-based chemical, epichlorohydrin, to make both epoxy and, more important, polycarbonate resins.

Propylene oxide enjoys the third largest use. Its hydroxyl-terminated oligomers are the major coreactants with isocyanates for polyurethane polymers. The fourth largest volume chemical from propylene in 2001 was acrylonitrile, whose major use is in polymers primarily for fibers. It is also used for elastomers and for ABS resins, familiar to everyone who uses a telephone. Oxo alcohols, some of which are not made from propylene, are used primarily as solvents and (combined with phthalic anhydride, Section 9.11) for plasticizers.

A marked difference can be seen in the growth rates of propylene-based chemicals compared to those of ethylene (Table 3.2). Propylene-based chemicals are less mature and, with the exception of isopropanol, have demonstrated better growth in the past decade. It is this faster growth that created a shortage of propylene in Europe, requiring importation of substantial amounts in the early 2000s.

The demand these chemicals make on propylene supplies is shown in the final column of Table 4.3. As might be expected, polypropylene is the biggest consumer of propylene; propylene oxide is next and then acrylonitrile. The chemicals where a figure is given in the final column make up only about 74% of propylene consumption and this reflects a substantial number of minor uses such as epichlorohydrin, ethylene–propylene elastomers, acrolein, allyl chloride and isopropyl acetate. Some of the smaller volume chemicals from propylene are described in Section 4.14.

4.14 LESSER VOLUME CHEMICALS FROM PROPYLENE

4.14.1 Allyl Chloride and Epichlorohydrin

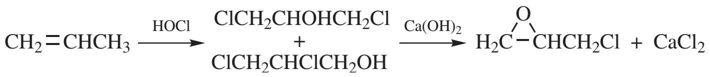
Allyl chloride is formed by the selective chlorination of the methyl group of propylene at 500°C. The high-temperature prevents addition to the double bond. Propylene and chlorine conversions are about 24 and 100%, respectively, at an allyl chloride selectivity of 86 mol %. Byproducts include dichloropropenes and minor amounts of isopropyl chloride and other chlorinated compounds.

$$CH_2{=}CHCH_3 + Cl_2 \xrightarrow{500^\circ C} CH_2{=}CHCH_2Cl + HCl$$

An as yet uncommercialized oxychlorination route to allyl chloride catalyzed by palladium and cupric chlorides (Section 3.4) has been devised. It proceeds at a much lower temperature of 240°C:

$$CH_2{=}CHCH_3 + HCl + 0.5O_2 \xrightarrow{PdCl_2,\ CuCl_2} CH_2{=}CHCH_2Cl + H_2O$$

The epoxidation of allyl chloride to epichlorohydrin proceeds like the traditional route to propylene oxide (Section 4.11). Treatment of allyl chloride with hypochlorous acid gives 1,3-dichloro-2-hydroxypropane $ClCH_2CHOHCH_2Cl$ and 1,2-dichloro-3-hydroxypropane $ClCH_2CHClCH_2OH$ in a ratio of 9:1. These react below 60°C with a 10–15 weight % aqueous slurry of calcium hydroxide to give almost 100% conversion to epichlorohydrin.



$$CH_2{=}CHCH_3 \xrightarrow{HOCl} \begin{matrix} ClCH_2CHOHCH_2Cl \\ + \\ ClCH_2CHClCH_2OH \end{matrix} \xrightarrow{Ca(OH)_2} H_2\overset{O}{C{-}C}HCH_2Cl + CaCl_2$$

In the overall process for epichlorohydrin from propylene, 75% of the chlorine is wasted, that is, it does not appear in the final product.

Because epichlorohydrin is made in far smaller quantities than ethylene and propylene oxides, the search for a replacement for the chlorohydrin process was less strongly motivated. Nonetheless, in the mid-1980s a process was instituted by Showa Denko in Japan. This process wastes only 50% of the chlorine. Propylene is oxidized to allyl acetate by oxygen in acetic acid with a palladium catalyst as shown in Figure 4.13. Hydrolysis yields allyl alcohol and acetic acid for recycle. There are other routes to allyl alcohol. In addition to direct oxidation, allyl chloride can be hydrolyzed. Acrolein, also obtained by the oxidation of propylene (Section 4.7), can be converted to allyl alcohol by the Meerwein–Pondorff reaction (isopropanol plus aluminum isopropoxide) as shown in Figure 4.14. There is also a curious isomerization of propylene oxide

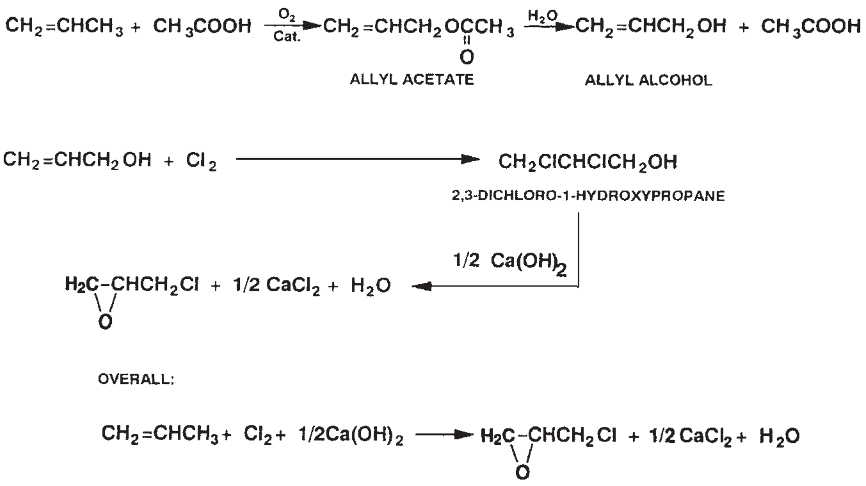


FIGURE 4.13 Showa Denko epichlorohydrin process.

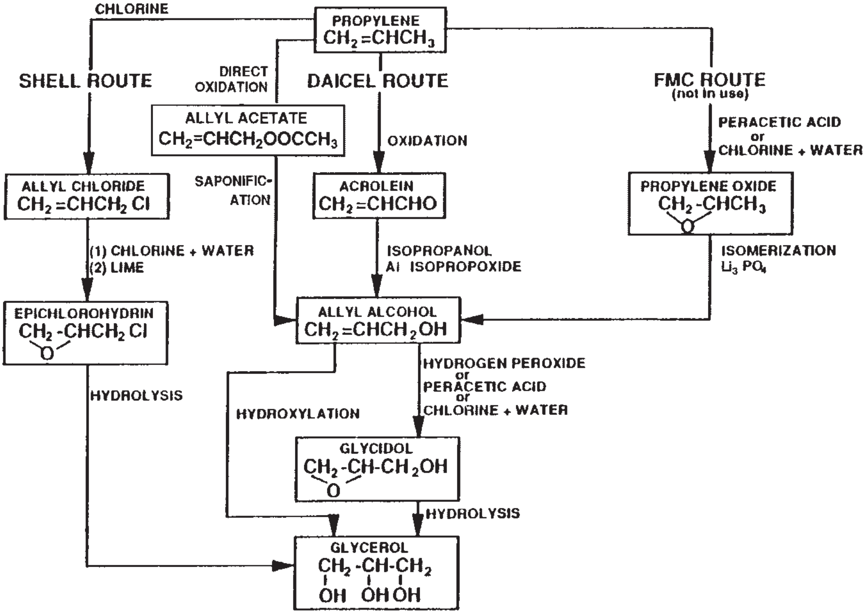
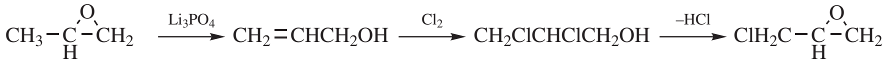


FIGURE 4.14 Synthetic routes to glycerol.

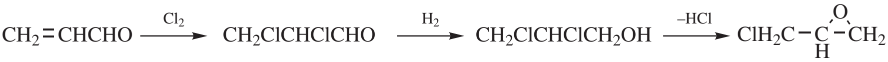
over lithium phosphate that gives allyl alcohol. The allyl alcohol is treated with chlorine and the resulting 2,3-dichloro-1-hydroxypropane is dehydrohalogenated to epichlorohydrin.



$$CH_3-\underset{H}{\overset{O}{C}}-CH_2 \xrightarrow{Li_3PO_4} CH_2{=}CHCH_2OH \xrightarrow{Cl_2} CH_2ClCHClCH_2OH \xrightarrow{-HCl} ClH_2C-\underset{H}{\overset{O}{C}}-CH_2$$

Propylene oxide — Allyl alcohol — 2,3-Dichloro-1-hydroxypropane — Epichlorohydrin

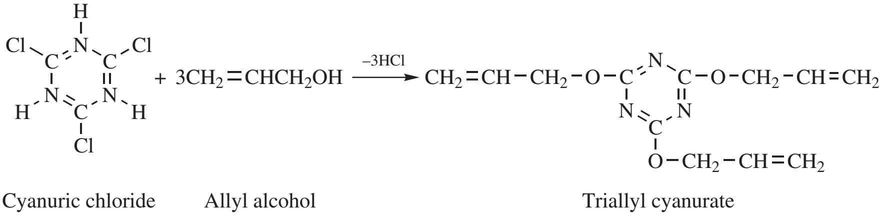
Dow was granted a patent that uses acrolein as the starting material for making epichlorohydrin. Addition of chlorine to acrolein gives 2,3-dichloropropanal. The dichloropropanal is hydrogenated to 2,3-dichloropropanol, which in turn undergoes dehydrohalogenation with calcium hydroxide to finally give epichlorohydrin.



$$CH_2{=}CHCHO \xrightarrow{Cl_2} CH_2ClCHClCHO \xrightarrow{H_2} CH_2ClCHClCH_2OH \xrightarrow{-HCl} ClH_2C-\underset{H}{\overset{O}{C}}-CH_2$$

Acrolein — 2,3-Dichloropropanal — 2,3-Dichloropropanol — Epichlorohydrin

Epichlorohydrin's major use is its reaction with bisphenol A (Section 7.1.2) to yield epoxy resins. It also plays a role in glycerol synthesis (Section 4.14.2). The major use of allyl alcohol is also in glycerol preparation. Allyl alcohol also reacts with phthalic anhydride to yield diallyl phthalate, a monomer for a thermoset polymer with good electrical properties, and with cyanuric chloride, to give triallyl cyanurate a polyester for thermoset resins with high heat resistance.



Allyl chloride is converted by ammonia to mono-, di-, and triallylamines.

4.14.2 Glycerol

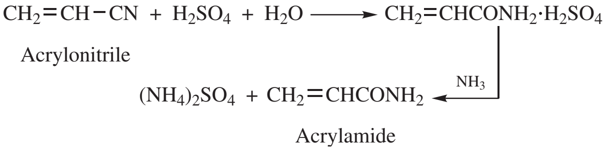
Natural fats and oils are triglycerides (Chapter 13) and give glycerol on hydrolysis. This source accounts for about 75% of the world's glycerol. The remainder comes from chemical synthesis, and the synthetic routes are summarized in Figure 4.14. The most important process (Fig. 4.14, Shell route) involves simply the hydrolysis of epichlorohydrin with 10% aqueous caustic soda at 150°C. Complete conversion is obtained. The reaction goes stepwise, the chlorine atom hydrolyzing first.

A route via acrolein (Fig. 4.14, Daicel route) involves a Meerwein–Pondorff reduction of acrolein to allyl alcohol (see above), which is epoxidized with hydrogen peroxide, hypochlorous acid, or peracetic acid to glycidol, whose hydrolysis yields glycerol. Alternatively, the allyl alcohol may be hydroxylated to glycerol directly. In the early 1990s, Daicel modified its process by oxidizing propylene directly to allyl acetate (Section 4.14.1), which on saponification yields allyl alcohol, as in the Showa Denko process (Section 4.14.1). This route is efficient but requires high capital investment. In the FMC route, shown in Figure 4.14, but no longer in use, propylene oxide is isomerized with a lithium phosphate catalyst to allyl alcohol. This can be converted to glycerol by the process already described. It is of interest that ARCO has adapted this route to allyl alcohol for a synthesis of 1,4-butanediol (Section 10.3).

Glycerol's uses are reviewed in Section 13.9. The pattern of glycerol manufacture varies around the world depending on indigenous production of fats and oils. In fat- and oil-rich countries like the United States, most glycerol comes from hydrolysis of natural fats and oils. In countries poor in agricultural produce, such as Japan, most glycerol is made synthetically. Synthetic glycerol is manufactured in the United States only by Dow. Its greater purity earns for it applications in cosmetics and personal care products.

4.14.3 Acrylamide

Hydrolysis of acrylonitrile with sulfuric acid gives acrylamide:



$$CH_2{=}CH{-}CN + H_2SO_4 + H_2O \longrightarrow CH_2{=}CHCONH_2{\cdot}H_2SO_4 \xrightarrow{NH_3} (NH_4)_2SO_4 + CH_2{=}CHCONH_2$$

Acrylonitrile

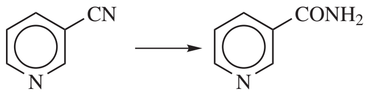
Acrylamide

As in the synthesis of caprolactam (Section 7.2.2) an undesirable low-value byproduct, ammonium sulfate, is generated, whose separation from the acrylamide is complex. This process has largely been replaced by an elegant catalytic hydrolysis using metallic copper. The reaction takes place at 100°C and gives almost 100% selectivity at 60–80% conversion.

$$CH_2{=}CHCN + H_2O \xrightarrow{\text{copper chromite}} CH_2{=}CHCONH_2$$

In the early 2000s, CDTECH, in collaboration with SASTECH (the technology arm of Sasol Industries), developed a process for acrylamide, similar to the above but using catalytic distillation to reduce the number of process steps, with savings in energy and equipment.

Nitto in Japan has developed a microbiological conversion of acrylonitrile to acrylamide. It provides the only example of the application of modern microbiology to the production of a reasonably large volume chemical other than fermentation-produced ethanol and high fructose corn syrup (Section 14.2). This conversion is brought about by an immobilized bacterial cell (e.g., species of nocardia, microbacterium, and corynebacterium) that contains the hydrolyzing enzyme. A temperature of 10°C and a pH of 7.5 provides a 15% aqueous solution of acrylamide in quantitative yield. At least six plants were using this process in the early 2000s. The process has since been extended to the synthesis of nicotinamide (niacinamide, part of the vitamin B complex) from cyanopyridine



Cyanopyridine

Nicotinamide

Most acrylamide is polymerized to a water-soluble polymer. Anionic character may be conferred by partial hydrolysis of amide linkages to carboxyl groups. Anionic functionality can also be achieved by copolymerization of acrylamide with monomers such as sodium acrylate. Conversely, monomers such as dimethylaminoethyl acrylate impart cationic character.

A potentially important use for the polymers is in enhanced oil recovery, where they increase the viscosity of the water used for the flooding that pushes oil through the rock formation so that it can be pumped. Their major use is for flocculents in industrial and municipal waste water treatment. They are included in formulations for paper and textile sizing, drilling muds for oil well drilling, and in the coagulation of slimes. With other acrylic monomers, acrylamide provides copolymers useful in the formulation of water-based protective coatings. If the amide group is converted to a methylol group with formaldehyde, a compound results that can cross-link with melamine resins (Section 10.5.1.1).

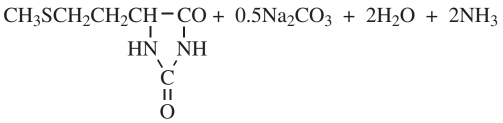
$$CH_2{=}CHCONH_2 + HCHO \longrightarrow CH_2{=}CHCONHCH_2OH$$

4.14.4 Acrolein

The preparation of acrolein as an intermediate in acrylic acid production was described in Section 4.7. Its role in glycerol synthesis was described in Section 4.14.2. The most important use for acrolein, however, is for the manufacture of DL-methionine, an essential amino acid added to poultry feeds. Methionine is the amino acid produced in third largest volume after L-glutamic acid, whose monosodium salt is a flavor enhancer in foods and L-lysine, also used in feeds. In the methionine synthesis, acrolein reacts almost quantitatively with methylmercaptan in the presence of pyridine to yield β-methylthiopropionaldehyde. The aldehyde is converted to a hydantoin with sodium cyanide and ammonium carbonate.

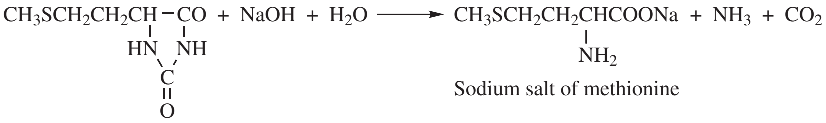
$$\underset{\text{Acrolein}}{CH_2{=}CHCHO} + \underset{\substack{\text{Methyl}\\\text{mercaptan}}}{CH_3SH} \xrightarrow{\text{pyridine}} \underset{\substack{\beta\text{-Methyl}\\\text{thiopropionaldehyde}}}{CH_3SCH_2CH_2CHO}$$

$$CH_3SCH_2CH_2CHO + NaCN + 1.5(NH_4)_2CO_3 \longrightarrow$$



$$\begin{array}{l} CH_3SCH_2CH_2CH-CO + 0.5Na_2CO_3 + 2H_2O + 2NH_3 \\ \qquad\qquad\qquad\quad\ HN\ \ NH \\ \qquad\qquad\qquad\qquad\ \ C \\ \qquad\qquad\qquad\qquad\ \ \| \\ \qquad\qquad\qquad\qquad\ \ O \end{array}$$

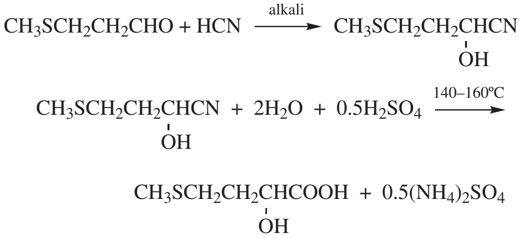
Aqueous hydrolysis of the hydantoin with sodium hydroxide and sodium carbonate at 6 bar provides the sodium salt of methionine with the release of ammonia.



$$\begin{array}{l} CH_3SCH_2CH_2CH-CO + NaOH + H_2O \longrightarrow CH_3SCH_2CH_2\underset{NH_2}{CH}COONa + NH_3 + CO_2 \\ \qquad\qquad\qquad\quad\ HN\ \ NH \\ \qquad\qquad\qquad\qquad\ \ C \\ \qquad\qquad\qquad\qquad\ \ \| \\ \qquad\qquad\qquad\qquad\ \ O \end{array}$$

Sodium salt of methionine

The sodium salt is then acidified and the methionine precipitates at its isoelectric pH of 5.7. The product of commerce is DL-methionine, the D-isomer being converted in the organism to the useful L-structure. Also effective in feeds is the DL-methionine hydroxy analogue developed by Monsanto. It is prepared by a simpler process, since an amino group does not need to be inserted into the molecule. This process too goes via β-methylthiopropionaldehyde, whose quantitative reaction with hydrocyanic acid at 40°C gives a cyanohydrin that can be hydrolyzed with sulfuric acid at 140–160°C and 3–4 bar to DL-methionine hydroxy analogue. The product is sold in aqueous solution.



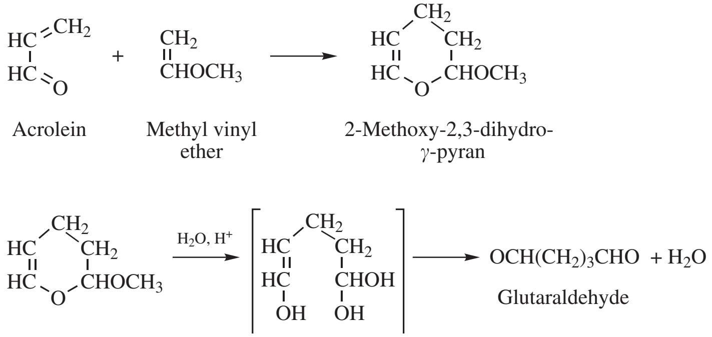
$$CH_3SCH_2CH_2CHO + HCN \xrightarrow{\text{alkali}} CH_3SCH_2CH_2\underset{\substack{|\\ OH}}{CH}CN$$

$$CH_3SCH_2CH_2\underset{\substack{|\\ OH}}{CH}CN + 2H_2O + 0.5H_2SO_4 \xrightarrow{140\text{–}160^\circ C}$$

$$CH_3SCH_2CH_2\underset{\substack{|\\ OH}}{CH}COOH + 0.5(NH_4)_2SO_4$$

Methionine
hydroxy analogue

Glutaraldehyde is manufactured in small quantities from acrolein, which undergoes a Diels–Alder reaction with methyl vinyl ether (Section 3.10.11) to yield 2-methoxy-2,3-dihydro-γ-pyran, whose hydrolysis in the presence of acid yields glutaraldehyde.



Glutaraldehyde is one of the two dialdehydes available commercially, the other being glyoxal (Section 3.11.6.7). They are useful for cross-linking hydroxyl-containing materials like leather, or cellulose for textile and paper treatment. They are also used in the immobilization of enzymes (Section 16.8).

A "new" use for acrolein is as an intermediate for making 1,3-propanediol. Addition of water to acrolein gives β-hydroxypropionaldehyde. This is the same material that Shell makes by hydroformylation of ethylene oxide (Section 3.11.6.6). Hydrogenation of β-hydroxypropionaldehyde yields the promising new polyester monomer 1,3-propanediol (Section 3.11.6.6).

4.14.5 Acrylonitrile Derivatives

Acrylonitrile production was described in Section 4.8, and its most important uses have been discussed in Section 4.8.1. It also participates in a reaction called cyanoethylation. A compound with a reactive hydrogen atom undergoes a base-catalyzed Michael addition to its double bond. A quaternary ammonium base such as trimethylbenzylammonium hydroxide is an excellent catalyst. Typical reactions are those with fatty amines and fatty alcohols. Reaction with octadecylamine yields octadecylaminopropionitrile. On hydrogenation, this yields octadecylaminopropylamine, a corrosion inhibitor valuable in the oil drilling industry.

$$\underset{\text{Octadecylamine}}{C_{18}H_{37}NH_2} + CH_2{=}CHCN \xrightarrow{\text{cat.}} \underset{\text{Octadecylaminopropionitrile}}{C_{18}H_{37}NHCH_2CH_2CN}$$

$$\xrightarrow[\text{cat.}]{H_2} \underset{\text{Octadecylaminopropylamine}}{C_{18}H_{37}NHCH_2CH_3CH_2NH_3}$$

The reaction with octadecanol provides cyanopropyl octadecyl ether whose nitrile group can also be hydrogenated to an amine. This compound is a flotation agent for the separation of silica and iron oxide in iron ore.

$$\underset{\text{Octadecanol}}{C_{18}H_{37}OH} + CH_2{=}CHCN \xrightarrow{\text{cat.}} \underset{\text{Octadecyloxypropionitrile}}{C_{18}H_{37}OCH_2CH_2CN} \xrightarrow[\text{cat.}]{H_2} \underset{\text{Octadecyloxypropylamine}}{C_{18}H_{37}OCH_2CH_2CH_2NH_2}$$

The graft polymerization of acrylonitrile onto starch provides a polymer capable of absorbing many times its own weight of water (Section 4.7), once the nitrile groups are partially hydrolyzed to amides and carboxyls.

NOTES AND REFERENCES

Section 4 The small amount of ethylene from catalytic cracking has in the past not been isolated. As the price of ethylene increases, its isolation becomes economically feasible. Thus almost 1.5 billion lb of ethylene was isolated from catalytic cracking in 2000 in the United States. Saudi Arabia initially opted only to steam crack ethane and exported the propane and butane in their associated gas. Subsequent crackers used as feedstock combinations of propane and the condensate fraction from gas. This is discussed in Chapter 2.

The propylene shortage of the late 1980s was experienced largely in Europe, where stream crackers had been shut down to decrease ethylene capacity. At the same time, however, this decreased propylene capacity. Although ethylene capacity was also shut down in the United States, there was no propylene shortage because of the large amount of it available from catalytic cracking. In Europe, where gasoline production is about one-third that of the United States, there was much less refinery propylene available. The building of new steam crackers in Europe ended the propylene shortage but added to ethylene overcapacity, and the shortage reappeared in the late 1990s and early 2000s.

For a thorough analysis of on-purpose propylene technologies and comparative economics see Nexant Chemsystems PERP report 97/98S3, Routes to Propylene (July, 2000).

Section 4.2 Catalysts and operating conditions for Deep Catalytic Cracking process is described in European Patent 0 305 720 B1 (April 13, 1994) assigned to RIPP and Sinopec.

Section 4.3 Propylene via metathesis of ethylene and butenes is described in "Maximizing Propylene from Ethylene and 2-Butene: The Meta-4 Process," J. Cosyns and C. Cameron, Chem Systems Annual European Seminar, London, February 12–13, 1997. Also, "Improving Steam Cracker Economics by Olefin Metathesis," S. Stanley and M. Shreehan, Chem Systems Annual U.S. Conference, January 28–29, 1998.

Section 4.5 Natta's application of Ziegler's catalyst proved seminal because it led to the discovery of synthetic methods for the preparation of stereoisomeric polymers. His life has been revisited in an article in *Chem. Eng. News*, February 10, 2003, p. 26. Although Ziegler was very helpful to him, Natta did not inform Ziegler of his results when he tried the catalyst on propylene, leaving Ziegler to learn about it from a paper published in the *J. Am. Chem. Soc.* in 1954. Ziegler, needless to say, did not take kindly to this.

Also of interest is Natta's desire to synthesize elastomeric propylene-based polymers. He visualized that atactic polypropylene should be elastomeric because of its lack of crystallinity. His work, of course, led to something far more valuable. It occurred to him, however, that a copolymer of ethylene and propylene should be noncrystalline and elastomeric. His co-workers prepared the first such polymer. Today EP copolymer and the modified EPDM copolymer are important articles of commerce (Section 3.2.5).

The Himont-Mitsui catalyst is described in US Patent 4,226,963 (October 9, 1980) to Montedison S.p.A.

Section 4.7 The reaction of acetic acid with formaldehyde to yield acrylic acid is claimed in US Patent 4,165,438 (August 21, 1979) to Chevron Research.

The catalysts described for the oxidation of propylene to acrylic acid are claimed in British Patent 1,346,626 (Feb 13, 1974) and in British Patent 1,361,246 (July 24, 1974) both to Nippon Shokubai. Other companies involved in the preparation of catalysts for propylene oxidation include Celanese, Union Carbide, Rohm GmbH, and BASF.

Selective vapor-phase oxidation of propylene to acrolein in a recirculating solids reactor is the subject of a patent assigned jointly to Du Pont and Elf Atochem (World Patent 99/03809, January 28, 1999). This approach is similar to that developed by Du Pont for oxidizing *n*-butane to maleic anhydride. The advantage to this is that, by avoiding oxygen in the gas phase, the riser reactor enables greater selectivity to acrolein.

The industry continues to try to use alkanes as feedstocks. For example, Sunoco and Rohm & Haas have jointly investigated the oxidation of propane directly to acrylic acid [US Patent 6,043,184, (March 28, 2000)]. However, yields are not good enough to consider commercialization.

The acrylates market is described in *Chem. Ind.*, September 2, 2002, p. 12, and in www.celanese.com/celanese_in_depth_2001_chemical_intermediates.pdf.

Section 4.8 The catalysts proposed for acrylonitrile formation are described in numerous patents typical of which are US Patent 4,473,506 (Sept 25, 1984) to Sohio and European Patent Application 0,109,259 (May 23, 1984) to Nitto Chemical Industries.

The technology for preparing acrylonitrile from acetonitrile and methane is found in West German Off. 2,616,275 (October 27, 1977). This provides an interesting example of how unwanted byproducts may be used. Either the technology can be advanced to the point where their production is eliminated (as has been done for acetonitrile) or else a use can be found for them. The latter approach is demonstrated both by this example with acetonitrile and by the conversion of unwanted isobutyraldehyde to neopentyl glycol (Section 4.12.1).

The mechanism of ammoxidation is discussed in several articles including R. K. Grasselli, *J. Chem. Educ.* **63**, 1986, 216 and R. K. Grasselli and J. D. Burrington, *Ind. Eng. Chem. Prod. Res. Dev.* **13**, 393 (1984).

The stability of the allyl radical is worth illustrating. The heat of the reaction of $CH_3CH_2CH_3 \rightarrow C_3H_7 + 0.5H_2$ is 45.8 or 42.4 kcal mol^{-1} depending on whether the *n*-propyl or isopropyl radical is formed, whereas the heat of $CH_3CH{=}CH_2 \rightarrow CH_2{\cdots}CH{\cdots}CH_2 + 0.5H_2$ is 35.7 kcal mol^{-1}, so that the allyl radical is stabilized to the extent of about 10 kcal mol^{-1}.

Conversion of propane to acrylonitrile continues to be an area of a high level of research. The economics of this conversion are nearing equivalency with propylene oxidation. Patents with promising results are US Patent 5,895,635 (April 20, 1999) to Standard Oil Company and Japanese Patent 10-028862 (February 3, 1998) to Mitsubishi Chemical Corporation.

Section 4.8.1 The ICI route to hexamethylene diamine via acrylonitrile coupling has been described in *Chem. Week*, March 7, 1990, p. 9.

Section 4.9 The conversion of cumene, via the hydroperoxide, to acetone and phenol is described in detail by H. Wittcoff, *J. Chem. Educ.* **56**, 810 (1979).

Nexant Chemsystems PERP report 01/02-2, Phenol/Acetone/Cumene (September, 2002) provides a good overview of the chemistry, process technology, economics, and markets for these materials.

Section 4.10.1 Nexant Chemsystems PERP report 99/00-2, Methyl Methacrylate (September 2001) provides a thorough assessment of the myriad approaches for making methyl methacrylate. A summary of the report is given by M. Morgan, *ECN*, 11–17 February 2002, pp. 20–23.

The Shell process for methyl methacrylate is described in European Patent Spec. 0,186,228 (August 23, 1989) and in European Patent Application 0,279,477 A1 (August 24 1988).

The Mitsubishi Gas Chemical Process for methyl methacrylate production is described in US Patent 4,613,684 (September 23, 1986).

Catalysts for isobutene oxidation to methyl methacrylate are described in numerous patents. Typical is German Offen 2,065,692 (January 2, 1975) to Japanese Geon and US Patent 3,875,220 (April 1, 1975) to Sohio.

The BASF route to methyl methacrylate from ethylene has been described in *Chem. Week*, January 26, 1989, p. 64. Various steps in the process provide the subject matter for US Patent 4, 118, 588 (October 3, 1978) to BASF, German Offen. 3,213,681 A1 (October 27, 1983), British Patent 1,573,272 (August 20, 1986) to BASF, and US Patent 4, 118, 588 (October 3, 1978) to BASF.

The Asahi process for methyl methacrylate via ammoxidation is described in *Chem. Econ. Eng. Rev.* **15**, 42 (1983).

Ashai's Direct Meta process for making methyl methacrylate from isobutene is described in US Patent 6,042,472 (March 21, 2000) to Asahi Kasei Kogyo Kabushiki Kaishsa.

Catalyst formulations for Mitsubishi Gas Chemical's HCN recycle process are described in US Patent 5,739,379 (April 14, 1998) to Mitsubishi Gas Chemical Company Inc.

The catalyst and reaction conditions for the ICI/Ineos methyl propionate/ condensation reaction is described in WO 99/52628 (October 21, 1999) to ICI, plc.

Section 4.11 The Sumitomo PO only technology based on cumene hydroperoxide is described in WO 030,270,87A1(April 3, 2003) to Sumitomo Chemical Company Limited. New routes to propylene oxide, described by J. Plotkin at a consultancy meeting, are summarized by S. Robinson, *ECN*, March 5–11, 2001, pp. 19–20.

Section 4.11.2 The preparation of propylene glycol via the hydroformylation of vinyl acetate is described in US Patent 4,723,036 (February 2, 1988) to Kuraray.

The Russian work on the direct oxidation of propylene to propylene oxide is found in US Patent 3,957,690 (May 18, 1986) issued to Bobulev *et al.*

The Union Carbide and Phillips work on the direct oxidation of propylene to propylene oxide is described in Canadian patents 968,364 (May 24, 1975) and 986,127 (March 23, 1976) to Union Carbide and in US Patent 4,380,659 (April 19, 1983) to Phillips Petroleum.

Typical of the peracid processes is one devised by Interox Chemicals using perpropionic acid. It is described in many patents including British Patent 1,591,497 (June 24, 1981) and US Patent 4,177,196 (December 4, 1979).

Typical of the processes for epoxidation of propylene with hydroperoxides is the process described in German Offen. 2,803,757 (August 3, 1978) to Pechiney Ugine Kuhlmann.

The Cetus process is described in an article in *Chem. Eng. News*, March 17, 1980, p. 15). The Exxon work with the methylotrophic organism is the subject of several patent applications including UK Patent appl. 2,081,306 (July 3, 1981).

The acetoxylation of propylene as a means for preparing propylene glycol and propylene oxide is described in several patents including German Patent 2,120,005 (August 31, 1978) to Scientific Design; US Patent 4,045,477 (August 30, 1977) to

Chem Systems; US Patent REISSUE 29597 (March 28, 1987) and 4,012,424 (March 15, 1977) to Chem Systems; US Patent 4,399,295 (August 16, 1983) to Chem Systems; US Patent 4,158,008 (June 12, 1979) to BASF.

Typical of the electrochemical processes for propylene oxide production is one described by Shell, *Chem. Eng. News*, September 28, 1987, p. 29.

Section 4.11.3.1 Hydro-oxidation of propylene to propylene oxide using a mixture of oxygen and hydrogen is described in US Patent 6,524,991 (February 25, 2003) to Dow Global Technologies Inc.

Section 4.11.3.2 The use of hydrogen peroxide as an oxidant to make propylene oxide is described in WO 03,011,845A1 (February 1, 2003) to BASF AG.

Section 4.12 The Union Carbide development of a high-boiling solvent to prevent loss of rhodium catalyst in hydroformylation is the basis for US Patent 4,148,830 (April 10, 1979).

Carbide's diorganophosphite liquids are described in *Chem. Eng. News* October 10, 1988, p. 270. The hydrogenation is carried out in two stages with a nickel catalyst. In the first stage, the vapor phase, conversion is ~7% at 10 bar and 140°C. The second stage is in the liquid phase at 100 bar and 60°C. The product is purified by distillation. Copper catalysts have also been used.

The technology associated with water-soluble rhodium catalysts for hydroformylation is described in European Patent Appl. 103,810 (March 28, 1984) to Ruhrchemie. Sulfonated triarylphosphines are described by Rhone Poulenc, US Patent 4,483,801 (November 20, 1984).

Section 4.14.1 Dow has patented a route to epichlorohydrin based on addition of chlorine to acrolein, followed by hydrogenation of the aldehyde group to the corresponding alcohol and finally dehydrohalogenation to give epichlorohydrin. [US Patent 6,008,419 (December 28, 1999) to Dow Chemical Company].

Section 4.14.2 The FMC process for hydroxylating allyl alcohol is described in German Offen. 2,439,879 (March 4, 1976).

Section 4.14.3 There is ongoing research and development on improving the performance of the microorganisms for making acrylamide via biotechnology (US Patent 5,698,629; December 16, 1997 to Nitto Chemical).

The catalytic distillation approach for making acrylamide is described in "Conversion of Acrylonitrile to Acrylamide via Catalytic Distillation," K. Rock, J. Almering, and S. Swart, European Petrochemical Technology Conference, June, 2001.

CHAPTER 5

CHEMICALS AND POLYMERS FROM THE C_4 STREAM

We have described the huge volume of chemicals based on ethylene and the somewhat smaller volume based on propylene. Quantitatively the C_4 stream provides far less chemicals than ethylene or propylene (Fig. 4.1). Only three C_4-based chemicals, butadiene, isobutene, and MTBE are among the 50 chemicals produced in highest volume in the United States. The C_4 stream usage is not in the same league as ethylene's 53 billion lb and propylene's 32 billion lb consumption in 2003. About 4.3 billion lb of butadiene were consumed. Chemical uses required 1.1 billion lb of isobutene, but the demand for MTBE in unleaded gasoline meant that of the order of 13 billion lb went into this application. In the late 1980s and 1990s, MTBE was the fastest growing chemical ever. Production rose from 1.2 billion lb in 1981 to 5.1 billion in 1986, 10.1 billion in 1990, and about 20 billion lb/year in 1999–2002. Isobutene requirements as MTBE feedstock were about 13 billion lb/year for 1999–2002. Western European demand for MTBE is about 8 billion lb/year, indicating the lower gasoline usage in Western Europe (Fig. 2.1).

Butadiene goes mainly into synthetic rubbers. There is a range of these of both chemical and historical importance. It was the C_4 stream that provided the synthetic rubber vital to both sides in World War II. Also the chemistry associated with the C_4 stream is interesting and different, so we shall deal with it in comparable detail.

Steam cracking of gas fractions gives far less C_4 fraction than does naphtha cracking (Section 2.2.3). Traditionally, *n*-butane has seldom been cracked in the United

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

States, because it occurs in relatively low volume in natural gas and is used largely for fuel for heating and cooking. This application in the United States increased in the mid-1980s and will increase further in the 1990s and 2000s because butane is being removed from gasoline, particularly in the summer months when it volatilizes and has an adverse affect on the ozone layer. A more important source of *n*-butane is LPG (Section 2.2.1), which is finding greater use as cracking feedstock. A C_4 unsaturated fraction is also obtained from catalytic cracking (Section 2.2.2). However, the fraction is dilute, and isolation of chemicals from it is more expensive. Most of it is used for alkylation (Section 2.2.5).

Because the United States has traditionally cracked natural gas fractions, there has always been a shortage of butadiene. The shortfall has been accommodated by imports from Japan and Western Europe where naphtha cracking yields an excess of the C_4 fraction. Japanese supplies have diminished because of demands in East Asia and India. Indeed, East Asia became an importer of butadiene in the early 2000s. It was this pending shortfall in the United States that motivated the discovery of the metathesis reaction (Section 2.2.8) and the dimerization of ethylene (Section 3.2.1), both aimed at providing C_4 chemicals. Butene dehydrogenation is also carried out in the United States.

The European surplus motivated five companies to convert butadiene to *n*-butenes, useful for alkylate (Section 2.2.5). At least one other plant has been hydrogenating butadiene to butanes for cracker feed (see note at the end of this chapter). This is all an ironic reversal of previous trends, in that butadiene has always been the premium product and butenes the unwanted byproduct.

The main components of the C_4 stream are *n*-butane, 1-butene, 2-butene, isobutene, and 1,3-butadiene. Table 5.1 shows a typical composition of the C_4 fraction from steam cracking. These can to some extent be interconverted (Fig. 5.1). *n*-Butane isomerizes to isobutane, which can be dehydrogenated to isobutene, a process commercialized in the early 1990s. Both *n*-butane and the butenes can be dehydrogenated to 1,3-butadiene. Dehydrogenation of butenes is practiced in the United States when it is favored by a high butadiene price. It is harder to dehydrogenate *n*-butane, and this is not currently done, although it has been in the past.

TABLE 5.1 Typical Composition of a C_4 Olefin Fraction from Steam Cracking of Naphtha

Component	Percentage
C_3	0.5
n-Butane	3
Isobutane	1
Isobutene	23
1-Butene	14
2-Butene	11
Butadiene	47
C_5, Other	0.5

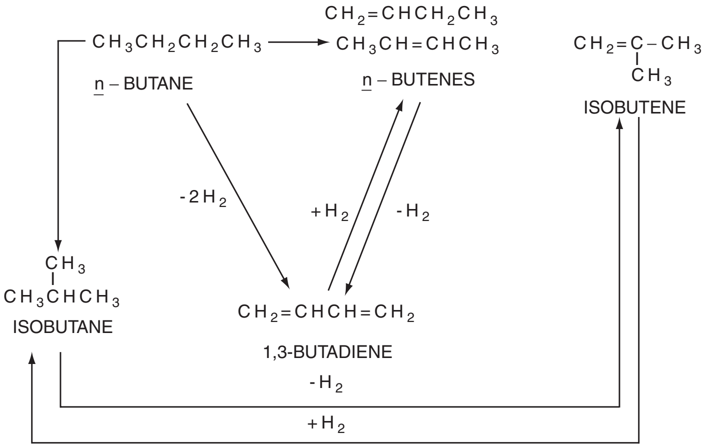


FIGURE 5.1 Major components of the C_4 stream.

Like propylene, the butenes have both fuel and chemical uses. When reacted with isobutane (Section 2.2.5) they provide alkylate for gasoline. When dimerized (Section 2.2.4) they become a component of high-octane polymer gasoline. Hydrogenation is not strictly necessary, although the double-bonded compounds tend to form tars. The dimers can be hydroformylated (Section 4.12) to provide nonanol for plasticizers (Section 9.1.1). Newer methods of dimerization (Section 5.1.3.2) yield more nearly linear products, which give more effective plasticizers. Alkylate has no chemical uses.

The separation of the C_4 olefins is complex and is outlined in Figure 5.2. The first step is removal of 1,3-butadiene by extractive distillation with an aprotic solvent, usually acetonitrile, *N*-methylpyrrolidone, or dimethylformamide. Each of these solvents is effective in depressing the volatility of components other than butadiene. However, a small amount of butadiene is left in the raffinate, which must be removed by after-treatment (selective hydrogenation) if pure 1-butene is desired later in the process.

The butadiene-free raffinate that results is called and traded as Raffinate I. It contains the two *n*-butenes and isobutene. The isobutene is reactive and may be separated by hydration to *tert*-butanol in the presence of sulfuric acid or, in more modern plants, by use of a fixed bed catalyst. *tert*-Butanol may be used as such or it may be dehydrated to pure isobutene.

In an alternative process, Raffinate I reacts with methanol to give MTBE (Section 5.2.1). This usually is used as such but, like *tert*-butanol, it may be cracked to give pure isobutene. The etherification process to MTBE is highly selective, on a par with the carboxylation of methanol to acetic acid (Section 10.5.2.2). It goes to about 97% conversion and, if all the isobutene must be removed, a second step is necessary in which the Raffinate I is reacted with a large excess of methanol.

Other processes for removing the isobutene involve an acid-catalyzed dimerization at 100°C to form isomers of 2,2,4-trimethylpentene, useful for the gasoline pool.

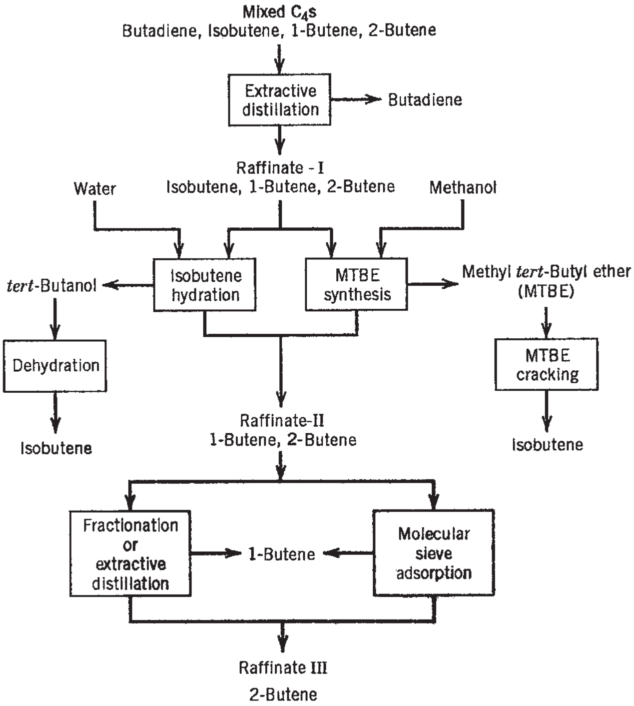


FIGURE 5.2 Separation of the C_4 olefins stream.

Another possibility is the polymerization of the isobutene to polyisobutene. The polymerization is catalyzed by aluminum chloride and the polymer is useful in adhesive and sealant formulations and petroleum product additives (Section 5.2.3).

The mixture of 1- and 2-butenes that remains is called and traded as Raffinate II. It may be hydrated to *sec*-butanol (Section 5.3) or oxidized to maleic anhydride (Section 5.4), although the latter is not done in the United States. In this process, 1-butene isomerizes to the more stable 2-butene.

The two butenes in Raffinate II may also be separated to yield pure 1-butene for linear low-density polyethylene production (Section 5.3). There are three procedures for separating the isomers. Fractionation requires a high multiplate low-temperature column because the boiling points are −6.47°C (1-butene) and 3.73°C (*cis*-2-butene). Extractive distillation and molecular sieve absorption (UOPs Sorbutene process) are also possible. The advantage of the UOP process is that pure 1-butene results even if appreciable isobutene remains in the Raffinate II. The other two processes are useful only if the butadiene and isobutene contents of Raffinate II are low. The *cis*- and *trans*-2-butene stream that results is called Raffinate III. The pure isomers do not have many uses, and the material is not ordinarily purified but is sent to the alkylation unit.

5.1 CHEMICALS AND POLYMERS FROM BUTADIENE

The United States and Western Europe traditionally have used the C_4 stream differently. In Europe, there is an excess of gasoline relative to diesel fuel and fuel oil. Hence, there is only a small market for alkylate gasoline (Section 2.2.5). Furthermore, naphtha is the major feedstock for steam cracking, and Western Europe's requirements for 1,3-butadiene can be satisfied by extraction from the copious C_4 stream that naphtha cracking produces. Hence, there is little demand for butenes and little difference in value between them and butanes. In the United States, on the other hand, alkylate gasoline is in ever greater demand for unleaded gasoline, and butenes are also required for dehydrogenation to butadiene, which is not provided in sufficient quantities by steam cracking of natural gas liquids or from catalytic cracking. Therefore, the butenes have greater value.

Figure 5.3 shows butadiene's end-use pattern. About 70% goes into synthetic rubbers Table 5.2 lists the major elastomers and their compositions. The most important one is styrene–butadiene rubber (SBR) for tires. This use was not growing until the advent of Sports Utility Vehicles, which use big tires with high rubber content, but the number of automobiles produced has nonetheless decreased because of overseas competition. Adding to butadiene's poor fortune is the longer life of modern tires and the virtual elimination of the spare tire. Modern radial ply tires contain less SBR and

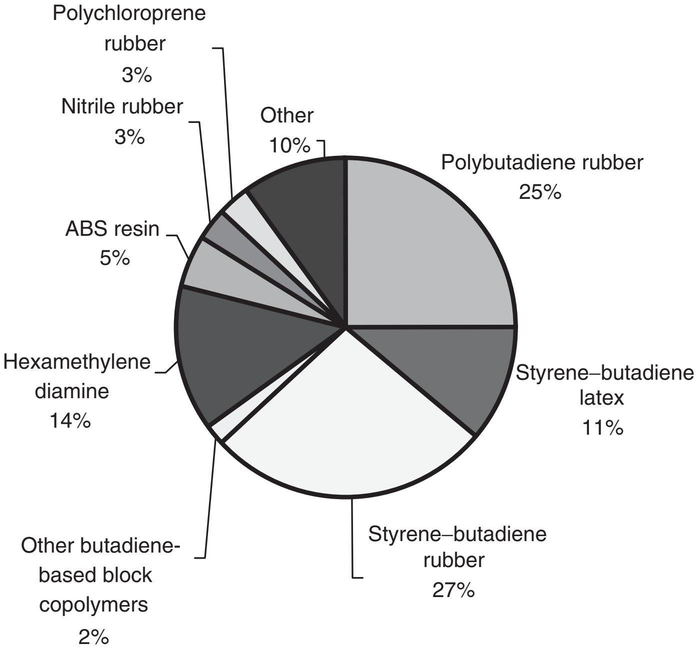


FIGURE 5.3 United States butadiene end-use pattern, 2001.

TABLE 5.2 Major Elastomers

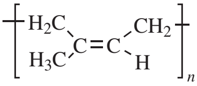
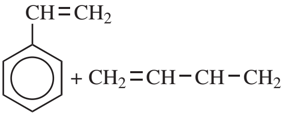
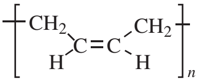
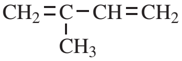
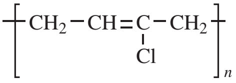
Elastomer	Monomers and/or structure	Polymerized by	Comments
Natural rubber	*cis*-1,4-Polyisoprene 	Enzymes	Obtained from *Hevea Brasiliensis*
Styrene-butadiene rubber (SBR)	~1 mol styrene to 6-mol butadiene 	Emulsion polymerization, free radical initiator often at low temperature (cold rubber)	~20% Butadiene units are in 1,2-configuration, ~60% are *trans*-1,4 and 20% *cis*-1,4
cis-1,4,-Polybutadiene rubber		Metal complex	High resiliency
Butyl rubber (Section 5.2.2)	Isobutene + 1–3% isoprene $CH_2=C(CH_3)_2$ +  $CH_2=\underset{CH_3}{\underset{\vert}{C}}-CH=CH_2$	Cationic initiator	High gas impermeability
Synthetic *cis*-1,4-polyisoprene	Isoprene  $CH_2=\underset{CH_3}{\underset{\vert}{C}}-CH=CH_2$	Metal complex	Properties similar to natural rubber
Polychloroprene rubber	Chloroprene  $\left[CH_2-CH=\underset{Cl}{\underset{\vert}{C}}-CH_2 \right]_n$ *trans*-1,4−Polychloroprene	Free radical initiator	Excellent ozone resistance
Nitrile rubber	Butadiene + 20–40% acrylonitrile $CH_2=CH-CH=CH_2$ + $CH_2=CHCN$	Free radical initiator	Similar to SBR but better oil resistance
Ethylene–propylene (EP) rubber and ethylene–propylene diene monomer (EPDM) rubber	C_2H_4, and C_3H_6 in EP. In EPDM, ethylidene norbornene, *trans*-1,4-hexadiene (Section 5.1.3.6) or dicyclopentadiene (Section 6.1) is added	Metal complex	EP vulcanized with peroxide; EPDM with normal vulcanizing agents

TABLE 5.2 (*Continued*)

Elastomer	Monomers and/or structure	Polymerized by	Comments
Thermoplastic rubber	Block copolymer of butadiene and styrene (and many others)	Ionic "living" polymerization	High strength, excellent solvent resistance, processability
Thiokol rubber	$n\mathrm{Na_2S} + n\mathrm{ClCH_2CH_2Cl} \longrightarrow$ $\left[\mathrm{CH_2CH_2{-}S{-}S{-}S{-}S}\right]_n + 2n\mathrm{NaC}$	Step growth polymerization	Used in sealants and as a rocket fuel binder

more natural rubber than the older cross-ply tires. Butadiene consumption in the United States in 1987 was about 3 billion lb and grew to about 4.5 billion lb in 2001, a higher than expected growth of about 3%/year.

Styrene–butadiene copolymers were the original basis for latex paint, but latices with superior properties result from poly(vinyl acetate), polyacrylates, polymethacrylates, and their copolymers, and these have since captured the market. Styrene–butadiene latices are still important as binders for paper, for carpet backing and for caulking compounds. Styrene–butadiene block copolymers were among the first thermoplastic elastomers and are the most important. They are discussed in Section 15.3.8. A specialty butadiene–styrene block copolymer with high styrene content, one version of which is called "K-Resin," can be blended with styrene homopolymer to increase its impact resistance. It can be used as such in adhesives and molded and extruded items, and it is stronger than polystyrene. Unlike other styrene–butadiene copolymers, "K-Resin" is transparent.

Several other synthetic rubbers are based on butadiene. The homopolymer, *cis*-1,4-polybutadiene rubber, which accounts for about 20% of total usage of butadiene (Fig. 5.3), is blended with natural and other rubbers such as SBR to aid their processing and to impart resilience and less heat build-up to tires. It is also used in tire treads to increase wear resistance, low-temperature flexibility, and resistance to aging. The sophistication of modern polymerization techniques is such that it is possible to polymerize butadiene to give any of the four possible stereoisomeric forms, which vary from elastomers to hard, resinous materials (Section 15.3.10). The elastomeric form is *cis*-1,4-polybutadiene. *trans*-1,4-Polybutadiene is used in the preparation of ABS copolymer (Section 5.1.1). The isotactic and syndiotactic 1,2 structures are not important commercially, although syndiotactic 1,2-polybutadiene can be fabricated into photodegradable film.

The chlorination of butadiene in the vapor phase at 250°C gives a mixture of 3,4-dichloro-1-butene, $\mathrm{CH_2{=}CH{—}CHCl{—}CH_2Cl}$, and 1,4-dichloro-2-butene, $\mathrm{ClCH_2{—}CH{=}CH{—}CH_2Cl}$. The former may be isomerized to the latter by heat in the presence of cuprous chloride (Section 5.1.2). Dehydrochlorination of 3,4-dichloro-1-butene leads to "chloroprene," the monomer for neoprene or polychloroprene rubbers. This use consumes about 3.7% of butadiene production.

$$\underset{\text{3,4-dichloro-1-butene}}{CH_2{=}CH{-}CHCl{-}CH_2Cl} \xrightarrow{-HCl} \underset{\text{2-Chloro-1,3-butadiene (Chloroprene)}}{CH_2{=}CH{-}CCl{=}CH_2}$$

Neoprene was an early synthetic rubber. It lacks the resilience necessary for use in tires, the major consumer of rubber, but it has good resistance to oil and ozone, which suits it for many specialized uses such as roofing and flexible hose. In the early days, it was made by reacting dimerized acetylene (i.e., vinylacetylene) with hydrogen chloride. Here is another example of petrochemicals replacing acetylene, for Du Pont phased out the last acetylene-based polychloroprene plant in the United States in 1974 and in Northern Ireland in 1977.

$$\underset{\text{Acetylene}}{2CH{\equiv}CH} \xrightarrow{CuCl/NH_4Cl} \underset{\text{Vinylacetylene}}{CH_2{=}CHC{\equiv}CH} \xrightarrow{+HCl} \underset{\text{Chloroprene}}{CH_2{=}CH{-}CCl{=}CH_2}$$

The market for neoprene is decreasing because EP or EPDM rubbers (Table 5.2) provide longer life, especially in roofing, where they resist exposure to oxygen and ozone. The materials are also useful for gasketing.

Nitrile rubber (Table 5.2) is a copolymer of acrylonitrile and butadiene, a typical ratio being 1:2. It is made with a redox initiator and is characterized by outstanding oil and abrasion resistance, which makes it suitable for oil seals, fuel tank fabrication, oil-resistant hoses, and ink rollers for printing presses. Dow and DSM have developed processes for dimerizing butadiene to vinylcyclohexene with subsequent dehydrogenation to styrene (Section 4.12).

5.1.1 Acrylonitrile–Butadiene–Styrene Resins (ABS)

Acrylonitrile–butadiene–styrene resins are two-phase systems of styrene–butadiene rubber dispersed in a glassy styrene–acrylonitrile matrix (Section 3.8). The copolymer has the best properties if there is sufficient input of energy in the mixing to cause grafting of the rubbery and glassy phases.

The ABS resins may be used between −40 and 107°C, not a very wide temperature range but a satisfactory one. They are flammable, but fire retardants can be added. Apart from these minor drawbacks, ABS resins have excellent properties. They process reasonably, have high gloss, do not mar, and have excellent dimensional stability and good mechanical properties. In terms of price and tonnage production (3145 million lb in 2000), they fit in a unique position between cheap, high-volume plastics, and expensive, low-volume engineering plastics. They can nonetheless be described as the first of the engineering plastics.

Injection molding of ABS resins gives housings for radios, telephones, business machines, pocket calculators, toilet seats, and parts for high-quality refrigerators, including the doors. Extrusion gives high-quality pipe and fittings (the biggest use) and also sheet that is thermoformed into vehicle covers and fittings, lawn mower housings, and snowmobile shrouds. Sheet is also used for luggage and the tops of skis. In most of these applications, ABS is replacing metal or, in the case of telephones, phenolics, and other plastics that are less impact-resistant.

The ABS resins may be painted, metallized, chromium plated, or printed and do not present the problems of a nonadhesive surface associated with the polyolefins. The plated plastic has replaced die cast metal in the radiator grilles of many automobiles.

A polymer alloy of ABS with polycarbonate is used for bumpers and side panels of automobiles. ABS has nonetheless suffered from interpolymer competition from polypropylene and polycarbonate.

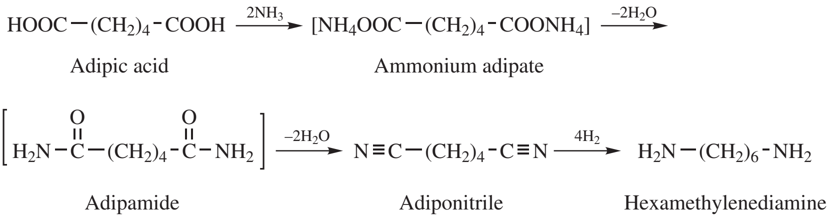
The first commercial grades of ABS, introduced in 1948, were simply blends of a rubber with styrene-acrylonitrile (SAN) copolymer. These blends reportedly used nitrile rubber since it was found to be more compatible with SAN than polybutadiene rubber. Modern ABS processes employ suspension, mass, or emulsion/mass hybrid polymerization of the three monomers: styrene, butadiene, and acrylonitrile. In these processes, an actual chemical linkage between the rubber phase and the elastomeric phase is formed. Properties of the ABS can be varied by adjusting the relative concentrations of the monomers, the degree to which the butadiene grafts to the SAN portion, or by adding an additional monomer. In general, the styrene contributes gloss and stiffness, the butadiene toughness and the acrylonitrile temperature resistance.

A polymer related to ABS is methyl acrylate–butadiene–styrene (MBS), produced in considerably lesser quantities than ABS. It is an impact modifier for PVC for bottles. PVC bottles are scarcely used in the United States, but in Western Europe they are used to package mineral water, cooking oil, and to a lesser extent alcoholic beverages. Usage of such bottles has decreased with the introduction of poly(ethylene terephthalate) (Section 9.3.3).

5.1.2 Hexamethylenediamine

The remaining major application for butadiene in Figure 5.3 is hexamethylenediamine (HMDA). Only two of the various routes to HMDA start with butadiene, but they include the most economic synthesis, and HMDA is butadiene's most important nonpolymer use. Accordingly the various routes to HMDA will be discussed here.

The evolution of syntheses for HMDA provides an excellent example of how sophisticated processes develop in the chemical industry. The first route to HMDA involved traditional reactions in which adipic acid (Section 7.2.1) and ammonia form ammonium adipate which, on dehydration first to the amide and then to the nitrile, provide adiponitrile. This in turn may be hydrogenated to HMDA.



$$HOOC-(CH_2)_4-COOH \xrightarrow{2NH_3} [NH_4OOC-(CH_2)_4-COONH_4] \xrightarrow{-2H_2O}$$

$$\left[H_2N-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH_2\right] \xrightarrow{-2H_2O} N{\equiv}C-(CH_2)_4-C{\equiv}N \xrightarrow{4H_2} H_2N-(CH_2)_6-NH_2$$

Under appropriate conditions, the reaction of adipic acid and ammonia leads to the nitrile without the isolation of intermediates. The vapor-phase reaction takes place at 275°C in the presence of a mixture of boric and phosphoric acids. It may also be conducted either in the liquid phase or as a melt at a somewhat lower temperature with a phosphoric acid catalyst. Selectivity is higher in the liquid and melt phases. The synthesis is simple but has the disadvantage of starting with expensive adipic acid.

Butadiene entered the picture because of a synthesis in which a mixture of *cis*- and *trans*-1,4-dichloro-2-butenes (see above) and 3,4-dichloro-1-butene was treated with sodium cyanide to give 1,4-dicyano-2-butene. The reaction takes place at about 80°C in the presence of cuprous chloride. The 1,4-dichloro compound yields the desired 1,4-dicyano compound as might be predicted. The 3,4-dicyano-1-butene, which forms from the corresponding 3,4-dichloro compound, however, undergoes an allylic rearrangement to give more of the desired 1,4,-dicyano-2-butene in both *cis* and *trans* forms at high selectivity.

$$\mathrm{ClCH_2{-}CH{=}CH{-}CH_2Cl} \xrightarrow[\mathrm{CuCl}]{\mathrm{NaCN}} \underset{\text{1,4-Dicyano-2-butene}}{\mathrm{N{\equiv}C{-}CH_2{-}CH{=}CH{-}CH_2{-}C{\equiv}N}}$$

$$\xrightarrow{\mathrm{H_2}} \underset{\text{1,4-Dicyanobutane}}{\mathrm{N{\equiv}C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C{\equiv}N}} \xrightarrow{\mathrm{H_2}} \underset{\text{Hexamethylenediamine}}{\mathrm{H_2N{-}(CH_2)_6{-}NH_2}}$$

In the final stage—the hydrogenation of adiponitrile to hexamethylenadiamine—excess ammonia is used to depress formation of a triamine, which nonetheless forms in small quantitites.

$$\mathrm{2NH_2(CH_2)_6NH_2} \longrightarrow \mathrm{NH_2(CH_2)_6NH(CH_2)_6NH_2 + NH_3}$$

The electrohydrodimerization of acrylonitrile (Section 4.8.1) was the next synthesis. It was an ingenious departure from classical chemistry. The hydrodimerization to adipontrile takes place by a complicated mechanism, which may be summarized as

$$\mathrm{2CH_2{=}CHCN + 2H^+ + 2e} \longrightarrow \mathrm{NC(CH_2)_4CN}$$

The first step is the reduction of acrylonitrile to its anion radical and this is followed by dimerization and protonation reactions. A necessary condition in the original process was the presence of a tetraalkylammonium salt as the electrolyte; otherwise propionitrile is the main product. The quaternary was thought to adsorb on the electrode to give a hydrophobic layer that prevented immediate protonation of the acrylonitrile anion radical as it was formed. A membrane to divide the cell was also required.

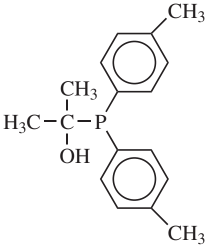
The newest version of the process employs an undivided cell and an emulsion of acrylonitrile with 10–15% disodium hydrogen phosphate solution containing 0.4% of a complex phosphate. The aqueous phase is saturated (7%) with acrylonitrile, and the adiponitrile extracts into the organic phase as it is formed. Conversion of acrylonitrile is 50 mol% and selectivity is about 92%. Byproducts include propionitrile C_2H_5CN, bis(cyanoethyl) ether $(NCC_2H_5)_2O$, and hydroxypropionitrile $HOCH_2CH_2CN$.

The newer process lowers utility costs. Acrylonitrile, the starting material, is more expensive than butadiene. Nonetheless, adiponitrile is manufactured by this clever Monsanto process in several United States and European plants, and it is the only example of the use of electrochemistry to manufacture a high-volume organic chemical.

Chemical means for dimerizing acrylonitrile have been studied extensively. Unlike the Monsanto process, the reaction is not a hydrodimerization. Thus it yields a mixture of the two possible 1,4-dicyanobutenes. The reaction proceeds at 1–2 bar and temperatures varying from 30 to 100°C to give 87% conversion with a selectivity to linear products of 84%.

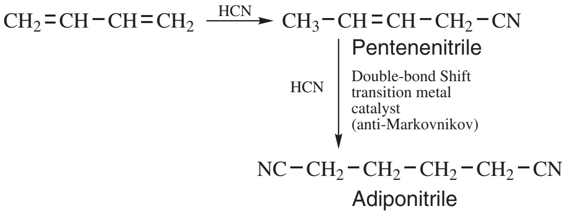
$$2CH_2{=}CHCN \longrightarrow NCCH_2CH{=}CHCH_2CN + NCCH{=}CHCH_2CH_2CN$$

These are hydrogenated to hexamethylenediamine. A branched isomer, methylene–glutaronitrile, $NC{-}C(CH_2){-}CH_2CH_2CN$, forms as a byproduct and may be isomerized to a linear product. The dimerization catalysts are phosphines. 2-Hydroxyisopropyl *bis*-*p*-tolylphosphine is typical.



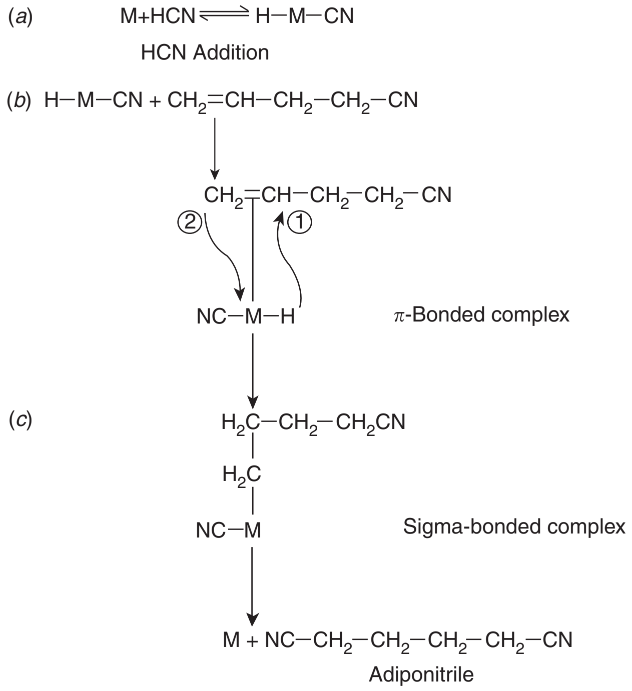
2-Hydroxyisopropyl-*bis*-*p*-tolylphosphine

These processes are rivaled by still another process that turns out to be the most economic. It starts with the 1,4-addition of hydrogen cyanide to butadiene. The catalyst, nickel with triaryl phosphite ligands, $Ni[P(OAr)_3]_4$, is remarkable. It not only effects the 1,4-addition, but it also isomerizes the byproduct 2-methyl-3-butenenitrile, which is produced in appreciable quantities, to the desired isomer. In addition, it shifts the double bond to a terminal position and then makes possible the addition of another mole of hydrogen cyanide anti-Markovnikov to the terminal bond. If it were not possible to use the same catalyst for both reactions, the double-bond shift could not be carried out in high yield because of an equilibrium. The resulting adiponitrile may be hydrogenated to hexamethylene diamine.



This synthesis, as opposed to the one starting with the chlorination of butadiene, eliminates the need for costly chlorine, uses hydrogen cyanide, which is now cheaper than sodium cyanide (but not when the synthesis based on 1,4-dichloro-2-butene was devised), eliminates the handling of carcinogenic 1,4-dichloro-2-butene, and solves the problem of disposing of ecologically unacceptable copper-contaminated sodium chloride.

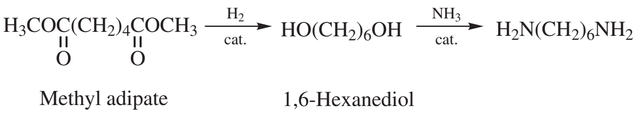
A simplified proposed mechanism for the HCN addition to the terminal double bond that results from the double bond shift in the initial pentenenitrile (Fig. 5.4) involves the formation of an H—M—CN complex in which M is the metallic catalyst. This complex in turn π-bonds with the terminal olefin after which a σ-bonded complex forms, which subsequently eliminates the metal to provide the adiponitrile.



Ligands omitted.

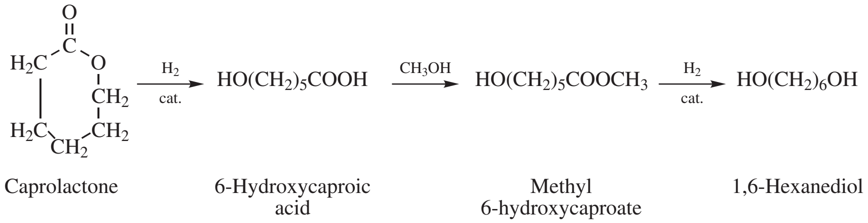
FIGURE 5.4 Mechanism of HCN addition.

An obsolete process for HMDA production involves the amination of 1,6-hexanediol with ammonia in the presence of Raney nickel. The diol, still manufactured for use in polyurethane formulations, results from the hydrogenolysis of methyl adipate.

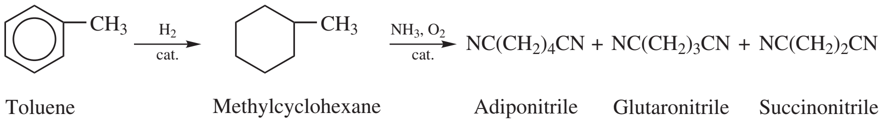


$$\underset{\text{Methyl adipate}}{H_3CO\underset{\|\atop O}{C}(CH_2)_4\underset{\|\atop O}{C}OCH_3} \xrightarrow[\text{cat.}]{H_2} \underset{\text{1,6-Hexanediol}}{HO(CH_2)_6OH} \xrightarrow[\text{cat.}]{NH_3} H_2N(CH_2)_6NH_2$$

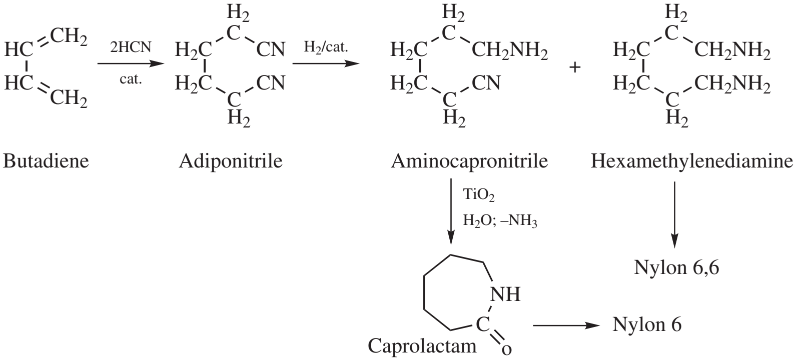
Another route to 1,6-hexanediol is via cyclohexanone, which is oxidized by hydrogen peroxide or peracetic acid to caprolactone (Section 7.2.2). The lactone can then be cleaved with hydrogen, in the presence of a reducing catalyst such as copper chromite, to 6-hydroxycaproic acid whose ester, on hydrogenolysis, gives 1,6-hexanediol. The amination of the diol takes place in the presence of ammonia and hydrogen at 200°C and 230 bar with a Raney nickel catalyst.



A proposed process for adiponitrile, never commercialized, involves the ammoxidation (Section 4.8) of methylcyclohexane (prepared by toluene hydrogenation) at 43°C over a tin oxide–antimony oxide catalyst. Adiponitrile is produced in relatively modest yields together with byproduct glutaronitrile and succinonitrile.



According to the patent literature, adiponitrile can be partially hydrogenated to a near 50:50 mixture of HMDA and aminocapronitrile. Aminocapronitrile, which is the compound made if only one of the two nitrile groups in adiponitrile is hydrogenated, is separated from the HMDA and is reacted with water at 240°C using a titanium dioxide catalyst. Caprolactam and ammonia are produced. This is a two-for-one process that yields monomers for both nylon 6 and nylon 6,6. Du Pont and BASF announced their intentions to commercialize this process, but Du Pont withdrew and BASF seems to be carrying on alone. Other butadiene to caprolactam routes are described in Section 7.2.1.

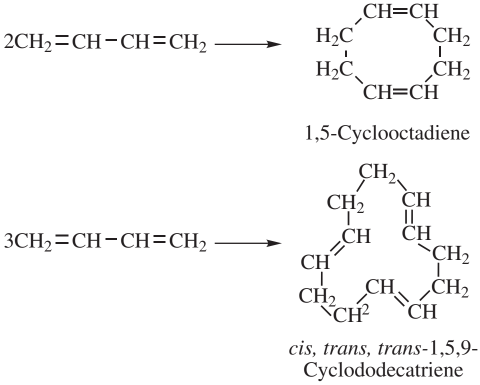


HMDA's major role is in the production of nylon 6,6 (Section 7.2.1). It can, however, be converted to an isocyanate by reaction with phosgene. This toxic product, used as a trimer to reduce its vapor pressure, is useful for the preparation of resistant, nonyellowing, glossy, low-temperature-curing coatings of which aircraft topcoats are an example.

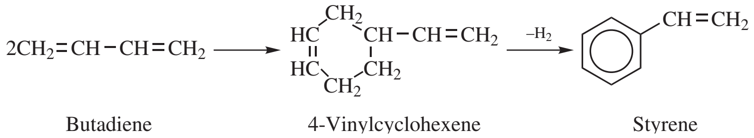
5.1.3 Lesser Volume Chemicals from Butadiene

Various lesser volume chemicals based on butadiene are generated by cyclization, di- and trimerization, and the Diels–Alder reaction. Carbonylation leads to an adipic acid synthesis.

5.1.3.1 Cyclization Cyclization of 2 and 3 mol of butadiene gives a dimer, 1,5-cyclooctadiene, and a trimer, *cis-trans-trans*-1,5,9-cyclododecatriene, an intermediate for perfumes.



Dimer formation is catalyzed by a nickel salt of 2-ethylhexanoic acid, triethylaluminum, and triphenylphosphine or triphenyl phosphite. A byproduct is another butadiene 237 dimer, 4-vinylcyclohexene, which is also produced in high yield in an uncatalyzed dimerization. It has been proposed as a precursor of styrene, which forms by oxidative dehydrogenation.



This styrene process has not been commercialized, although Dow described an improved catalyst in the mid-1990s (see note at the end of this chapter). A catalyst with large ligands that suppresses 4-vinylcyclohexene formation is nickel in combination with *tris-O*-phenylphenyl phosphite. At 80°C and 1 bar, selectivity to 1,5-cyclooctadiene is 96%.

DSM has developed a related approach to styrene via butadiene. Vinylcyclohexene is dehydrogenated in the gas phase over a proprietary Pd/MgO catalyst to give ethylbenzene (Section 3.8). The ethylbenzene can then be converted to styrene by conventional techniques.

At typical butadiene prices, both the Dow and DSM approaches are less economic than the conventional ethylbenzene route to styrene. In addition, it would take the output from three to four steam crackers to provide enough butadiene to supply a world-class styrene plant.

5.1.3.2 Dimerization and Trimerization Linear dimers of butadiene are formed in several ways. One is 1,3,7-octatriene, which forms with a nickel catalyst and appropriate ligands.

$$2CH_2{=}CH{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$$

1,3,7-Octatriene

More important are the products intended for hydroformylation to yield plasticizer alcohols (Section 4.6).

Dimers with terminal functionality, such as 1,7-octadiene, result from 2 mol of butadiene with formic acid as the source of hydrogen.

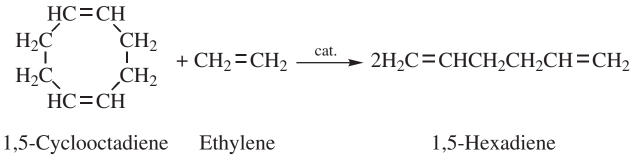
$$2CH_2{=}CH{-}CH{=}CH_2 + HCOOH \longrightarrow CH_2{=}CH(CH_2)_4CH{=}CH_2 + CO_2$$

Formic acid 1,7-Octadiene

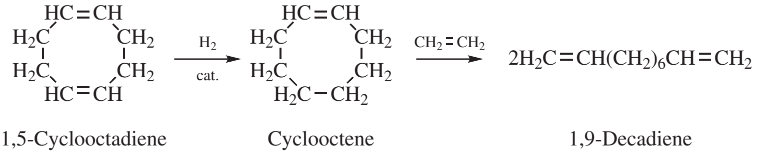
The catalyst is palladium acetate with triethylamine. The reaction is run in an aprotic solvent, dimethylformamide. Ligands such as triethylphosphine must be present. Conversion and selectivity are high, 95 and 93%, respectively.

Butadiene trimerizes over a titanium tetrachloride–dialkylaluminum chloride catalyst at 70°C and 1 bar to provides the *cis*, *trans*, *trans* isomer. The coproducts are minor amounts of the all *trans* isomer, polybutadiene, 1,5-cyclooctadiene, and 4-vinylcyclohexene. The *trans, trans, trans* isomer results if a nickel catalyst is used, but this is not done commercially. The catalyst is similar to the Ziegler polyethylene catalyst.

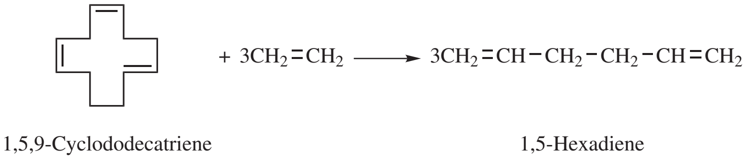
In the late 1980s, Shell developed routes to two terminal olefins, 1,5-hexadiene and 1,9-decadiene. The first compound results from the metathesis (Section 2.2.9) of 1,5-cyclooctadiene with ethylene.



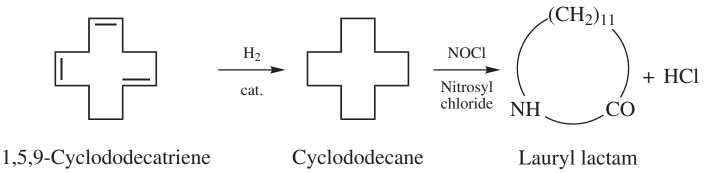
1,9-Decadiene is made by the reaction of cyclooctene with ethylene, the starting material resulting again from the selective hydrogenation of 1,5-cyclooctadiene. The heterogeneous reaction makes use of a rhenium catalyst at 5–20°C and 1–2 bar. Yields are better than 90%.



1,5-Hexadiene can also be prepared by the metathesis of 1,5,9-cyclododecatriene with 3 mol of ethylene.

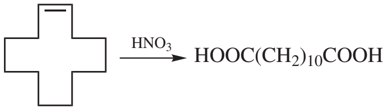


1,5,9-Cyclododecatriene can be hydrogenated to cyclododecane. Treatment with nitrosyl chloride gives lauryl lactam, the monomer for nylon 12.

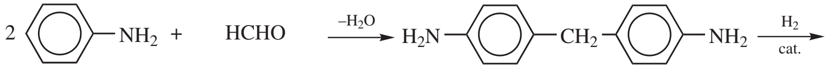


The same process is one of several used to obtain caprolactam from cyclohexane, the monomer for nylon 6 (Section 7.2.2).

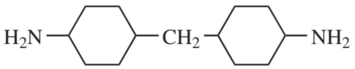
The partly hydrogenated triene, cyclododecene, can be oxidized with nitric acid to dodecanedioic acid. This was part of a now defunct Du Pont process to make the nylon “Qiana,” a condensate of dodecanedioic acid with *p,p′*-diaminodicyclohexylmethane, which in turn was made by hydrogenation of the adduct from the condensation of aniline and formaldehyde.



Cyclododecene Dodecanedioic acid



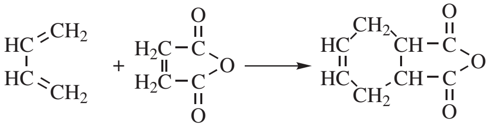
Aniline Formaldehyde *p,p′*-Diaminodiphenylmethane



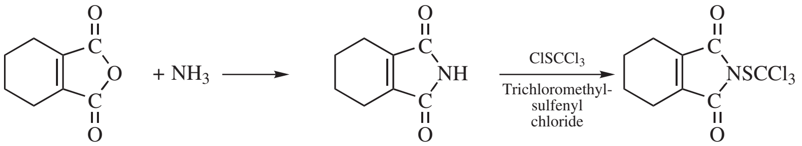
p,p′-Diaminodicyclohexylmethane

Qiana was said to have the drape and feel of silk, but still did not succeed in the marketplace.

5.1.3.3 Diels–Alder Reactions In contrast to the laboratory, the Diels–Alder condensation is used industrially only on a small scale. Nonetheless, butadiene is the classic diene for the reaction. It reacts with cyclopentadiene (Section 6.3) to give ethylidene norbornene, a monomer useful in ethylene–propylene–diene monomer rubber (Section 3.2.5). It also reacts with maleic anhydride to give tetrahydrophthalic anhydride, used in polyester and alkyd resins and as an ingredient in the fungicide, captan. The preparation of the reagent trichloromethylsulfenyl chloride is shown in the notes at the end of this chapter.

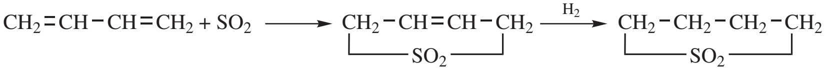


1,3-Butadiene Maleic anhydride Tetrahydrophthalic anhydride



Tetrahydrophthalic anhydride Tetrahydrophthalimide Captan

Diels–Alder addition of sulfur dioxide to butadiene at room temperature followed by hydrogenation yields tetramethylene sulfone (Sulfolane), which is used to extract aromatic compounds (Section 2.2.3) from catalytic reformate in petroleum refineries.



$$CH_2{=}CH{-}CH{=}CH_2 + SO_2 \longrightarrow \underbrace{CH_2{-}CH{=}CH{-}CH_2}_{SO_2} \xrightarrow{H_2} \underbrace{CH_2{-}CH_2{-}CH_2{-}CH_2}_{SO_2}$$

Sulfolene Sulfolane

It is also mixed with diisopropanolamine and water in the so-called Sulfinol process for the removal of hydrogen sulfide, carbon dioxide, carbonyl sulfide, and other acid components from so-called "sour" gas. The acid components are absorbed chemically by the amine and physically by the sulfolane. Being aprotic, sulfolane is also useful in extractive distillations, for example, for the separation of butadiene from other C_4 isomers (Chapter 5).

The Diels–Alder reaction between maleic anhydride and cyclopentadiene is discussed later (Section 6.2). The Diels–Alder reaction between two molecules of butadiene yields vinylcyclohexene (Section 5.1.3.1).

5.1.3.4 Adipic Acid Adipic acid is produced in large quantities by the classical synthesis based on cyclohexane (Section 7.2.1). It is being made by BASF in the 2000s by dicarbonylation of butadiene. This technology appears competitive with the classical route at typical butadiene costs. The reaction proceeds in two stages since the dicarbonylation is difficult. Carbon monoxide and methanol react with butadiene in the presence of dicobalt octacarbonyl in quinoline or a related base at 600 bar and 120°C to give methyl-3-pentenoate at 98% selectivity. The second step takes place at a higher temperature of 185°C but at a lower pressure of 30 bar in the presence of additional CO and methanol.

$$CH_2{=}CH{-}CH{=}CH_2 + CO + CH_3OH \xrightarrow{\text{cat.}} CH_3CH{=}CHCH_2COOCH_3$$

Methyl 3-pentenoate

$$CH_3CH{=}CHCH_2COOCH_3 + CO + CH_3OH \xrightarrow{\text{cat.}} CH_3OOC(CH_2)_4COOCH_3$$

Dimethyl adipate

$$CH_3OOC(CH_2)_4COOCH_3 + 2H_2O \xrightarrow{H^+} HOOC(CH_2)_4COOH + 2CH_3OH$$

Adipic acid

Selectivity at this point is ~85% to the desired dimethyl adipate. The migration of the double bond in the second step (cf. a similar shift in the hexamethylenediamine synthesis from butadiene, Section 5.1.2) makes linearity possible. Other catalyst systems include platinum and palladium halides, phosphine-promoted cobalt complexes and rhodium complexes. Byproducts include methyl 3-pentenoate, methyl glutarate, methyl

ethyl succinate, dimethyl and diethyl succinate, and methyl pentanoates. The first two materials are obtained in largest amounts.

Between 1995 and 2000, Du Pont/DSM, Rhone Poulenc, and Union Carbide each disclosed related work on the conversion of butadiene to adipic acid. However, no announcements of commercialization have been forthcoming.

5.1.3.5 1,4-Butanediol Butadiene is the basis for one of the important routes to 1,4-butanediol by way of a double acetoxylation, which is described in Section 10.3.1.

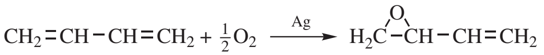
5.1.3.6 trans-1,4-Hexadiene *trans*-1,4-Hexadiene (Section 16.7.1) results from the condensation of ethylene and butadiene in the presence of a rhodium catalyst. This was the first rhodium-catalyzed homogeneous reaction to be used industrially.

$$CH_2{=}CH{-}CH{=}CH_2 + CH_2{=}CH_2 \xrightarrow{\text{cat.}} CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH_3$$

The compound is a useful comonomer for the production of EPDM rubber (Table 5.2). The terminal double bond enters into the polymerization, and the less reactive *trans* double bond then becomes pendant and provides a site for cross-linking or vulcanization with sulfur compounds.

5.1.3.7 Dimethyl-2,6-Naphthalene Dicarboxylate Amoco (now BP) has commercialized a process to make dimethyl-2,6-naphthalene dicarboxylate from butadiene and *o*-xylene. This material is used as a monomer to make a specialty high-temperature resistant, barrier polyester, poly(ethylene naphthalate) (Section 9.3.3). The synthesis is shown in Figure 5.5. An alkenylation reaction over an alkali metal catalyst gives 5-(*o*-tolyl)-pentene-2, which cyclizes over a platinum and copper on zeolite catalyst to give 1,5-dimethyltetralin. Liquid-phase dehydrogenation at 220–420°C and moderate pressure over platinum and rhenium on γ-alumina gives a mixture of 1,5- and 1,6-dimethylnaphthalenes. The latter is separated by crystallization and the 1,5-product recycled for isomerization. Oxidation, similar to that in terephthalic acid/dimethyl terephthalate production (Section 9.3.1) gives dimethyl-2,6-naphthalene dicarboxylic acid or its dimethyl ester.

5.1.3.8 Butadiene Monoepoxide Eastman Chemical has built a small plant to commercialize a process that converts butadiene to the corresponding monoepoxide:



$$CH_2{=}CH{-}CH{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow{\text{Ag}} H_2C{-}CH{-}CH{=}CH_2$$

Butadiene monoepoxide

The chemistry is analogous to that of the silver-catalyzed direct oxidation of ethylene to ethylene oxide. Just as with ethylene, butadiene contains no allylic hydrogens and is able to undergo epoxidation smoothly to afford 3,4-epoxy-1-butene

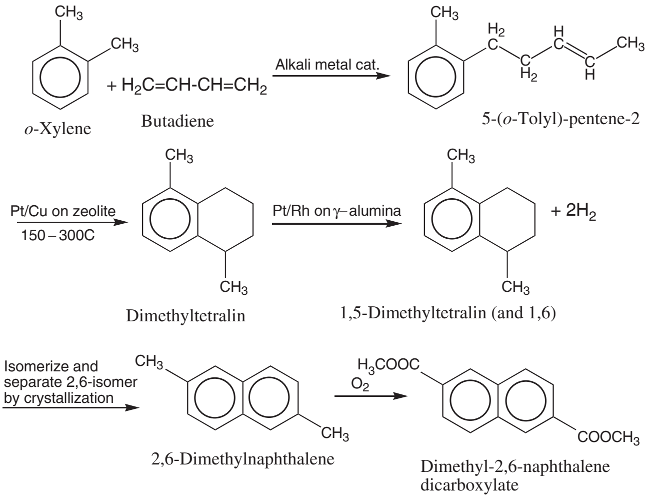
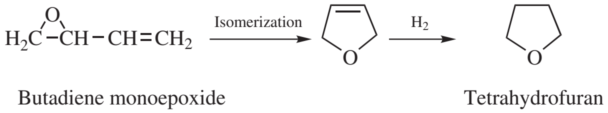


FIGURE 5.5 Synthesis of dimethyl-2,6-naphthalene dicarboxylate.

(butadiene monoepoxide) in good yield. Eastman is using this material as a convenient synthon to make a variety of specialty intermediates for the pharmaceutical and agricultural markets. This monoepoxide also has the potential to be converted economically to tetrahydrofuran (THF) for Spandex (Section 15.3.8) via the following reactions:



Although consumed on a scale almost an order of magnitude less than ethylene, butadiene has no fewer nor less interesting reactions. They are carried out, however, on a smaller scale.

5.2 CHEMICALS AND POLYMERS FROM ISOBUTENE

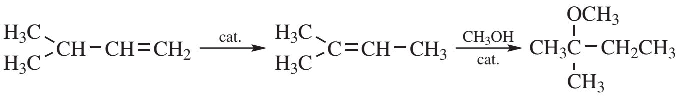
Isobutene was a lackluster chemical until the 1980s. Between 1981 and 1999, however, United States production grew from 1.2 to 20.9 billion lb (Section 2.3.2 and the beginning of this chapter). Its growth results from its role as a precursor for MTBE, the preferred oxygen-containing additive for increasing the octane number of unleaded gasoline. Other uses for isobutene include formation of butyl rubber

(Table 5.2, Section 5.2.2), polyisobutenes, alkylates for gasoline (Section 2.2.5), *tert*-butanol, methyl methacrylate (Section 4.6.1), and isoprene (Section 6.2).

The production of isobutene from the mixed C_4 stream was described in Section 5. A second major source of isobutene is the dehydration of the *tert*-butanol produced as a coproduct in a propylene oxide process (Section 4.7).

Because there was insufficient isobutene in the late 1980s and 1990s to satisfy the need for MTBE, processes were devised for dehydrogenating isobutane to isobutene in the same way that the butenes may be dehydrogenated to butadiene. The dehydrogenation goes more readily because isobutane has an excellent leaving group—the hydrogen on the tertiary carbon atom. The first step, the isomerization of *n*-butane to isobutane, is a well-defined refinery reaction. By 2002, owners of many plants around the world designed to dehydrogenate isobutane to isobutene were wondering what to do with their isobutene, if the use of MTBE is reduced.

A related route to octane-improving tertiary ethers is BP's Etherol process. It is intended to produce the higher analogues of MTBE by making use of the isoalkenes from catalytic cracking. These include 3-methyl-1-butene and 3-methyl-1-pentene. The catalyst, a Pd-impregnated ion exchange resin, isomerizes these to isopentene and isohexene and catalyzes the addition of methanol to the newly created, reactive double bond. Also, in the presence of hydrogen, it selectively catalyzes the hydrogenation of diolefins to monoolefins. Thus, it has three functions. An example is the formation of *tert*-amyl methyl ether (TAME) from 3-methyl-1-butene.



$$(H_3C)_2CH{-}CH{=}CH_2 \xrightarrow{\text{cat.}} (H_3C)_2C{=}CH{-}CH_3 \xrightarrow[\text{cat.}]{CH_3OH} CH_3\overset{\overset{\displaystyle OCH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_2CH_3$$

3-Methyl-1-butene 2-Methyl-2-butene TAME

5.2.1 Methyl *tert*-Butyl Ether

The role of MTBE as an octane improver in gasoline was mentioned above. Its production and isolation directly from Raffinate I, a portion of the C_4 fraction from either steam or catalytic cracking, was discussed in Section 5. It can be made similarly from isolated isobutene by reaction with methanol in a highly selective reaction in the presence of an acid catalyst, usually an acidic ion exchange resin.

The phaseout of MTBE will present two problems—the need for an alternative method of enhancing octane number and how best to revamp MTBE production equipment for alternative uses. The role of octane number enhancement is likely to be filled by ethanol. An alternative use of equipment that is being pursued by a number of engineering contractors is to convert the MTBE etherification reactor to dimerize isobutene to diisobutenes (see below). The diisobutenes can then be hydrogenated in a new and separate reactor to give isooctane, itself a high-octane gasoline component (Section 2.2.5), although its octane number is considerably less than that of MTBE.

Isooctane production has the benefit of using the same equipment (with the addition of a hydrogenation reactor) and process conditions as MTBE production and also provides an alternative use for the isobutene.

5.2.2 Butyl Rubber

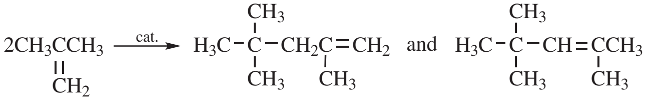
An important outlet for isobutene is in butyl rubber, a copolymer of isobutene with 2–5% of isoprene. Butyl rubber was used for inner tubes before the advent of the tubeless tire because of its impermeability to air. It is still used as an inner liner for tubeless tires, for truck inner tubes, for tire sidewall components, and for air cushions and bellows. Without the isoprene, the polymer would contain no double bonds and would not vulcanize with sulfur. The isoprene comonomer leaves only a small number of double bonds to be cross-linked, and the resulting polymer contains little if any unsaturation. For this reason, it resists aging and is therefore useful in constructions such as tops for convertibles.

5.2.3 Polyisobutenes and Isobutene Oligomers and Polymers

Isobutene can be polymerized to polyisobutene under the influence of Friedel–Crafts catalysts such as boron trifluoride or aluminum chloride. The lower molecular weight liquid products are adhesives and tackifiers. The higher molecular weight products are used in caulking compounds and as a chewing gum base.

An oligomer produced in much higher volume, about 750 million lb/year in the United States, is so-called polybutenes, made by polymerizing Raffinate I (Section 5) with an acid catalyst such as aluminum chloride and with hydrochloric acid as an activator. The *n*-butenes act largely as chain stoppers since the isobutene polymerizes much more rapidly. The resulting low molecular weight (1000–1500) polymers, functionalized by reaction with maleic anhydride, are widely used as additives for lubricating oils and gasoline.

Like propylene and the butenes, isobutene is used for alkylates for gasoline (Section 2.2.5) and may be dimerized or oligomerized (Section 2.2.4), to give diisobutenes, unsaturated precursors of 2,2,4-trimethylpentane. Both the unsaturated and subsequently hydrogenated compounds increase the octane number of gasoline, the latter of course being more stable. This reaction may become more significant if MTBE is phased out (see above).



$$2CH_3\underset{\underset{CH_2}{\|}}{C}CH_3 \xrightarrow{\text{cat.}} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2\underset{\underset{CH_3}{|}}{C}=CH_2 \text{ and } H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=\underset{\underset{CH_3}{|}}{C}CH_3$$

Isobutene Diisobutenes

The diisobutenes may be hydroformylated (Section 4.8) to branched-chain aldehydes that can be hydrogenated to branched nonanol. Alkylation of phenol with nonanol gives nonylphenol, which can subsequently be ethoxylated to give nonionic surfactants. Diisobutenes are also used to alkylate phenol directly to provide branched-chain octylphenol for the preparation of ethoxylated nonionic surfactants. The octyl compound is used on a much smaller scale but, in spite of conflicting claims, both are likely to be phased out because of their lack of biodegradability.

5.2.4 *tert*-Butanol

Isobutene may be hydrated to *tert*-butanol with an acid catalyst such as 60% sulfuric acid at a low temperature of 10–30°C with very high selectivity and yield. This is the major route for isolating isobutene from Raffinate I (Section 5). *tert*-Butanol is also produced concurrently with propylene oxide as described in Section 4.7. A third route is acidification of *tert*-butyl hydroperoxide, which in turn results from the reaction of isobutane with oxygen. This is not done commercially since the major interest in *tert*-butanol has been for dehydration to isobutene, which is also readily obtained by isobutane dehydrogenation. The dehydrogenation is more difficult than the dehydration, but most isobutene for MTBE still comes from isobutene because there is not enough *tert*-butanol.

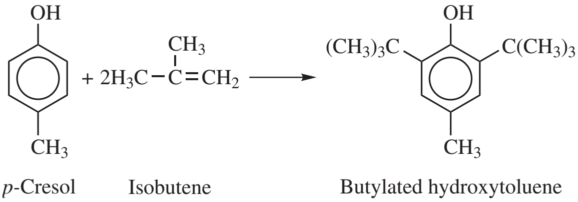
tert-Butanol is a solid that dissolves readily in gasoline and has been used as an octane improver. It may be mixed with an equal quantity of methanol, which by itself is not useful in gasoline because it separates out as a second layer in the presence of moisture. However, neither the *tert*-butanol nor the methanol-*tert*-butanol combination is as effective as MTBE. The fate of most *tert*-butanol is its dehydration to isobutene, which is done in the refinery in the separation of C_4s and as a step in methyl methacrylate production in Japan (Section 4.10.1).

5.2.5 Methyl Methacrylate

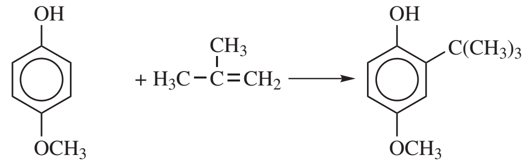
Both isobutene and *tert*-butanol can be oxidized to methacrylic acid (Section 4.10.1). Methacrylaldehyde is an intermediate. Both undergo ammoxidation to methacrylonitrile, an intermediate for the preparation of methacrylic acid in one Japanese process (Section 4.10.1) that is not currently in use.

5.2.6 Lesser Volume Chemicals from Isobutene

Two small volume but widely used products based on isobutene are butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA). The BHT results from the interaction of isobutene and *p*-cresol with a silica catalyst.



BHA results from the reaction of 1 mol of isobutene with the monomethyl ether of hydroquinone.

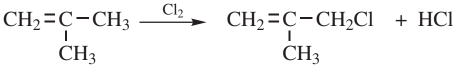


Hydroquinone monomethyl ether

BHA

Both BHT and BHA are oil-soluble antioxidants for rubbers and plastics and for fatty foods such as shortenings. Small quantities protect huge tonnages of products as diverse as elastomers and shortening from deterioration and thus have great economic significance. The food usage has been investigated repeatedly by the Food and Drug Administration, but thus far no evidence against them has been found. Even so, their use in food products is decreasing.

Liquid-phase chlorination of isobutene at 400–500°C leads to methallyl chloride (cf. allyl chloride, Section 4.14.1). Treatment with aluminum and hydrogen gives triisobutyl aluminum and diisobutyl aluminum hydride, both important as Ziegler–Natta polymerization catalysts. The hydride is also a reducing agent.



$$\mathrm{CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \xrightarrow{Cl_2} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2Cl + HCl}$$

Isobutene

Methallyl chloride

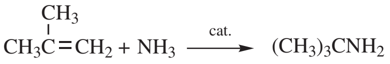
$$\mathrm{CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3 \xrightarrow[H_2]{Al} [(CH_3)_2CH_2CH_2]_3Al + [(CH_3)_2CH_2CH_2]_2AlH}$$

Isobutene

Triisobutylaluminum

Diisobutylaluminum hydride

Isobutene figures prominently in a synthesis of isoprene as discussed in Section 6.1. Isobutene and ammonia yield *tert*-butylamine with a catalyst of ammonium iodide promoted with chromium chloride.

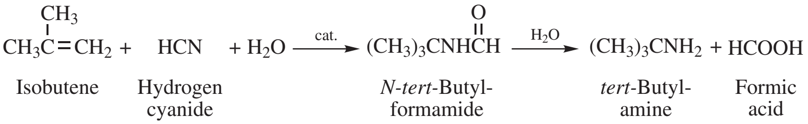


$$\mathrm{CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + NH_3 \xrightarrow{cat.} (CH_3)_3CNH_2}$$

Isobutene

tert-Butylamine

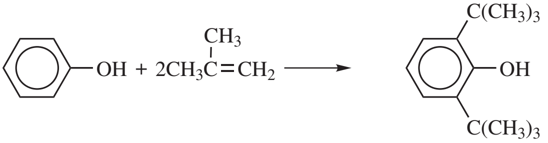
Conversion is 19% at 100% selectivity. The reaction is probably not yet used industrially. This is a demonstration of the high reactivity of the double bond of isobutene, since ammonia addition to a double bond normally takes place only with difficulty, and with specialized homogeneous catalysts. *tert*-Butylamine is normally made by the Ritter reaction of isobutene with hydrogen cyanide, which involves the addition of hydrogen cyanide and water to a double bond, followed by *in situ* hydrolysis of the resultant formamide.



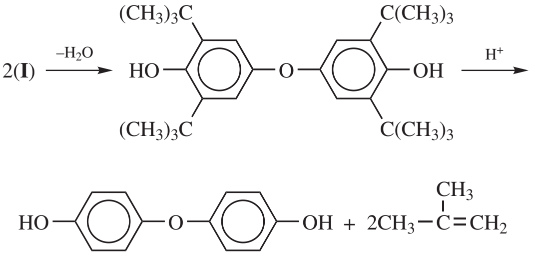
$$CH_3\overset{CH_3}{\overset{|}{C}}{=}CH_2 + HCN + H_2O \xrightarrow{\text{cat.}} (CH_3)_3CNH\overset{O}{\overset{\|}{C}}H \xrightarrow{H_2O} (CH_3)_3CNH_2 + HCOOH$$

Isobutene Hydrogen cyanide *N*-*tert*-Butylformamide *tert*-Butylamine Formic acid

tert-Butylamine is used in the formulation of lubricating oil additives. The labile nature of the *tert*-butyl group makes isobutene valuable in chemical synthesis. An example is the use of isobutene as a shielding group for the synthesis of *p,p′*-biphenol, a monomer for liquid-crystal polymers. Phenol is alkylated with isobutene to give 2,6-di-*tert*-butylphenol (I). Then, 2 mol can be coupled in the *para* position to give a diquinone, which can be hydrogenated to the substituted biphenol. The protective *tert*-butyl groups can be removed by acid catalysis and the recovered isobutene can be recycled.

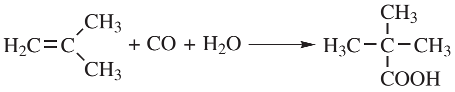


2,6-Di-*tert*-butylphenol (**I**)



p,p′-Biphenol

Acid-catalysed carbonylation of isobutene in the presence of water gives pivalic acid, the simplest member of a class of acids known as Koch acids. ExxonMobil (neoacids) and Shell (Versatic acids) are the two largest producers of pivalic acid. It is as an intermediate for the production of specialty organic peroxides, agrochemicals, and pharmaceutical actives. Glycidyl esters of pivalic acid are finding increasing use in coatings formulations while vinyl esters find application as specialty monomers.



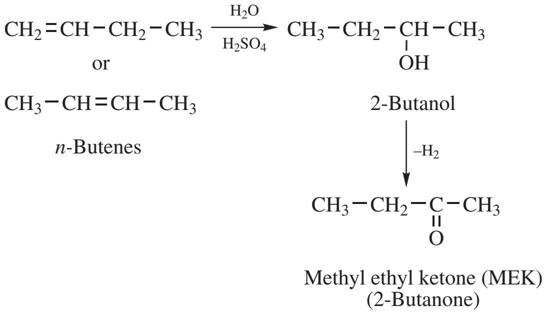
Pivalic acid

5.3 CHEMICALS AND POLYMERS FROM 1- AND 2-BUTENES

Most uses for the butenes are relatively low volume. Pure 1-butene plays an important role in the production of linear low-density polyethylene and to a lesser extent of high-density polyethylene (Section 3.1.1).

In combination with isobutene, the mixture of 1- and 2-butenes is polymerized to so-called polybutenes (Section 5.2.3). 1-Butene can be polymerized to poly(1-butene) with a Ziegler–Natta catalyst. Like the polypropylene of commerce (Section 4.5) it has an isotactic structure. Its advantages over polypropylene are that it is less prone to stress crack and has high-temperature tensile strength and less cold flow. Its major use, which is small, is in construction of pipes and vessels for handling and storing corrosive liquids at high temperatures and pressures. It is not useful in molding because of postcrystallization, which leads to shrinking.

Like propylene and isobutene, 1- and 2-butene mixtures can be hydrated with concentrated sulfuric acid to give 2-butanol.



Direct hydration, as with ethylene and propylene, is also possible (Section 3.9). 2-Butanol has a few minor uses as a solvent, but most of it is dehydrogenated to MEK, an important solvent for vinyl and nitrocellulose lacquers and acrylic resins. In the United States, a vapor-phase process with a zinc oxide or zinc-copper catalyst is used, while in Europe a liquid-phase reaction with finely divided nickel or copper chromite is preferred.

The mixture of 1- and 2-butenes (raffinate II) can also undergo the oxo reaction to give a mixture of pentanals and, more important, amyl alcohols. With the latest generation of oxo catalysts (bisphosphite-modified rhodium), hydroformylation of raffinate II gives *n*-valeraldehyde as the major product. Valeraldehyde can be converted to 2-propylheptanol, a C_{10} plasticizer range alcohol. Alternatively, the raffinate II can be dimerized to mixed octenes using IFP's Dimersol X process (Section 4.6), and then converted to C_9 plasticizer range alcohols via oxo chemistry (Section 4.12). The amyl alcohols are useful as solvents as such or as their esters. As described previously (Section 4.12), catalysts are available that lead to a high percentage of *n*-amyl alcohol from 1-butene.

Like propylene, 1- and 2-butenes have uses in gasoline, for they may be alkylated with isobutane to provide branched-chain structures (Section 2.2.5). Indeed, they are preferred to propylene for alkylate because they provide more highly branched molecules. They also may be components of polygas (Section 2.2.4). If the oligomerization takes place with propylene, heptenes are produced, which can be used as the basis for C_8 oxo alcohols (Section 4.12).

2-Butene is the starting material for a process, as yet uncommercialized, for isoprene (Section 6.2). It undergoes metathesis with ethylene to give propylene. This “on-purpose” route to propylene is discussed in Section 4.1.

A small amount of 1-butene is converted to butene oxide, a homologue of ethylene oxide, by epoxidation with a peracid. Like isobutene (Section 5.2.6) it forms aluminum derivatives such as tributylaluminum, a useful Ziegler–Natta catalyst.

1- and 2-Butenes may be dehydrogenated to butadiene (Section 5.1) at a temperature of 650°C in the presence of steam, which not only minimizes butadiene polymerization but also inhibits carbon deposition on the catalyst. The dehydrogenation is endothermic and thus a pressure of 0–1 bar is used at a contact time of 0.2 seconds. The catalyst comprises calcium nickel phosphate. Oxidative dehydrogenation is also possible, and is in fact preferred since it makes possible operation at lower temperatures of about 550°C with a fixed-catalyst bed. The hydrogen released reacts with oxygen to form water, an exothermic reaction that compensates for the heat lost by the endothermic dehydrogenation.

5.4 CHEMICALS FROM *n*-BUTANE

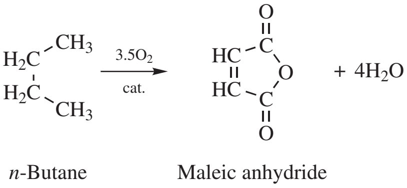
5.4.1 Acetic Acid

One of the earliest routes to acetic acid was based on the liquid-phase oxidation of hydrocarbons such as *n*-butane and light naphtha. This process is discussed in Section 10.5.2.2

5.4.2 Maleic Anydride

Both 1- and 2-butenes may be oxidized to maleic anhydride analogously to the oxidation of propylene to acrylic acid (Section 4.7), the 1-butene isomerizing to the more thermodynamically stable 2-butene. The original catalyst was vanadium pentoxide. Maleic anhydride traditionally has been prepared by the oxidation of benzene over the same catalyst (Section 7.5). A benzene shortage in the early 1970s motivated the development of an alternate route based on butenes, and the new route also had the advantage that two carbon atoms were not lost. *n*-Butenes are not as important for refinery reactions in Europe as they are in the United States, and therefore are not much more expensive than *n*-butane.

n-Butane, cheaper in the United States, was investigated as a feedstock for maleic anhydride and unexpectedly proved adequate. It was an early and successful example of alkane functionalization, a topic discussed in more detail in Chapter 11.



The pathway for the oxidation of 2-butene to maleic anhydride is analogous to the oxidation of propane to acrylic acid, but there is no analogous reaction involving the oxidation of a saturated hydrocarbon in reasonably high selectivity with only carbon dioxide and water as byproducts. The oxidation of *n*-butane or naphtha to acetic acid (Section 10.5.2.2) is not analogous because numerous byproducts are produced.

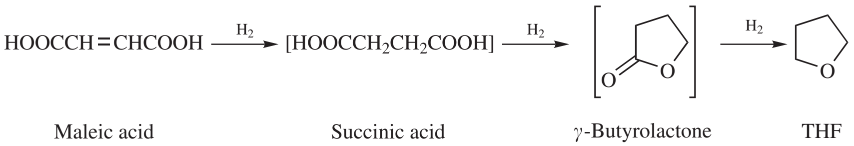
It is impressive that a catalyst system can be found that will oxidize methyl groups to carboxyls and insert a double bond while refraining from promoting C—C bonds scission. The reason is that maleic anhydride, with its conjugated double-bond system, is remarkably stable. The formation of an activated complex through which further oxidation could take place involves disruption of this conjugation and hence has a high activation energy.

By the early 1980s *n*-butane oxidation had become the preferred method for maleic anhydride manufacture. The reaction may be carried out either in a fixed or fluid-bed reactor, the latter requiring an attrition-resistant catalyst. The secondary products, as in ethylene oxidation to ethylene oxide (Section 2.7), are carbon dioxide and water. The fluid-bed reaction, instituted in Japan in the early 1990s, is carried out with a butane concentration in air of 4.5% at a temperature of 440°C with a contact time of about 11 seconds. The catalyst is based on vanadium pentoxide and various phosphoric acids. Other catalysts described in the patent literature contain boron, lithium, and zinc as activators.

Butane-based maleic anhydride processes are conventionally carried out without hydrocarbon recycle and thus maximum yield, not selectivity, is important. The nitrogen in air complicates recycle loops but, because no recycle is employed in this process, air can be used as the oxidant rather than expensive oxygen. Typical selectivities range from 50 to 52%. Mitsubishi and BOC are together developing the opposite approach. The oxidant is oxygen and butane is recycled so that butane conversion per pass is reduced but selectivity is increased.

Mitsubishi/BOC claim that the feedstock cost savings offset the increased cost of using oxygen and the increase in capital investment from the recycling equipment.

In the late 1990s, Du Pont developed a process to convert maleic acid to tetrahydrofuran (THF). Du Pont oxidizes butane to maleic anhydride and then isolates the product as an aqueous solution of maleic acid. The aqueous solution is subjected to hydrogenolysis to yield THF (Section 10.3.1) with a newly developed catalyst that makes possible the use of milder temperatures and pressures than are commonly required for hydrogenolyses.



Du Pont requires THF for oligomerization to a polybutene ether for use in their Spandex polymer. Spandex is a block copolymer comprising hard urethane blocks and flexible polyether blocks, useful for hosiery, swimsuits, sports clothes, and elastic in undergarments. Although it is an old polymer, its use increased rapidly in the late 1980s and early 1990s when pantyhose and tights became fashionable.

Maleic anhydride, which is produced at a level of about 700 million lb a year in the United States in the early 2000s, finds its greatest market in unsaturated polyester resins (Section 9.1.1). Its other important uses are conversion to fumaric acid for use as a food acidulant and in the formulation of agricultural chemicals (Section 6.3) and lube oil additives (Section 5.2.3). Its newest use is for conversion to 1,4-butanediol (Section 10.3.1).

NOTES AND REFERENCES

Butenes are known trivially as butylenes and this terminology is consistent with the terms ethylene and propylene. However, the systematic name butene has made deep inroads into industrial chemical literature. Therefore we use it here, along with the systematic names for the other higher olefins, like pentenes, hexenes, and so on.

The most recent specialist book in this area is J. Schulze and M. Homann, *C_4*-Hydrocarbons and Derivatives—*Resources, Production and Marketing*, Springer-Verlag, Berlin, 1989. It provides an authoritative overview of the technology, chemical engineering, marketing, and economics of the C_4 stream.

Statistics of MTBE production vary widely, and we have used the Nexant/Chemsystems data here in preference to *Chem. Eng. News* and *Guide to the Business of Chemistry.* This may affect the internal consistency of other data in this chapter derived from the last two sources.

One estimate indicates that 1.3 billion lb/year of butadiene was hydrogenated in Western Europe in 2000. This was intended to reduce the European surplus, which in the early 2000s did not develop because of increased demand in the United States. The technology of butadiene hydrogenation has been discussed by B. Torck, *Chem. Ind.* October 4, 1993, p. 742. This article also presents a valuable overview of the state of the C_4 market.

For a discussion of C_4 production processes and economics see Nexant Chemsystems' PERP report 01/02-3, Butadiene/Butylenes (February, 2003).

Section 5.1 Syndiotactic 1,2-polybutadiene is discussed by Y. Takeuchi *et al.*, in Chapter 3 of *New Industrial Polymers,* R. D. Deanin, Ed., American Chemical Society, ACS Symposium Series 4, Washington, DC, 1972.

Goodyear's seminal discovery in 1839 of how to make natural rubber practical by vulcanizing it with sulfur is well known. Less well known is that in southern Mexico and northern Central America the Olmecs were vulcanizing or curing rubber as early as the second millennium B.C. Subsequently, the Mayas, and later the Aztecs, took on this technology. When Cortez came to Mexico he was startled to see the natives playing a complex ball game with a solid rubber ball 8 in. in diameter, The ball bounced many feet into the air. The rubber was apparently cured by the juice of a morning glory vine that wrapped itself around the rubber tree. How convenient of nature that it placed the two components in such proximity. The critical components in the juice are apparently not clearly defined but traces of sulfonic acids and sulfonyl chlorides are present. The story is well told by Dick Teresi, *Lost Discoveries*, Simon & Schuster, New York, 2002, pp.337–340. The analysis of the morning glory juice is described by D. Hostler et al., *Science*, June 18, 1999, pp. 1988–1989.

Nexant Chemsystems' PERP report 99/00S13, *Chemicals from Butadiene* (January, 2001) presents of thorough overview of the commercially employed process technologies of the major derivatives of butadiene.

Section 5.1.2 A detailed discussion of the development of processes for HMDA manufacture has been provided by H. A. Wittcoff, *J. Chem. Educ.* **56**, 654 (1979).

The ICI dimerization of acrylonitrile is described in *Chem. Week*, March 7, 1990, p. 9, in European Patent Publication 0,352,007A2 (January 24, 1990), and in US Patent 4,958,042 (September 18, 1990). It is also discussed in three West German Offen. 2,694,904 (May 17 1977); 2,720,279 (November 24, 1977); and 2,721,808 (December 8, 1977). Related work by Halcon is described in West German Offen. 2,559,185-7 (July 1, 1976).

The Du Pont process for preparing HMDA by the hydrocyanation of butadiene is described in US Patents 4,339,395 (July 13, 1982) and 4,080,374 (March 21, 1978). It is also described by V. D. Luedeke in *Encyclopedia of Chemical Processing and Design*, Vol. 2, J. J. McKetta and W. A. Cunningham, Eds., Dekker, New York, 1977, p. 146.

Patents describing the coproduction of caprolactam and HMDA include US Patents 5,151,543 (September 29, 1992) to Du Pont and 5,496,941 (March 5, 1996) to BASF and World Patent 96/20931 (July 11, 1996) to BASF.

The ammoxidation of methylcyclohexane is described in US Patent 3,624,125 (November 30, 1971) to Imperial Chemical Industries (now ICI). Also described is the ammoxidation of cyclohexane [West German Offen. 1,807,354 (July 3, 1969)]. In fact, it is the cyclohexane that undergoes ammoxidation, the methylcyclohexane being dehydroalkylated in the process.

The mechanism for the hydrodimerization of acrylonitrile is explained well by D. Pletcher, *Industrial Electrochemistry*, 2nd ed., Chapman & Hall, London, 1990 (paperback, Blackie, 1993).

Section 5.1.3.1 The preparation of 1,5-hexadiene and 1,9-decadiene have been described in three patents; Great Britain Patent 1,482,745 (August 10, 1977) to Shell Research; US Patent 3,792,102 (February 12, 1984) and US Patent 3,878,262 (April 15, 1975) both to Phillips Petroleum.

The Dow process for conversion of butadiene to styrene involves dimerization of butadiene to vinylcyclohexene followed by an oxidative dehydrogenation of the vinylcyclohexene to styrene. The dimerization is catalyzed by copper loaded Y zeolite. The oxidative hydrogenation uses proprietary mixed-oxide catalysts. A DSM process has three steps, the first being dimerization and the second dehydrogenation to ethylbenzene followed by further dehydrogenation to styrene. The first dehydrogenation uses a Pd/MgO catalyst. The ethylbenzene–styrene conversion is conventional. Typical patents are US Patents 5,196,621 (March 23, 1993) and 5,329,057 (July 12, 1994) and World Patent 94/01385 (January 20, 1994), all to Dow Chemical Co.

Section 5.1.3.2 The dimerization of butadiene to 1,5-cyclooctadiene is described in US Patent 3,250,817 (May 10, 1966) to Chevron Research. The reaction is also discussed by P. W. Jolly and G. Wilke, *The Organic Chemistry of Nickel*, Vol. 2, Academic Press, New York, 1975.

Section 5.1.3.3 Trichloromethylsulfenyl chloride is made by perchlorination of methyl mercaptan or dimethyl sulfide:

$$CH_3OH \xrightarrow{H_2S} \underset{\text{Methyl mercaptan}}{CH_3SH} \xrightarrow[\text{Fe cat.}]{\text{Air}} \underset{\text{Dimethyl sulfide}}{CH_3S-SCH_3} \xrightarrow{\text{Perchlorination}} \underset{\text{Trichloromethylsulfenyl chloride}}{ClS-CCl_3}$$

Section 5.1.3.4 BASFs process for adipic acid by the dicarbonylation of butadiene is described in numerous patents including US Patent 4,310,686 (January 12, 1982); US Patent 4,360,695 (November 23, 1982); US Patent 4,350,572 (September 21, 1982); and West German Offen. 2,630,086 (January 12, 1978); and 2,646,955 (April 20, 1978). Rhone Poulenc's work on converting butadiene to adipic acid is described in US Patents 5,625,096 (April 29, 1997) and 5,312,979 (May 17, 1994). Butadiene-based approaches to adipic acid are described in joint patents to Du Pont and DSM, European Patent 0 662 467B1 (May 6, 1998) and US Patents 5,710,325 (January 20, 1998) and 5,840,959 (November 24, 1998).

Section 5.1.3.6 The mechanism of the formation of *trans*-1,4-Hexadiene is described by G. W. Parshall, *Homogeneous Catalysis*, John Wiley & Sons, Inc. New York, 1980, pp. 63–65.

Section 5.1.3.7 The BP Amoco route to 2,6-dimethylnaphthalene is described in US Patents 4,990,717 (February 5, 1991), 5,073,670 (December, 17, 1991), and

5,510,563 (April 23, 1996). 2,6-Dimethylnaphthalene is the key material in the production of the corresponding diacid, 2,6-naphthalene dicarboxylic acid. Because of the complicated multistep chemistry used in the BP Amoco process, the resulting dicarboxylic acid product is expensive and is inhibiting the growth of poly(ethylene naphthalate).

Section 5.1.3.8 Patents describing the direct oxidation of butadiene to the corresponding monoepoxide include US Patents 5,362,890 (November 8, 1994) and 5,312,981 (May 17, 1994) both to Eastman Chemical.

Section 5.2.1 The isomerization of butenes to isobutene is described in two patents to ARCO, US Patent 4,778,943 (October 18, 1988) and 4,654,463 (March 31, 1987).

Section 5.3 The direct hydration of *n*-butenes to 2-butanol is described in German Offen. 3,512,518-A1 (October 9, 1986), to Deutsche Texaco AG.

Section 5.4 The Du Pont process for achieving high yields of maleic anhydride is described in US Patents 4,371,702 (February 1, 1983) and 4,442,226 (April 10, 1984) and in European Patent Appl. 0,189,261 A1 (July 30, 1986).

CHAPTER 6

CHEMICALS AND POLYMERS FROM THE C_5 STREAM

The C_5 olefins are not a major source of chemicals, and US consumption in 2002 was less than one billion lb. Consumption in Western Europe and Japan is considerably less. Demand for isoamylene (a mixture of 2-methyl-2-butene and 2-methyl-1-butene also known as isopentenes) for conversion to the octane improver *tert*-amyl methyl ether (TAME) was expected to increase. With the likely demise of MTBE (Section 5.2), the fate of similar fuel oxygenates such as TAME is also in jeopardy.

Like propylene and the C_4 olefins, the C_5 olefins are produced by both catalytic and steam cracking (Sections 2.2.1, 2.2.2). Just as catalytic cracking produces butenes but no butadiene, it produces pentenes but practically no diolefins such as isoprene and cyclopentadiene. The steam cracking of naphtha or gas oil, on the other hand, produces isoprene equivalent to 2.5% of the ethylene formed. The C_5 fraction from gas oil cracking as well as from high-temperature naphtha cracking contains more cyclopentadiene (15–25%) than isoprene (which is present to the extent of 10–15%). The former results from the temperature-induced cyclization of the latter. From naphtha cracked at lower temperatures, consequently, there is more isoprene than cyclopentadiene.

Steam cracking of liquids produces a fraction called pyrolysis gasoline (Section 2.2.1), which contains both the C_5 olefins and an aromatic fraction. It may all be sent to the gasoline pool, usually after hydrogenation of the double bonds. Alternatively, the C_5 fraction is recovered by distillation, and the remainder hydrotreated to remove any remaining olefins. After this it is processed like catalytic reformate

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

(Section 2.2.3) to remove benzene and toluene. The residue is then sent to the gasoline pool.

Since the United States has cracked ethane and propane predominantly, pyrolysis gasoline has not been a major source of C_5 olefins, which accounts for the fact that in 2001 only 436 million lb of isoprene were produced.

The number of hydrocarbon isomers increases with increasing chain length. One can list 3 pentanes, 6 pentenes plus cyclopentane and methylcyclobutane, 6 pentadienes plus cyclopentene, methylcyclobutanes, cyclopentadienes, and so on. In the C_5 fraction, there are appreciable quantities of 11 components as shown in Figure 6.1. Of these, isoprene and cyclopentadiene are isolated as pure compounds.

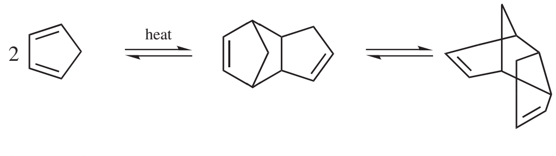
The isopentenes (methylbutenes) are isolated as mixed isomers. One use is dehydrogenation to isoprene. Isopentane can also be dehydrogenated to isoprene, and this is believed to be done in the CIS. Synthetic natural rubber (Section 5.1) is more important there than in the United States. For dehydrogenation, the olefin–alkane mixture can be used, the olefin dehydrogenating first. In the United States, the 3-methyl-1-butene is isomerized to 2-methyl-2-butene and 2-methyl-1-butene. These may be extracted as mixed isomers as described below, just as isobutene is isolated from the C_4 olefin fraction.

Isopentane is not isolated from the C_5 cracking fraction because separation from C_5 olefins is too difficult. Instead it is obtained from the C_5 fraction of straight run gasoline (Section 2.1). The separation of isopentane from C_5 olefins can be brought about with molecular sieves, but this process is not yet practiced industrially. The separation from *n*-pentane is brought about either by distillation or with molecular sieves. Isopentane is useful as a solvent.

6.1 SEPARATION OF THE C_5 STREAM

The separation of the many C_5 components is difficult and is done differently around the world. Figure 6.2 provides a conceptualized scheme, which combines processes used in several refineries.

Cyclopentadiene must be removed first because it polymerizes and can foul the reboilers of the downstream distillation columns. Its isolation depends on a facile and reversible dimerization that takes place when the remaining C_5 fraction is heated at 100°C for 2–3 hours or at 150°C under pressure for a shorter period. The dimer, dicyclopentadiene, forms by a Diels–Alder reaction and normally has the endo form. Since it boils 130°C higher than the monomer, it is readily separated from the other components by vacuum distillation. At 350°C in a tubular reactor, the monomer is rapidly regenerated.



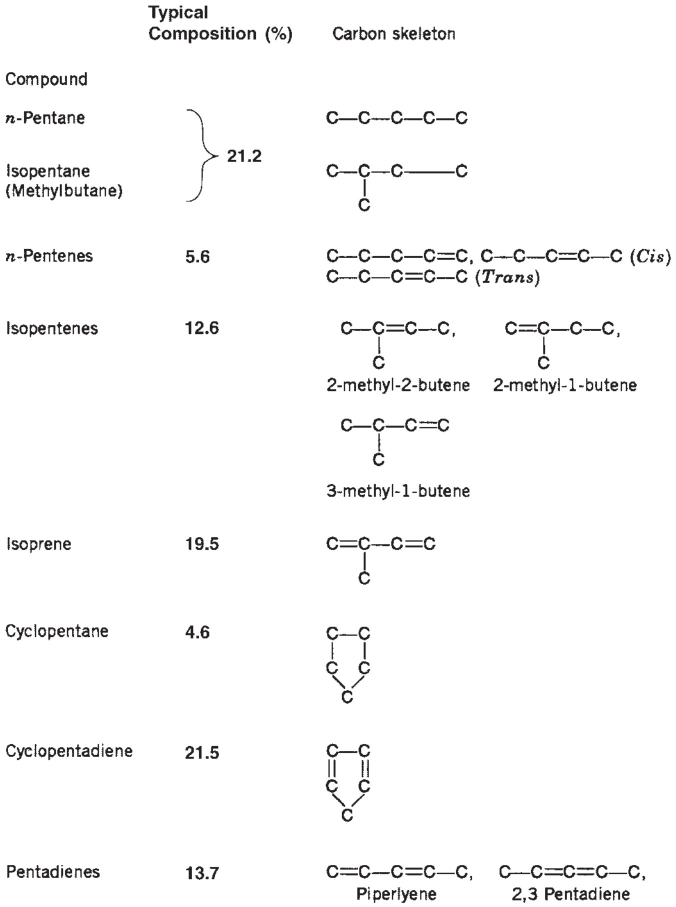


FIGURE 6.1 Components of the C_5 fraction and typical composition of standard severity steam cracking of naphtha, C_5 stream (balance of 1–3% is C_6^+).

Isoprene is removed next, by extractive distillation with an aprotic solvent such as acetonitrile or *N*-methylpyrrolidone. Almost all the alkanes and most of the olefins distil overhead, while the solvent, the diolefins, and the C_5 acetylenes appear at the bottom of the column. Successive distillations of this bottom stream regenerate the solvent for recycle, split the hydrocarbon stream into acetylenes and diolefins, and split the diolefins into isoprene and piperylene (1,3-pentadiene). Polymerization grade isoprene requires a further distillation for adequate purification.

The overhead stream from the extractive distillation can be further distilled to give 1-pentene, isopentenes (methylbutenes), and a mixture of the remaining C_5 alkanes and olefins. The isopentenes, mainly 3-methyl-1-butene, are isomerized by 65% sulfuric acid primarily to 2-methyl-2-butene $(CH_3)_2C{=}CHCH_3$, and to a

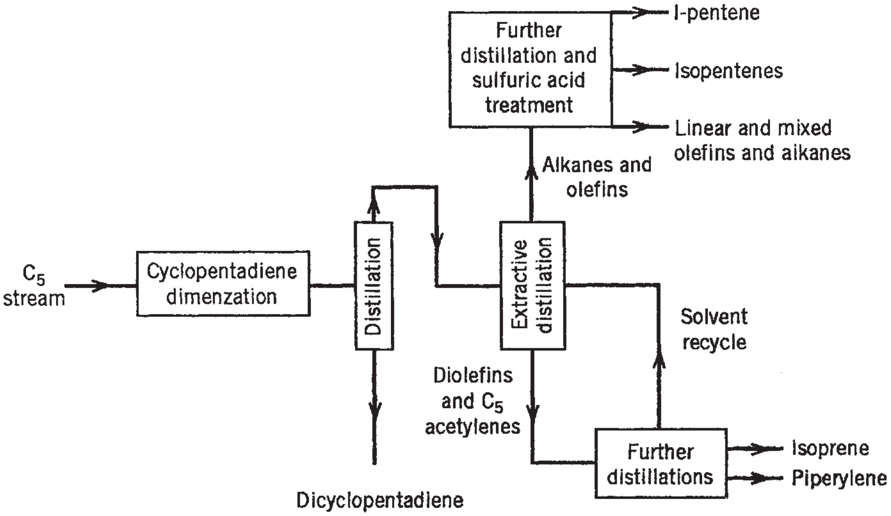


FIGURE 6.2 Conceptualized scheme for separation of mixed C_5 stream.

lesser extent to 2-methyl-1-butene, $CH_2{=}C(CH_3)CHCH_3$. These react readily with water in the presence of sulfuric acid at 0–10°C to yield a tertiary alcohol, 2-methyl-2-butanol, just as isobutene does in the process for separating the C_4 olefins (Section 5). The 2-methyl-2-butanol is separated and heated to 350°C to regenerate the alkene. The methylbutanol can be dehydrogenated to isoprene with a catalyst based on iron, chromium oxides and potassium carbonate at 60°C. Selectivity is 85% at 35% conversion. Just as with isobutene, methanol may be used instead of water (Section 5.2.1). With 2-methyl-2-butene, TAME results (Section 5.2).

$$\underset{\text{2-Methyl-2-butene}}{(CH_3)_2C{=}CHCH_3} + CH_3OH \longrightarrow \underset{\text{TAME}}{(CH_3)_2C(OCH_3)CH_2CH_3}$$

The residual C_5 stream contains linear and mixed olefins. They can be separated without difficulty but there is little demand for them. The mixture can be polymerized to give an inexpensive hydrocarbon resin (Section 6.3) useful in coatings and adhesives.

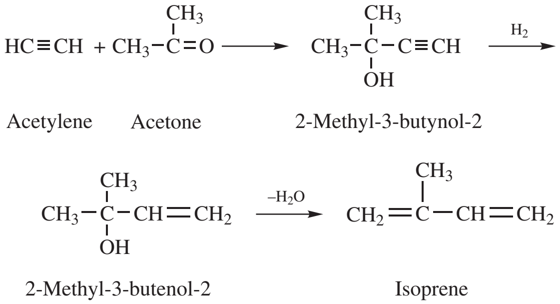
Exxon Chemical developed a catalyst that could crack TAME to give isoamylene (a mixture of 2-methyl-2-butene and 2-methyl-1-butene) and methanol. This reaction is a convenient way to separate isoamylene from other close boiling C_5 olefin components. The 2-methyl-1-butene can be isomerized to desired 2-methyl-2-butene.

Exxon Chemical is believed to use these techniques to extract high purity 2-methyl-2-butene for use in tackifier resins.

6.2 ISOPRENE

There are three possible sources of isoprene starting with the C_5 fraction, all mentioned in Section 6.1. The first is isolation from the C_5 fraction from steam cracking; the second is dehydrogenation of isopentenes; and the third is dehydrogenation of isopentane.

There are several synthetic routes to isoprene. In an Italian process devised by Snamprogetti and still in use, acetylene reacts with acetone to yield 2-methyl-3-butyn-2-ol. Hydrogenation gives 2-methyl-3-butenol, which on dehydration provides isoprene.



$$HC{\equiv}CH + CH_3-\overset{CH_3}{C}=O \longrightarrow CH_3-\underset{OH}{\overset{CH_3}{C}}-C{\equiv}CH \xrightarrow{H_2}$$

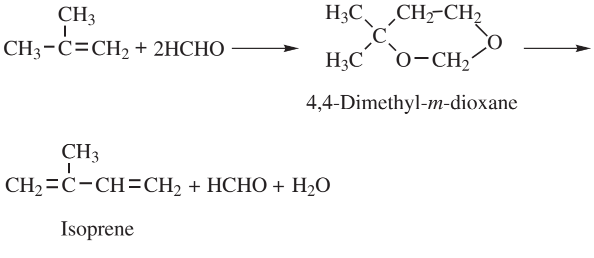
Acetylene Acetone 2-Methyl-3-butynol-2

$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH=CH_2 \xrightarrow{-H_2O} CH_2=\overset{CH_3}{C}-CH=CH_2$$

2-Methyl-3-butenol-2 Isoprene

The condensation of acetylene and acetone is carried out in liquid ammonia at low temperatures with potassium hydroxide as the catalyst. The hydrogenation must be carried out selectively so that a double bond forms. This is reminiscent of the hydrogenation of 1,4-butynediol to 1,4-butenediol (Section 10.3.1). The dehydration goes well at 250–300°C with alumina.

A second process, devised by the Institut Français du Pétrole and said to be used in the CIS, involves the reaction of isobutene with formaldehyde, via the Prins reaction, to give dimethyl-*m*-dioxane, which can be cracked to isoprene.



$$CH_3-\overset{CH_3}{C}=CH_2 + 2HCHO \longrightarrow$$

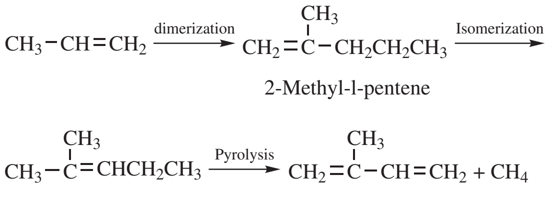
4,4-Dimethyl-*m*-dioxane

$$CH_2=\overset{CH_3}{C}-CH=CH_2 + HCHO + H_2O$$

Isoprene

The Prins reaction is catalyzed by strong acid or acid ion exchange resin. Raffinate I (Section 5.1) may be used instead of pure isobutene. The second step of the reaction requires a high temperature with a phosphoric acid–charcoal or calcium phosphate catalyst with water.

Another synthetic process, used only briefly by Goodyear because it proved uneconomical, involves the dimerization of propylene to 2-methyl-1-pentene (Section 4.6). The reaction goes in 90% yield at about 300°C and elevated pressures with a tri-*n*-propylaluminum catalyst. The dimer is isomerized at about 100°C with a silica–alumina catalyst to the more stable 2-methyl-2-pentene, which in turn is demethanated to isoprene and methane at 660°C in the presence of superheated steam and catalytic amounts of hydrogen bromide.



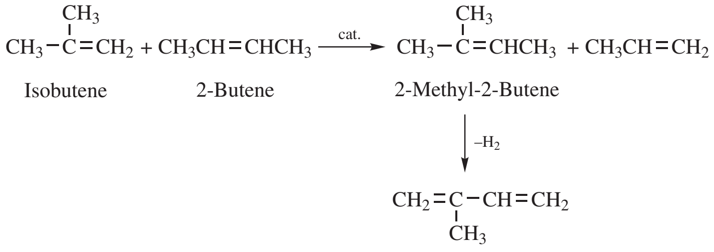
$$CH_3{-}CH{=}CH_2 \xrightarrow{\text{dimerization}} CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH_2CH_2CH_3 \xrightarrow{\text{Isomerization}}$$

2-Methyl-l-pentene

$$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2CH_3 \xrightarrow{\text{Pyrolysis}} CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}CH{=}CH_2 + CH_4$$

2-Methyl-2-pentene Isoprene

An attractive process for isoprene formation, which has never been commercialized, involves a metathesis reaction between isobutene and 2-butene to yield propylene and 2-methyl-2-butene which, as indicated above, can be dehydrogenated to isoprene.



$$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 + CH_3CH{=}CHCH_3 \xrightarrow{\text{cat.}} CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_3 + CH_3CH{=}CH_2$$

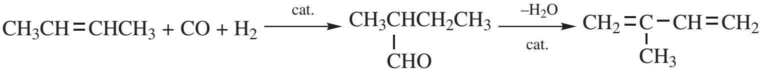
Isobutene 2-Butene 2-Methyl-2-Butene

$$\Big\downarrow {-H_2}$$

$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2$$

Isoprene

A clever synthesis of isoprene, also not commercialized, involves the hydroformylation of 2-butene with a rhodium catalyst such as rhodium (cyclooctadiene) acetylacetonate with triphenylphosphine at 115°C and 8 bar. A branched aldehyde, 2-methylbutanal, results.

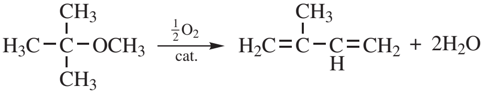


$$CH_3CH{=}CHCH_3 + CO + H_2 \xrightarrow{\text{cat.}} CH_3\underset{\substack{|\\ CHO}}{C}HCH_2CH_3 \xrightarrow[\text{cat.}]{-H_2O} CH_2{=}\underset{\substack{|\\ CH_3}}{C}{-}CH{=}CH_2$$

2-Butene 2-Methylbutanal Isoprene

With a cobalt catalyst, a linear compound would form because cobalt facilitates migration of the double bond to the terminal position, a property important in the hydroformylation step of the Shell SHOP process (Section 3.3.4). The 2-methylbutanal is dehydrated with crystalline boron phosphate catalyst. Conversion to isoprene is 80%, with 85% selectivity. A proposed mechanism for the dehydration is shown in Figure 6.3. It is unusual for aldehyde groups to participate in this type of dehydration reaction.

Yet another route to isoprene that has been under investigation is Sumitomo's air oxidation of MTBE using molybdenum, tungsten, or vanadium oxide catalysts.



$$H_3C{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}{-}OCH_3 \xrightarrow[\text{cat.}]{\frac{1}{2}O_2} H_2C{=}\overset{\substack{CH_3\\ |}}{C}{-}\underset{H}{C}{=}CH_2 + 2H_2O$$

MTBE Isoprene

The major use for isoprene is its stereospecific polymerization to *cis*-1,4-polyisoprene, a polymer closely related to natural rubber. Its preparation was not possible prior to the advent of Ziegler–Natta catalysis. The catalyst may comprise a titanium tetrachloride–trialkylaluminum combination or an alkyl lithium. Modern radial ply tires require increased amounts of natural rubber because it has greater resilience and lower hysteresis losses (i.e., less heat build-up) than styrene–butadiene rubber. The demand can be satisfied with synthetic *cis*-1,4-polyisoprene, provided that it is competitive in price with natural rubber.

The second important use for isoprene is in styrene–isoprene–styrene (S–I–S) block copolymers similar to S–B–S copolymers (Section 5). These thermoplastic elastomers contain about 85% isoprene and 15% styrene and are used in applications where elasticity combined with easy processing is desired. These include bitumen–asphalt modification, adhesives, sealants, and coatings, polymer modification, and polymers for footwear soles and heels. The S–I–S block copolymers are made commercially in a semicontinuous process (the polymerizations are carried out batchwise while the polymer and solvent recovery stages are run continuously). Batch polymerizations make it easier for the producer to control the extent of polymerization and provides flexibility for production of various product grades. The heart of the process is the block polymerization reaction, which can be divided into three separate stages: styrene polymerization, diene polymerization, and finally coupling of the "living" polymer chains (Section 15.3.7). In the first polymerization stage, styrene is polymerized in cyclohexane with butyllithium as the initiator. After about an hour, the resulting polystyryllithium living

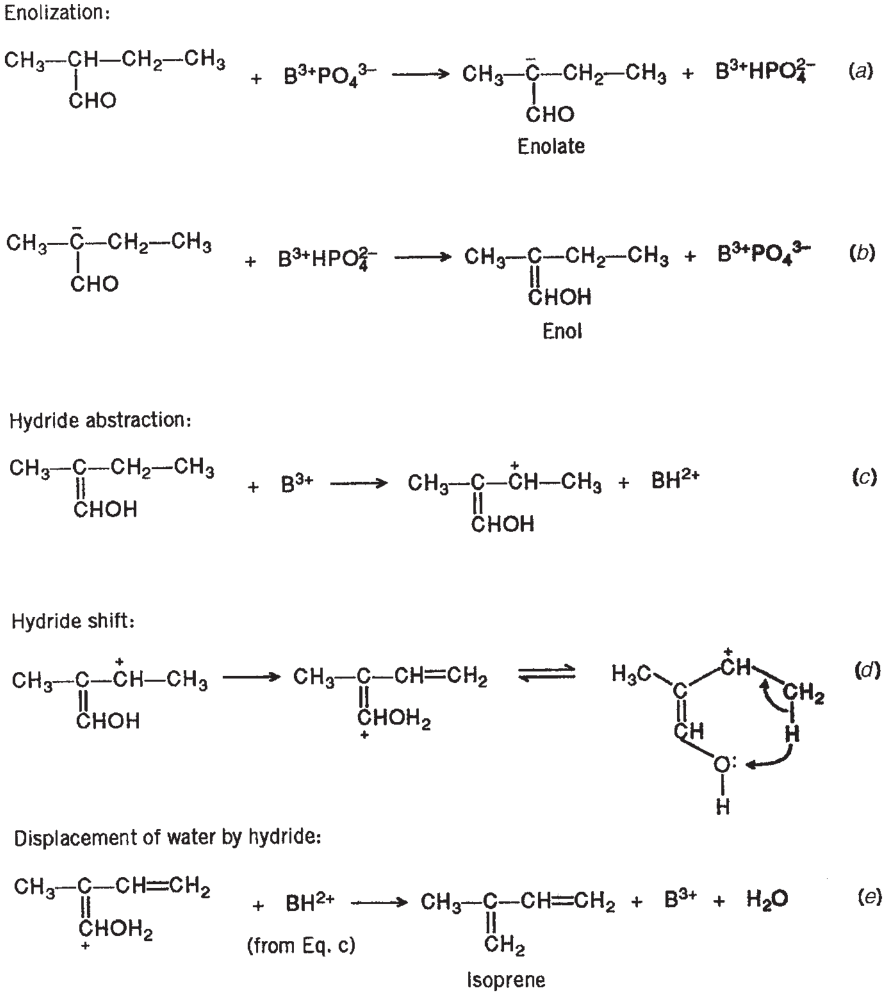
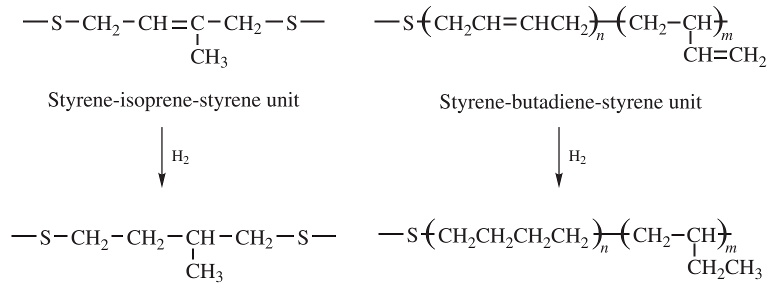


FIGURE 6.3 Proposed mechanism for the production of isoprene by dehydration of 2-methylbutanal.

polymer solution is transferred rapidly into a separate reactor containing isoprene (or butadiene) in cyclohexane. Isoprene polymerization is initiated via the polystyryllithium and is completed in about two hours. At this stage, a two-block polystyrene–polyisoprenyllithium species is present. Finally, the S–I–S block copolymer can be made in one of two different ways. In one way, the two-block copolymer is coupled with a coupling agent such as dibromoethane. In the other, the additional styrene is added to the living two block copolymer to give a linear three block polystryrene–polyisoprene–polystyrene copolymer.

An extension of S–B–S and S–I–S technology is the partial hydrogenation of the polymers to produce styrene–ethylene–butenes–styrene (S–E–B–S) and styrene–ethylene–propylene–styrene (S–E–P–S), respectively (S = Styrene unit):



Styrene-isoprene-styrene unit

Styrene-butadiene-styrene unit

Styrene-ethylene-propylene-styrene unit

Styrene-ethylene-butene-styrene unit

These partially hydrogenated polymers were initially developed by Shell using a high pressure hydrogenation step, but they sold the business in 2001. Kuraray is reportedly working on a lower cost process employing low pressure hydrogenation technology. The hydrogenated derivatives have the advantage of increased weather and temperature resistance.

Another use for isoprene is in the manufacture of butyl rubber, a copolymer of isobutene and 3–5% isoprene (Section 5.2.2), which shows very low gas permeability and thus is useful to line tires.

A small volume isoprene derivative is *trans*-1,4-polyisoprene. The *trans* double bond makes the molecule crystalline, removing all the elastomeric properties of the *cis* isomer. The product resembles two natural materials, balata and gutta percha, and is useful for golf ball covers. This use has declined because of the superior properties of ionomers such as “Surlyn” (Section 3.2.3). Gutta percha is still used by dentists for temporary fillings for teeth, particularly in “root canal” work. Balata and gutta percha are both polyisoprenes and are believed to be stereoisomers.

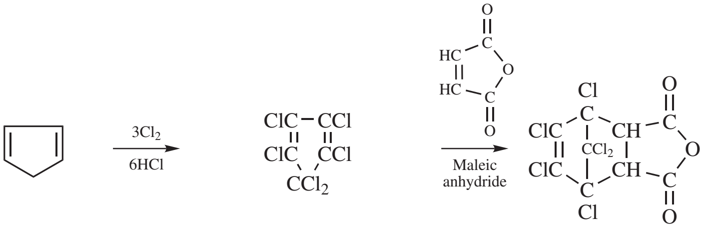
6.3 CYCLOPENTADIENE AND DICYCLOPENTADIENE

Cyclopentadiene is typically the largest component in the C_5 stream from standard severity steam cracking of naphtha and accounts for 15–25% of the total C_5 fraction. It also occurs in distillate from coke ovens. Like butadiene, it is not formed in catalytic cracking. The US production in 2002 is estimated at about 400 million lb.

Owing to the difficulty of separating cyclopentadiene from the other close boiling C_5 olefins in the C_5 stream, it is usually recovered as its dimer, dicyclopentadiene (Section 6.1).

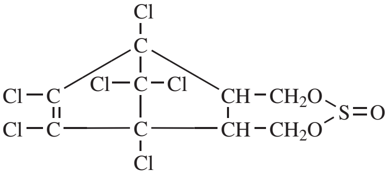
The main use for cyclopentadiene is in the formulation of inexpensive low molecular weight (under 2000) oligomers, which fall into the category of hydrocarbon resins. There are two types, linear aliphatic and cycloaliphatic. The former are made from unsaturated C_5 cuts containing primarily piperylene (1,3-pentadiene) and pentenes. The cycloaliphatics contain these and cyclopentadiene. The resins are used in thermoplastic and contact adhesives and in printing inks. In rubber formulations, they increase hardness and flex life.

The liquid-phase chlorination of cyclopentadiene provides hexachlorocyclopentadiene, which undergoes a Diels–Alder reaction with maleic anhydride to form so-called chlorendic anhydride, used as a flame retardant in unsaturated polyester resins (Section 9.1.1).



Cyclopentadiene Hexachlorocyclopentadiene Chlorendic anhydride

Hexachlorocyclopentadiene undergoes a similar Diels–Alder reaction with 1,4-dihydroxy-2-butene (Section 10.3.1) to give a diol adduct, which reacts with thionyl chloride to give the insecticide, endosulfan.



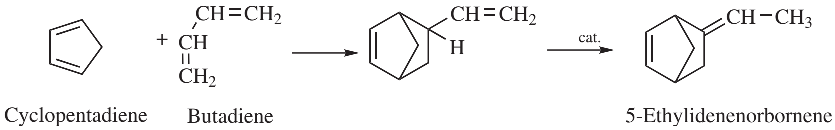
Endosulfan

Like most organochlorine compounds, endosulfan is suspect because its persistence leads to its accumulation in the food chain and subsequently in body fat.

An emerging application for cyclopentadiene is as a starting material for monomers for use in cyclic olefin copolymers (COCs). The COCs are amorphous transparent polymers made via copolymerization of ethylene with cyclic olefin monomers such as norbornene and tetracyclododecene. Norbornene is made by the Diels–Alder reaction of ethylene and cyclopentadiene, while tetracyclododecene is made by the Diels–Alder reaction of cyclopentadiene and norbornene. It is believed that COCs, because of their good optical and physical properties, may present a lower cost alternative to polycarbonate for CD–ROMs, although commercialization has been slow.

The main use for dicyclopentadiene is in unsaturated polyester resins (Section 9.1.1), where it terminates the maleate ester chains. In addition, dissociated cyclopentadiene participates in Diels–Alder reactions with the double bonds in the unreacted maleate esters. The result is a low viscosity resin with high strength. Because of this low viscosity, not as much styrene need be added to give a low viscosity easy-to-apply resin. The styrene can be thought of as a "reactive diluent," and the system is more environmentally friendly. The product is said to be more brittle but to have a smoother surface.

Because dicyclopentadiene has two double bonds of varying reactivity, it can be used as a monomer in ethylene–propylene diene monomer elastomers (Section 3.2.5). In this application, it competes with *trans*-1,4-hexadiene (Section 5.1.3.6.) and 5-ethylidenenorbornene. The latter results from a Diels–Alder condensation of cyclopentadiene and butadiene. The adduct is isomerized with an alkaline earth metal catalyst to 5-ethylidenenorbornene.



In all these compounds, the active double bond enters into the copolymerization, leaving the less active double-bond pendant for cross-linking or vulcanization with sulfur-containing compounds.

In an interesting application, dicyclopentadiene is a monomer for the production of a thermoset polymer useful in reaction injection molding (RIM). In conventional injection molding, the size of moldings made from viscous polymers like polyethylene is limited by the amount of pressure available to push the molding compound into the mold. In RIM, low molecular weight components react in a mold almost instantaneously. The advantage is that large moldings can be made. Dicyclopentadiene undergoes ring-opening metathesis polymerization (Section 2.2.9) in the mold in the presence of a catalyst comprising tungsten hexachloride in *p-tert*-butylphenol to give a cross-linked polymer.

Dicyclopentadiene can be oxidized to maleic anhydride but this reaction has never been commercialized.

6.4 PENTENE-1 AND PIPERYLENE

Pentene-1, while present in C_5 steam cracker streams, is rarely isolated. However, a much larger source of pentene-1 is available in Sasol's Fischer–Tropsch "Synthol" stream (Section 12.2). The uniqueness of olefins in the Synthol stream is that a large percentage are linear α-olefins with both odd and even numbers of carbon atoms. Ethylene oligomerization, the conventional route to α-olefins, gives only even carbon numbered compounds (Section 3.3.2). Pentene-1 has potential application as a comonomer in linear low-density polyethylene, but because of the historical lack of supply and even now only a single supplier, adoption of pentene-1 as a comonomer has been very slow. Piperylene (1,3-pentadiene) finds use almost exclusively in premium aliphatic hydrocarbon resins.

NOTES AND REFERENCES

Section 6.1 Separation technologies for C_5's are discussed in Nexant Chemsystems' Process Evaluation/Research Planning (PERP) report 98/99S4, Options for Refinery C_5's (September, 1999). ExxonMobil's isoamylene process is covered in US Patents 4,714,788 (December 22, 1987) and 4,691,073 (January 9, 1987).

Section 6.2 The process for isoprene production via 2-methylbutanal is covered in European Patent Appl. 0,080,449 (January 6, 1983) to Monsanto. The chemistry, process technology, production economics, and end-use markets for isoprene are discussed in Nexant Chemsystems' Process Evaluation/Research Planning (PERP) report 98/99S2, *Isoprene* (September, 1999).

Section 6.3 The use of polycyclopentadiene in reaction injection molding is described in US Patent 4,400,340 (August 23, 1983) to Hercules. The chemistry, process technology, production economics, and end-use markets for cyclopentadiene are discussed in Nexant Chemsystems' Process Evaluation/Research Planning (PERP) report 97/98S7, *Dicyclopentadiene and Derivatives* (August, 1998).

CHAPTER 7

CHEMICALS AND POLYMERS FROM BENZENE

In the United States, most benzene comes from the catalytic reforming of naphtha (Section 2.2.3), which yields a mixture of benzene, toluene, and the xylenes (BTX). Benzene is also a volatile byproduct of the conversion of coal to coke. Benzene from coke oven distillate is available only to the extent that coke is required by the steel industry, and this has not expanded to accommodate the expanding benzene market. Furthermore, such benzene contains sulfur-based impurities such as thiophene that can be removed only with difficulty, and these render it unacceptable for many purposes. In 1949, all US benzene was produced from coal tar; by 1959 the proportion had dropped to 50%. In 1972 it was down to only 6.4%, and in the early 2000s it was less than 2%.

That is not the whole story, however. In Europe and Japan, pyrolysis gasoline, (Section 2.2.1) is the major source of benzene and toluene. It results from the steam cracking of hydrocarbons, particularly naphtha and gas oil. Xylenes also occur in pyrolysis gasoline but are not easily isolated because of a high concentration of ethylbenzene. In the United States, only 24% of benzene comes from this source. Figure 7.1 shows the sources of benzene in the United States and Western Europe. Somewhat more benzene comes from coke oven distillate in Europe than in the United States.

Catalytic reforming typically leads to a BTX mixture containing 50–55% toluene, 30–35% xylenes, but only about 10–15% benzene, the end product most in demand for chemical production. Toluene and the xylenes, on the other hand, have been favored for raising the octane number of unleaded gasoline, and they are less toxic than benzene.

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

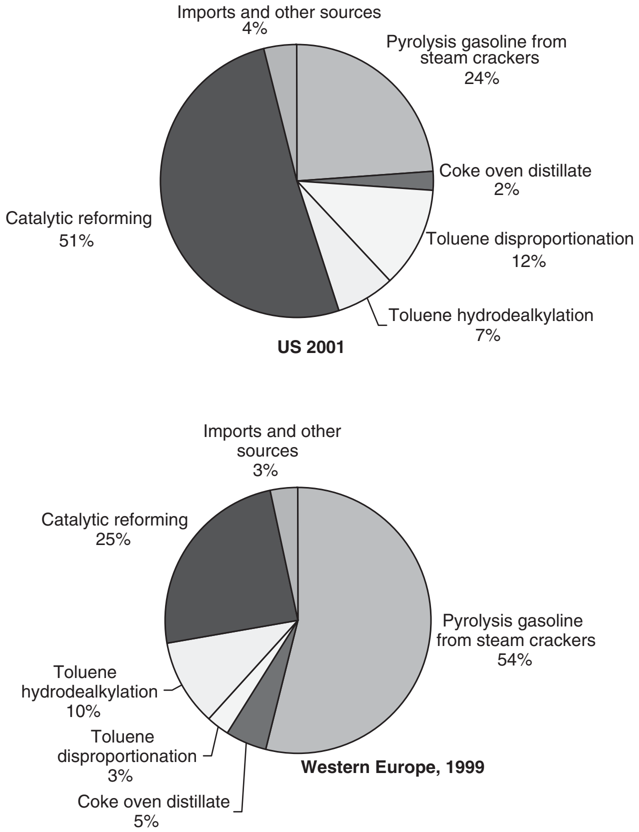


FIGURE 7.1 Sources of benzene in United States and Western Europe.

Since there have always been large surpluses of chemical toluene, a process was devised to convert toluene to benzene by hydrodealkylation (Section 8.1). In 2001 this accounted for about 7% of the United States and 11% of Western European toluene consumption, down from 24 and 28%, respectively, in the early 1990s. The amount of toluene hydrodealkylated fluctuates partly because it is a function of the price differential between benzene and toluene. Toluene must be at least 15% cheaper to warrant hydrodealkylation. Hydrodealkylation also assumed less importance in the United States by the early 2000s because it was largely replaced by toluene disproportionation (Section 8.1). This shift was motivated by the fact that disproportionation provides *p*-xylene, the demand for which has burgeoned in the Far East since the late 1980s as feedstock for terephthalic acid for poly(ethylene terephthalate). In 2001, toluene disproportionation provided 12% of United States benzene but still only 3% in Western Europe.

The US Clean Air Act, which came into effect in 1995, changed the aromatics supply picture. It stipulates that benzene in gasoline must be decreased to 1% and the remaining aromatics content must be no greater than 25%. In 1990, gasoline contained as much as 3% benzene and 36% total aromatics. This means that catalytic reforming (Section 2.2.2) will have to be carried out as usual for BTX for the chemical industry.

For gasoline, naphtha, stripped of the C_5 and C_6 fraction, must be lightly reformed to produce as little benzene as possible (see note at the end of this chapter).

Pyrolysis gasoline from steam cracking (Section 2.2.1) is yet another source of benzene and toluene. It also contains xylenes but they are not easily isolated because of high concentrations of ethylbenzene. In the United States, about 20% of benzene comes from this source (Section 8.1). The remainder of the benzene the United States uses comes from imports. The pattern is shown in Figure 7.1.

As the figure indicates, the picture in 2001 in Western Europe is quite different. Pyrolysis gasoline is much more important and accounts for 54% of benzene consumption. Toluene hydrodealkylation accounts for about 10% and much of this toluene is also derived from pyrolysis gasoline. Toluene disproportionation accounts for 3% and catalytic reforming—the major source in the United States—for 25%. Slightly more benzene comes from coke oven distillate than in the United States.

In 2002, about 20 billion lb of benzene was used in the United States as a chemical feedstock as compared to 33 billion lb of propylene (Section 1.5). The corresponding figures for Western Europe were 17 and 33 billion lb. This makes benzene the third most important basic chemical.

The major uses for benzene are shown in Figure 7.2. In addition to these, we shall discuss a number of small volume chemicals from benzene. The biggest use for benzene is its reaction with ethylene to give ethylbenzene for dehydrogenation to styrene (Section 4.6) and for peroxidation to ethylbenzene hydroperoxide for propylene oxide and styrene (Section 4.6). These processes have already been described. Next is its reaction with propylene to give cumene for conversion to phenol and acetone (Section 4.9). In 2002, ethylbenzene and cumene accounted for 74% of the total benzene consumption. In contrast to the sources of benzene in the US and Western Europe, the end-use patterns are similar.

7.1 PHENOL

Phenol (Section 4.9) is yet another chemical for which a variety of processes is available. The cumene hydroperoxide process, by far the dominant one, was described in Section 4.9, but there are various obsolete routes worthy of mention. The earliest process was the sulfonation of benzene to benzenesulfonic acid followed by fusion of the sodium salt of the acid with alkali (Fig. 7.3*a*). During the Boer War (1899–1902) the British used picric acid (trinitrophenol), an uncertain and unreliable explosive, in their shells. The phenol in coal tar did not provide enough picric acid for the war effort, and the benzenesulfonate process thus became the first tonnage organic chemical process to be operated. Large amounts of byproduct Na_2SO_3 and $NaHSO_3$ made this process cumbersome. To be economical, a benzenesulfonate plant requires cheap sulfuric acid and caustic soda and a nearby paper mill that can use the sodium sulfite byproduct for pulping. Labor costs are high but capital costs are low. No synthetic phenol is made in this way now in either the United States or Western Europe.

The second route appeared in 1924 (Fig. 7.3*b*) and involved the direct chlorination of benzene to chlorobenzene, which was then hydrolyzed to the sodium salt of phenol

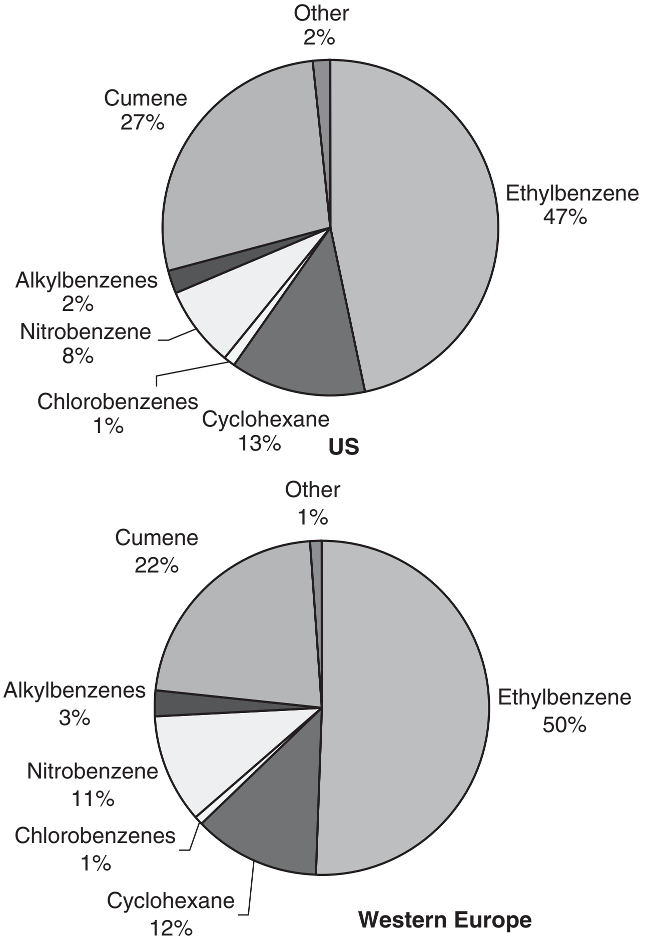


FIGURE 7.2 Consumption of benzene in United States and Western Europe by derivative, 2001.

by means of sodium carbonate or sodium hydroxide. The chlorobenzene process is expensive because of chlorine and alkali usage and must be operated on a very large scale to be economical. The closure of Dow-Midland's massive 100,000 tons/year plant in the 1980s means that no US synthetic phenol is made in this way. Plants are still operating in Argentina, India, Italy, and Poland.

In a later process, the Raschig–Hooker regenerative process (Fig. 7.3*c*), chlorobenzene was prepared from hydrogen chloride, air, and benzene [a reaction comparable to the oxychlorination of ethylene, (Section 3.4)] at 250°C with a $CuCl_2 / FeCl_3$ catalyst supported on alumina. Hydrolysis by steam in the vapor phase with a Ca_3PO_4 / SiO_2 catalyst at 450°C yields phenol and HCl for recycle. The oxychlorination is run to a conversion of only 10–15% to diminish dichlorobenzene formation, which takes place to the extent of 6–10%. In the hydrolysis of the chlorobenzene, diphenyl ether,

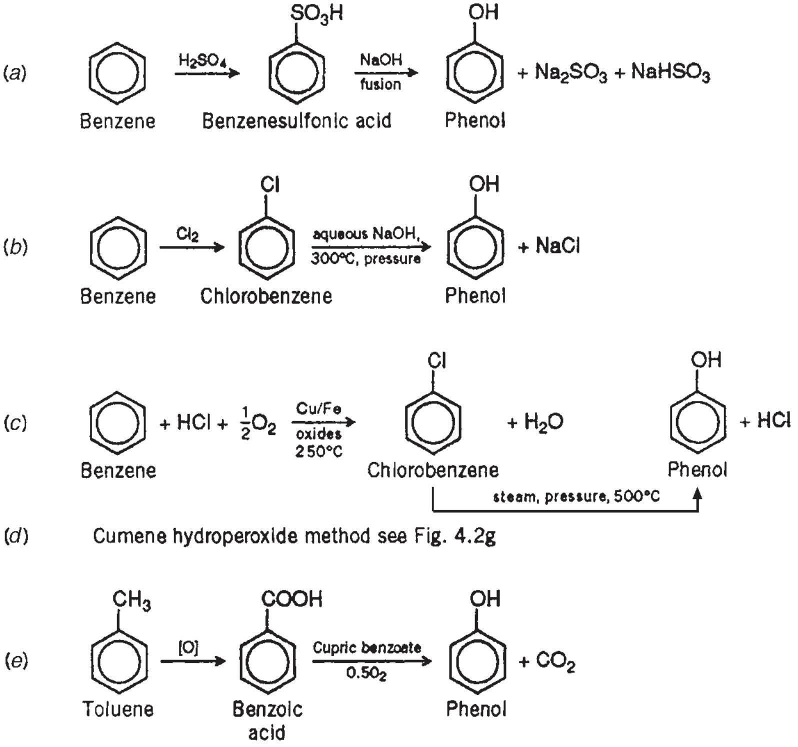


FIGURE 7.3 Processes for phenol manufacture.

and *o*- and *p*-hydroxydiphenyl ethers are formed as byproducts. The dichlorobenzenes are recycled to the chlorination reaction, their presence preventing the formation of additional more highly chlorinated products. The Raschig–Hooker process requires highly corrosion-resistant equipment because of the presence of HCl at high temperatures. It is not as wasteful of chlorine and alkali as the chlorobenzene route, but conversions per pass are low, and therefore capital costs are high. Also, the high temperatures and acid conditions cause corrosion problems, and the high pressures increase operating costs. The process has been obsolete since 1971.

Another reaction was motivated by surplus toluene (Fig. 7.3*e*), which is first oxidized in the liquid phase to benzoic acid. Molten benzoic acid then reacts with air and steam in the presence of cupric benzoate promoted with magnesium benzoate as catalyst. The volatile phenol is removed by distillation. This process, which gives a selectivity approaching 90%, has the advantage of starting with a lower cost raw material. However, the process was only a limited success, in part because the economics of the cumene process benefited from the acetone coproduct credit (see note at the end of this chapter). The economics of toluene oxidation depend to a degree on whether toluene provides greater value in this reaction or in hydrodealkylation (Section 8.1). In the early 2000s, only about 70 million lb of phenol were manufactured by this route in the United States by NOVEON, Inc. (originally Kalama), and 110 million lb in Western Europe by DSM. The process is economically feasible because valuable benzaldehyde and benzoic acid byproducts are formed. In this sense, it is a 2-for-1 process like the cumene hydroperoxide process. It demonstrates, however, the tyranny of 2-for-1 reactions, namely, that for widespread use the two products must be produced in the ratio that the market demands. It is unlikely that this process will ever grow much beyond its current level, as benzaldehyde and benzoic acid demand is limited.

Although the mechanism for the conversion of benzoic acid to phenol is uncertain, it may proceed through phenyl benzoate, as shown in Figure 7.4. The phenyl benzoate decomposes to phenol and benzoic acid, and the cuprous benzoate is reoxidized to cupric benzoate. An alternative mechanism postulates the formation of salicylic acid or *p*-hydroxybenzoic acid, either of which may decompose to phenol and carbon dioxide.

The dominant cumene process (Section 4.9) thus has much in its favor. No expensive chlorine, sodium hydroxide, or sulfuric acid is wasted; conditions are mild; and utility costs are low. Its sole drawback is that a demand must exist for both chemicals in the ratio in which they are produced. Market disruptions during the mid-1980s motivated research for a new process that produces phenol only. Thus, a plant was built in Australia in which a cyclohexanol–cyclohexanone mixture (Section 7.2.1) was dehydrogenated to phenol, but it was soon closed as uneconomical. A Japanese process (Section 4.9) operates with cumene made from benzene and

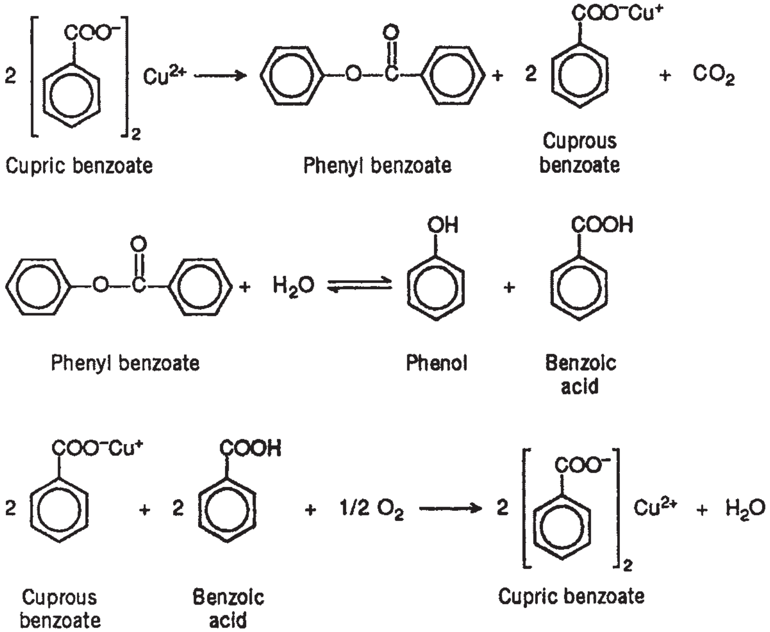
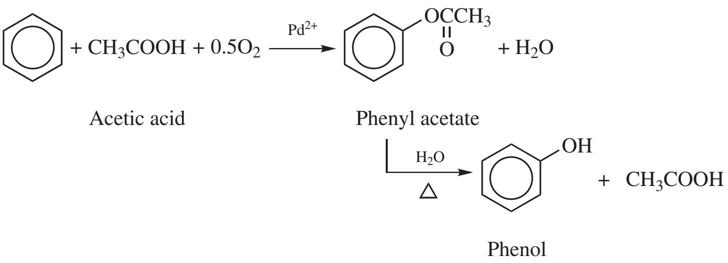


FIGURE 7.4 Conversion of benzoic acid to phenol.

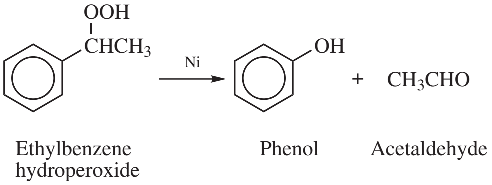
isopropanol rather than propylene. The isopropanol is made by hydrogenation of the surplus acetone produced in the process. In a related process, Mitsui Chemical is believed to dehydrate isopropanol back to propylene for recycle to the front-end of the cumene process. Mitsui uses this process when acetone demand is slack.

The direct air oxidation of benzene to phenol is a research goal. One route involves the reaction of benzene with acetic acid in the presence of palladium and oxygen to give phenyl acetate. This reaction is analogous to the formation of acetaldehyde (Section 3.5) by the Wacker reaction or vinyl acetate (Section 3.6) by a related reaction.



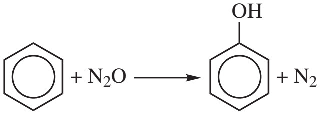
As in the Wacker reaction, the palladium is rendered catalytic by the incorporation of an oxidant. As in the vinyl acetate process, the reaction may be carried out in the vapor phase over a supported palladium metal catalyst. The phenyl acetate may then be hydrolyzed to phenol and acetic acid, which is recycled.

Ethylbenzene hydroperoxide (Section 4.11) may be decomposed with a nickel catalyst to phenol and acetaldehyde in very high yield. However, this too is a coproduct process and the demand for acetaldehyde had decreased by the mid-1980s (Section 3.5).



Asahi Chemical has developed a process for the production of phenol from benzene via selective hydrogenation to cyclohexene. About 20% of the cyclohexene is unavoidably further hydrogenated to cyclohexane. Cyclohexene is separated from the cyclohexane and unconverted benzene by a series of extractive distillations. The purified cyclohexene is either oxidized to a mixture of cyclohexanone, cyclohexenone, and cyclohexanol or hydrated to cyclohexanol. These oxygenated compounds are finally dehydrogenated to phenol. The cyclohexane could be dehydrogenated to benzene for recycle.

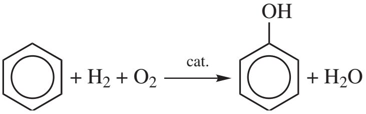
In the mid-1990s, Solutia (formerly Monsanto) developed a direct route to phenol in collaboration with the Boreskov Institute of Catalysis in Russia. It was based on the discovery by a Japanese professor in 1983 that certain metal impregnated zeolites could catalyze the oxidation of benzene to phenol with nitrous oxide as oxidant. Selectivity with respect to phenol is over 95%.



The drawback to this approach is that it requires a low-cost source of nitrous oxide. Solutia had an answer to this. Nitrous oxide is an unavoidable byproduct of modern adipic acid production (Section 7.2.1), by a process already operated by Solutia. For every pound of adipic acid, 0.32 lb of nitrous oxide is produced. Nitrous oxide is a greenhouse gas and must be disposed of safely. Thus, the Solutia phenol process takes a process debit and converts it into a process credit. Solutia had announced their intent to commercialize this process but, because of overbuilding of phenol plants, their plans are on hold. Only two other US companies have byproduct nitrous oxide from adipic acid production.

If required, nitrous oxide can be produced by the catalytic oxidation of ammonia. This chemistry is used in Japan for making small quantities of very high purity nitrous oxide for medical application. It would be a significant development if this approach gave nitrous oxide at low enough cost to make the Solutia process competitive with the conventional cumene-based route.

The Korea Research Institute of Chemical Technology has developed a one-step route to phenol by the passage of hydrogen, oxygen, and nitrogen into a 50:50 solution of benzene and acetic acid at 50°C containing a slurry of two different zeolite catalysts.



Ninety-seven percent selectivity is claimed with a zeolite mixture also containing palladium and ethylanthraquinone. The latter presumably promotes formation *in situ* of hydrogen peroxide. The snag is that the catalyst has low productivity before regeneration is required.

Japanese researchers at the Institute for Materials and Chemical Processes, National Institute of Advanced Science and Technology have discovered a one-step benzene-to-phenol process. In the Japanese process, benzene, oxygen, and hydrogen are passed over a catalyst composed of palladium supported on alpha-alumina at 250°C. Phenol was produced in greater than 90% selectivity but per pass conversions were less than 3%.

As the above examples show, the “holy grail” of phenol production technology—direct benzene hydroxylation with either oxygen or hydrogen peroxide—remains distant. While some progress has been reported, catalysts capable of simultaneously achieving high selectivity, activity, and run length have eluded researchers.

7.1.1 Phenolic Resins

The major applications for phenol are shown in Figure 7.5. The biggest use in the past was the manufacture of phenol–formaldehyde resins (Section 15.4.1), which in 2000–2001 consumed 34% of the US phenol and 24% of Western Europe's. It has now been overtaken by bisphenol A. Annual phenolic resin production in the United States was about 4.6 billion lb in the early 2000s.

Phenolic resins have good chemical, heat, and water resistance, good dielectric properties, and high surface hardness and dimensional stability. They are cheap and can be formulated to meet the needs of the electrical, automotive, appliance, and adhesives industries. Adhesives comprise the largest market for phenolic resins, with bonding of plywood, particle board, and hardboard the largest single application. Phenolic resins are also used in the fabrication of laminates such as "Formica" in which a phenolic bound composite, which has an unattractive brown color, is faced or coated with a layer of a high-quality, colorless, nonyellowing melamine–formaldehyde resin. Under the layer is placed the pattern—often an actual photograph of wood grain or, in cheaper formulations, a printed picture of wood grain. Phenolic resins are frequently compounded with other adhesives to provide water resistance and tack or stickiness.

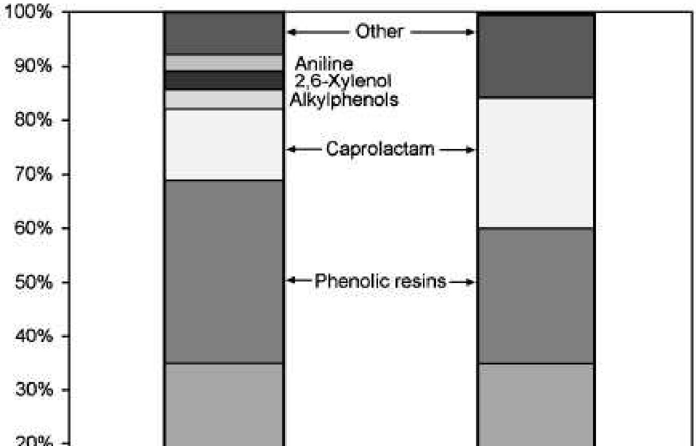
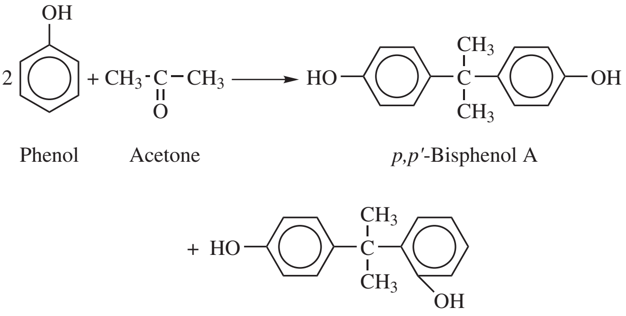


FIGURE 7.5 United States (2001) and Western Europe (2000) phenol end-uses. In Western Europe statistics, alkylphenols, 2,6-xylenol and aniline are included in the "other" category.

Phenolic moldings inevitably have a poor color, and moldings can be produced only in dark colors. They are used for the characteristic electrical plugs and were formerly used for telephones. Other applications include insulation, abrasives, and foundry and shell moldings. They are used in brake linings, clutch facings, and other friction parts where a high temperature-resistant binder is required. Phenolics are also cross-linking agents for epoxy resins in the formulation of structural adhesives and resistant coatings, particularly for can linings. Although usage is large, growth has been inhibited, as it has been for all thermoset resins, because of the difficulty of fabrication and the low-molding speeds. The water resistance of the resins is a positive point but the poor color is a negative one.

7.1.2 Bisphenol A

Phenol condenses with acetone to give bisphenol A, which in turn reacts with epichlorohydrin to give epoxy resins (Section 7.1.2.1) and with phosgene to give polycarbonates (Section 7.1.2.2). In the early 2000s, this became the largest consumer of phenol. For epoxy resins, a mixture of the *o*- and *p*-isomers is acceptable, but the other polymers require the *p,p'*-isomer.



Phenol Acetone *p,p'*-Bisphenol A

o,p-Bisphenol A

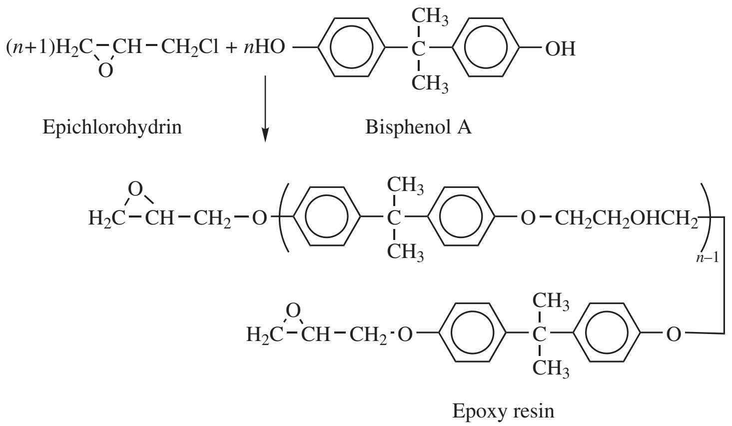
Polycarbonate grade bisphenol A is 99.5% pure, whereas the epoxy grade is 95% pure and is a mixture of the two isomers. The condensation of acetone and bisphenol A was traditionally catalyzed with hydrogen chloride at about 50°C. The substitution of a solid catalyst, such as a sulfonated cation exchange resin, for the corrosive hydrogen chloride, provides a more ecologically acceptable reaction because disposal of the spent hydrogen chloride is fraught with problems. The ion exchange resin is used at 70–90°C. It leads to production cost savings of 6–8 ¢/lb in a 200 million lb/year plant. Materials of construction are cheaper, less maintenance is required, waste water production is minimal, and treatment facilities and product purification are simpler.

A variety of byproducts is produced and these can be rearranged to bisphenol A at 75°C in the presence of a catalyst comprising a cation exchange resin partially esterified with a mercaptoalcohol.

The separation of the *o,p*-isomer from the *p,p*-isomer is accomplished by a combination of distillation and crystallization. In the United States in 2001, 62% of bisphenol A was required for production of polycarbonate resins and 23% for epoxy resins. Two percent went into the fire retardant tetrabromobisphenol A and 13% to exports and other uses. In Western Europe, polycarbonates take 57%, and epoxy resins take 35.5%. Other uses include polysulfones, poly(ether imides), polyarylates, and specialty polyester resins.

7.1.2.1 Epoxy Resins

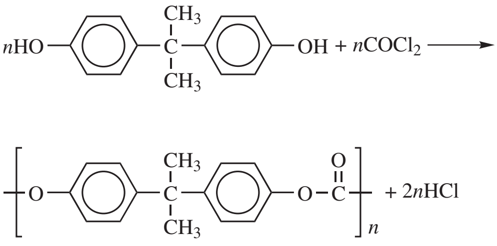
Epoxy resins (Section 15.4.3) are oligomers resulting from the condensation of bisphenol A and epichlorohydrin.



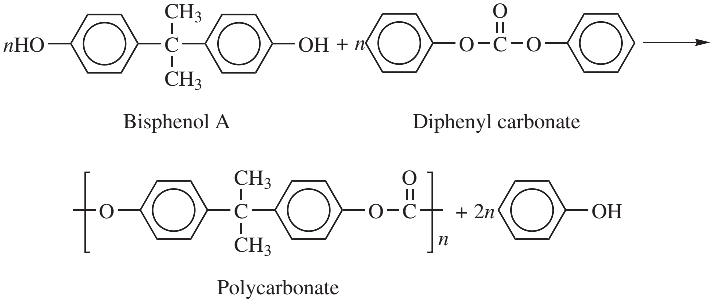
When cross-linked they provide hard, chemically resistant, and dimensionally stable polymers with superb electrical properties. Their largest use is for protective coatings for metal containers, appliances, and ships, as well as for general maintenance where resistance to severe corrosion is required. They are used in the computer industry for "potting" electrical components. The second largest use is in fiber-reinforced composites for circuit boards, aerospace components, and sporting equipment. Other uses include adhesives, sealants, patching and flooring compounds, and castings.

7.1.2.2 Polycarbonate Resins

The conventional route to polycarbonate resins is via the condensation of bisphenol A and phosgene. They are thermoplastics with exceptional clarity, impact strength, flame resistance, and low warpage. The problem of reacting a high-melting solid, the sodium salt of bisphenol A, with a gas, phosgene, has been solved by the use of phase-transfer catalysis (Section 16.10). The salt is slurried in water, whereas the phosgene is dissolved in an organic phase such as dichloromethane containing a catalytic amount of a base such as pyridine. A 1995 General Electric patent suggests that they now prefer tetrabutylammonium hydroxide in 50% sodium hydroxide solution, which permits the use of a phosgene excess of only 2% compared with a 30% excess in the older method because of hydrolysis. The phosgene–pyridine complex is sufficiently lipophilic so that it migrates to the organic layer where the condensation takes place. The pyridine returns to the aqueous layer to repeat the operation. This was probably the first industrial use for phase-transfer catalysis.



Phosgene is highly toxic; indeed it was used as poison gas in World War I. In the early 1990s, General Electric built a polycarbonate plant in Japan that did not use phosgene, and other companies, such as Bayer and Asahi, developed similar routes. It is believed that all the non-phosgene-based plants use the same basic reaction to produce polycarbonate. Diphenyl carbonate, prepared without phosgene as indicated below, is reacted with bisphenol A in the absence of solvent to give an intermediate low molecular weight prepolymer and phenol, which is reused to make additional diphenyl carbonate. The prepolymer is further heated under high vacuum to build molecular weight. Regenerated diphenyl carbonate is recycled. This transesterification process, also called the melt process, has an advantage over the commonly used interfacial route in that the product is obtained in undiluted form and may be directly pelletized. Disadvantages of the melt process are the high vacuums needed and limitation on molecular weight imposed by the high-melt viscosity.



While all producers of non-phosgene polycarbonate use the melt-phase transesterification process described above, they use different technologies to make the diphenyl carbonate and diphenyl carbonate precursors. For example, it is believed that GE Plastics uses the route shown in Figure 7.6, starting with the oxidative carbonylation of methanol to dimethyl carbonate (Section 10.5.2.5). An exchange reaction between phenol and dimethyl carbonate provides diphenyl carbonate. Diphenyl carbonate is used as the source of the carbonate linkage rather than dimethyl carbonate because the phenyl group is a much better leaving group.

Bayer and Ube are believed to use nitric oxide as a redox reagent in the synthesis of dimethyl carbonate. The chemistry of this approach involves the formation of

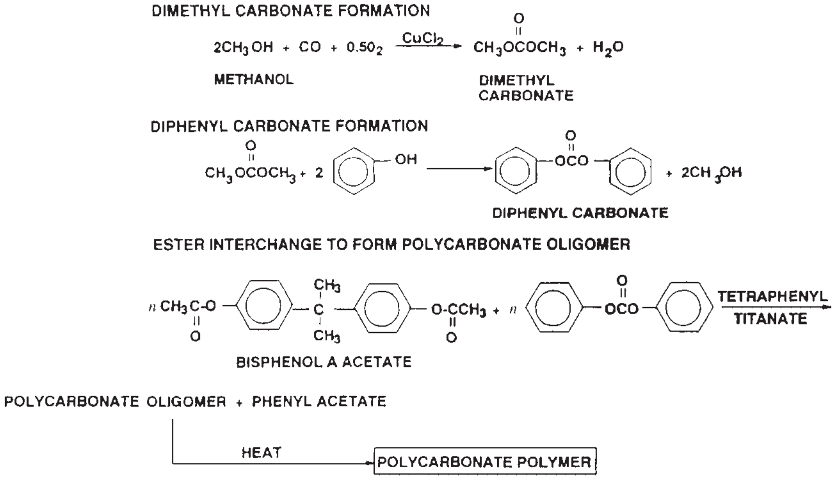


FIGURE 7.6 Preparation of polycarbonate resin without phosgene.

methyl nitrite from methanol, nitric oxide, and oxygen. Methyl nitrite is subsequently reacted with carbon monoxide to give dimethyl carbonate along with nitric oxide for recyle. Asahi Chemical, in a joint venture with Chi Mei, constructed a non-phosgene-based polycarbonate plant that pieces together two previously known reaction steps to make precursor dimethyl carbonate. The first step is reaction of ethylene oxide with carbon dioxide in the presence of a catalytic amount of quaternary ammonium salts to give ethylene carbonate. The ethylene carbonate is then transesterified with methanol to give two products—dimethyl carbonate and ethylene glycol. Shell has also developed similar technology but based on propylene oxide in place of ethylene oxide.

Yet another approach for making dialkylcarbonates is via alcoholysis of urea. The tin-catalyzed reaction of methanol and urea is well known but suffers from low yields because intermediate methyl carbamate is prone to decompose to isocyanuric acid. Mitsubishi Gas Chemical has disclosed that reaction of urea with *n*-butanol works well and that di-*n*-butyl carbonate has an advantage over dimethyl carbonate when making diphenyl carbonate because it avoids the troublesome azeotropes that plague the separation of diphenyl carbonate and dimethyl carbonate.

A non-phosgene route, still at the devlopment stage, is the oxidative carbonylation method, where carbon monoxide and oxygen, together with a palladium catalyst, replace phosgene. Figure 7.7 summarizes the various approaches for making diphenyl carbonate.

The largest application for polycarbonates is in the electrical and electronics sector for compact disks, business machine enclosures, connectors and plugs, telephones, and electrical distribution devices. The second largest application is for window glazing and related applications such as binoculars, where a virtually unbreakable molding with exceptional optical properties is required. Polycarbonates are also blended with

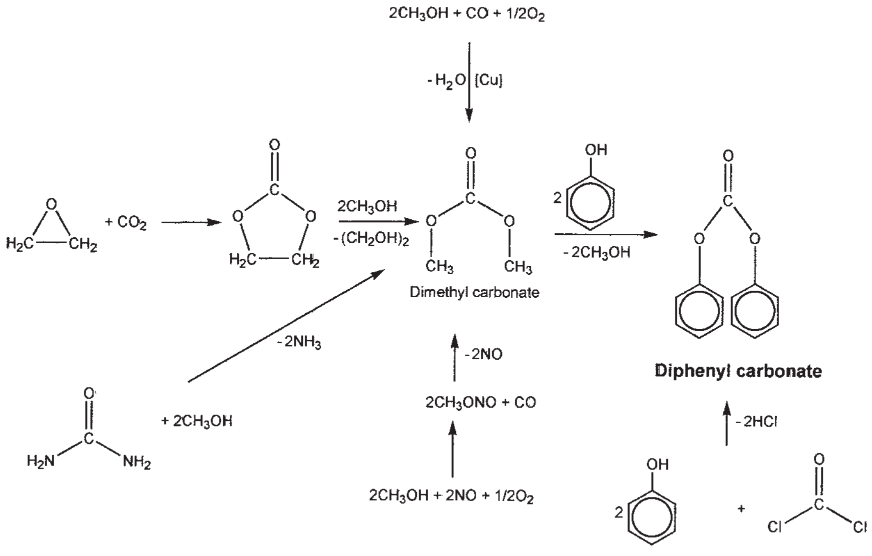
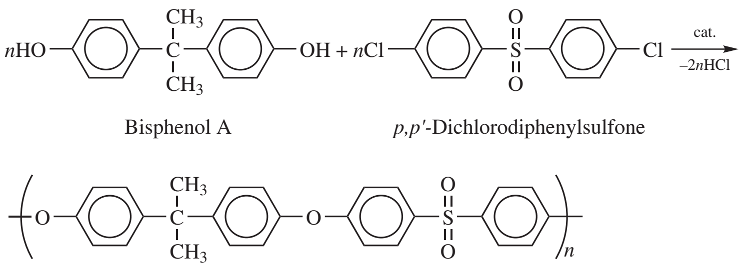


FIGURE 7.7 Routes to diphenyl carbonate.

poly(ethylene terephthalate) (Section 9.3.3) or poly(butylene terephthalate) (Section 9.3.4) to make impact-resistant polymer alloys useful, for example, for automobile bumpers and even for side panels and doors.

7.1.2.3 Lesser Volume Uses for Bisphenol A Bisphenol A (BPA) is used in the synthesis of several engineering polymers because its stiffness contributes strength. The low-volume polysulfone and polyether sulfone polymers require less than 3% of the BPA produced. An example is the condensate of BPA and *p,p′*-dichlorodiphenylsulfone. The hydrogen chloride produced in the condensation is neutralized with base as the reaction progresses.



Bisphenol A

p,p′-Dichlorodiphenylsulfone

Polysulfone

These polymers are used in electrical, automotive, and electronics applications because of their thermal stability and excellent anticorrosive properties. Their superior corrosion resistance and stability to hydrolysis make them useful for medical instruments that require repeated sterilization. They are also used for ultrafiltration membranes in biotechnology and for the "Prism" separators by which hydrogen is separated from argon and nitrogen in a modification of the Haber process. The Haber process gives low yields per pass and much hydrogen and nitrogen must be recycled. The argon left from the air accumulates. To prevent an unacceptable level, a purge was necessary to remove nitrogen, argon, and also valuable hydrogen, which had to be used as fuel. The Monsanto process passes the recycled gases over a microporous polysulfone membrane. The hydrogen diffuses rapidly through the pores and is recycled without waste.

Produced in even smaller quantities than polysulfones are the polyarylates and the poly(ether imides). Polyarylates are condensates of BPA with isophthalic and terephthalic acids. They have excellent resistance to ultraviolet radiation and good impact resistance. They are used in fog lamp lenses and to a larger degree in the rear tail lights of automobiles that are at eye level.

Poly(ether imides) (General Electric's "Ultem") have been designed to have some of the excellent properties of a polyimide but with greater tractability. They are condensates of *m*-phenylenediamine with a bisphenol-based dianhydride, made by a nucleophilic displacement between the sodium salt of bisphenol A (**I**) and *N*-methyl-4-nitrophthalic anhydride (**II**). The sequence of reactions is shown in Figure 7.8. Reaction 1 shows the formation of the bis(ether substituted phthalimide) (**III**). Reaction 2 shows the reaction of the *N*-methyl-4-nitrophthalimide anhydride (**III**) with *o*-phthalic acid to give a bis(ether phthalic acid) (**IV**) and Reaction 3 shows the loss of water by this tetracarboxylic acid to give a dianhydride (**V**). Reaction 4 is the polymerization reaction of (**V**) with *m*-phenylenediamine to give the polyimide (**VI**).

Bisphenol A is also the basis for a specialty corrosion–resistant, unsaturated polyester (Section 9.1.1) based on its reaction with phthalic and maleic anhydrides. Bromination of BPA provides tetrabromobisphenol A, a flame retardant useful in its own right and as a monomer for flame retardant epoxy resins. Among many other lipophiles, however, it is under intense scrutiny as an environmental hazard and endocrine disrupter. It was banned in Holland in early 2001, and there are concerns about its safety.

7.1.3 Cyclohexanone

The third largest use for phenol in both the United States and Western Europe is for caprolactam. Its conversion to caprolactam is described in Section 7.2.2.

Approximately 33% of caprolactam comes from this source and the remainder from cyclohexane oxidation (Section 7.2.2). The starting material for caprolactam is cyclohexanone, and this could come from phenol by a straightforward two-stage process in which the phenol is first hydrogenated to cyclohexanol and then dehydrogenated to cyclohexanone.

By a unique hydrogenation, however, phenol may be converted directly to cyclohexanone in high yield in a single step with a supported palladium catalyst at

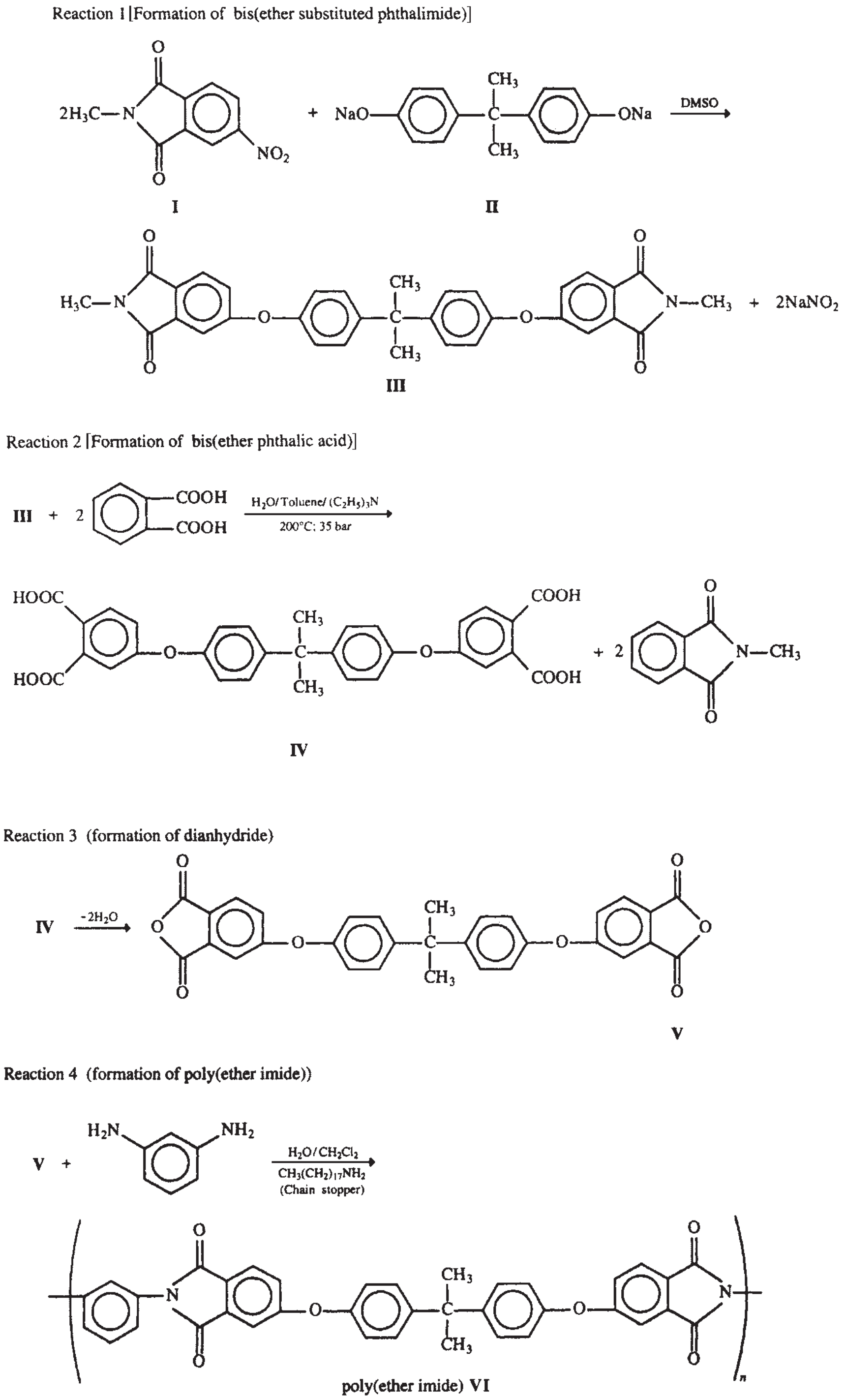
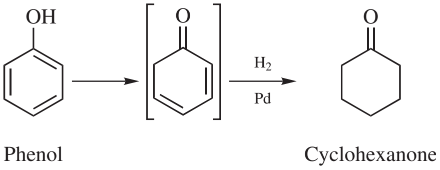


FIGURE 7.8 Preparation of a poly(ether imide).

12–13 bar and 200°C. Selectivity is about 97%. Presumably the cyclohexanol converts to a keto form, which on hydrogenation provides cyclohexanone:



Benzene is the starting material in the Asahi route (Section 7.1). It is selectively hydrogenated to cyclohexene, and the cyclohexene is converted to cyclohexanol by hydration. The cyclohexanol may then be oxidized or dehydrogenated to cyclohexanone. The key to the process is the ability to obtain high selectivity to the cyclohexene.

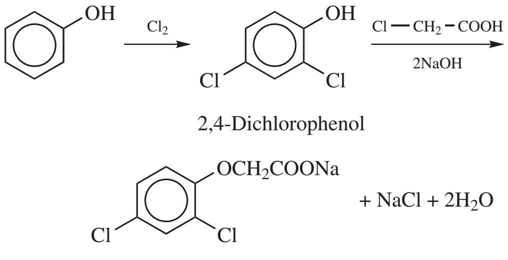
7.1.4 Alkylphenols

Phenol may be alkylated with olefins by a Friedel–Crafts reaction (Section 5.2.3) to provide alkylphenols. When alkylated with propylene trimer (Sections 2.2.4, 4.2) nonylphenol results which, when reacted with ethylene oxide, provides an ethoxylate. This is an important surfactant for industrial detergents and has also been used in liquid dishwashing detergents. It has low-foam properties and good detergency. Because of questions of biodegradability, however, it is being replaced by other surfactants including the more expensive ethoxylated fatty alcohols, alcohol sulfates, and alcohol ethoxysulfates. It is also converted to antioxidants for rubbers and plastics and for lube oil additives.

Octylphenol is made (Section 5.2.3) by alkylating phenol with diisobutene. Ethoxylation gives nonionic surface cleaners. Reaction with formaldehyde provides an oil-soluble phenolic resin. Dodecylphenol results from the condensation of propylene tetramer (Section 4.6) with phenol. Most of the product is used for lube oil additive formulations.

7.1.5 Chlorinated Phenols

The most important chlorinated phenol is 2,4-dichlorophenol, the raw material for the widely used herbicide, 2,4-dichlorophenoxyacetic acid or 2,4-D.

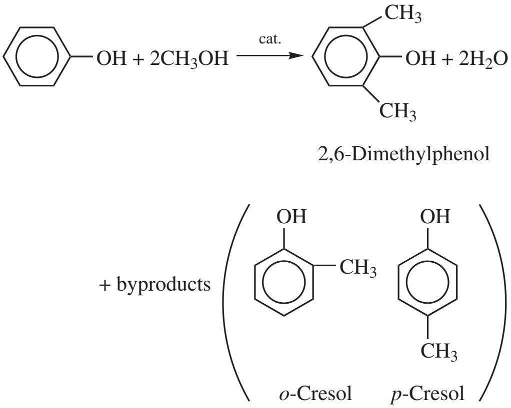


2,4-Dichlorophenoxyacetic acid, sodium salt

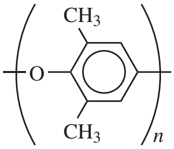
Pentachlorophenol, made by exhaustive chlorination of phenol, is a wood preservative and slimicide. Like other chlorinated compounds it has been outlawed in the United States because of its adverse environmental affects. The chlorine atoms make it highly lipophilic and, when it enters the body via the food chain, it accumulates in fatty tissue. The same is not true of 2,4-D, whose carboxyl group may facilitate its excretion.

7.1.6 2,6-Xylenol and Cresols

The synthesis of 2,6-xylenol (2,6-dimethylphenol) provides a small application for phenol. It is made by methylation of phenol at about 500°C at almost atmospheric pressure with a methanol/phenol molar ratio of 6:1 and a catalyst comprising magnesium oxide on an inert carrier pretreated with methanol vapor. Ten percent water provides continuous catalyst regeneration. Both *o*- and *p*-cresol are byproducts.



The xylenol is converted by oxidative coupling to poly(phenylene ether) whose recurring unit is



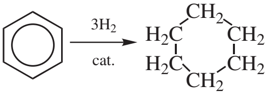
o-Cresol finds use in the manufacture of pesticides.

7.1.7 Aniline from Phenol

Aniline is normally prepared by hydrogenation of nitrobenzene (Section 7.3). An alternative route involves the ammonolysis of phenol. Both of these processes are described in Section 7.5.

7.2 CYCLOHEXANE

Small quantities of cyclohexane are extracted from naphtha (Section 2.1) but most is produced by hydrogenation of benzene. The process is operated in refinery complexes using hydrogen from catalytic reforming (Section 2.2.3). However, since the Clean Air Act reduced the permissible aromatics content in gasoline, less hydrogen is available for such reactions.



Cyclohexane

Either nickel or platinum catalysts may be used, but both require benzene feed with a sulphur content of less than one part per million. Hydrogenation is carried out at an upper temperature of 230°C at 1.5–2.5 bar. Although liquid-phase hydrogenations are more common, gas-phase processes are available. These operate at temperatures as high as 600°C with moderate pressures of 25–50 bar.

Although some cyclohexane is used as a solvent, its major market is for the production of adipic acid and caprolactam.

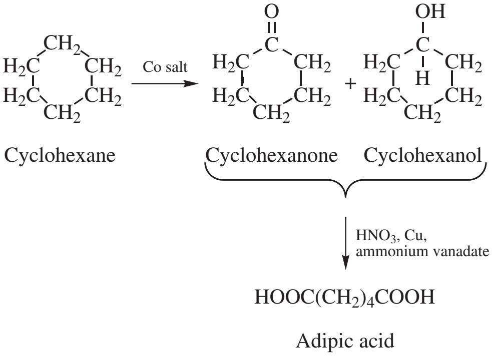
7.2.1 Adipic Acid

Benzene is the source of the two most important nylons, nylon 6,6 and nylon 6. Nylon 6,6 is the polymer formed when adipic acid condenses with hexamethylene diamine. Nylon 6 (Fig. 7.2.2) is the self-condensation product of caprolactam, which is the dehydration product of 6-aminocaproic (6-aminohexanoic) acid. The numbers used to designate nylons refer to the number of carbon atoms in the diamine and dibasic acid in that order. A single number indicates that the amino and carboxyl functions are in one molecule. Thus $[NH(CH_2)_6NHCO(CH_2)_4CO]_n$ is nylon 6,6, whereas $[NH(CH_2)_5CO]_n$ is nylon 6, and $[NH(CH_2)_6NHCO(CH_2)_8CO]_n$ is nylon 6,10, a specialty nylon made with sebacic rather than adipic acid.

In the early days of nylon, Du Pont created a mystique about their product by advertising that it was made from coal, air, and water. Coal at that time was the source of the benzene or phenol feedstocks. Now both are derived from petroleum, and “made from petroleum, air and water” does not sound nearly as good.

Nylon 6,6 is the preferred polymer in both Western Europe and the United States. In Europe in 2001, it enjoyed a little over 50% of the market. In the United States, there is twice as much capacity for manufacturing nylon 6,6 as nylon 6. In Japan, however, nylon 6 is more popular. Nylon 6 can be manufactured from merchant caprolactam whereas, until the 1950s, merchant hexamethylene diamine was not available. Many of the producers of caprolactam were fertilizer manufacturers who could use the byproduct ammonium sulfate.

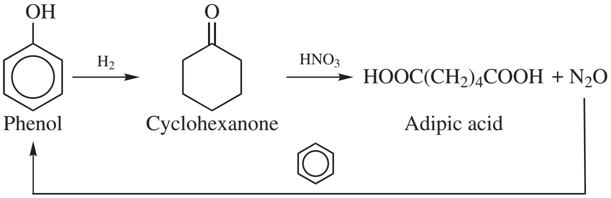
The first step in the manufacture of the adipic acid needed for nylon 6,6, is the hydrogenation of benzene to cyclohexane. Thereafter the cyclohexane may be oxidized directly to adipic acid with nitric acid or with air over cobalt acetate, but yields are low, production of valueless byproducts is high, and large amounts of nitric acid are consumed. Instead, a two-stage process is used. The initial oxidation at about 150°C and 10–15 bar over cobalt or manganese naphthenate or octanoate gives a cyclohexanol/cyclohexanone "mixed oil" or "KA oil" (ketone/alcohol oil). In the first stage of the reaction, cyclohexyl hydroperoxide forms and this is converted catalytically to the ol/one.



Conversions of the order of 10–12% are accepted in order to minimize the formation of adipic acid, which at this stage presents processing problems and, more important, to minimize the degradation reactions that provide glutaric (C_5) and succinic (C_4) acids. The selectivity to the ol/one does not surpass 85%, but unreacted cyclohexane can be recycled. The desired ol/one mixture is purified by distillation.

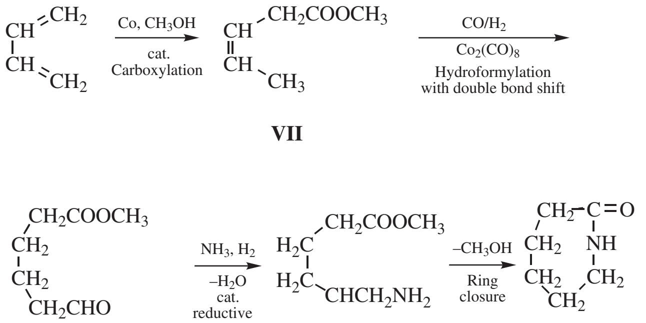
The ratio of cyclohexanol/cyclohexanone may be increased from between 1:1 and 2:1 to about 9:1 by the addition of boric acid, which esterifies the "ol" as it is formed and prevents its further oxidation to cyclohexanone. The boric acid also increases the selectivity of the reaction. The cyclohexanol/cyclohexanone "mixed oil" is then oxidized to adipic acid with nitric acid at high selectivity over a copper catalyst with ammonium vanadate. Conversions per pass are of the order of 12%. No way of circumventing the use of nitric acid has yet been found, and this is the only example in industrial chemistry of the use of nitric acid as an oxidant for the production of a large volume chemical.

While nitric acid is an effective oxidizing agent for converting KA oil to adipic acid, an unavoidable byproduct is nitrous oxide. For every pound of adipic acid, 0.32 lb of nitrous oxide is also produced. Nitric acid manufacture also produces 2.9 lb of nitrous oxide per 1000 lb of nitric acid, and together they were responsible in the mid-1990s for about 100,000 tonnes of nitrous oxide emissions per year in the United States. Nitrous oxide is a "greenhouse" gas that is believed to contribute to global warming by absorbing reflected infrared radiation. It has been estimated that its warming potential is three times that of carbon dioxide. In 1997, it was estimated that adipic acid production contributed about 10% of all nitrous oxide emissions in the United States. Motor vehicles and fertilizers were the largest generators of nitrous oxide, each causing ~33–34% of total emissions. Most adipic acid producers now employ catalytic or thermal processes to destroy their nitrous oxide byproduct, but Alsachimie, a Rhodia subsidiary, has developed a process that converts it to nitric acid for recycle. This approach is of double benefit as further nitrous oxide production from conventional nitric acid production is reduced. Solutia plans to avoid nitrous oxide emissions by using it in an adipic acid plant as an oxidant to convert benzene to phenol (Section 7.1). This offers the opportunity to couple phenol and adipic acid production:



Researchers have long sought another method for oxidizing cyclohexane to adipic acid, to avoid the cost of the nitric acid and to eliminate the environmental problems associated with nitrous oxide. In the 1960s, Halcon constructed a semiworks plant for Rohm and Haas that employed a two-stage air oxidation of cyclohexane. The second stage used a copper and magnesium catalyst in acetic acid solvent and gave an 80% yield based on KA oil. This was substantially less than the 93–95% yield achieved by conventional nitric acid oxidation, and the approach was abandoned. In a 1994 Patent Application, BASF disclosed a catalyst system that was able to achieve selectivities of 88.2% to adipic acid, 6.2% to glutaric acid, and 3.6% to succinic acid. No plans for commercializing this process have been announced. Nagoya University researchers reported in 1998 that cyclohexane could be oxidized by hydrogen peroxide at over 90% selectivity by a phase-transfer catalyst containing small amounts of tungsten.

A number of non-cyclohexane-based routes to adipic acid have been explored over the years. Most of them have been based on a butadiene feedstock, and one is described in Section 5.1.2. Arco, BASF, Shell, Du Pont, DSM, Idemitsu, and Rhone-Poulenc have all studied hydrocarbonylation of butadiene, which is typically performed in two stages in the presence of an alcohol, so that the end-product is the corresponding dialkyl adipate. This is hydrolyzed to adipic acid, freeing the alcohol for recycle. In a joint 1998 patent, Du Pont and DSM disclosed some promising results with a palladium, ferrocene, phosphorus-containing ligand catalyst system. Du Pont and DSM together developed another butadiene route to caprolactam called Altam. The first step, a carbonylation, is the same as the first step in BASFs adipic acid synthesis (Section 5.1.3.4) and gives methyl 3-pentenoate (**VII**). This is hydroformylated with a cobalt catalyst rather than the more efficient rhodium catalyst because it shifts the double bond to the terminal position to provide the aldehyde (**VIII**). Reductive amination introduces an amine group to give an aminoester (**IX**) and this cyclizes to caprolactam (**X**) with the elimination of methanol.

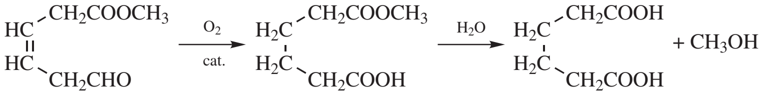


VII

VIII **IX** **X** Caprolactam

Du Pont withdrew, as they did from the two-for-one process in Section 5.1.2, prompted by their coincident withdrawal from the fibers business in 2003. Shell came in to help with catalyst development. The process is available for license but by 2002 had not been commercialized.

In 1998, Du Pont and DSM disclosed a variation to the above reaction scheme in which compound (**VIII**) is oxidized to the half-ester of adipic acid and then hydrolyzed to the free acid. Butadiene was converted to adipic acid by sequential reaction steps that included hydrocarboxylation, isomerization, hydroformylation, oxidation, and hydrolysis:



VIII Adipic acid

In a 1994 European Patent, researchers at the University of North Carolina disclosed a means for dimerizing methyl acrylate to give a precursor that can be easily converted to dimethyl adipate by hydrogenation.

$$2CH_2{=}CH{-}COOCH_3 \longrightarrow H_3COOCCH_2{-}CH{=}CH{-}CH_2COOCH_3 \xrightarrow{H_2}$$

Methyl acrylate

$$H_3COOCCH_2CH_2CH_2CH_2COOCH_3 \xrightarrow{2H_2O,\ -2CH_3OH} HOOC(CH_2)_4COOH$$

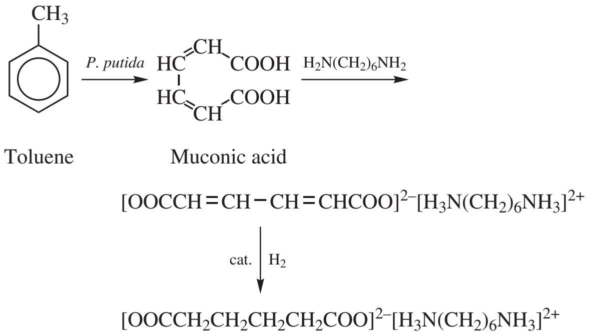
Adipic acid

An obsolescent route to adipic acid starts with tetrahydrofuran (Sections 10.3.1, 14.1):

Tetrahydrofuran 1,4-Dichlorobutane Adipic acid

The waste of chlorine, which does not appear in the end-product, and the use of poisonous sodium cyanide make the process unattractive. Tetrahydrofuran was originally an agricultural product derived from furfural (Section 14.1.1) obtained in turn by hydrolysis of the pentosans in cereal hulls. Today it is largely made from 1,4-butanediol or maleic anhydride (Section 10.3.1), although the furfural-based product is still produced.

A microbiological process for the production of adipic acid proposed by Celanese is not likely to be commercialized in the near future but is mentioned here because, like the microbiological process for propylene oxide (Section 4.11.2), it demonstrates the potential of modern biotechnology. Nylon 6,6 salt (an equimolar mixture of adipic acid and hexamethylene diamine) is produced from toluene via muconic acid. Toluene is first converted to muconic acid by a mutant strain of *Pseudomonas putida*.



Muconic acid is much less soluble than adipic acid and is neutralized with hexamethylene diamine as it is formed in the fermenter to yield a solution of hexamethylene diammonium muconate in concentrations as high as 3.9%, which is separated from the cells by ultrafiltration. The salt may be precipitated by addition of isopropanol. Thereafter it is hydrogenated to give nylon salt for nylon preparation. The key to the process is the ability to isolate the product from dilute aqueous solution without expensive removal of water by distillation or other means.

7.2.1.1 Nylons from Adipic Acid Once adipic acid has been made, it must be reacted with hexamethylenediamine, whose manufacture has already been described (Section 5.1.3), to obtain nylon 6,6.

$$\underset{\text{Adipic acid}}{\mathrm{HOOC(CH_2)_4COOH}} + \underset{\text{Hexamethylenediamine}}{\mathrm{H_2N(CH_2)_6NH_2}} \longrightarrow \underset{\text{Nylon 6,6}}{\left[\mathrm{OC(CH_2)_4CONH(CH_2)_6NH}\right]_n}$$

Nylon 4,6 is another polyamide based on adipic acid, combined in this case with 1,4-diaminobutane. It is used as an engineering plastic rather than as a fiber. It has a higher melting point than either nylon 6,6 or nylon 6, with better toughness and temperature stability, but with the high water absorption that bedevils nylons. 1,4-Diaminobutane results from the addition of hydrocyanic acid to acrylonitrile to provide succinonitrile, which on hydrogenation gives the diamine. This reaction is an excellent example of how to gain value from the HCN byproduct from acrylonitrile production (Section 4.4).

$$\underset{\text{Acrylonitrile}}{\mathrm{NCCH{=}CH_2 + HCN}} \longrightarrow \underset{\text{Succinonitrile}}{\mathrm{NCCH_2CH_2CN}} \xrightarrow{\mathrm{H_2/cat.}} \underset{\text{1,4-Diaminobutane}}{\mathrm{H_2N(CH_2)_4NH_2}}$$

The addition of HCN to the highly activated double bond of acrylonitrile takes place at 80°C in the presence of an alkaline catalyst such as triethylamine. The hydrogenation to 1,4-diaminobutane may take place with a cobalt oxide catalyst in a tetrahydrofuran solvent at 100°C and 190 bar.

Nylon raw materials cannot be made sufficiently pure to form a satisfactory polymer. Therefore, the diamime and dicarboxylic acid are reacted at mild temperature to form a salt, which can be purified further by crystallization. Thereafter, the salt is heated further to polymerize it.

7.2.2 Caprolactam

There are competing routes to caprolactam. In the initial and most widely used one, cyclohexanone is the starting material. The cyclohexanone component of "mixed oil" (Section 7.2.1) may be separated by distillation, and the cyclohexanol may be dehydrogenated to cyclohexanone at 425°C and atmospheric pressure with metallic catalysts such as zinc or copper. Cyclohexanone may also be obtained from phenol (Section 7.1.3).

The cyclohexanone (Fig. 7.9*a*) reacts with hydroxylamine sulfate to give cyclohexanone oxime and sulfuric acid, which is converted to ammonium sulfate by the ammonia injected into the reaction mixture to drive the reaction to the right. Oximes undergo the Beckmann rearrangement, and this one is no exception; treatment with sulfuric acid gives caprolactam and ammonium sulfate.

The production of hydroxylamine also gives an ammonium sulfate byproduct. Ammonium bicarbonate and ammonia give ammonium carbonate. Oxidation of ammonia gives an NO/NO_2 mixture that reacts with the carbonate to give ammonium nitrite for conversion with sulfur dioxide and ammonium hydroxide solution to hydroxylamine sulfate and ammonium sulfate.

$$\underset{\substack{\text{Ammonium}\\ \text{bicarbonate}}}{\mathrm{NH_4HCO_3}} + \mathrm{NH_3} \longrightarrow \underset{\substack{\text{Ammonium}\\ \text{carbonate}}}{\mathrm{(NH_4)_2CO_3}} \xrightarrow{\mathrm{NO/NO_2}} \underset{\substack{\text{Ammonium}\\ \text{nitrite}}}{\mathrm{2NH_4NO_2}}$$

$$\mathrm{NH_4NO_2 + SO_2/NH_4OH} \longrightarrow \underset{\substack{\text{Hydroxylamine}\\ \text{sulfate}}}{\mathrm{[HONH_3]^+HSO_4^-}} + \underset{\substack{\text{Ammonium}\\ \text{bisulfate}}}{\mathrm{NH_4HSO_4}} \xrightarrow{\mathrm{NH_3}}$$

$$\underset{\text{Hydroxylamine}}{\mathrm{NH_2OH}} + \underset{\text{Ammonium sulfate}}{\mathrm{(NH_4)_2SO_4}}$$

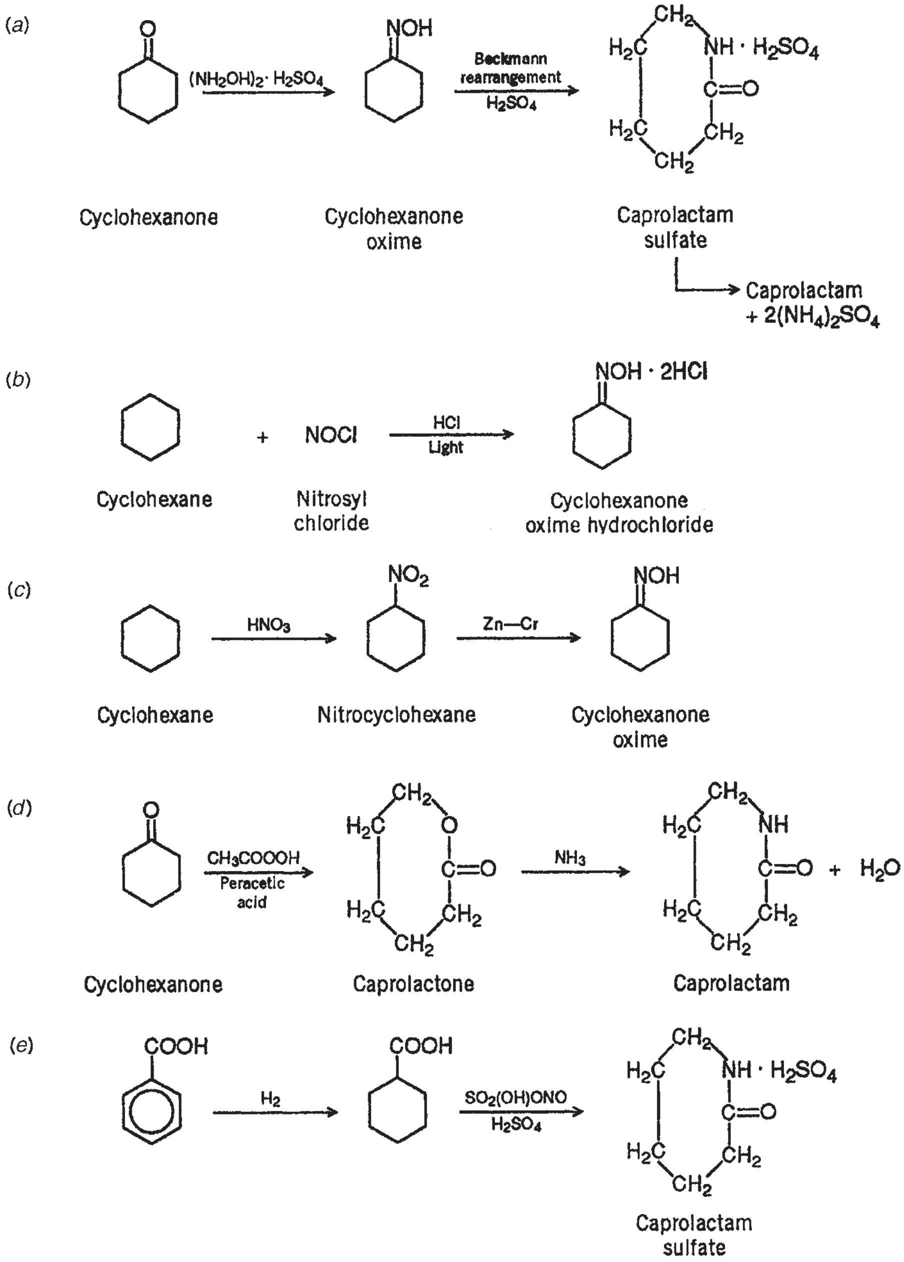


FIGURE 7.9 Routes to caprolactam.

Each pound of caprolactam produced generates 4.4 lb of ammonium sulfate byproduct. Of this, 1.6 lb arises from the production of hydroxylamine sulfate, 1.1 lb from the production of the oxime and 1.7 lb from the Beckmann rearrangement. This large amount of ammonium sulfate finds its way to the fertilizer market particularly if a fertilizer plant is close to the source of the ammonium sulfate.

To add to these difficulties, hydroxylamine decomposes rapidly at room temperature especially in the presence of atmospheric moisture and carbon dioxide. Ammonium nitrite is an explosive similar to the nitrate. In 1999, explosions wrecked the Nisshin Chemical plant in Japan and the Concept Sciences plant in Allentown, PA, leaving BASF as the only producer.

The production of cumbersome amounts of unwanted ammonium sulfate stimulated the search for alternative methods for caprolactam production. One of them involves the use of phosphoric rather than sulfuric acid to effect the Beckmann rearrangement, because ammonium phosphate has greater value as a fertilizer.

A Japanese (Toray) process (Fig. 7.9*b*) involves treatment of cyclohexane with nitrosyl chloride and hydrogen chloride under actinic light (500 μm) to give the oxime hydrochloride without a Beckmann rearrangement. The nitrosyl chloride is made in three steps. Ammonia is burned in air to nitrogen trioxide; the trioxide is absorbed in sulfuric acid to give nitrosylsulfuric acid; hydrogen chloride is then added to the nitrosylsulfuric acid:

$$2NH_3 + 3O_2 \longrightarrow N_2O_3 + 3H_2O$$

$$2H_2SO_4 + N_2O_3 \longrightarrow 2HNOSO_4 + H_2O$$

$$HNOSO_4 + HCl \longrightarrow NOCl + H_2SO_4$$

This process is wasteful of chlorine since the cyclohexanone oxime hydrochloride must be converted to the free oxime. On the other hand, the sulfuric acid that results in the NOCl reaction is recycled so that ammonium sulfate production is virtually eliminated. Nonetheless, it still results from the Beckmann rearrangement. The major problem with photonitrosation is the engineering of an appropriate mercury light source. This same reaction is useful on cyclododecane (Section 5.1.2.2) to provide the monomer for nylon 12.

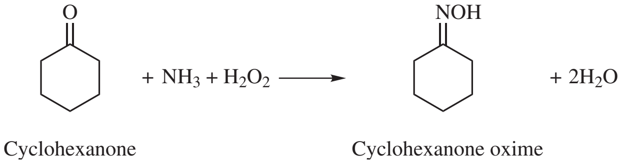
Another process (Fig. 7.9*c*), now largely of historical interest but used at one time by Du Pont, involves liquid-phase nitration of cyclohexane to nitrocyclohexane. This can be converted by careful reduction over a zinc–chromium catalyst to cyclohexanone oxime, the precursor of caprolactam. The manufacture of hydroxylamine is avoided, and about 66% of the ammonium sulfate is eliminated. The nitration step is akin to the gas-phase nitration of propane to a mixture of nitroparaffins (Section 11.2) and is difficult to carry out in high selectivity.

A fourth route to caprolactam (Fig. 7.9*d*) uses peracetic acid (from acetaldehyde and air) to convert cyclohexanone, at 50°C and atmospheric pressure, to caprolactone, which on reaction with ammonia provides caprolactam. Only the first step is now in use for the production of caprolactone.

A toluene-based route to caprolactam has been pioneered by Snia Viscosa. It was used in Italy until the early 1990s and is now used in China. Benzoic acid (Fig. 7.9*e*), prepared by the cobalt-catalyzed oxidation of toluene, is hydrogenated to hexahydrobenzoic acid, over a palladium catalyst at 170°C and 15 bar. This is treated with nitrosylsulfuric acid (see above) to obtain caprolactam sulfate. This process also eliminates 66% of the ammonium sulfate. In a variation of it, the caprolactam sulfate is diluted with water to dissociate the salt, after which the caprolactam is extracted from the 50% sulfuric acid solution with toluene or an alkylphenol. Thus the byproduct is sulfuric acid rather than the salt. The acid can be pyrolyzed to sulfur dioxide for conversion via sulfur trioxide to concentrated sulfuric acid. This processes may be the most economical of all.

A clever approach to the problem of eliminating ammonium sulfate formation is found in a DSM process in which a buffered solution of hydroxylamine reacts with cyclohexanone in solution to produce the oxime. The buffered hydroxylamine solution is produced by hydrogenation of nitrate ions to hydroxylamine in the presence of a phosphate buffer with a palladium catalyst. This solution reacts with hydroxylamine, and the oxime can be extracted with toluene. The aqueous solution can be recycled. DSM originally obtained caprolactam technology from Germany in lieu of reparations for World War II and is today Europe's largest producer of caprolactam for the merchant market.

Several new caprolactam developments were announced in the mid-1990s and early 2000s. Some are discussed in Sections 5.1.2 and 7.2.1, but there were several others, which were not mentioned. Enichem built a demonstration facility in 1994 that employed hydrogen peroxide to produce cyclohexanone oxime directly from ammonia and cyclohexanone. Enichem refers to this reaction as "ammoximation."



The elimination of the conventional steps for making hydroxylamine and converting it to the oxime reduce the capital expenditure and levels of ammonium sulfate byproduct are lower.

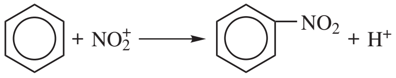
Sumitomo has developed a heterogeneous catalyst to carry out the Beckmann rearrangement of cyclohexanone oxime to caprolactam in the gas phase (Fig. 7.9*a*). The catalyst is believed to be a metal modified zeolite capable of withstanding the rigors of fluidization. The key benefit of this reaction step is the elimination of ammonium sulfate byproduct. It has been demonstrated by Sumitomo in a 5000-tonne/year pilot plant. Combined with Enichem's ammoxidation of cyclohexanone, production of ammonium sulfate may be eliminated altogether. Sumitomo started this new process in 2003 in a 67,000 tonne/year plant in Japan.

Of all these processes, only three were in use in 2002, the cyclohexanone-based process first described, the photonitrosation, and the DSM process. Of the new processes, there seem to be firm plans for commercialization only of the Sumitomo/Enichem process. The many processes for caprolactam production nonetheless provide an example of the imagination that chemists bring to bear to solve a troublesome problem, in this instance the formation of large amounts of ammonium sulfate.

7.3 ANILINE

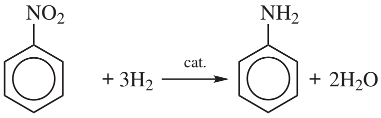
Next in the line of benzene-based chemicals is aniline. Production in 2002 in the United States was 1.8 billion lb, 75% of which was used to produce isocyanates (Section 7.3.2). In the traditional process, benzene is first nitrated with mixed acids (H_2SO_4/HNO_3), which form a nitronium ion (NO_2^+), which attacks the benzene ring. The reaction is exothermic and the mixture must be cooled to maintain a temperature of about 50°C. An adiabatic process has been described, in which 65% rather than 98% sulfuric acid is used. The water in the acid absorbs the heat eliminating the need for external cooling. In the nitration of benzene, a small amount of *meta* isomer is obtained.

$$HNO_3 \longrightarrow NO_2^+ + OH^-$$



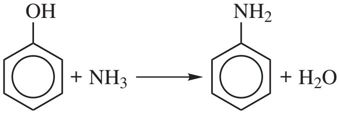
Nitrobenzene

Nitrobenzene is reduced to aniline in almost quantitative yield by vapor-phase hydrogenation at 270°C and 1.25 bar in a fluidized bed of a copper-on-silica catalyst. Also feasible is a vapor-phase hydrogenation over a fixed bed of nickel sulfide on alumina.



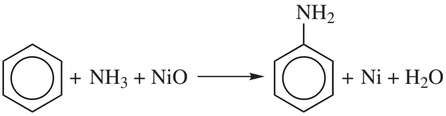
Nitrobenzene Aniline

An older process employed iron turnings and hydrochloric acid as a source of hydrogen. This liquid-phase process, in which the iron was converted to Fe_3O_4, useful as a pigment, is little used today. Another process involving the ammonolysis of chlorobenzene was wasteful of chlorine and has not been used since 1967. The newest method for aniline preparation involves the ammonolysis of phenol.

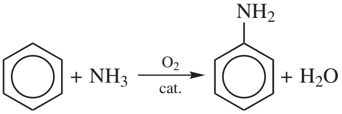


This reversible reaction is driven to the right by a high ammonia/phenol ratio, which also retards formation of diphenylamine. The reaction takes place at 200 bar and 425°C. The catalyst is proprietary, although initially a mixture of alumina and silica was proposed. Oxides of magnesium, aluminum, and tungsten are also effective in the presence of cocatalysts such as cerium and vanadium. Aniline selectivity is lower (~90%) than in the nitrobenzene process, and diphenylamine and carbazole form as byproducts by dehydrogenation. The lower capital cost of this process as compared to the nitrobenzene process is partly offset by higher raw material costs. On the other hand, the process eliminates ecological problems associated with the use of sulfuric and nitric acids.

The direct amination of benzene with ammonia via intermolecular dehydrogenation has been studied by Du Pont but has never been commercialized. Obviously, such a process could provide the lowest possible raw material costs. The capital investment for the nitrobenzene section of a nitrobenzene–aniline plant is about half of the total, and its elimination would also reduce capital costs. The "cataloreactant," a term apparently coined for this reaction, comprises nickel with small amounts of rare earth metal oxides together with a stoichiometric amount of nickel oxide, which reacts with the released hydrogen. The reaction takes place at 350°C and 290 bar with a high selectivity of 97% and a low conversion of 10% benzene per pass.

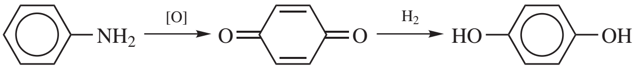


ICI reported a similar oxidative technique.



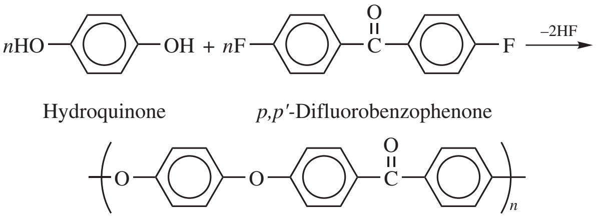
Selectivities as great as 96% are said to be attainable by use of a vanadium pentoxide on a γ-alumina catalyst that has been hydrogenated and in which the vanadium has an average oxidation state between 4 and 5. It is similar to the $V_2P_2O_7$ catalysts used for maleic anhydride production (Section 5.4.2). Intermolecular dehydrogenations such as these are rare in organic chemistry. Another example is found in HCN preparation (Section 10.1), from ammonia and methane.

Aniline's major use is for conversion to 4,4′-diphenylmethane diisocyanate, discussed below. The second most important use is for rubber chemicals (see note at the end of this chapter). A third use is as an intermediate for dyes, drugs such as antihistamines (bamipine and thenaldine), and intermediate chemicals. It is also used in the synthesis of riboflavin. A small use is for the preparation of hydroquinone (Section 7.7) largely for photographic uses. Aniline is oxidized by manganese or chromic oxides in acid solution to *p*-quinone, which in turn can be reduced to hydroquinone with hydrogen.



Aniline *p*-Quinone Hydroquinone

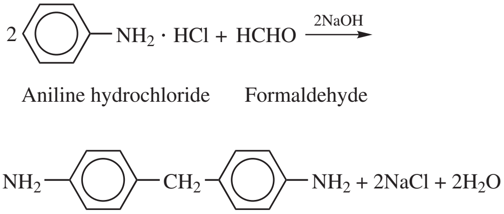
Another use for hydroquinone is as a component of a high performance plastic, poly(ether ether ketone) (PEEK) a condensate of hydroquinone and *p,p′*-difluorobenzophenone.



Poly(ether ether ketone)

7.3.1 4,4′-Diphenylmethane Diisocyanate (MDI)

4,4′-Diphenylmethane diisocyanate (MDI, standing for methylenediphenyl diisocyanate) is produced by the reaction of aniline hydrochloride with formaldehyde to form the 4,4′, 2,4′, and 2,2′ isomers of diaminodiphenylmethane. The equation shows only the 4,4′ isomer:

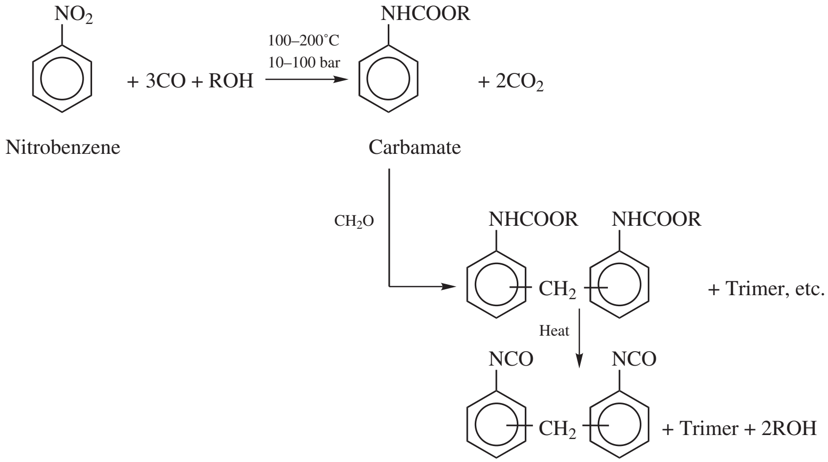


4,4'-Diaminodiphenylmethane

The diamine reacts with additional formaldehyde to give trimers, tetramers, and higher oligomers. The diisocyanate from the diamine is known as MDI, whereas the isocyanate from the oligomers is known as poly MDI or PMDI. When MDI is required, the diamine is removed from the mixture by distillation and phosgenated. Conversely, the entire mixture may be phosgenated and the MDI separated from the mixed isocyanates by distillation.

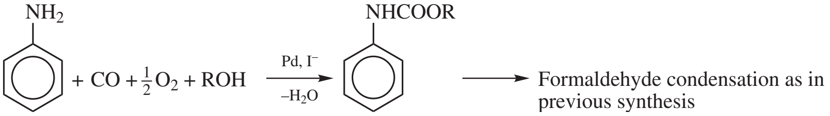
For the condensation of aniline and formaldehyde, aniline is treated with a stoichiometric amount of hydrochloric acid, and the hydrochloride is reacted with 37% formaldehyde for a few minutes at 70°C. The condensation is completed at 100–160°C for one hour. The mixture of di- and higher amines is recovered and phosgenated by reaction with phosgene in chlorobenzene solution. The carbamoyl chloride forms at 50–70°C, and this is decomposed to the isocyanate at 90–130°C with release of HCl.

Several non-phosgene routes have been proposed for the preparation of MDI, but none has been commercialized. An ARCO process developed further by Japanese companies, involves the direct carbonylation of nitrobenzene in the presence of a lower alcohol with a sulfur or selenium catalyst. A carbamate forms that can be reacted with formaldehyde to give dimers and oligomers, after which the carbamate groups are converted to isocyanates by heating with or without a catalyst. The recovered alcohol is recycled.

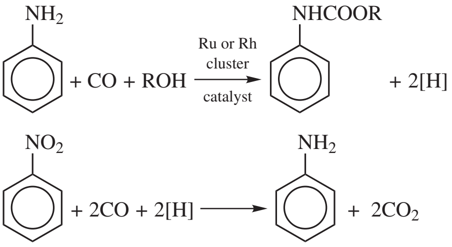


ARCO never commercialized the process, presumably because residual selenium could not be completely removed from the product. The catalysts proposed by the Japanese companies are said to be superior and include iodide-promoted palladium metal and a ruthenium carbonyl complex.

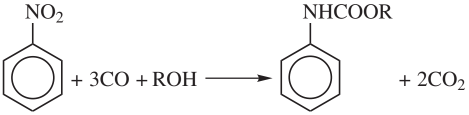
An Asahi process starts with aniline, which makes necessary an oxidative carbonylation. The catalyst is palladium metal with an iodide promoter. In this redox system, in which the palladium is catalytic rather than stoichiometric, Pd is reduced to Pd^{2+} and the iodide I^- is oxidized to iodine I_2. Ethylene phenylcarbamate forms, which reacts with formaldehyde to give a dicarbamate, which in turn decomposes to the diisocyanate. An advantage of this process is that it is said to give a minimum of polymeric products in the formaldehyde condensation.



In a clever process developed by Catalytica Associates, Nippon Kokan, and Haldor Topsøe, a mixture of aniline and nitrobenzene is carbonylated in the presence of an alcohol to give methyl *N*-phenyl carbamate. Since oxygen is not present, the nascent hydrogen that forms reacts immediately with nitrobenzene to give aniline, which is further carbonylated.



The overall reaction is



No net aniline need be supplied since the nitrobenzene is reduced to aniline in the process. A redox catalyst, which often leads to corrosion, is not required. Instead the process uses a cluster catalyst (an agglomeration of metal atoms) based on rhodium or ruthenium carbonyl complexes incorporating biphosphino or poly tertiary-amino ligands.

Urea may also provide the CO for carbonylating the amine and a process of this type was commercialized in 1995 by Hüls for the manufacture of isophorone diisocyanate. An amine, urea, and an alcohol will form a carbamate, which can be converted to an isocyanate:

$$\mathrm{RNH_2 + NH_2CONH_2 + R'OH \longrightarrow RNHCOOR' + 2NH_3}$$

$$\mathrm{RNHCOOR' \longrightarrow RNCO + R'OH}$$

In the Hüls process, *n*-butanol is used for the alcohol. This type of chemistry seems to be effecive only for aliphatic isocyanates, and thus the challenge of making the large volume aromatic isocyanates without the use of phosgene still remains unmet.

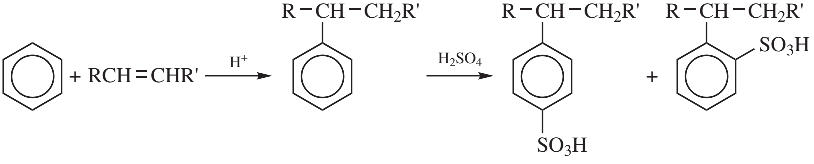
Polyurethanes (Section 15.4.2) are made by reaction of diisocyanates with hydroxyl-containing compounds, primarily polyether polyols (Section 4.11.1). If the hydroxyl compound is bifunctional, a linear polymer results, but usually a polyfunctional alcohol is used to give a cross-linked, thermosetting resin. The polyols are sometimes replaced by polyamines. The products have a urea structure, and in industry these materials are commonly referred to as polyurethanes. The two major diisocyanates are MDI/PMDI and toluene diisocyanate (Section 8.3). Their application is primarily for foams. The MDI/PMDI provides most of the rigid foams, which are largely used for insulation, whereas TDI provides the flexible ones, which are used in upholstery, bedding, and automobiles. Of particular interest is RIM, an acronym for reaction injection molding. In this process, the isocyanate and a polyamine, which reacts faster than a polyol, are pumped into a mold together with a catalyst, so that they may react in the mold. This makes large moldings possible. The steering wheels of cars are frequently made by RIM, because a skin forms that provides a leather-like feel.

There are also noncellular applications for isocyanates, mostly in corrosion-resistant maintenance coatings, which use primarily MDI/PMDI if yellowing is not a problem. Nonyellowing urethane coatings are based on aliphatic isocyanates derived from hexamethylene diamine, bis(aminocyclohexylmethane), "isophorone diamine," xylylene diamine, and tetramethylxylylene diisocyanate. These are all termed aliphatic, even though two of them contain aromatic rings. The isocyanate groups, however, are attached to aliphatic carbon atoms. The structures are shown in Figure 7.10.

Nonyellowing isocyanates are useful for aircraft topcoats over epoxy primers. A more recent application, which could develop into large volume usage, is clear automotive topcoating.

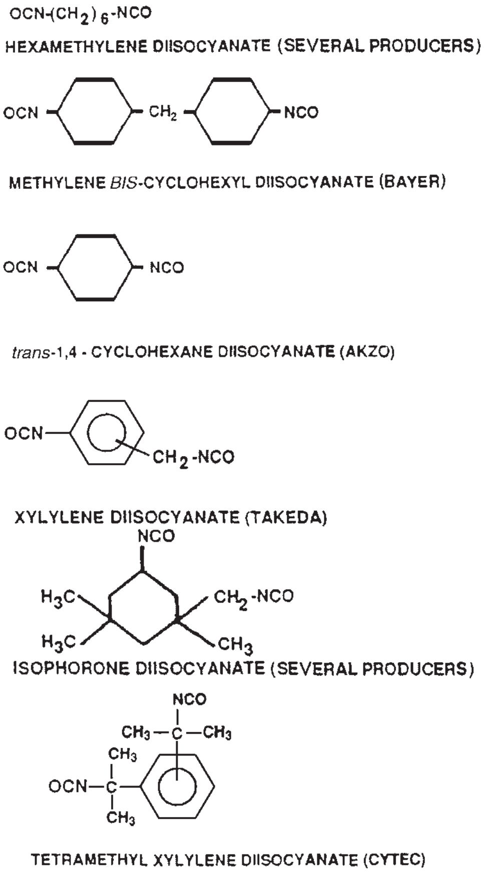
7.4 ALKYLBENZENES

The most important alkylbenzenes are those with C_{10}–C_{14} side chains. These are sulfonated to provide the alkylbenzenesulfonate surfactants, useful in detergent formulations. The equation is written for an internal olefin:



Alkylbenzene sulfonates

There are several sources of the side chains for the Friedel–Crafts alkylation of benzene for surfactants. Initially propylene tetramer, from polygas (Section 2.2.4), a highly branched dodecene, was used, and this is still important in developing countries (Section 4.6). In the United States and Western Europe, it has been outlawed because branched-chain surfactants biodegrade very slowly with resultant foaming in rivers and sewage plants.



HEXAMETHYLENE DIISOCYANATE (SEVERAL PRODUCERS)

METHYLENE *BIS*-CYCLOHEXYL DIISOCYANATE (BAYER)

trans-1,4 - CYCLOHEXANE DIISOCYANATE (AKZO)

XYLYLENE DIISOCYANATE (TAKEDA)

ISOPHORONE DIISOCYANATE (SEVERAL PRODUCERS)

TETRAMETHYL XYLYLENE DIISOCYANATE (CYTEC)

FIGURE 7.10 Selected “aliphatic” diisocyanates.

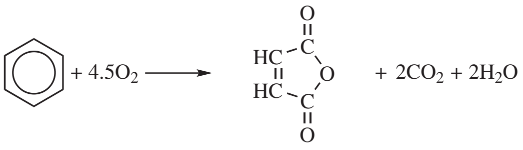
The move to biodegradable detergents made necessary the manufacture of linear olefins. High molecular weight paraffins (C_{20}–C_{30}), which occur in the wax separated from lubricating oil, can be separated into linear and branched molecules by use of molecular sieves, particularly by UOP’s Molex process. The linear fraction can then be steam-cracked, just as lower hydrocarbons can, to provide α-olefins with both even and odd numbers of carbon atoms with chain lengths varying from C_6 to C_{18}. These are impure but suitable for surfactants. Alternatively, paraffins from C_6 to C_{19} may be dehydrogenated catalytically to internal olefins.

The Friedel–Crafts alkylation of benzene can also be carried out with alkyl chlorides (monochloroparaffins) made by chlorinating *n*-alkanes with 10–15 carbon atoms. The dehydrochlorination of the monochloroparaffins also provides useful olefins. The supply of wax, however, is limited, which makes necessary the use of olefins from ethylene oligomerization (Section 3.2). Either linear or internal olefins with chain lengths of C_{10}–C_{13} can be used, the major source of the latter being the Shell SHOP process (Section 3.3.3). From internal olefins, as in the equation above, a molecule with two side chains results, but since both of these are linear they are biodegradable.

The Friedel–Crafts alkylations were traditonally brought about by hydrogen fluoride or aluminum chloride catalysts. These are noxious and have largely been replaced by solid acid catalysts such as zeolites, certain synthetic clays and solid Lewis acids.

7.5 MALEIC ANHYDRIDE

Most maleic anhydride is made by the oxidation of butane or, less frequently, 1- and 2-butenes (Section 5.3.1). An older method still used to a slight extent in Europe is based on the oxidation of benzene and is analogous to the process for phthalic anhydride from naphthalene (Sections 9.1.1, 12.1). The vapor-phase oxidation is carried out with a supported vanadium pentoxide catalyst at 400°C. A mixture of maleic acid and maleic anhydride results, and the acid may be dehydrated to the anhydride directly without separation. The product is purified by batch vacuum distillation. The uses for maleic anhydride were described in Section 5.4.

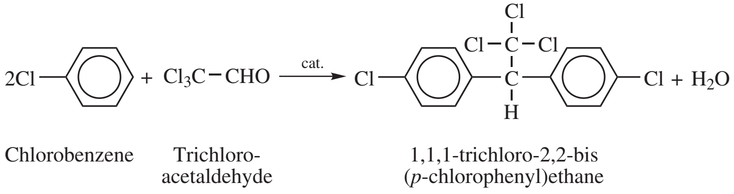


Maleic anhydride

7.6 CHLORINATED BENZENES

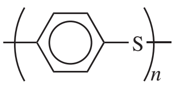
Chlorobenzene results from the liquid-phase chlorination of benzene at slightly above room temperature with a ferric chloride catalyst. Small amounts of di- and trichlorobenzene form. Oxychlorination achieves the same result (Section 3.4) with hydrogen chloride and air instead of chlorine, and an alumina-supported cupric chloride-ferric chloride catalyst. This was in fact the first use for oxychlorination, which today makes a key contribution to vinyl chloride manufacture (Section 3.3). Conversion is kept at 10–15% to supress the formation of di- and polychlorobenzenes and to control the reaction's exothermicity.

Chlorobenzene is used primarily as a solvent (cf. phosgenation of diaminodiphenylmethane, Section 7.3.1). It may be converted to aniline (Section 7.3) and has been used in the past as a raw material for phenol (Section 7.1). Chlorobenzene condenses with trichloroacetaldehyde (chloral) to yield the insecticide 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDT). In about 80% of the product the chlorines are *para–para* but *ortho–para* and *ortho–ortho* forms are also produced.



DDT was remarkably effective in mosquito control but was banned because its stability and lipophilicity caused it to accumulate in body fat. Strains of mosquitoes immune to DDT have emerged either because they have developed enzymes that hydrolyze DDT or because natural selection has retained only immune strains. In many areas DDT is now useless, and there was a drive to ban it completely at the United Nations Environment Programme negotiations on persistent organic pollutants in Johannesburg in 2000. There are, however, places where it is remains effective, and it is still used in 23 countries in Africa, Asia, and South America, including Ethiopia, India, South Africa, Madagascar, and Swaziland. In most cases, its use is restricted to spraying the insides of houses to limit malaria. In spite of support for the ban from the major environmental groups, the threat of even more deaths from malaria resulted in a treaty permitting its restricted use in disease vector control.

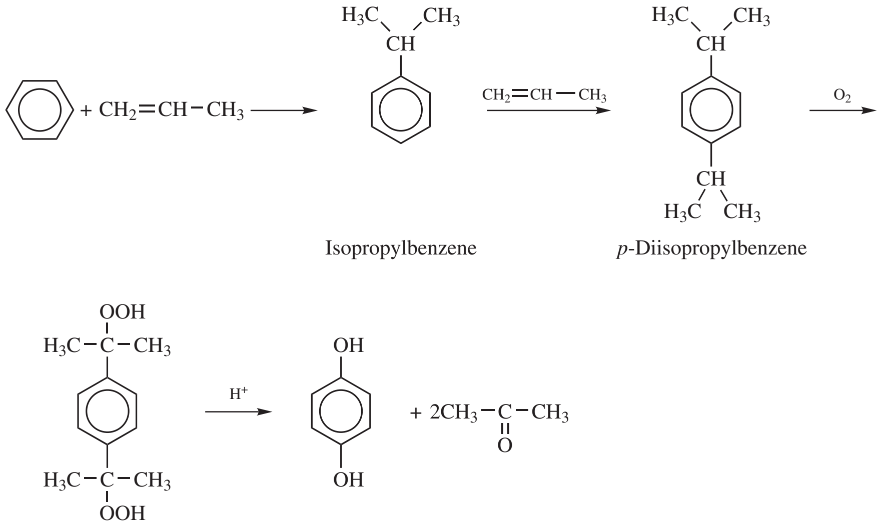
Dichlorobenzenes are small-volume chemicals which, like many chlorine derivatives, are being phased out. *p*-Dichlorobenzene is used as a moth repellant and deodorant. On reaction with sodium sulfide, the specialty polymer, poly(phenylene sulfide) results. Its recurring unit is



o-Dichlorobenzene is a solvent for toluene diisocyanate.

7.7 DIHYDROXYBENZENES

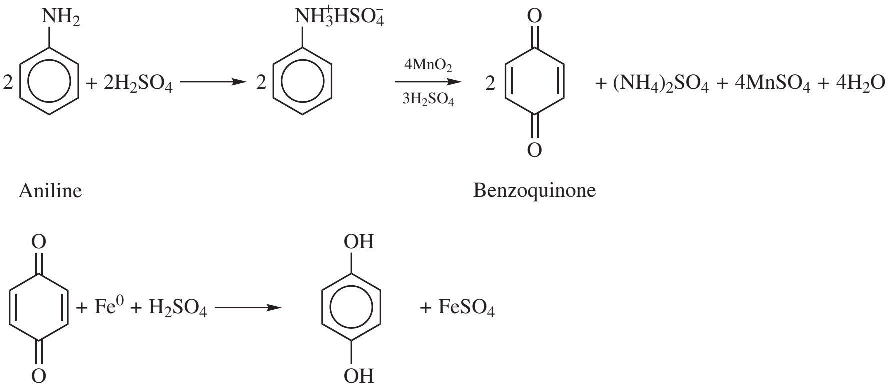
Of the three dihydroxybenzenes—hydroquinone, resorcinol, and catechol—hydroquinone is the most important. Numerous processes have been proposed for its preparation. One is analogous to the cumene-based phenol process (Section 4.9). *p*-Diisopropylbenzene is prepared by alkylating cumene with isopropyl chloride in the presence of aluminum chloride at 90°C to achieve a 98% molar yield. Peroxidation takes place at 90–100°C with air in the presence of dilute sodium carbonate. A mixture of mono- and dihydroperoxides results. Extraction with aqueous alkali separates the two. The oxidation gives 10% conversion and the ultimate molar yield of dihydroperoxide is 65%. It is decomposed in acetone solution with dilute sulfuric acid at 90°C and 2 bar. Hydroquinone is formed in an overall yield of 60 mol%. Acetone is a coproduct.



Isopropylbenzene p-Diisopropylbenzene

p-Di(2-hydroperoxy-2-propyl)benzene Hydroquinone

The earliest procedure for hydroquinone manufacture but still in use involves aniline sulfate oxidation (Section 7.3) to benzoquinone in the presence of manganese dioxide. Reduction of the quinone with iron and sulfuric acid provides hydroquinone and ferrous sulfate, which can subsequently be converted to ferric oxide, useful as a pigment but whose consumption is declining.

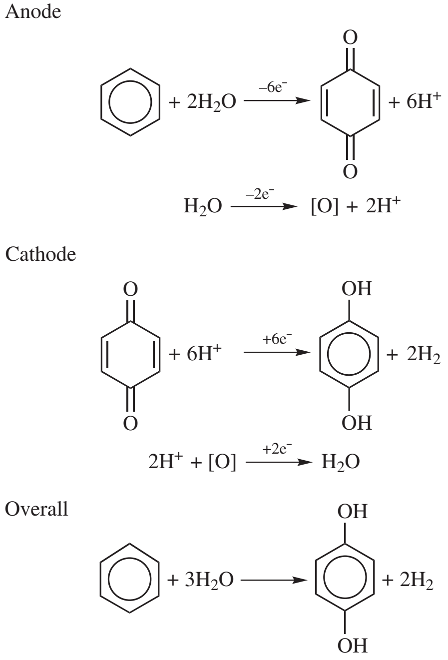


Aniline Benzoquinone

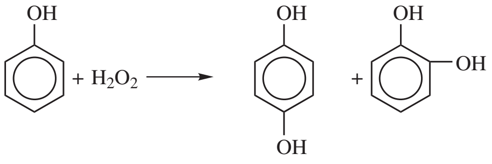
Hydroquinone

The initial oxidation is carried out below 10°C. Chromic acid may be used instead of manganese dioxide. In either instance, ammonium sulfate residues provide a disposal problem.

The electrolytic oxidation of benzene to hydroquinone has never been commercialized although it appears attractive economically. The benzene is oxidized continuously at the anode of an electrolytic cell to produce benzoquinone, which is concurrently reduced to hydroquinone at the cathode.

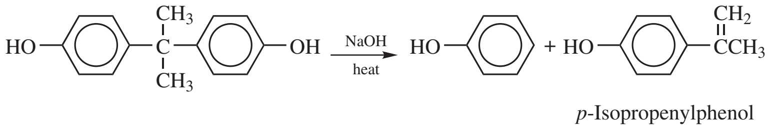


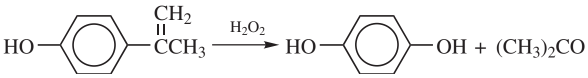
The direct hydroxylation of phenol with hydrogen peroxide provides a mixture of catechol and hydroquinone. The process is believed to be used in Europe and Japan.



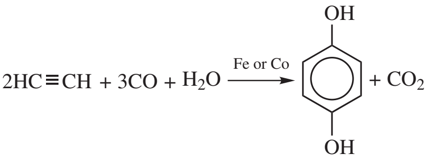
Phenol Hydroquinone Catechol

A process based on bisphenol A involves its conversion to *p*-isopropenylphenol either by a base-catalyzed or thermal decomposition. Reaction of *p*-isopropenylphenol with hydrogen peroxide yields hydroquinone and acetone.





A Reppe process involves simultaneous cyclization and carbonylation of acetylene with iron or cobalt catalysts. A more modern version makes use of ruthenium or rhenium catalysts at 600–900 bar with hydrogen instead of water. If carbonyl cluster catalysts are used, lower pressures are possible at temperatures of 100–300°C. These processes have not been commercialized.



A biological route to hydroquinone and benzoquinone is described in the literature (see note to Section 16.8).

The major uses for hydroquinone are as an antioxidant and antiozonant in rubber manufacture and in chemical formulations for the development of photographic films. It is also a polymerization inhibitor in the manufacture and storage of monomers such as acrylonitrile, vinyl acetate, and acrylic and methacrylic esters. It is a precursor of butylated hydroxyanisole (BHA) a food grade antioxidant prepared by alkylating the monomethyl ether of hydroquinone with isobutene. A related food grade antioxidant is butylated hydroxytoluene (BHT) (Section 5.2.6). Growth in hydroquinone usage is not expected because tires last longer and new photographic films require less hydroquinone for developing.

Resorcinol is made by benzene disulfonation analogous to an obsolete process for phenol manufacture (Section 7.1). Isomers are avoided because of the *meta* directiveness of the sulfonic acid group. Monosulfonation is carried out at 100°C with 100% sulfuric acid made by adding oleum to 96% acid (Fig. 7.11). Oleum is used at 80°C for the second sulfonation because the water produced dilutes the acid and, if the strength drops below 80%, sulfonation ceases. The disulfonic acid is neutralized with sodium sulfite or sodium carbonate to produce SO_2 or CO_2. Sodium sulfite is preferred because it is a byproduct of the overall reaction and can be recycled.

Sodium sulfate is also formed as a byproduct because excess sulfuric acid is used, which must be neutralized. A variation of the neutralization step, which eliminates the excess sulfuric acid, involves the use of calcium carbonate to complete the 90% neutralization achieved with sodium sulfite. A 9:1 mixture of sodium and calcium salts of the benzenedisulfonic acid is obtained, which is further treated with

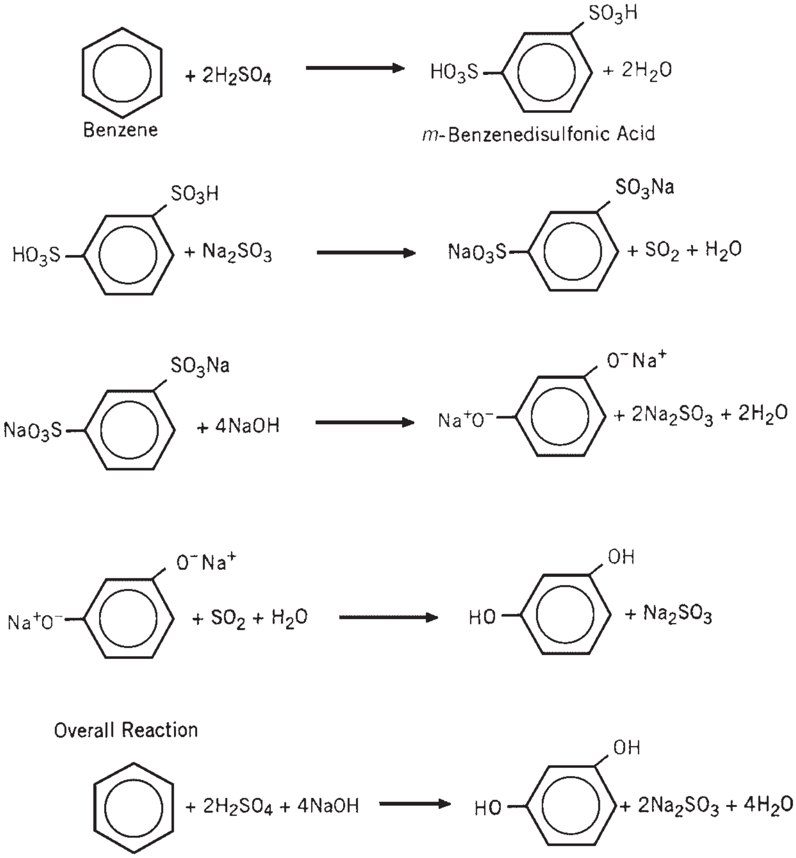


FIGURE 7.11 Resorcinol from benzene.

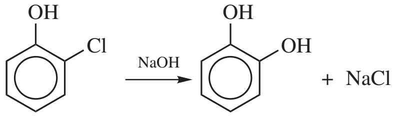
sodium carbonate. The sodium displaces the calcium and produces calcium carbonate together with the completely neutralized sodium salt of benzenedisulfonic acid.

This sodium salt is fused with sodium hydroxide in a batch process at 300°C at a four to one molar ratio of caustic to sodium salt. The resulting mixture is neutralized either with sulfuric acid or with the SO_2 evolved in the initial neutralization of the benzenedisulfonic acid. A mixture of resorcinol, sodium sulfate, and sodium sulfite results. Resorcinol may be extracted from the aqueous solution by several solvents including isopropyl ether.

Resorcinol is used in the formulation of high-performance adhesives; primarily resorcinol–formaldehyde condensates for the rubber and wood product industries and for bonding tire cord to the rubber tire matrix. These adhesives have better properties than phenol–formaldehyde resins (Section 7.1.1) for the production of laminated beams where high strength is required and the application of heat is impractical. Resorcinol is also a raw material for the production of pharmaceuticals, dyes, and ultraviolet absorbers. Typical is its conversion to *m*-aminophenol by reaction with ammonia, a reaction analogous to the amination of phenol to aniline (Section 7.1.5).

The lead salt of mononitroresorcinol is made by mild nitration of resorcinol. It is used in modern firework displays, often set to music, where split second timing of ignition is essential. It is one of the few explosives capable of igniting reliably when a “bridgewire” running through it glows transiently red hot after an electric current is switched on. It produces a flame that burns for about four milliseconds, depending on the applied current, and is used with more conventional oxidizers and fuels.

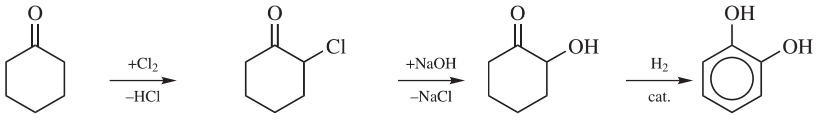
o-Dihydroxybenzene (catechol or pyrocatechol) results from the caustic hydrolysis of *o*-chlorophenol in the presence of copper powder at 190–230°C and 3–6 bar. In the process, a chlorine atom is replaced by a hydroxyl group. Conversion is 69%, of which 89% is catechol and 11% resorcinol and higher phenols. This is no longer used commercially.



o-Chlorophenol

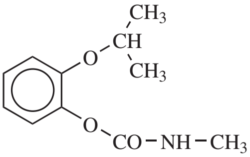
A second route to catechol involves the direct hydroxylation of phenol with hydrogen peroxide in the presence of formic and phosphoric acids. A mixture of three parts catechol to two of hydroquinone results. Formic acid alone favors increased formation of hydroquinone. The two products are separated by distillation.

A third synthesis involves the chlorination of cyclohexanone to 2-chlorocyclohexanone. Caustic hydrolysis of the chlorine provides 2-hydroxycyclohexanone, which can then be dehydrogenated to catechol.



Cyclohexanone 2-Chlorocyclohexanone 2-Hydroxycyclohexanone Catechol

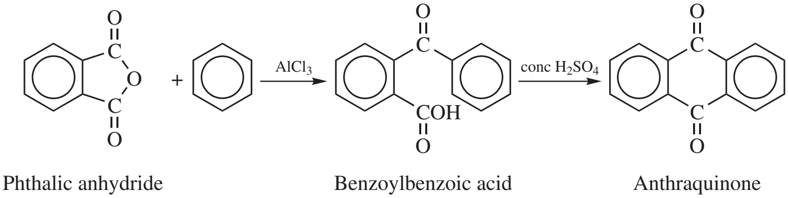
The major use for catechol is for the preparation of a carbamate insecticide, propoxur, used to kill household pests.



Propoxur

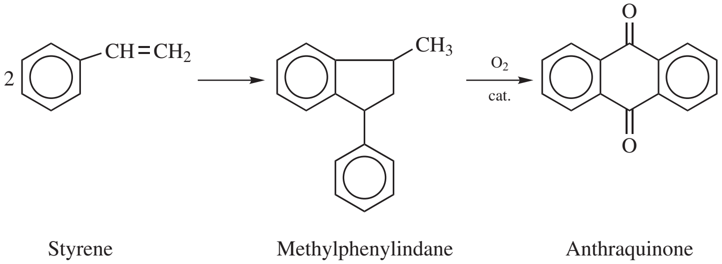
7.8 ANTHRAQUINONE

The Friedel–Crafts condensation of benzene and phthalic anhydride (Section 9.1) in the presence of aluminum chloride at 25–60°C produces benzoylbenzoic acid. The product is cyclized with oleum to anthraquinone, which is purified by sublimation at 380°C. Yields are of the order of 95%.



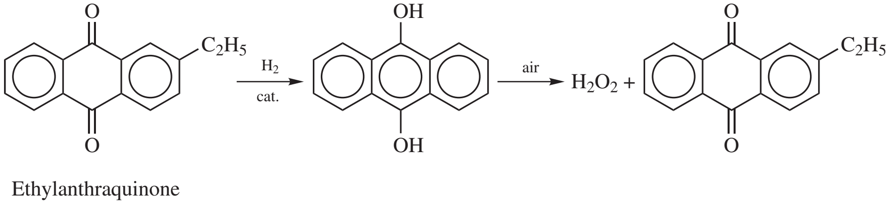
A second route to anthraquinone involves the direct oxidation of anthracene, a process still practiced in Europe, where high-purity anthracene has traditionally been available from coal tar fractionation.

In a third process, styrene is dimerized to methylphenylindane, which can be oxidized in the vapor phase to anthraquinone. The dimerization is catalyzed by sulfuric acid at reflux temperature. The complex vapor-phase conversion to anthraquinone takes place over a promoted vanadium pentoxide catalyst.



Anthraquinone has been used primarily for the production of dyes and pigments. Tetrahydroanthraquinone is used as a catalyst to facilitate the chemical pulping of wood for paper manufacture. This technology has been pioneered in Japan, where it is used primarily with Kraft pulping, which employs sodium hydroxide and sodium sulfide to disengage lignin from the wood and leave cellulose fibers. In conventional pulping, the 1,4-glycosidic linkages of cellulose are hydrolyzed and reduce the yield of pulp. Tetrahydroanthraquinone apparently accelerates the delignification process while inhibiting attack on the cellulose. Higher yields of pulp result.

Ethylanthraquinone is the catalyst in the autooxidation route for the manufacture of hydrogen peroxide. It is reduced by hydrogen on palladium to the hydroquinone, and then reoxidized with air to give hydrogen peroxide and the original anthraquinone.



NOTES AND REFERENCES

The standard work on benzene is still *Benzene and its Industrial Derivatives*, E. G. Hancock, Ed., Benn, London, 1975. More recent is H-G. Franck and J. W. Stadelhofer, *Industrial Aromatic Chemistry*, Springer, Berlin, 1988. There is a slim paperback *Benzene*, VCH Publishers, 1993, but no author is listed.

For a good discussion of benzene process technology and production economics see Nexant Chemsystems' PERP report 02/03-5, Benzene/Toluene (April, 2003).

Catalytic reforming (Section 2.2.3) works best with C_7 and C_8 molecules but less well with C_6 alkanes, which tend to form cracked products, thus reducing the yield of benzene. Also higher temperatures are required to reform C_6 alkanes. Thus, by using lower temperatures, the C_7 and C_8 molecules reform preferentially. If the naphtha is stripped before reforming, most of the C_6 alkanes are removed so that benzene cannot form. Even so, benzene results in the reforming process from hydrodealkylation of the toluene and xylenes.

In the early 1990s, Chevron instituted a catalytic reforming process called Aromax, based on a metal-doped zeolite catalyst, which reforms the C_6 fraction more effectively to give a higher yield of benzene. (Section 2.2.3).

Section 7.1 The Japanese process for producing phenol only from cumene has been described by Mitsui Petrochemical in Japanese Patents 300,300 (November 28, 1988) and 328,722 (December 26, 1988). Oxidation of benzene to phenol maintaining a high-product ratio is reviewed by J. Plotkin, *Eur. Chem. News*, September 25–October 2, 2000, pp. 59–62.

Benzene acetoxylation has been described by J. Davidson and C. Triggs, *Chem. Ind.* 1361 (1976) and in Ger. Offen 1,643,355 (1967). The Korea Research Institute process is described in *Eur. Chem. News*, May 22–28, 2000, p. 33, and in World Patent Appl. 99/64,129. The Japanese one-step palladium-catalyzed phenol process is described in *Eur. Chem. News*, January 14–20, 2002, p. 23.

Perhaps the first citation that describes the nitrous oxide oxidation of benzene to phenol is by Japanese workers M. Iwamoto, J. Hirata, K. Matsukami, and, S. Kagawa, *J. Phys. Chem.*, **87,** 903 (1983).

Patents describing Boreskov Institute of Catalysis' nitrous oxide based oxidation of benzene to phenol include WO 95/27,560 (April 12, 1995) and WO 95/27,561 (April 12, 1995).

Solutia patented a fluidized-bed reactor for the nitrous oxide oxidation of benzene to phenol, US Patent 5,892,132 (April 6, 1999).

Section 7.1.2 The rearrangement of BPA byproducts to BPA is described in US Patent 3,221,061 (November 30, 1965) to Union Carbide.

Section 7.1.2.2 The preparation of dimethyl carbonate is described in US Patent 4,360,477 (November 23, 1982) to General Electric. The use of this reagent in the polycarbonate synthesis is described in US Patent 4,452,968 (June 5, 1984) to General Electric. The 1995 patent involving tetrabutylammonium hydroxide is US Patent 5,391,692. The oxidative carbonylation route to polycarbonate is mentioned in www.nedo.go.jp/kiban/zairyo/eng/poly/poly005.html.

The Bayer route to dimethyl carbonate is described in US Patents 5,449,9806 (September 12, 1995) and 5,523,452 (June 4, 1996) both to Bayer. The Bayer approach to diphenyl carbonate is described in US Patent 5,334,742 (August 2, 1994) to Bayer. Asahi has a patent that discloses the use of reactive distillation to effect the methanolyis of ethylene carbonate to dimethyl carbonate and ethylene glycol, US Patent 5,847,189 (December 8, 1998).

Section 7.2.1 The microbiological route from toluene to adipic acid is described in Celanese patents including US Patent 4,355,107 (October 19, 1982) and European Patent Appl. 0,074,168 (March 16, 1983) and 0,117,048 (August 29, 1984).

The Gulf process for adipic acid formation in one step is described in US Patent 3,231,608 (January 25, 1966) and US Patent 4,263,453 (April 21, 1981).

Nagoya University's route to adipic acid via hydrogen peroxide oxidation of cyclohexane using phase-transfer catalysis is described in *Jpn. Chem. Week*, September 28, 1998, p. 2.

The University of North Carolina process for adipic acid via dimerization of methyl acrylate is disclosed in European Patent 0,475,386 B1 (August 9, 1995).

The attempts to reduce emissions of nitrous oxide are reviewed by A. Scott, *Chem. Week*, February 18, 1998.

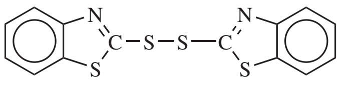
Section 7.2.1.1 Nylon 4,6 is described in US Patent 4,408,036 (October 4, 1983) to Stamicarbon BV.

Section 7.2.2 The 1999 hydroxylamine plant explosions are described in *Chem. Eng. News*, June 19, 2000, p. 15 and July 3, 2000, p. 8. The Mitsubishi Kasei and Enichem catalysts for caprolactam production are described briefly in *Chem. Week*, August 3, 1994, p. 21.

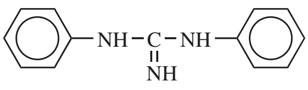
Sumitomo and Enichem's announcement about combining each company's developments to allow a ammonium sulfate-free caprolactam process is found in *Chem. Mkt. Rep.*, October 16, 2000.

Section 7.3 The adiabatic process for nitrobenzene formation is described in US Patent 4,021,498 (May 3, 1977) to American Cyanamid. The ICI process is disclosed in World Patent Appl. 00/09473 and *Eur. Chem. News*, 22–28 May 2000, p. 33.

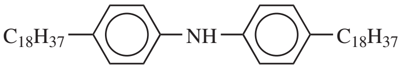
Aniline is the basis for several rubber compounding agents. Thus dibenzthiazole disulfide is a primary accelerator. Diphenylguanidine, is a secondary accelerator and *p,p′*-distearyldiphenylamine, is an antioxidant and antiozonant.



Dibenzthiazole disulfide



Diphenylguanidine



p,p′-Distearyldiphenylamine

Section 7.3.1 The ARCO process for carbonylation of nitrobenzene is described in a number of patents including US Patents 3,595,054 (July 15,1975); 3,962,302 (June 8, 1976); 4,041,139 (May 8, 1977); and 4,038,377 (August 1, 1977).

The Asahi process is described in numerous Japanese Patents including 58-159,751 (1983); 57-158,746-8 (1982); 58-67,660 (1983); and 58-96,054 (1983).

Section 7.6 The consensus that DDT is wholly bad was debated at the Johannesburg negotiations. Some details are given at www.sciencenews.org/20000701/bob2.asp. A fairly partisan web site www.malaria.org/DDTpage.html provides an extensive bibliography and www.junkscience.co./ddtfaq.htm calls into question the evidence that DDT is responsible for the various problems with birds and their eggs. See also a collection of articles at www.malaria.org/DDTpage.html.

Section 7.7 The electrolytic oxidation of benzene to hydroquinone is a URBK–Wesseling process described in *Chem.-Ing.-Tech.* **46**(15) (1974). Related processes have been patented by Du Pont (US Patent 3,884,776, June 20, 1975). The electrolytic oxidation of phenol is described in patents to Union Carbide (French Patent 15,444,350, October 31, 1968) and to Eastman Kodak (US Patent 4,061,548, December 6, 1977). Phenol oxidation with hydrogen peroxide is also described by Goodyear in US Patents 3,870,731 (March 11, 1975) and 3,859,317 (January 7, 1975). The process involving *p*-isopropenylphenol is patented by Upjohn in German Offen. 2,214,971 (November 16, 1972).

Mononitroresorcinol plus other fireworks chemistry is described in M. Russell, *Chem. Brit.* **38**, 36 (2002).

Section 7.8 The use of anthraquinone for pulping of wood has been described by J. M. MacLoed, *TAPPI Proceedings*, 1983 Pulping Conference.

CHAPTER 8

CHEMICALS AND POLYMERS FROM TOLUENE

Toluene is the major product from catalytic reforming (Section 2.2.3). The chemical industry requires considerably more benzene than toluene, but toluene is preferred for unleaded gasoline because of its low toxicity and high-octane number. Catalytic reforming is the major source of toluene in the United States but in Western Europe pyrolysis gasoline (Section 2.2.1) is the major source.

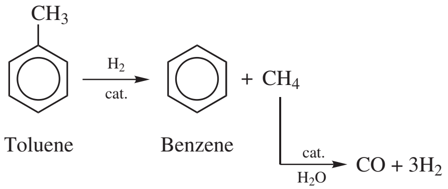
Just as propylene has traditionally been cheaper than ethylene, toluene has similarly been cheaper than benzene. Propylene's ready availability and its reactive allylic hydrogens led to the development of a series of brilliant chemical reactions. Attempts to find broad usage for toluene were less successful despite its reactive benzylic hydrogens. Its main chemical uses are hydrodealkylation to benzene and disporportionation to benzene and xylenes. These are "swing" operations and occur when the price differential is sufficient. In 2002, they consumed 70% of the toluene isolated from catalytic reforming in the United States.

With a US consumption in 2001 of about 9.1 billion lb for chemical uses, toluene is the smallest of the seven basic chemicals. The fact that so much of it is used to augment benzene and xylenes output by hydrodealkylation and disproportionation (Section 8.1) indicates that even this figure of 9.1 billion lb exaggerates its chemical importance.

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

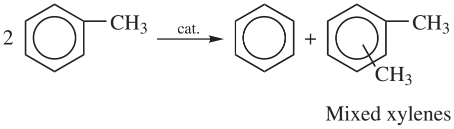
8.1 HYDRODEALKYLATION AND DISPROPORTIONATION

In situ hydrodealkylation during catalytic reforming was discussed in Section 2.2.3 as an additional source of benzene in that reaction. Hydrodealkylation in a dedicated plant may be purely thermal or it may be catalyzed by metals or supported metal oxides. Hydrogen is always present. Typical reaction conditions are 600°C and 40–60 bar over oxides of chromium, platinum, molybdenum or cobalt, supported on alumina. The uncatalyzed reaction requires a higher temperature of up to 800°C and a pressure up to 100 bar.



Methane forms and, in one version of the process, it is subjected to the synthesis gas reaction (Section 10.4) to provide hydrogen for the hydrodealkylation. Despite the cost of catalyst, the catalytic method is preferred because it allows for higher conversion and gives greater selectivity so that more than 92% benzene results.

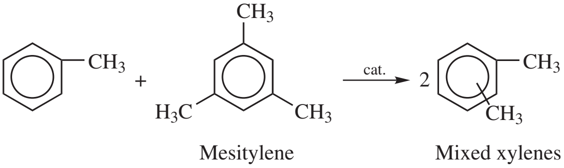
A variation of hydrodealkylation is disproportionation. Two molecules of toluene react to give one of benzene and one of mixed xylenes.



Disproportionation is important as a source of mixed xylenes from which the *para* isomer, the one most in demand, can be isolated. The reaction is carried out in the vapor phase in the presence of a non-noble metal catalyst. Even a casual estimate of the energetics of the reaction indicates that the equilibrium constant is close to unity, so large volumes of reactants must be recycled from the product-recovery section of the plant to the reactor. The advantage of the process, compared with catalytic reforming, is that the reactor effluent is free from ethylbenzene. This makes the separation of the xylene isomers easier, and crystallization may be used (Section 9).

Disproportionation is formally (but not mechanistically) similar to metathesis (Section 2.2.9). Both produce two more valuable products from one less valuable one. It has assumed major importance in the United States, and in 2001 4.3 billion lb of benzene was produced by this process. This figure is expected to grow, primarily because of a dramatic improvement developed by Mobil in the mid- to late-1980s. This comprised a liquid-phase process based on a shape selective, antimony-doped zeolite ZSM-5 catalyst at 300°C and 45 bar. A xylene fraction results with as much as 95–99% of the desired *p*-xylene. The disproportionation takes place inside a zeolite cage whose "mouth" is shaped such that benzene, toluene and *p*-xylene have ready access but *o*- and *m*-xylenes cannot escape (Section 16.9). Accordingly these isomers remain in the cage to undergo further isomerization and to supply the equilibrium quantities required each time 2 mol of toluene disproportionate. These types of process, termed "selective toluene disproportionation," are now offered by several licensors such as UOP, Axens, and GTC. *p*-Xylene selectivities in the range of 95–99% can now be achieved, but at these high selectivities toluene conversion per pass is reduced to 20–23%.

Another form of disproportionation, called transalkylation, involves the interaction of toluene with 1,3,5-trimethylbenzene or mesitylene, a compound produced during catalytic reforming.



A methyl group migrates from a trimethylbenzene molecule to a toluene molecule giving two molecules of mixed xylenes. The reaction is carried out in the presence of hydrogen. In practice, benzene is also produced, but its volume can be kept low by use of a high ratio of trimethylbenzene to toluene.

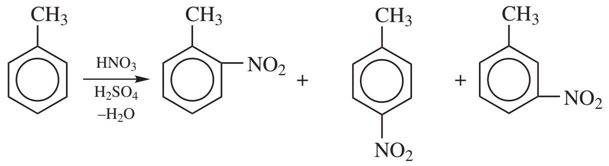
8.2 SOLVENTS

Toluene's second largest use is as a solvent mainly for coatings. The finding in the United States that benzene is carcinogenic has increased toluene's solvent usage at the expense of benzene, although the latter is in any case small. Toluene is a primary solvent for coatings based on medium and short oil alkyd resins (Section 9.1.1) but is a so-called latent solvent for nitrocellulose lacquers, which require as primary solvents polar compounds such as esters, ketones, and glycol ethers.

8.3 DINITROTOLUENE AND TOLUENE DIISOCYANATE

The largest outlet for toluene in which its chemical properties are of value in their own right is as a raw material for a mixture of 2,4- and 2,6-toluene diisocyanate (tolylene diisocyanate, diisocyanatotoluene, TDI) used for polyurethane resins. The TDI is made by chemistry similar to that used for 4,4′-diphenylmethane diisocyanate (MDI) (Section 7.3.1). Various non-phosgene routes have been suggested but none has been commercialized.

Commercial TDI contains about 80% of the 2,4-*ortho,para*-isomer and 20% of the 2,6- *ortho,ortho*-isomer. The three-step process comprises the dinitration of toluene; the hydrogenation of the nitro compounds to diaminotoluenes; and the reaction of these with phosgene to commercial grade TDI. Toluene is nitrated with a mixture of nitric and sulfuric acids in two stages. The first produces the three isomers of mononitrotoluene.



Toluene

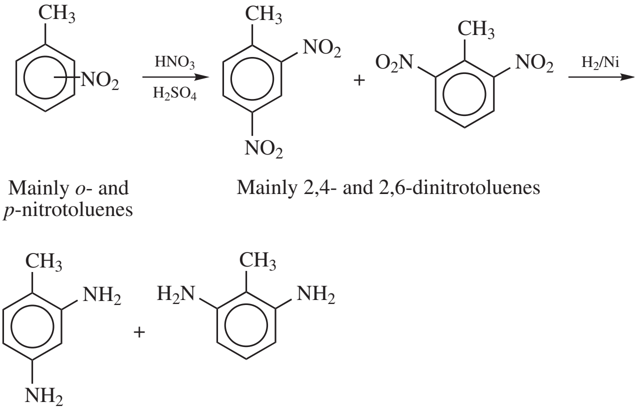
o-Nitrotoluene (65%)

p-Nitrotoluene (31%)

m-Nitrotoluene (4%)

These are subsequently nitrated further to obtain the six possible dinitrotoluene isomers. The 2,4-isomer comprises 74–76% of the mixture and the 2,6-isomer 19–21%. The concentrations of the other four isomers are minimal. The 3,4-compound forms at a level of 2.4–2.6%. The 2,3, 2,5- and 3,5-isomers are present at a level no greater than 1.7%. The concentration of the acids is carefully controlled so that very little of the trinitro isomers form.

The dinitrotoluenes are dissolved in methanol and hydrogenated continuously to diaminotoluenes by reaction with hydrogen in the presence of Raney nickel at 150–180°C and 65–130 bar. Numerous other catalysts such as supported platinum or palladium may be used.



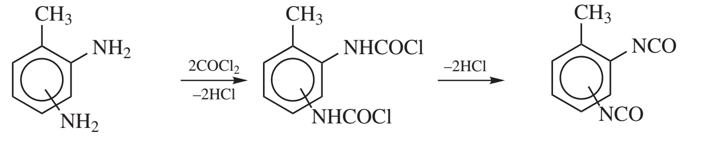
Mainly *o*- and *p*-nitrotoluenes

Mainly 2,4- and 2,6-dinitrotoluenes

Mainly 2,4- and 2,6-diaminotoluenes

The possibility of eliminating the nitration step by an intermolecular amination of toluene with ammonia is of some interest. Similar chemistry has been discussed for the possible preparation of aniline (Section 7.3) and *m*-aminophenol (Section 7.7).

The carbonylation with phosgene occurs in two stages, the first yielding a carbamoyl chloride and the second the isocyanate. In both reactions, HCl is liberated. The reaction is carried out with a 10–20% solution of the diamine mixture in chlorobenzene (Section 7.6). This is combined with a chlorobenzene solution of phosgene.



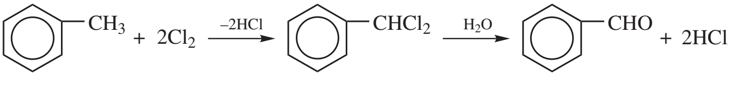
Mixture of 2,4 and 2,6-diaminotoluenes   Isomeric carbamoyl chlorides   Mixture of 2,4- and 2,6-tolune diisocyanate

Carbamoyl chloride formation occurs at 0–30°C and isocyanate formation at 160–180°C. Conversion is about 80%. Treatment of the residue with alkali provides unreacted diaminotoluene for recycle.

Dinitrotoluene is also used as a gelatinizing and waterproofing agent in explosive compositions. Additional nitration gives trinitrotoluene (TNT), an explosive formerly used in military and civilian applications but now of importance only to the military. It is safer than picric acid (Section 7.1) because it does not form detonation-sensitive salts with metals and has a lower melting point (80°C) so that it can be conveniently loaded into shells in the molten state. For civilian explosives, such as those used in mining, ammonium nitrate is the preferred material.

8.4 LESSER VOLUME CHEMICALS FROM TOLUENE

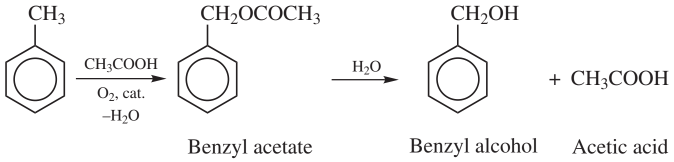
Toluene may be converted to phenol (Section 7.1). It also provides the starting material for one route to caprolactam (Section 7.2.2). In a reaction analogous to the formation of allyl chloride from propylene (Section 4.14.1), the methyl group of toluene can be chlorinated to yield benzyl chloride, which may be used to quaternize tertiary amines such as lauryldimethylamine to give germicidal compounds. Its main use is as a raw material for the minor PVC plasticizer, butyl benzyl phthalate. The presence of the aromatic ring appears to confer stain resistance to PVC floor coverings. Dichlorination of the methyl group of toluene leads to benzal chloride, which on hydrolysis provides benzaldehyde, an ingredient of flavors and perfumes. This is the most important route to benzaldehyde, which is also a valuable byproduct of the toluene-to-phenol process (Section 7.1).



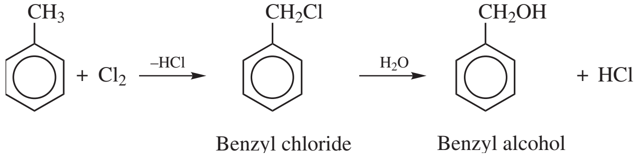
Benzal chloride   Benzaldehyde

It may also be made by direct oxidation of toluene, which is usually accomplished in the liquid phase with air at about 100°C and 3 bar with cobalt salt catalysts. In another process, the oxidation is carried out in acetic acid with cobalt and manganese acetates as catalysts. This is analogous to the process used for the preparation of terephthalic acid (Section 9.3).

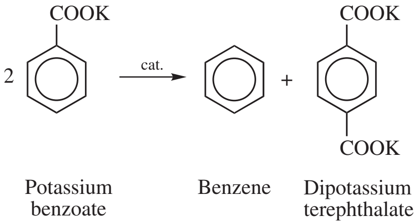
The oxidation of toluene gives not only benzaldehyde but also benzyl alcohol, just as the oxidation of propylene provides acrolein and allyl alcohol (Sections 4.7, 4.14.2), although the mechanisms are different. These normally occur as recyclable byproducts during benzoic acid formation. If benzyl alcohol is required by direct oxidation, the reaction is carried out in the presence of acetic acid, which captures the alcohol as benzyl acetate before it is oxidized further to benzoic acid. The same technique is used in the oxidation of propylene to allyl alcohol.



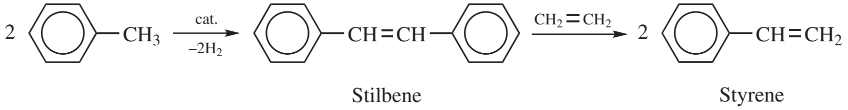
The most important route to benzyl alcohol, however, is by the hydrolysis of benzyl chloride.



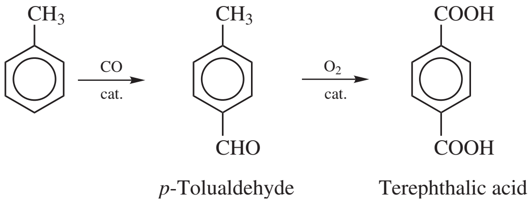
Benzoic acid is a halfway state in a minor process for phenol manufacture (Section 7.1), but benzoic acid itself has a few small uses. Sodium benzoate is a preservative in some foods. Diethylene glycol dibenzoate is a useful nonstaining plasticizer for PVC flooring where it competes with butyl benzyl phthalate. Butyl benzoate is a perfume ingredient. Benzoic acid is an intermediate in a caprolactam synthesis (Section 7.2.2) and in a process for the production of terephthalic acid known as the Henkel II reaction. This involves the disproportionation of potassium benzoate to benzene and the potassium salt of terephthalic acid. It is noteworthy because of the *para* directiveness of the potassium ion. The process has been used in Japan.



The conversion of toluene to *p*-methylstyrene has already been described (Section 3.8). There is, however, an uncommercialized but chemically interesting process for styrene from toluene. Toluene is dehydrocoupled to stilbene followed by a metathesis (Section 2.2.9) reaction with ethylene. The first step takes place at 600°C in the presence of a lead magnesium aluminate catalyst and the second at 500°C with a calcium oxide–tungsten oxide catalyst on silica.



The carbonylation of toluene leads to *p*-tolualdehyde, which can be oxidized to terephthalic acid (Section 9.3.2). The reaction is catalyzed by a combination of HF and BF_3 to give selectivities of about 97% at 85% conversion. This process has not been commercialized because, despite the use of low cost toluene as feedstock, it cannot compete economically with the conventional *p*-xylene based route. In addition, the HF/BF_3 catalyst system is corrosive and difficult to handle.



NOTES AND REFERENCES

Toluene is discussed in Franck and Stadelhofer, cited in the bibliography to Chapter 7. There is yet another standard work edited by E. G. Hancock, *Toluene, the Xylenes and their Industrial Derivatives*, Elsevier, Amsterdam, The Netherlands, 1982.

Section 8.1 For an excellent review of toluene production process technology see Nexant Chemsystems' PERP report 02/03-5, Benzene/Toluene (April, 2003).

Typical of the many patents describing the disproportionation of toluene to *p*-xylene is West German Offen. 2,633,881 (June 2, 1977) to Mobil Oil. UOP has recently issued a series of patents relating to improvements in toluene disproportionation and transalkylation technology: US Patent 6,383,967 (May 7, 2002), US Patent 6,359, 185 (March 19, 2002), US Patent 6,191,331 (February 20, 2001), US Patent 6,355,852 (March 12, 2002), US Patent 6,008,423 (December 28, 1999), US Patent 6,239,056 (March 29, 2001), and US Patent 6,063,977 (May 16, 2000).

Section 8.3 For a review of TDI production technology see Nexant Chemsystems' PERP report 98/99S8, MDI/TDI.

Section 8.4 The conversion of toluene to styrene is described in numerous patents to Monsanto, including the following: West German Offen. 2,500,023 (July 10, 1975), US Patent 3,965,206 (June 22, 1976), US Patent 4,091,044 (May 23, 1978), West German Offen. 2,748,018 (May 11, 1978), British Patent 1,578,994 (October 26, 1977), US Patent 4,243,825 (January 6, 1981), US Patent 4,247,727 (January 27, 1981), US Patent 4,254,293 (March 3, 1981), US Patent 4,255,602 (March 10, 1981), US Patent 4,255,603 (March 10, 1981), US Patent 4,255,604 (March 10, 1981), US Patent 4,268,703 (May 19, 1981), US Patent 4,268,704 (May 19, 1981).

The production of terephthalic acid by toluene carbonylation has been claimed in three patents issued to Mitsubishi Gas Chemcial Co. as follows: West German Offen. 2,422,197 (November 28, 1974), 2,460,673 (July 3, 1975), and 2,425,571 (December 12, 1974). The oxidation of the tolualdehyde to terephthalic acid is claimed in West German Offen. 1,943,510 (June 18, 1970), also assigned to Mitsubishi Gas Chemical Co.

The oxidative coupling of toluene to stilbene and stilbene's subsequent metathesis with ethylene to styrene is described in US Patent 3,980,580 and in *CHEMTECH*, March 1977, p. 140.

CHAPTER 9

CHEMICALS AND POLYMERS FROM XYLENES

Xylenes are produced mainly by catalytic reforming (Section 2.2.3). This is so even in Europe where most of the benzene and about one-half of the toluene comes from pyrolysis gasoline (Section 2.2.1). The xylenes are isolated only with difficulty from pyrolysis gasoline because it contains about 50% ethylbenzene with a similar vapor pressure. Accordingly, the C_8 fraction of pyrolysis gasoline is usually returned to the gasoline pool.

A comparison of the C_8 fractions from catalytic reforming and pyrolysis gasoline was shown in Figure 2.10 together with the end-use requirements. The chemical industry needs to separate the xylene isomers (*ortho*, *meta*, *para*) isomerize the unwanted ones to an equilibrium mixture, separate the desired *p*-xylene and repeat the process to extinction.

The separation of the three xylene isomers and ethylbenzene from each other is an awesome task. Their physical constants are shown in Table 9.1. The boiling points of all four compounds are within 9°C. *o*-Xylene boils 5°C above the others, however, and may be separated by fractional distillation on a huge column with 150–200 plates and a high reflux ratio. The mixture at the top of the column contains about 40% *m*-xylene, 20% *p*-xylene, and 40% ethylbenzene. If required, the low-boiling ethylbenzene can be removed by an involved extractive distillation. Energy costs are high and the ethylbenzene is sometime allowed to remain for further processing.

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

TABLE 9.1 Physical Constants of the C_8-Stream

Compound	Melting Point (°C)	Boiling Point (°C)
o-Xylene	−25.2	144.4
m-Xylene	−47.9	139.1
p-Xylene	13.2	138.3
Ethylbenzene	−95.0	136.2

The isomers in the intermediate fraction differ markedly in melting point and, in the older process, they are separated, by low-temperature crystallization. The mixture is carefully dried to avoid icing of the equipment and then cooled. Crystallization of *p*-xylene starts at −4°C and continues until −68°C, at which point the *p*-xylene/*m*-xylene eutectic starts to separate, so the procedure is halted. The first stage only raises the *p*-xylene concentration in the crystalline mass to 70%, but a series of melting, washing and recrystallization steps eventually increases this to 99.5%.

If *m*-xylene is required, it may be extracted from the C_8 stream by complex formation. Treatment of the stream with $HF{-}BF_3$ gives two layers. The *m*-xylene selectively dissolves in the $HF{-}BF_3$ layer as the complex $C_6H_4(CH_3)_2 \cdot HBF_4$. The phases are separated and the *m*-xylene regenerated by heating.

The drawbacks of the low-temperature crystallization are the high-energy requirements for cooling and the problems of handling the solid *p*-xylene which, for example, deposits on the walls of the cooling vessel and thus reduces the rate of heat transfer. Nonetheless, it is still used particularly if *p*-xylene content is high, as it is if produced by disproportionation (Section 8.1).

The more recent processes for separating the *m*- and *p*-xylenes make use of molecular sieves for which the feed components show small differences in affinity. The UOP Parex process is the most widely used. A newer related process, called Eluxyl, has been pioneered by Chevron and Axens (formed by a merger of IFP and Procatalyse, but now wholly owned by IFP). These are analogous to the process used to separate linear and branched-chain hydrocarbons (Section 7.4). They are based on a continuous countercurrent flow of liquid and solid adsorbent. This is achieved in a novel way. The solid bed of adsorbent cannot easily be moved countercurrent to the liquid flow. Instead, countercurrent flow is simulated with a stationary bed of adsorbent by periodically displacing the positions at which the process streams enter and leave the bed. That is, the positions of the liquid feed and withdrawal points are shifted in the same direction as the fluid flow down the bed.

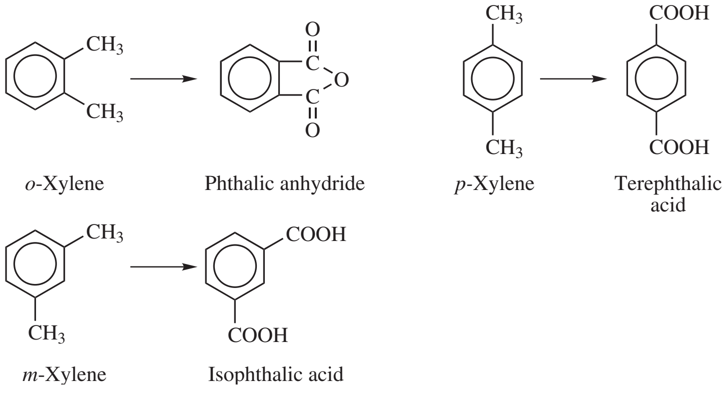
Alternatively, if *m*-xylene is targeted for separation, it can be selectively absorbed from the C_8 stream by passing it through an isothermal bed of solid adsorbent. In UOP's MX Sorbex process, countercurrent contact of the fluid and solid adsorbent is simulated using the same methodology described for the Parex process above.

The exit streams from both the low-temperature crystallization and the adsorption processes contain unwanted products, primarily *m*-xylene, ethylbenzene (if it was not removed earlier) and the portion of *o*-xylene that the market does not require. They are catalytically isomerized in the presence of acid catalysts to provide another equilibrium mixture, which is somewhat more favorable in that it contains about 48% *m*-xylene, 22% each of *o*- and *p*-xylenes, and 8% ethylbenzene. Acidic catalysts include silica–alumina, and silica with $HF{-}BF_3$, the same material that complexes with *m*-xylene. The drawback of silica–alumina is that it promotes disproportionation and transalkylation. If platinized alumina is added to the silica–alumina, as in a dual function catalyst (Section 16.5), the system will isomerize ethylbenzene as well as the xylenes.

The most important isomerization catalyst today is the zeolite, ZSM-5. This is the same zeolite catalyst useful for toluene disproportionation to benzene and *p*-xylene (Section 8.1). The silica-alumina–platinized-alumina catalyst operates at 23–33 bar in a hydrogen atmosphere with substantial recycle. ZSM-5 has a major economic advantage because it operates at low pressures either in the vapor or liquid phase and requires less or even no hydrogen and much less recycle than does the noble metal catalyst. Its one disadvantage is that it does not isomerize ethylbenzene but rather dealkylates it to benzene. Because the ZSM-5 process requires less capital investment and provides lower operating costs, it has been widely accepted. A recently announced but not commercialized process makes use of non-zeolite molecular sieves, primarily silicoaluminophosphates. This process is claimed not only to isomerize ethylbenzene to xylenes but also to provide a higher level of the desired *p*-xylene.

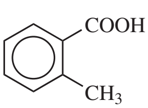
Several unconventional processes for producing aromatics were commercialized in the late 1990s. They catalytically converted low valued materials such as LPG, light olefins, and C_6 and C_7 alkanes to aromatics. Examples include BP/UOP's Cyclar process, Chevron's Aromax process, and Asahi's Alpha process. Xylenes are typically the smallest fraction of aromatics from these processes.

Mixed xylenes are used as solvents, particularly in the paint industry, and are valued components of the gasoline pool because of their high octane number. The major chemical use for the individual xylenes is oxidation of *p*-xylene to terephthalic acid, *m*-xylene to isophthalic acid, and *o*-xylene to phthalic anhydride.

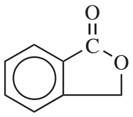


9.1 *o*-XYLENE AND PHTHALIC ANHYDRIDE

o-Xylene may be oxidized to phthalic anhydride in gas- or liquid-phase processes and in fixed or fluidized beds. The liquid-phase oxidation makes use of metal salt catalysts that are soluble in the reaction medium. The gas-phase fluidized-bed process takes place at 375–410°C over a classical vanadium pentoxide catalyst. The process is highly exothermic, and the fluidized bed offers better temperature control and less risk of explosion. It also enables the handling of phthalic anhydride as a liquid (melting point 130.8°C). Yields are rather low, probably less than 80%, and there are side reactions leading to *o*-toluic acid, phthalide, benzoic acid, and maleic anhydride as well as to the complete oxidation to carbon dioxide and water.

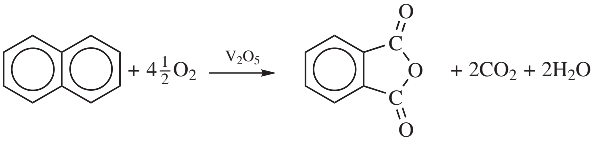


o-Toluic acid



Phthalide

As a result of the low yields, an older route to phthalic anhydride, based on naphthalene (Section 12.1) has remained viable to a limited degree. The oxidation is similar, again with a vanadium pentoxide catalyst. Indeed some plants can operate with either feedstock. The reaction is analogous to the oxidation of benzene to maleic anhydride (Section 5.4).



Naphthalene

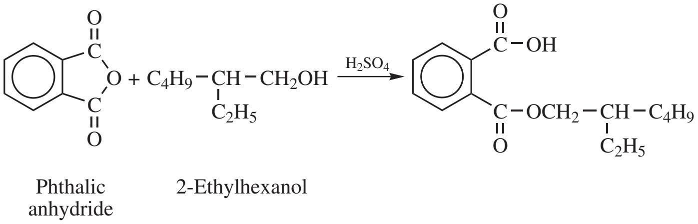
Phthalic anhydride

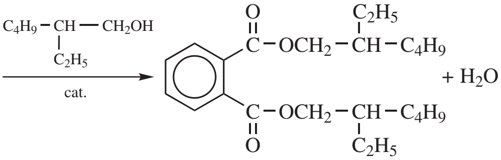
The *o*-xylene process is somewhat less exothermic (265 *vs*. 429 kcal mol^{-1}) because there are fewer carbon atoms to be oxidized. The loss of two carbon atoms from naphthalene as carbon dioxide is an economic drawback of the process, which is balanced by the higher yields.

Naphthalene is available from the distillate from coke ovens and is one of the few coal tar chemicals still of importance. It is also made by the hydrodealkyation of the methylnaphthalenes produced by the catalytic reforming (Section 2.2.3) of gas oil fractions. Only about 2.0% of US phthalic anhydride comes from naphthalene. The proportion is higher in Europe.

9.1.1 Uses of Phthalic Anhydride

About 40% of phthalic anhydride production was used for plasticizers (Section 4.12.2) in 2002. About 17% goes into alkyd resins (Section 9.1.1) and most of the remainder is used for unsaturated polyesters Section 9.1.1) All three of these applications involve esterification of phthalic anhydride and are mature. As with all anhydrides, the esterification proceeds in two stages. The first, shown below with 2-ethylhexanol, the most important plasticizer alcohol, goes readily to form the half ester, whereas the second step proceeds only with the aid of a catalyst such as *p*-toluenesulfonic acid and a temperature of 160°C.





Di-(2-ethylhexyl) phthalate

At a temperature between 185 and 205°C, a noncatalytic esterification takes place, obviating the catalyst removal steps. With both routes color development must be avoided. The plasticizer has a high boiling point and, once formed, is difficult and expensive to distill or otherwise purify. Phthalic anhydride melts at 130.8°C, and it is frequently shipped in bulk as a liquid in heated tankers.

Alkyd resins (Section 9.1.1) are oligomers in which polyester functions have been inserted into natural "drying oils" such as linseed or soybean oil. Air-drying alkyds were developed in the early 1930s. Before that, gloss paints were based on drying oils themselves. Drying oils (e.g., linseed and tung oil) are triglycerides containing unsaturated fatty acids (Section 13.1). About 50% of the fatty acid in linseed oil is linolenic acid:

$$CH_3—CH_2—CH{=}CH—CH_2—CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—COOH,$$

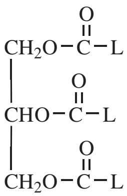
while linoleic acid has one fewer double bond:

$$CH_3—CH_2—CH_2—CH_2—CH_2— CH{=}CH—CH_2—CH{=}CH—(CH_2)_7—COOH.$$

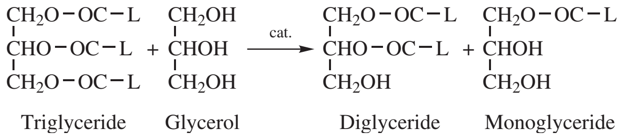
It comprises about 50% of the fatty acids in soybean oil, which, because less unsaturation is present, is called a semidrying oil.

The drying oil was dissolved in a solvent and mixed with pigment. An oil-soluble metal salt such as lead or cobalt naphthenate was added as an initiator. It induced peroxide formation when the paint was spread as a thin film. The peroxide in turn catalyzed the polymerization of the double bonds in the linseed oil to a cross-linked paint film. The drying oils used were primarily linseed and tung oil. Soybean oil could not be used because it does not contain enough unsaturation to achieve adequate cross-linking. It is valuable in alkyds (see below) because the alkyd has 6–10 fatty acid residues, whereas the oil has only three. In other words, the alkyd has greater functionality.

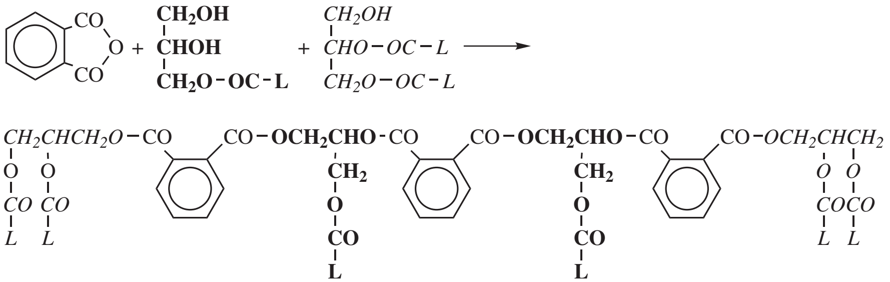
The oil-based paints had little resistance to solvents, chemicals or ultraviolet light. They were largely replaced by oil-modified alkyd resins which are made by heating or interesterifying a drying oil with a polyol such as glycerol and esterifying the mono- and diglycerides produced with a dibasic acid or anhydride such as phthalic anhydride. If linoleic or linolenic acid is written L—COOH then the triglyceride is



Interesterification with glycerol gives a mixture of esters:



These react with phthalic anhydride to give a more or less linear polymer, the chain length of which is determined by the ratio of mono- to diglycerides in the mixture, the latter acting as chain stoppers. (Monoglyceride units are shown in bold; diglyceride units in italic.) This polymer is called an alkyd.

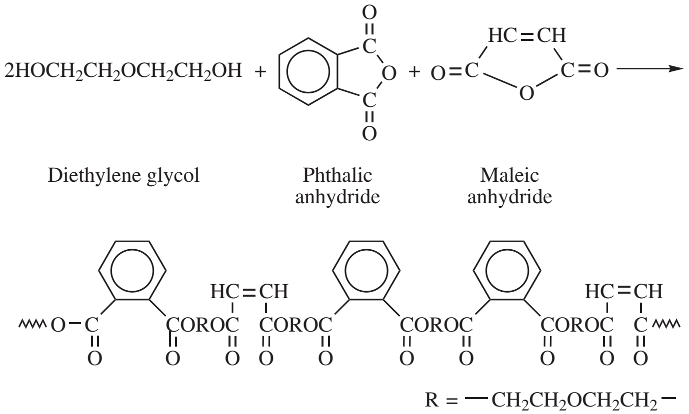


The incorporation of the polyester function gives the paint film greater solvent and uv resistance and also imparts somewhat greater corrosion resistance.

Most alkyd resins are made either from soybean oil, which is rich in a mixture of oleic and linoleic acids or from tall oil acids (Section 13.1), which are also mixtures of these acids. Over 400 different alkyds are available commercially, varying in the type and amount of fatty acid present. Also, instead of the glycerol nature provides in fats and oils, the more highly functional pentaerythritol (Section 3.1.1.3) may be used. Maleic anhydride or occasionally other dibasic acids can replace some of the phthalic anhydride. In another variation, part or all of the phthalic anhydride can be replaced by toluene diisocyanate (Section 8.3) to impart solvent and chemical-resistant urethane linkages.

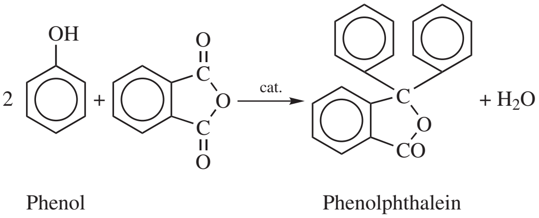
Although alkyd resins are the most important vehicles for oil-based paints, their market is decreasing because of competition from water-based paints, corrosion-resistant paints based on epoxy, polyurethane and vinyl polymers, and solventless coatings such as radiation-cured and powder coatings.

Unsaturated polyester resins are oligomers that result from the condensation of phthalic anhydride, maleic anhydride, and a glycol such as diethylene glycol. The unsaturated oligomers are copolymerized with styrene or less frequently with methyl methacrylate in the presence of a peroxide initiator. Isophthalic acid may be used to replace part or all of the phthalic anhydride (Section 9.2.1).

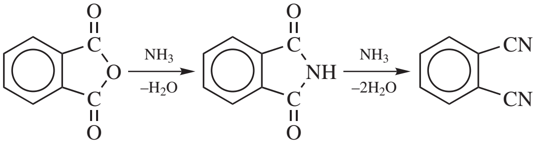


Unsaturated polyester reinforced with glass cloth or fiber is used for the classic automobile, the Corvette. It replaces metal in the fabrication of pipe and storage tanks, and in the manufacture of small boats, and even large minesweepers, where the absence of metal is essential. The fabrication, however, must be done largely by hand (the lay-up and spray-up technique), which introduces an expensive labor component. Some of the hand labor can be eliminated by the use of a process called sheet molding, which makes use of a polyester-impregnated glass cloth and an initiator, which does not become effective until the assembly is heated beyond a threshold temperature. Nonetheless, the technique is primarily of value for short runs of products.

Among the lesser volume uses for phthalic anhydride is its reaction with benzene to form an intermediate which, on dehydration, leads to anthraquinone (Section 7.8). Phthalic anhydride reacts with phenol in the presence of sulfuric acid to form the pH indicator, phenolphthalein.

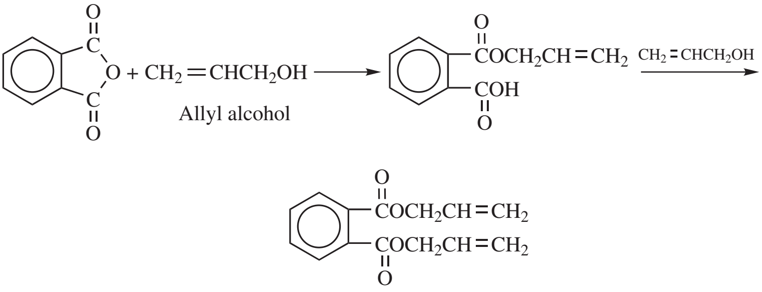


On reaction with ammonia, phthalic anhydride gives phthalimide which, on further heating with ammonia, dehydrates to give phthalonitrile, the starting material for phthalocyanine dyes.



Phthalimide Phthalonitrile

Esterification with allyl alcohol gives diallyl phthalate, a monomer for high-performance thermoset polymers, useful for glass-reinforced plastics. The esterification takes place in two steps as with di-2-ethylhexyl phthalate (Section 9.1.1).

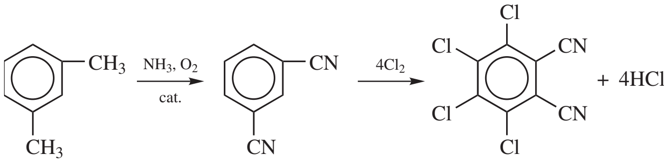


Diallyl phthalate

A high-performance poly(ether imide) “Ultem,” developed by General Electric, involves the condensation of *m*-phenylenediamine with an *o*-phthalic-based dianhydride related to bisphenol A (Section 7.1.2.3).

9.2 *m*-XYLENE AND ISOPHTHALIC ACID

m-Xylene undergoes ammoxidation (Section 4.8) to yield isophthalonitrile which, on chlorination of the ring positions, gives the fungicide Daconil.



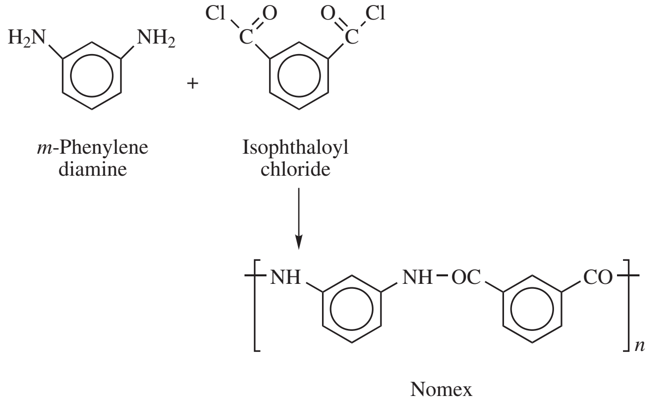
m-Xylene Isophthalonitrile Daconil

Hydrogenation of the nitrile provides *m*-xylylenediamine, a curing agent for epoxy resins.

Isophthalic acid is made by the oxidation of *m*-xylene by the Amoco-Mid Century process (Section 9.3.1). The highly exothermic reaction takes place at about 200°C and 12 bar with a yield of 95 mol%. Excess oxygen is used.

9.2.1 Uses of Isophthalic Acid

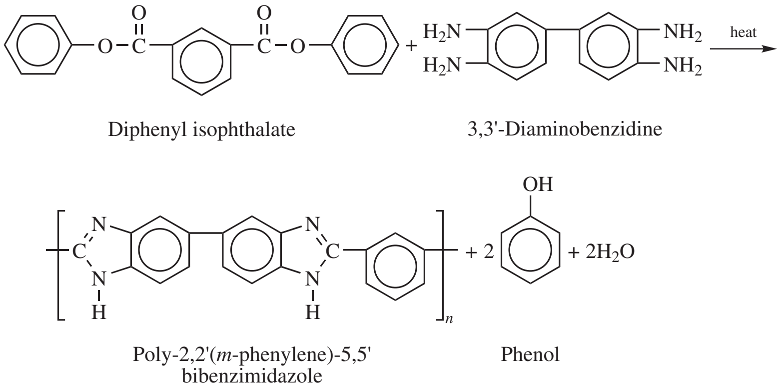
Isophthalic acid has a number of low-volume uses. A major one is in unsaturated polyesters (Section 9.1.1), where the greater stability to alkali of the ester linkages enhances the corrosion resistance of the final product. To a lesser extent, it is used in alkyd resins. It goes into specialty plasticizers and its acid chloride, isophthaloyl chloride, is condensed with *m*-phenylene diamine to give Nomex, a high-temperature-resistant aramid (aromatic polyamide) polymer useful for fire-resistant cloth for fire fighters and race car drivers' uniforms and more recently for plant workers' clothing.



A growing application for isophthalic acid is as a modifier for poly(ethylene terephthalate) for use in carbonated soft-drink bottle resin. Isophthalic acid, when used to replace a few percent of the terephthalic acid in polyester formulations, serves to disrupt the crystallization of the molten resin as it cools. This feature gives resins that can be processed at lower temperatures saving energy and processing time, and reducing formation of acetaldehyde (a heat degradation product). Isophthalic acid-containing copolyesters also have improved gas barrier properties, an important feature for carbonated beverage bottles (see below). Because crystallization has been reduced, the bottles are more transparent.

Polybenzimidazoles are high temperature-resistant resins made from the diphenyl ester of isophthalic acid and a tetramine such as 3,3′-diaminobenzidine

(3,3′,4,4′-tetraaminobiphenyl). They find use as adhesives and laminants for the aerospace industry. Honeycomb bonding provides an example.

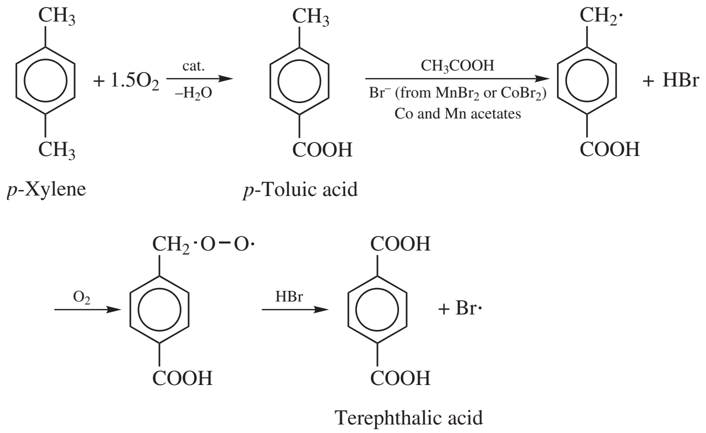


9.3 *p*-XYLENE AND TEREPHTHALIC ACID–DIMETHYL TEREPHTHALATE

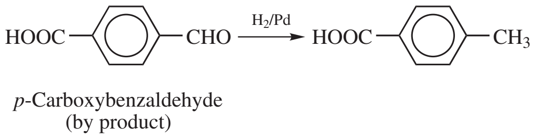
The major use for *p*-xylene is oxidation to terephthalic acid which, as such or less often as its methyl ester, is reacted with ethylene glycol to give polyester resins for fibers, films, molding resins, and for biaxially oriented bottle resins. Terephthalic acid–dimethyl terephthalate is the most widely used xylene-based chemical by a wide margin, about 10 billion lb having been produced in the United States in 2002 compared with 1.2 billion lb of phthalic anhydride, the next largest derivative.

9.3.1 Oxidation of *p*-Xylene

Although *o*-xylene oxidizes readily, *m*- and *p*-xylenes present a problem. The *m*- and *p*-toluic acids formed in the first stage of oxidation contain a methyl group that defies further oxidation, because the carboxyl group is electron withdrawing. There are several ways to overcome this, the most important being the Mid-Century Process developed jointly by Amoco and Scientific Design. The oxidation is carried out in acetic acid solution with a catalyst comprising a manganese or cobalt salt with a bromine promoter, which may actually be bromine itself but is usually manganous or cobaltous bromide. The bromide converts the recalcitrant methyl group to a free radical, which is then much more susceptible to oxidation.



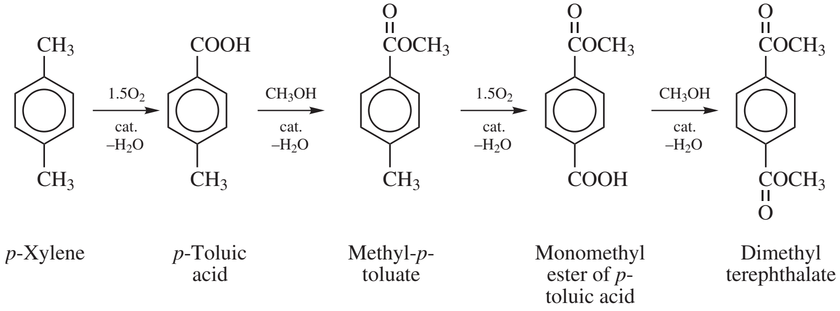
Acetic acid is used as a solvent because terephthalic acid (TPA) is much less soluble in it than are the intermediate products, and this allows for the separation of relatively pure TPA. Much of the acetic acid is oxidized and must be replaced. This is now a growth area for acetic acid (Section 10.5.2.2). Even in its presence, impurities are formed in the reaction, the most important of which is *p*-carboxybenzaldehyde. Crude terephthalic acid containing parts per million of this impurity in aqueous solution is subjected to hydrogenolysis with a palladium catalyst at 250°C and 36 bar. The impurity is converted to *p*-toluic acid, which, in turn, is separated from the terephthalic acid by fractional crystallization.



This hydrogenolysis provides the most important industrial use for palladium catalysts. It is this step that made possible the production of terephthalic acid sufficiently pure to be used directly in the esterification reaction to produce polyester fibers and resins. The purified acid is called PTA (purified terephthalic acid).

Although the mechanism that causes the cobalt bromide to function as a cocatalyst is not completely understood, it has been suggested that the aromatic molecule becomes a free radical because of electron extraction by the cobalt cation. The free radical expels a proton and interacts with oxygen to form a peroxy radical that then maintains the chain reaction by hydrogen abstraction. Reaction chains are probably very short and the bromide is present to produce oxygen-containing radicals at an optimum rate.

Prior to the development of this process for pure terephthalic acid, it was necessary to use dimethyl terephthalate, which can be purified by distillation, for polyester formation. In early processes, nitric acid oxidized *p*-xylene to crude terephthalic acid, which was then converted for purification to the methyl ester. In another process, *p*-xylene was oxidized to toluic acid, which was esterified to give methyl toluate. The oxidation of the second methyl group is then possible, and the second carboxyl group may then be esterified to give dimethyl terephthalate.



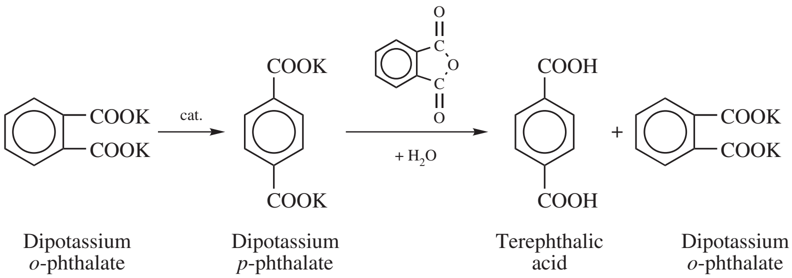
Currently, all new facilities produce purified terephthalic acid rather than the ester, and the latter is being phased out. In 2002, 70% of capacity in both the United States and Western Europe produced terephthalic acid. There has been burgeoning growth of polyester fiber production in the Far East in the late 1980s that will probably continue until the year 2020.

Emphasis on recycling of plastics has made discarded polyester bottles a source of scrap. Polyester bottles can be recycled simply by chopping them up and melting and reprocessing the chips. This is the commonest method. Carpet fiber is the big use for recycled poly(ethylene terephthalate) in the United States. Nonetheless, polyester scrap is also a source of dimethyl terephthalate or related polyester oligomers. Two main processes are available. In the first, poly(ethylene terephthalate) scrap is treated with methanol to generate dimethyl terephthalate and ethylene glycol, which may be purified by distillation. The second process achieves only a partial depolymerization. A small amount of ethylene glycol is added to the scrap to give a low-viscosity oligomer, which is purified by adsorption and filtration. It is then repolymerized under partial vacuum, which removes volatile contaminants and the ethylene glycol formed during the reaction. Costs of collecting, sorting, and cleaning scrap are a major part of the recycling cost, but it appears that the overall process is similar in cost to the conventional process starting with virgin material. Plastics recycling has been most successful with polyesters.

9.3.2 Alternate Sources for Terephthalic Acid

There are various other sources for terephthalic acid. The disproportionation of toluene to *p*-xylene, which in turn may be oxidized to terephthalic acid, has been described in Section 8.1 as was the carbonylation of toluene in Section 8.4, and the *para*-directed disproportionation of potassium benzoate in Section 8.4 (the Henkel II process).

The Henkel I process is related, and involves the isomerization of *o*-potassium phthalate to the *para* isomer, in the presence of a zinc–cadmium catalyst at temperatures somewhat greater than 400°C and a modest pressure below 20 bar. Potassium is an expensive material and must be recovered. This can be done by reacting the potassium terephthalate with phthalic anhydride to yield more of the *o*-potassium phthalate.



Like *m*-xylene, *p*-xylene can be ammoxidized. Terephthalonitrile results, which can be hydrolyzed to terephthalic acid. This process is not in use. It is interesting that the ammoxidation is carried out without added oxygen, the vanadium pentoxide–alumina catalyst giving up its oxygen in the process. The concept of an oxide as both a catalyst and a coreactant for oxidations has been attempted recently by Du Pont in a process for the oxidation of *n*-butane to maleic anhydride (Section 5.4) and in an unused process for aniline (Section 7.3).

9.3.3 Poly(ethylene terephthalate)

The formation of poly(ethylene terephthalate) was described in Section 3.7.1. In 2002, about 70% of the production globally was used for polyester fibers. Another 25% was used for bottle resin, largely for containers for carbonated beverages. This application grew at almost 15%/year during the 1980s and at 8–10%/year into the 2000s. The polyester is biaxially oriented, that is, it is drawn in two dimensions by blowing rather than in one dimension as is the case when it is drawn into a fiber. It has sufficient mechanical strength to withstand the pressure in carbonated beverages, but it does not have sufficient resilience to withstand the sharp bend required at the bottom of the bottle. For this reason, the first bottles made from polyester had a hemispherical end, and the bottle was set into a polyethylene cup. A later version distributed the stresses created in making the sharp bend by molding a bottom comprising four convolutions, all of which have rounded edges. The elimination of the polyethylene makes recycling easier.

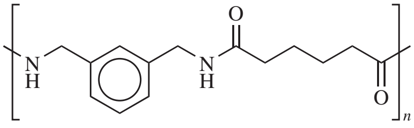
The significant properties of polymers are usually their mechanical characteristics—crystallinity, Young's modulus, glass transition temperature, and so on (Section 15.5 and note at end of this chapter). In the case of bottles for beer and carbonated beverages, however, the permeability of polymers to oxygen and carbon dioxide is crucial. The permeabilities of several polymers are shown in Table 9.2. HDPE and PVC are clearly unsuitable. PET is better, but beer in a two liter PET bottle at

TABLE 9.2 Oxygen and Carbon Dioxide Permeabilities of Various Polymers

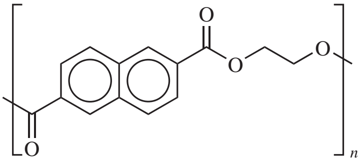
	Transmission of 25-μm Films, cm^3 m^{-2} atm. Pressure Drop over 24 h	
Polymer	Oxygen	Carbon Dioxide
High-density polyethylene	2900	9100
Poly(vinyl chloride)	120	500
Poly(ethylene terephthalate)	95	240
Poly(vinylidene chloride)	10	75
Ethylene–vinyl alcohol (dry)	2	
Ethylene–vinyl alcohol	100	

about 4.6 bar would lose about one-third of its fizz in six months and would be oxidized more rapidly. This is acceptable for carbonated beverages where oxidation is not a problem and the level of fizz above a certain threshold is not important. Carbon dioxide can be put in at 6 bar and any losses are unimportant. Nor is it a problem with less carbonated ("flat") highly flavored British beers, as long as the polymer is colored, because beer photodegrades. For light lager-style beers, however, it cannot compete with conventional glass bottles and aluminum cans other than in fast-turnover venues such as sports stadiums, concert arenas, and swimming areas, where there is concern about safety of glass bottles. In 2002, global beer consumption was approximately 300 billion units, hence the "Holy Grail" application for plastic bottles is beer containers.

Numerous approaches for improving the shortcomings of homopolymer PET bottles are in place or under development. One solution is to make multilayer bottles using low-permeability polymers such as ethylene–vinyl alcohol copolymer or poly(vinylidene chloride) (Section 3.11.7). The ethylene–vinyl alcohol copolymer is



Nylon MXD6



Poly(ethylene naphthalate)

moisture sensitive, so must be sandwiched between two layers of PET. Aluminizing the bottle also reduces gas transmission but prevents the consumer from seeing the product, which is one of the benefits of glass. Gas transmission through the cap has also been reduced by the use of a specialty nylon (MXD6 from *m*-xylylenediamine and adipic acid) rather than nylon 6 for the screw cap.

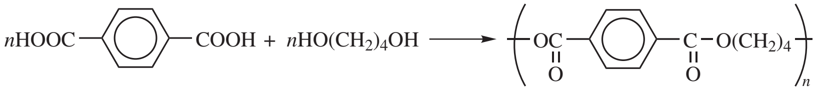
Copolymers (such as with terephthalic acid and naphthalene dicarboxylic acid), high barrier monolayers [such as poly(ethylene naphthalate)], and incorporation of oxygen scavengers in the plastic layers or in the cap lining have also been tried. The problems are the expense and the difficulty of recycling. PET homopolymer is readily recyclable; coated materials less easily so. Some recyclers have permission to use the recycled material in nonfood applications. Carpeting fiber provides the most important application. There were 3768 billion PET bottles of all kinds in 2001. The recycling rate was 22%, down from 40% in 1995.

About 5% of poly(ethylene terephthalate) goes into a strong, biaxially oriented film known as Mylar. It is used in photographic and X-ray film, magnetic tapes for sound and video recordings, and containers for microwave and boil-in-the-bag cooking.

A small but growing amount of polyester is used as a molding compound. Because the polymer has a glass transition temperature of about 80°C, the molding does not crystallize well on cooling. Crystallization can be induced by nucleating the polymer, which makes molding possible only in specialized applications. Dimensional stability can also be achieved by addition of glass fiber.

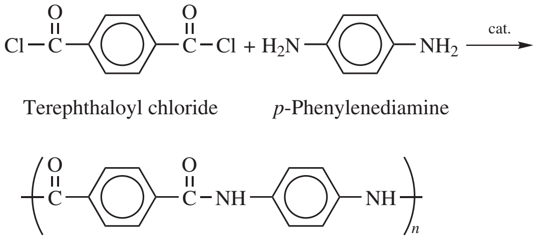
9.3.4 Lower Volume Polymers from Terephthalic Acid

Poly (butylene terephthalate), made by condensing terephthalic acid or its dimethyl ester with 1,4-butanediol (Section 5.1.3.5), is a relatively inexpensive molding resin useful for pipe, automotive parts, and toothbrush bristles. It is also alloyed with polycarbonate to give a plastic useful for automobile bumpers and even for side panels.



1,4-Butanediol Poly(butylene terephthalate)

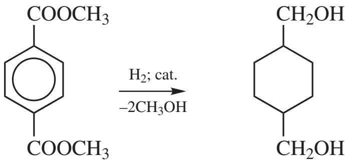
The condensation of terephthaloyl chloride with *p*-phenylenediamine leads to an aramid known as Kevlar. That it must be spun into fibers from concentrated sulfuric acid solution is an indication of its properties. The resulting fibers are stronger than steel fibers of the same dimension. Kevlar was probably the first of the liquid-crystal polymers, a category of polymers whose rigid chains allow them to maintain a crystalline structure either in the melt form or in solution. It finds its major application as an asbestos replacement. Other uses include cord for tires for large vehicles and reinforcement for bullet-proof vests and military helmets. It is used for canoe manufacture combined with epoxy resin, and as cloth for boat sails. Its most important use, however, was not anticipated by Du Pont. Kevlar is the most important replacement for the now outlawed asbestos for brake linings, clutch facings, and related uses. Dyneema (Section 3.1.5) competes where temperature resistance is not required. Nomex (Section 9.2.1) is a polymer related to Kevlar.



Terephthaloyl chloride p-Phenylenediamine

Kevlar

Dimethyl terephthalate may be subjected to hydrogenolysis to convert the ester groups to alcohols. At the same time the ring is hydrogenated. 1,4-Bis(hydroxymethyl)cyclohexane otherwise known as cyclohexane dimethanol results.



Dimethyl terephthalate

1,4-Bis(hydroxymethyl)-cyclohexane

This diol may exist in the *cis* or *trans* form, and the ratio must be carefully controlled if the product is to be used for the formation of polyester fibers by condensation with terephthalic acid. Eastman's "Kodel" contains this diol. It is also useful for the preparation of specialty polyurethane resins.

Both Shell and Du Pont are pursuing commercialization of a new polyester resin, poly(trimethylene terephthalate), which is based on the polymerization of terephthalic acid and 1,3-propanediol (Sections 3.11.6.6, 4.14.4). This material, particularly in carpet applications, combines the inherent stain resistance of polyester with the elastic recovery and resilience of nylon. It dyes more easily and is less abrasive. The price of carpeting from it will probably be intermediate between the prices of traditional polyester and nylon carpeting.

9.4 MAJOR CHEMICALS FROM XYLENES: A SUMMARY

Table 9.3 shows the US production of major chemicals from xylenes. All grew healthily over the period 1993–2000 except for polyester fibers. These have grown only slowly in the United States but very rapidly in East Asia reflecting their burgeoning textile industries. Global production of polyester fibers rose from 17.6 billion lb in 1990 to 39.4 billion lb in 2000. The major growth area in the United States has been thermoplastic polyesters, that is, the market for PET bottles and related artifacts. This growth is reflected in the construction by M&G Polymer of a

TABLE 9.3 Production of Chemicals from Xylenes, United States 1993–2000

	Million lb 1993	Million lb 2000	Average Annual % Increase 1993–2000
Mixed xylenes	6600	9840	5.9
p-Xylene	5791	8850	6.2
o-Xylene	834	1170	5.0
Phthalic anhydride	854	1140	4.2
Terephthalic acid (purified)	6740	9470	5.0
Polyester resins and fibers	4944	5600	1.8
Thermoplastic polyesters[a]	2549	5140	10.5
Polyester fibers[b]	3557	3804	1.0

Source: Guide to the Business of Chemistry.

[a] Poly(ethylene terephthalate) and poly(butylene terephthalate).

[b] From *Chem. Eng. News*, June 24, 2002, p. 64.

275,000 tonne/year PET plant in Texas due to come onstream in 2003. It will be the biggest in the world.

NOTES AND REFERENCES

Xylenes are discussed in Franck and Stadelhofer, cited in the bibliography to Chapter 7. The standard work is *Toluene, the Xylenes and their Industrial Derivatives*, E. G. Hancock, Ed., Elsevier, Amsterdam, The Netherlands, 1982. The economics of xylenes production is presented in Nexant Chemsystems PERP report 01/02-7, Xylenes (May, 2002).

Section 9 The use of silicoaluminophosphates for xylene isomerization is described in European Patent Appl. 0,249,914A1 (December 23, 1987), to Union Carbide.

The UOP process for separation of *m*- and *p*-xylenes is described in detail by Spitz, p. 192, cited in the general bibliography.

Section 9.1 For a more detailed discussion of both alkyd and polyester resins and for a chapter on plasticizers, see H. A. Wittcoff and B. G. Reuben, *Perspective*, Part 2, cited in Section 0.4.2.

Section 9.2 Nexant Chemsystems PERP report 94/95S14, *meta-Xylene/Isophthalic Acid* (February, 1997) highlights UOPs MX Sorbex process and Mitsubishi Gas Chemical's HF/BF3 extraction process for separating and purifying *m*-xylene and production and uses for isophthalic acid.

Section 9.3.1 The chemistry and production economics of PTA manufacture are given in Nexant Chemsystem's PERP report 01/02-4, *Terephthalic Acid* (December, 2002). Recycling of poly(ethylene terephthalate) bottles is described in *Plast. Eur.*, December 1992, p. 750 and in Nexant Chemsystems PERP report 99/00S4, *Developments in PET Recycling* (July, 2000).

Section 9.3.3 The use of poly(ethylene terephthalate) in beer bottles is partly based on D. Birkett, *Chem. Brit.* **38**, July 2002, p. 28, and H. Hansler, *Chem. Ind.*, 429, (2000). Nexant Chemsystems PERP report 00/01S1, *Plastic Beer Bottles* provides a good summary of the various approaches for making plastic beer bottles. General information about mechanical properties of polymers is available in standard texts but is also summarized in H. A. Wittcoff and B. G. Reuben, *Perspective*, Parts 1 and 2, cited in Section 0.4.2.

Section 9.3.4 A good review of the chemistry, process technology, production economics, and markets for poly(butylene terephthalate) can be found in Nexant Chemsystem's PERP report 98/99S6, *Polybutylene Terephthalate* (July, 1999).

CHAPTER 10

CHEMICALS FROM METHANE

So far, we have described six natural gas and/or petroleum-derived products as raw materials for chemicals—ethylene, propylene, the C_4 stream, benzene, toluene, and the xylenes. To complete the picture, we must add methane, whose major use is conversion to synthesis gas, $CO + H_2$ useful for ammonia and methanol production. Lesser uses include chlorination, conversion to acetylene, and ammoxidation to hydrocyanic acid.

The major source of methane is natural or associated gas (Section 2.4). It is also available from refinery gases, which are usually used for fuel and not recovered for chemicals. Although there has been an "explosion" in the discovery of natural gas in many places the world, notably the CIS and Qatar, the reserves in the United States between 1981 and 2001 dropped by about 11%. Fresh reserves almost matched consumption, and the reserves to production ratio dropped from 11.5 to 9 years. If necessary, methane may be synthesized from petroleum (Section 10.4.2) or coal (Section 12.5).

10.1 HYDROCYANIC ACID

Hydrocyanic acid (hydrogen cyanide or HCN) is produced in the United States at a level of about 1.7 billion lb/year in 2002. It was formerly made by the reaction of sodium, carbon (charcoal), and ammonia. In the first stage of the process, ammonia and sodium react to form sodamide, $NaNH_2$. This reacts with carbon to form sodium cyanamide $NaHCN_2$, which in turn reacts with more carbon to provide sodium

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff, Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

cyanide NaCN at temperatures as high as 850°C. Yields based on sodium and ammonia were high. Acidification with sulfuric acid provides hydrocyanic acid.

$$2Na + 2C + 2NH_3 + 1.5O_2 \xrightarrow{-3H_2O} 2NaCN \xrightarrow{H_2SO_4} 2HCN + Na_2SO_4$$

The process has been superseded by the more economical Andrussow reaction between methane, air, and ammonia at 1000°C and slightly above atmospheric pressure over a platinum catalyst with 10–20% rhodium to prevent volatilization.

$$2NH_3 + 2CH_4 + 3O_2 \xrightarrow{\text{Pt-Rh } 1000^\circ\text{C}} 2HCN + 6H_2O$$

In a modified process used by DeGussa, air is omitted, and methane (or any other hydrocarbon feedstock including naphtha) reacts directly with ammonia at 1400°C.

$$CH_4 + NH_3 \xrightarrow{\text{Pt-Rh } 1400^\circ\text{C}} HCN + 3H_2$$

This provides one of the few examples in industrial chemistry of an intermolecular dehydrogenation and is possible because of the high temperature. Other examples are provided by the interaction of benzene with ammonia (Section 7.3) and the condensation of two oleic acid molecules to form so-called dimer acid (Section 13.3).

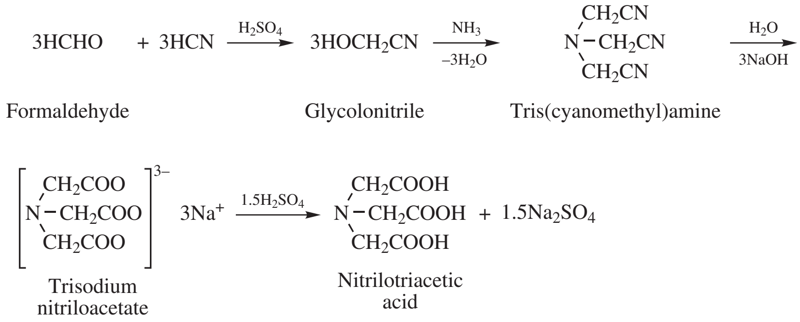
Hydrocyanic acid is also a byproduct of the ammoxidation of propylene to acrylonitrile (Section 4.8). It was this lower cost source of the chemical that motivated the more economical methane-based route. Byproduct hydrocyanic acid from acrylonitrile production (Section 4.8) enjoyed about 18% of the market in 2002.

Another route to hydrocyanic acid is the dehydration of formamide (Section 10.8), a process that has been revived as a basic step in a synthesis of methyl methacrylate (Section 4.10.1). Hydrocyanic acid also results from the interaction of carbon monoxide and ammonia.

$$CO + NH_3 \longrightarrow HCN + H_2O$$

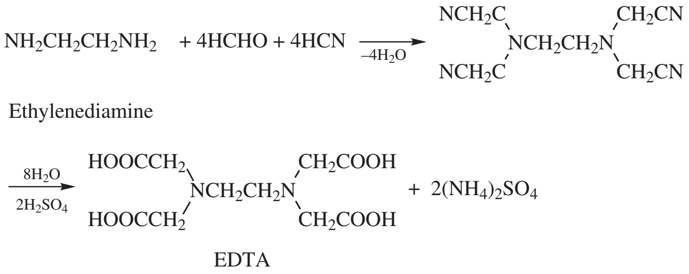
Hydrocyanic acid and its sodium salt undergo a number of industrially important reactions. Its largest application, hexamethylenediamine production, is described in Section 5.1.1. Its second largest use is for methyl methacrylate (Section 4.10.1.). It has been used in two obsolete routes to acrylic acid (Section 4.7) and one to acrylonitrile (Section 4.8).

The powerful chelator, sodium nitrilotriacetic acid, was used notably in Holland to replace the sodium tripolyphosphate “builder” in some detergents. It is made from ammonia, methanol, and hydrocyanic acid. In the first step, 37% formaldehyde is reacted with HCN in the presence of sulfuric acid to give glycolonitrile. This reacts at 60°C with ammonia to give tris(cyanomethyl)amine. Hydrolysis with aqueous sodium hydroxide at 140°C and 3 bar at a pH of 14 gives sodium nitrilotriacetate. Acidification with sulfuric acid provides nitrilotriacetic acid.



Its use as a builder in the United States has been inhibited because of the suggested toxicity of the heavy metal chelates, such as iron chelate, which could form in a washing machine. These are now believed to be nontoxic, and the product is one of the several phosphate replacements used more in Europe than in the United States. The others include zeolites, which act as ion exchangers, and polyacrylic acids (Section 4.7). Phosphates are frowned upon because they lead to eutrophication in rivers and lakes (Section 17.2.5).

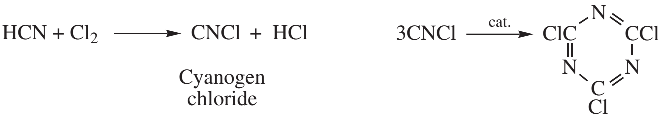
Other uses for hydrocyanic acid include conversion to sodium cyanide for gold recovery and preparation of ethylenediaminetetraacetic acid (EDTA). The latter is made via a modified Mannich reaction in which ethylenediamine is condensed with formaldehyde and hydrocyanic acid. Hydrolysis of the nitrile gives EDTA.



Single-step processes are also used, either with sodium hydroxide or with an aqueous solution of sodium cyanide. In each instance the sodium salt results.

$$H_2NCH_2CH_2NH_2 + 4HCHO + 4NaCN + 4H_2O \xrightarrow{\text{NaOH } 80^{\circ}\text{C}} (NaOOCCH_2)_2NCH_2CH_2N(CH_2COONa)_2$$

Another use for hydrogen cyanide is in the production of cyanuric chloride. Cyanogen chloride is first produced from chlorine and aqueous hydrocyanic acid at 40°C. The gas is trimerized to cyanuric chloride in the gas phase at over 300°C with activated charcoal and metal salts as catalysts. Cyanuric chloride is a starting material for the important triazine herbicides and fiber-reactive dyes. It is also used for the manufacture of triallyl cyanurate, useful for specialty polyesters and for certain pharmaceutical syntheses.



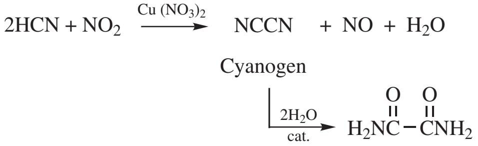
$$HCN + Cl_2 \longrightarrow CNCl + HCl \qquad 3CNCl \xrightarrow{cat.}$$

Cyanogen chloride

Cyanuric chloride

An important use for hydrocyanic acid, or more frequently sodium cyanide, is in the synthesis of amino acids by the Strecker reaction. The most important application of this reaction is for the synthesis of DL-methionine, a poultry feed additive (Section 4.7).

Oxamide is a specialty fertilizer, not widely used, that releases ammonia slowly into the soil. It melts at 419°C without decomposition, making it one of the highest melting of all organic compounds. It results from the hydrolysis of cyanogen, which in turn is made by the cupric nitrate catalyzed oxidation of hydrocyanic acid with nitrogen dioxide at 0–5°C.



$$2HCN + NO_2 \xrightarrow{Cu(NO_3)_2} NCCN + NO + H_2O$$

Cyanogen

$$\xrightarrow[cat.]{2H_2O} H_2N\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}NH_2$$

Oxamide

The cyanogen hydrolyzes quantitatively with hydrochloric acid at room temperature. It has been proposed that the process be used with the byproduct hydrocyanic acid from ammoxidation (Section 4.8). However, this use is precluded by the imbalance between fertilizer usage, which is very large, and hydrocyanic acid production, which is relatively small. Because fertilizers must be cheap, large capital investment in expensive hydrocyanic acid production is not warranted.

Hydrogen cyanide absorbed on a diatomaceous earth such as celite was the notorious Zyklon B used by the Nazis in their extermination camps. It boils at 25.6°C so that the solid pellets provided abundant vapor. Carbon monoxide was also used in gas chambers. At Auschwitz–Birkenau, about 1.25 million people were gassed with Zyklon B—about 900,000 Jews together with 350,000 Poles, Russian prisoners of war, gypsies, and the disabled. Stutthof was another Zyklon B camp, while Majdanek used both hydrogen cyanide and carbon monoxide. All in all, about 3 million people were killed with cyanide (see note at end of this chapter), out of the 6 million Jews and 6 million non-Jewish civilians murdered by the Nazis.

10.2 HALOGENATED METHANES

Chlorination of methane yields a mixture of mono-, di-, tri-, and tetrachloromethanes (see note at end of this chapter). These can be separated by distillation, which provides a route to their preparation but is not the preferred one. Chloromethane (methyl chloride) chlorinates more readily than methane, the formation of dichloromethane becoming significant after 18% of the methane has been converted to chloromethane. Indeed, a high conversion to chloromethane can be obtained only if the methane/chlorine ratio is greater than 10:1. Consequently, the preferred route to chloromethane is the reaction of methanol with hydrogen chloride.

$$CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$$

In contrast, chloroethane (ethyl chloride) can be made by the chlorination of ethane since dichlorination does not start until about 75% of chloroethane has been produced.

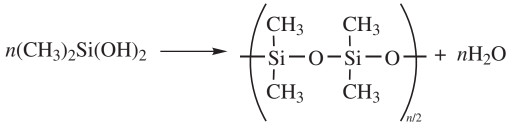
10.2.1 Chloromethane

In 2002, capacity for chloromethane was 535 million lb in the United States. Its major use in the past has been for conversion to dichloromethane (Section 10.2.2), whose use has declined markedly in the 1990s because of its toxicity. About 80% of chloromethane production is used to make silicone resins (or, more appropriately, polysiloxanes), which result from the hydrolysis of dimethyldichlorosilane. This monomer is made by reaction of chloromethane with silicon, which is usually in the form of a copper alloy.

$$CH_3Cl + \underset{\text{Silicon/ copper alloy}}{Si(Cu)} \longrightarrow \underset{\text{Dimethyldichlorosilane}}{(CH_3)_2SiCl_2} + Cu$$

The silane hydrolyzes with water to provide dimethyldihydroxysilane, which converts to a polysiloxane. Trimethylhydroxysilane from trimethylchlorosilane acts as a chain stopper.

$$(CH_3)_2SiCl_2 + 2H_2O \longrightarrow \underset{\text{Dimethyldihydroxysilane}}{(CH_3)_2Si(OH)_2} + 2HCl$$



$$n(CH_3)_2Si(OH)_2 \longrightarrow \left(-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O- \right)_{n/2} + nH_2O$$

Polysiloxane

The type of organic groups attached to the siloxane backbone and the extent of cross-linking between the chains determines whether the silicone will be an oil, an elastomer, or a resin. Silicones are used in water-repellent coatings, mold release agents, and slip agents. They are formulated as elastomers, caulking compounds and sealants, and as resins for lamination with glass. Silicone oils are used as antifoam agents in detergents and in aerobic fermentation processes such as penicillin production.

A smaller volume use for chloromethane is in the preparation of methylcellulose (Section 14.3). Its use in the manufacture of tetramethyl and tetraethyllead for gasoline has practically been phased out in the United States, but some of the gasoline additive was still manufactured in the early 2000s and exported. Chloromethane is used in the preparation of quaternary ammonium compounds such as difatty dimethylammonium chloride (Section 13.1) and has a small use as a catalyst and solvent in the production of butyl rubber.

10.2.2 Dichloromethane

Dichloromethane (methylene chloride) is made by the chlorination of chloromethane. Further chlorination of the mixture of chlorinated methanes provides chloroform and carbon tetrachloride. Dichloromethane production in 2001 was estimated to be 200 million lb, compared with 650 million lb in 1996, and 607 million lb in 1984. Western European consumption remained level at 351 million lb in 2001 compared with 310 million lb in 1996.

$$\underset{\text{Chloromethane}}{CH_3Cl + Cl_2} \longrightarrow \underset{\text{Dichloromethane}}{CH_2Cl_2 + 2HCl}$$

Dichloromethane has been used as a paint stripper, especially for jet aircraft that must be stripped at intervals and examined for cracks. It had the advantage over alkaline paint removers of not attacking aluminum. On the other hand, many chlorinated hydrocarbons are health hazards. Dichloromethane is described as a possible carcinogen–mutagen but it is not nearly as dangerous as tri- and tetrachloromethane because its appreciable water solubility means it does not accumulate in body fat. Nonetheless, dichloromethane's use as a paint stripper has declined precipitously. A more expensive substitute is *N*-methylpyrrolidone (Section 10.3.1). It has also been important in solvent degreasing, an application that is similarly being eliminated. Thirty-five percent of dichloromethane production was for synthesis of chlorofluorocarbons, which are being phased out, as is the application for solvent extraction of caffeine, cocoa, and edible oils. Production is nonetheless predicted to remain significant because of its use in the production of chlorosilanes, which is expected to grow at 2–3%/year in the 2000s.

10.2.3 Trichloromethane

Trichloromethane production in 1998 was 525 million lb and increased to about 650 million lb in 2002, because it is used in the production of hydrofluorocarbons, the replacements, if temporary, for fluorocarbons. It does, however, attack the liver and is carcinogenic in animals. On the basis of evidence of its mode of action, the EPA is trying to have it classified as a threshold carcinogen, so that tiny concentrations in water that has been disinfected with chlorine would still be acceptable (Section 17.3.7).

Trichloromethane is made by chlorination either of methane or chloromethane. The chlorination of methane can be carried out either thermally with chlorine without catalysts or by oxychlorination (Section 3.4) with hydrogen chloride and a potassium chloride–cupric chloride catalyst. Both processes are highly exothermic. The oxychlorination is carried out at 400–450°C at slightly elevated pressure. The chlorination may be initiated by photons or by chlorine atoms formed when chlorine molecules are heated. Trichloromethane was once an important anesthetic.

At one time, 97% was used for production of chlorofluorocarbon refrigerants and aerosol propellants, applications phased out in 1995 because the products destroy the ozone layer (Section 17.2.1). Fluorocarbons are made from both chloroform and

TABLE 10.1 Fluorocarbon Replacements[a]

Application	Fluorocarbon Being Phased Out	Transitional Replacement 1996–2005	Long-Term Replacement 2003 and Beyond
Domestic refrigeration Refrigerant	CFC-12	HFC-134a; isobutane	HFC-134a; isobutane
Domestic refrigeration Foam blowing	CFC-11	HCFC-141b Cyclopentane HFC-134a HCFC-22	HFC-245fa Cyclopentane HFC-134a Pentane
Mobile air conditioning	CFC-12 replaced by HFC-134a by 1996	HFC-134a	Propane HFC-152a Transcritical CO_2 (150 bar)
Unitary air conditioning	HCFC-22 CHF_2Cl monochlorodifluoromethane	HCFC 22 (until 2009)	HFC blends, R407C or R410A, and with HFC-134a propane (HC-290), ammonia, CO_2
Chillers (for building air conditioning)	CFC-11 CFC-12	HCFC-123 (until 2020) HFC-22 (until 2009)	HFC-134A HFC-245FA HFC-134A R-407C R-410A, NH_3
Commercial refrigeration	CFC-11 CFC-12 CFC-502	HCFC-22 and blends R404A R507	HFC blends R404A R507, NH_3, CO_2

Foam blowing	CFC-11 CFC-12	HCFC-141B HCFC-142B	HFC-245fa HFC-365mfc Blends of pentane isomers HFC-245fa HFC-365mfc HFC-134a Blends of the above HFC-134a, CO_2
Solvents	CFC-113 $C_2F_3C_{l3}$ 1,1,2-trichlorotrifluoroethane	HCFC-141b HCFC-123	HFC-365mfc (expensive) methylsiloxane, *n*-propyl bromide, HFC-43-10, HFC-245fa, Methyl perfluorobutyl ether, volatile methyl siloxanes, *n*-propyl bromide, flammable hydrocarbons, alcohols and ketones, aqueous cleaning, semiaqueous cleaning, no-clean fluxes, and inert gas soldering.
Aerosols	CFC-11 and CFC-12 banned in 1977. Replaced by	Hydrocarbons, HCFCs and HFCs, CFCs for metered dose inhalers (Montreal Treaty exemption)	HFC-134a, CF_3CH_2F HFC-227ea, CF_3CHFCF_3 Propane, butane, isobutane, dimethyl ether
Firefighting	Halon 1301 bromotrifluoromethane CF_3Br Halon 1211 bromochlorodifluoromethane CF_2ClBr		HFC-23 Trifluoromethane HFC-125 Pentafluoroethane HFC-227ea 1,1,1,2,3,3,3-heptafluoropropane HFC-236fa Hexafluoropropane Water-based systems,foam, dry powder, inert gas mixtures, CO_2

---

[a] Fluorocarbons are referred to by the code ABCD, where ABCD is a number with up to four digits. D is the number of fluorine atoms in the molecule; C is the number of hydrogen atoms plus one; B is the number of carbon atoms minus one, and A is the number of double bonds. If A = 0 or B = 0, they are omitted.

carbon tetrachloride by stepwise displacement of the chlorine atoms with hydrofluoric acid (HF). The higher the temperature and pressure, the more substitution results. Thus tetrachloromethane yields $CFCl_3$, CF_2Cl_2, and CF_3Cl. Trichloromethane yields $CHFCl_2$, CHF_2Cl_2, and CHF_3.

Catalysts for the reaction are fluorides or oxyfluorides of aluminum or chromium. Substitutes are compounds that contain fluorine and hydrogen, but no chlorine in most instances. In some replacements, a reduced number of chlorine atoms is considered acceptable. These too are believed to destroy the ozone layer, but at a lower rate. Thus their use is considered a temporary measure, and they are being phased out in the early part of the twenty-first century. Fluorinated ethers are potential replacements. The most important fluorocarbons and their applications and proposed replacements are shown in Table 10.1.

Trichloromethane reacts with hydrofluoric acid as noted above to give chlorodifluoroethane which, on pyrolysis at 700°C, gives tetrafluoroethylene and hexafluoropropylene. The former is the monomer for Teflon.

$$\underset{\text{Trichloromethane}}{2CHCl_3 + 2HF} \xrightarrow[-2HCl]{} \underset{\text{Chlorodifluoromethane}}{2CHClF_2} \xrightarrow{700^\circ C} \underset{\text{Tetrafluoroethylene}}{F_2C{=}CF_2} + 2HCl$$

$$3CHClF_2 \xrightarrow{700^\circ C} \underset{\text{Hexafluoropropylene}}{F_3CCF{=}CF_2} + 3HCl$$

10.2.4 Tetrachloromethane and Carbon Disulfide

Tetrachloromethane (carbon tetrachloride) was the raw material for trichlorofluoromethane and dichlorofluoromethane, discussed above and now phased out. It has no alternate uses. It may be made by exhaustive chlorination of methane or chloromethane, but there are two more important routes. The most widely used is a "two-for-one" reaction that produces both tetrachloromethane and perchloroethylene by the chlorolysis of a propane–propylene mixture at ~500°C:

$$\underset{\text{Propylene}}{CH_2{=}CHCH_3} + 7Cl_2 \longrightarrow \underset{\substack{\text{Carbon}\\\text{tetrachloride}}}{CCl_4} + \underset{\substack{\text{Perchloro-}\\\text{ethylene}}}{Cl_2C{=}CCl_2} + 6HCl$$

$$CH_3CH_2CH_3 + 8Cl_2 \longrightarrow CCl_4 + Cl_2C{=}CCl_2 + 8HCl$$

The quantity produced is dependent on the demand for perchloroethylene and the shortfall is made up by a route starting with methane but proceeding via carbon disulfide, another important methane-based chemical. An iron catalyst at 30°C brings about the chlorination:

$$CS_2 + 2Cl_2 \longrightarrow CCl_4 + 2S$$

Excess chlorine gives sulfur monochloride, also of interest industrially:

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$$

Carbon disulfide is made by reaction of methane and sulfur vapor in the presence of a catalyst:

$$CH_4 + aS_x \longrightarrow CS_2 + 2H_2S$$

where $ax = 4$ and x is between 2 and 8 since it is an equilibrium mixture of S_2, S_6, and S_8.

A major use for carbon disulfide is in the manufacture of regenerated cellulose for rayon, cellophane, and synthetic sponges (Section 14.3), all mature products.

10.2.5 Bromomethane

Bromomethane (methyl bromide) is made from methanol and hydrobromic acid:

$$CH_3OH + HBr \longrightarrow CH_3Br + H_2O$$

or from methanol plus bromine and a reducing agent to convert the HBr produced to the more valuable bromine.

World production in 1998 was 61,436 tonnes. It is widely used as a soil and grain fumigant and less widely to fumigate private residences infested with termites. It was a latecomer to the list of chemicals believed to affect the ozone layer. Its future is still in doubt (Section 17.2.1). Manufacture was scheduled to end in the United States in 2000 but this has been delayed because of lack of a suitable replacement.

10.3 ACETYLENE

Acetylene rose in importance as a chemical feedstock after World War II and reached a peak in the mid-1960s. But its use has since declined precipitously. Coal was not only a source of aromatics, by way of coke oven distillate (Section 7), but was also the raw material for acetylene, and hence the source of many early plastics and aliphatic organic chemicals.

In the oldest process, coke and lime, are heated in an electric furnace to 2000°C to give calcium carbide. This is hydrolyzed by water to give acetylene.

$$CaO + 3C \longrightarrow CaC_2 + CO$$

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + \underset{\text{Acetylene}}{CH{\equiv}CH}$$

The process has many of the characteristics of nineteenth century industry. It is a batch process. It is labor intensive because of the handling of solids and energy intensive because of the electric furnace. It is environmentally unattractive because every ton of acetylene produced is accompanied by 2.8 tons of calcium hydroxide, usually in a slurry with 10 times as much water. The capital cost of the furnace is high and it has a short life because of the "heroic" conditions used.

Even in the days of cheap energy, the problems with the carbide process provided an impetus for its replacement. In the early 1960s, many attempts were made to derive acetylene from petroleum. Thermodynamically, it is the stable C_2 hydrocarbon above 1300°C, but the pyrolysis of other hydrocarbons is not so simple. It is difficult to quench the reaction mixture rapidly enough to prevent reverse reactions and to keep residence times short enough to prevent coking. Separation of acetylene from byproduct hydrogen provides an additional problem.

These difficulties were addressed in the Wulff and Sachsse processes, which in theory can start with naphtha or natural gas. The naphtha-based plants, mainly European, gave continuous trouble and were closed after short lives.

Today there are four sources of acetylene. The calcium carbide route is one, but much of US acetylene produced in this way is for the nonchemical application of arc welding. Calcium carbide has played an honorable role in the history of the US chemical industry and even gave its name to the Union Carbide Corporation, whose name disappeared when the company was absorbed by Dow. Its derivative, calcium cyanamide, gave its name to the American Cyanamid Corporation, a veteran US chemical company that split into Cytec and American Cyanamid in 1994. Its name disappeared when the latter was taken over by American Home Products. Carbide's energy requirements, however, mean that today it can only be made economically in countries such as Norway, which have cheap hydroelectric power and unproductive land where the waste calcium hydroxide can be dumped.

For most chemical processes in the United States, acetylene is obtained from three other sources. The first is as a byproduct from thermal or steam cracking (Section 2.2.1) The cracking of propane at high severity, that is, high temperatures, can yield up to 2% of acetylene. Such conditions also produce a maximum amount of ethylene. Steam cracking of ethane–propane accounts for about half of US acetylene production. Before the C_2 fractionation, the acetylene in the C_2 stream is selectively absorbed in dipolar aprotic solvents such as dimethylformamide or *N*-methylpyrrolidone. If the acetylene is not wanted, it must be selectively hydrogenated to ethylene, and most crackers operate in this way.

A second process is thermal, the above-mentioned Wulff process, operated not with naphtha but with natural gas, which is primarily methane. The reactor consists of a furnace containing a hot brick lattice. The bricks are heated for a minute to about 1300°C by burning a gaseous fuel. The feed methane is then pyrolyzed for one minute. The same sequence of operations is then carried out in the opposite direction through the furnace, giving a four minute cycle with a final temperature below 400°C. The product is quenched and comprises a mixture of acetylene and ethylene in a ratio of 1:2.

The third process requires oxygen and is known as the partial oxidation process. There are several variations, but the Sachsse process is the most important of them. Methane and oxygen are preheated to 600°C and reacted in a special burner with flame formation. A temperature of about 1500°C is achieved. After a residence time of a few milliseconds, the mixture is quenched to 40°C with water or quench oil to inhibit soot and hydrogen formation. This yields a gaseous product containing 8–10% acetylene, corresponding to 30% of the carbon in the feedstock. Synthesis gas (Section 10.4) is the major product and about 1.5% of the initial carbon emerges as soot.

The Wulff and Sachsse processes, although not as "heroic" as the carbide process, are energy intensive. Thus acetylene has become steadily more expensive in comparison with ethylene, and almost everything that used to be done with acetylene can now be done more cheaply with olefins.

The list of obsolete or nearly obsolete acetylene-based processes is impressive—vinyl chloride from acetylene and hydrogen chloride; vinyl acetate from acetylene and acetic acid; acrylonitrile from acetylene and hydrocyanic acid; acetaldehyde from acetylene and water; chloroprene from acetylene dimer (vinylacetylene) and HCl; acrylate esters by way of acetylene, an alcohol, and carbon monoxide; and perchloroethylene (Section 10.3.2) by a multistage chlorination–dehydrochlorination process. Between 1967 and 1974, 25 acetylene plants in the United States closed, and consumption for chemical use dropped from 1.23 to 0.40 billion lb between 1962 and 1977. In 2000, acetylene demand was estimated at about 300 million lb, and in 2002 the supply dropped to under 200 million lb as Borden closed its acetylene-based vinyl chloride plant and ISP (International Specialty Products) shuttered its two 1,4-butanediol plants in the United States (see below).

The major area for the remaining acetylene use is in Reppe chemistry. Reppe was a German chemist who studied the interaction of acetylene with aldehydes, ketones, alcohols, and carbon monoxide, during World War II. The acrylate process mentioned above (Section 4.3) is a Reppe reaction as is the 1,4-butanediol process below.

10.3.1 1,4-Butanediol

Acetylene reacts with formaldehyde to give 1,4-butynediol, which may be hydrogenated stepwise to butenediol and butanediol.

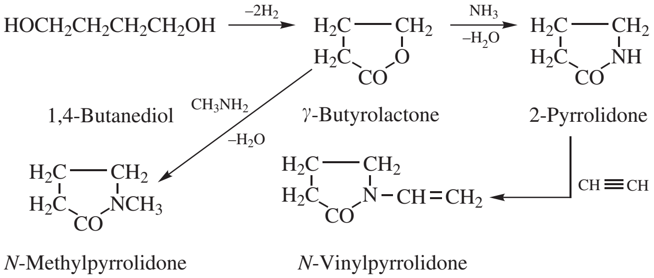
$$\underset{\text{Acetylene}}{HC{\equiv}CH} + \underset{\text{Formaldehyde}}{2HCHO} \longrightarrow \underset{\text{1,4-Butynediol}}{HOCH_2{-}C{\equiv}C{-}CH_2OH} \xrightarrow{H_2}$$

$$\underset{\text{1,4-Butenediol}}{HOCH_2{-}CH{=}CH{-}CH_2OH} \xrightarrow{H_2} \underset{\text{1,4-Butanediol}}{HOCH_2{-}CH_2{-}CH_2{-}CH_2OH}$$

The condensation of 37% aqueous formaldehyde and acetylene takes place at about 100°C and 5 bar in the presence of a cuprous acetylide catalyst deposited on magnesium silicate. In this process, the formation of byproduct propargyl alcohol $CH{\equiv}CCH_2OH$ is minimized. The hydrogenation is carried out in two stages because a purer product results. The first stage is operated at 50–60°C at 7–15 bar with a Raney nickel catalyst to yield 1,4-butenediol, which finds application in the manufacture of the pesticide Endosulfan (Section 6.3). The second stage requires a temperature of 120–140°C with hydrogen at 150–200 bar with a nickel–copper–manganese catalyst on a silica gel carrier and yields 1,4-butanediol.

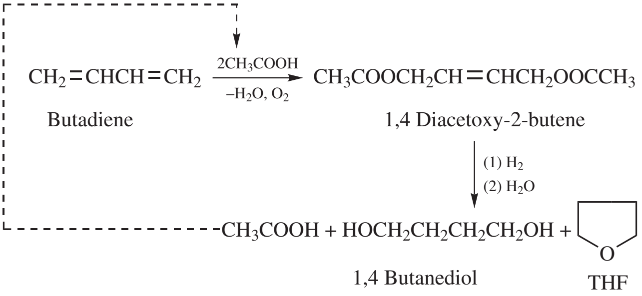
About 35% of 1,4-butanediol production is converted to tetrahydrofuran (THF). This is converted to poly(tetramethylene ether glycol) in the same way that ethylene oxide can be converted to poly(ethylene oxide). The product is used in the formulation of polyurethanes and elastomeric fibers such as Spandex (Section 3.1) and a thermoplastic elastomer, Hytrel (Section 15.3.8).

1,4-Butanediol is used as such in specialized polyurethane compositions for the manufacture of wheels for skates. It is also the basis for the so-called acetylenic chemicals γ-butyrolactone, pyrrolidone, and *N*-vinylpyrrolidone. γ-Butyrolactone is an aprotic solvent with limited end-use applications and some notoriety as a date rape drug. The great majority of γ-butyrolactone is converted to 2-pyrrolidone or *N*-methylpyrrolidone, a replacement for chlorinated solvents.



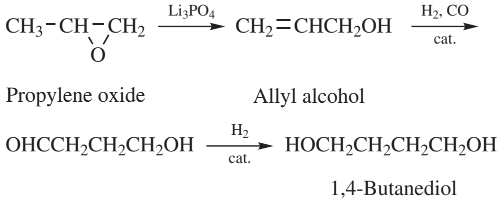
2-Pyrrolidone's major use is for conversion to *N*-vinylpyrrolidone. This can be polymerized to poly(*N*-vinylpyrrolidone) or copolymerized with vinyl acetate. These polymers are formulated into hair sprays, used as excipients in pharmaceutical pill manufacture, and as clarifying agents for beer and wine. During World War II poly(*N*-vinylpyrrolidone) was of interest in Germany as a replacement for blood plasma. The other important use for 1,4-butanediol is in the synthesis of poly(butylene terephthalate) (Section 9.3.4).

Although 1,4-butanediol has a relatively modest market (US production in 2002 was about 775 million lb) numerous possible routes to it have been developed. In 1979 in Japan, Mitsubishi Chemical commercialized a process from butadiene by an acetoxylation, reminiscent of an unsuccessful process for the manufacture of ethylene glycol (Section 3.7.2). The acetoxylation proceeds more readily with the conjugated butadiene than with ethylene because the double-bond system is more reactive (Section 3.7.1). Thus it is possible to use a palladium–tellurium catalyst without the iodine promoter required for ethylene, alleviating much of the corrosion, which was the Achilles' heel of the earlier process. After the initial acetoxylation, the 1,4-diacetoxy-2-butene is hydrogenated to 1,4-diacetoxybutane, which is saponified to the desired product and acetic acid for recycle.

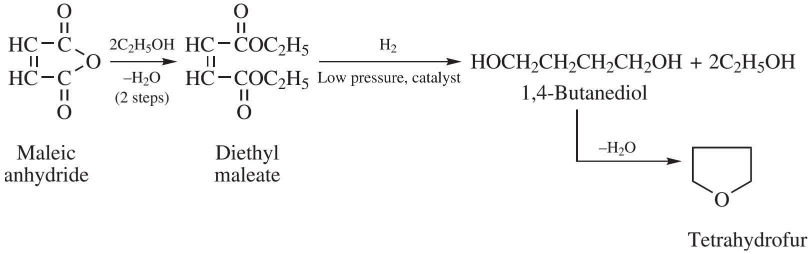


As indicated above, this process can also be run to give THF as the major product. BASF licensed this process in 2000 for a new plant in South Korea.

Another process for 1,4-butanediol production, commercialized in the United States by ARCO Chemical (now Lyondell) in 1990, starts with propylene oxide, which may be isomerized to allyl alcohol with a lithium phosphate catalyst. This was a step in an obsolete glycerol process (Section 4.14.2). Hydroformylation of the allyl alcohol yields an aldehyde, which on hydrogenation gives 1,4-butanediol. The hydroformylation is difficult and does not provide maximum selectivity to a linear product. Thus the branched aldehyde $CH_3CH(CHO)CH_2OH$ forms, which on hydrogenation provides a coproduct, 2-methyl-1,3-propanediol, $CH_3CH(CH_2OH)_2$. Lyondell is developing markets for this new diol and, in the early 2000s, it was beginning to find applications in unsaturated polyester resin formulations.



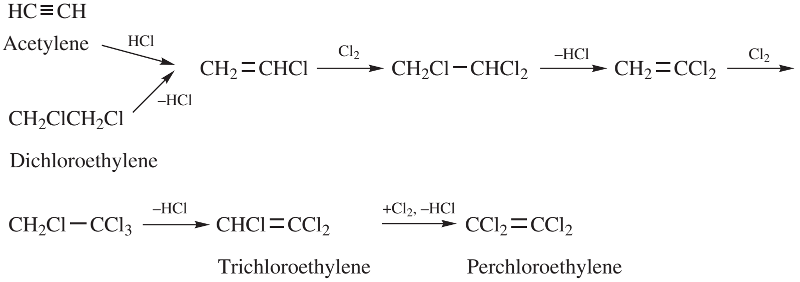
A process developed by Davy McKee and instituted in Japan in 1993 starts with maleic anhydride (Section 5.4), which is converted to ethyl or methyl maleate in two steps. This unsaturated ester is hydrogenated and subjected to hydrogenolysis in one step to give the desired product and ethanol for recycle.



A Du Pont process, for which a plant was completed in Spain in 1995, makes possible the conversion of maleic anhydride to tetrahydrofuran in one step. A major use for 1,4-butanediol is for conversion to THF, hence the Du Pont process accomplishes in one step what the Davy McKee process does in four steps. The Du Pont process entails hydrogenolyis of an aqueous solution of maleic acid. Besides the desired THF, a range of intermediate products including succinic acid, γ-butyrolactone, and 1,4-butanediol are formed. Since some unreacted maleic acid is always present, the 1,4-butanediol undergoes acid catalyzed cyclic dehydration to give additional THF. The unreacted maleic acid, succinic acid, and γ-butyrolactone are recycled back to the hydrogenolysis reactor. BP and Lurgi have combined to develop a similar process, which converts *n*-butane to an unisolated maleic acid intermediate, and then to 1,4-butanediol and/or THF. BP has built a plant using this technology in Lima, Ohio. In the mid-1990s, Sisas, a small Italian entrepreneurial company, developed and operated a process that converted maleic anhydride to γ-butyrolactone in one step. The butyrolactone was then converted to 1,4-butanediol, THF, or *N*-methyl pyrrolidone depending on market requirements. Sisas ran into financial difficulty and BASF bought the Sisas assets in 2001. Thus, BASF now operates 1,4-butanediol or THF plants based on acetylene (United States and Germany), butadiene (South Korea) and *n*-butane (Belgium).

10.3.2 Lesser Uses for Acetylene

Trichloroethylene (for degreasing) and perchloroethylene (for dry cleaning) may be made from acetylene. Most perchloroethylene, however, is produced from simultaneous chlorination and pyrolysis of hydrocarbons or by oxychlorination of dichloroethylene. (Sections 3.11.7, 10.2).



$$HC{\equiv}CH \text{ (Acetylene)} \xrightarrow{HCl} CH_2{=}CHCl \xleftarrow{-HCl} CH_2ClCH_2Cl \text{ (Dichloroethylene)}$$

$$CH_2{=}CHCl \xrightarrow{Cl_2} CH_2Cl{-}CHCl_2 \xrightarrow{-HCl} CH_2{=}CCl_2 \xrightarrow{Cl_2}$$

$$CH_2Cl{-}CCl_3 \xrightarrow{-HCl} CHCl{=}CCl_2 \text{ (Trichloroethylene)} \xrightarrow{+Cl_2,\,-HCl} CCl_2{=}CCl_2 \text{ (Perchloroethylene)}$$

Both products suffer from the same ecological problems as other chlorinated compounds, and their consumption decreased rapidly in the early 1990s.

Vinyl fluoride results from the addition of hydrogen fluoride to acetylene (Section 3.11.8). It can be polymerized to poly(vinyl fluoride), a specialty polymer, with outstanding weathering properties.

$$nCH{\equiv}CH + nHF \longrightarrow nCH_2{=}CHF \longrightarrow \left[CH_2{-}CHF \right]_n$$

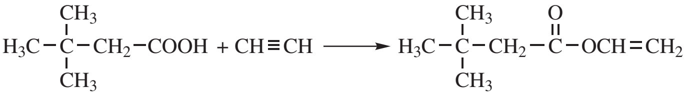
Partial carbonylation of acetylene with formaldehyde gives propargyl alcohol, used in the petroleum and metallurgical industries, and as an intermediate in the manufacture of the miticide, propargite; the antibacterial, sulfadiazine, and various propargyl carbonate fungicides:

$$HCHO + HC{\equiv}CH \xrightarrow[100^\circ C,\ 5\ bar]{Cu\ acetylide} HC{\equiv}CCH_2OH$$

Propargyl alcohol

Higher carbonyl compounds also give acetylenic alcohols, and these form parts of synthetic routes to terpenes, vitamins A and E and various perfumes and steroids.

Other small uses for acetylene include vinyl ester formation by the zinc or mercury salt-catalyzed reaction between an acid and acetylene. Thus, the so-called neo or Koch acids may be converted to vinyl esters as may fatty acids such as stearic or oleic.



$$H_3C-C(CH_3)_2-CH_2-COOH + CH{\equiv}CH \longrightarrow H_3C-C(CH_3)_2-CH_2-C(=O)-OCH{=}CH_2$$

Neohexanoic acid Vinyl neohexanoate

Vinyl esters may also be made by an exchange reaction or transvinylation between an acid and a vinyl compound such as vinyl acetate or vinyl chloride. The major use of these materials is as internal plasticizers or modifiers for polymers based on vinyl chloride and vinyl acetate to provide enhanced water resistance.

$$RCOOH + CH_2{=}CHOOCCH_3 \xrightarrow{\text{cat.}} RCOOCH{=}CH_2 + CH_3COOH$$

Vinyl acetate Vinyl ester Acetic acid

In a related reaction, vinyl ethers result from the interaction of alcohols and acetylene. The reaction is catalyzed by alkali. These too are used as comonomers for the modification of vinyl polymers.

$$n\text{-}C_{18}H_{37}OH + CH{\equiv}CH \longrightarrow n\text{-}C_{18}H_{37}OCH{=}CH_2$$

Stearyl alcohol Vinyl stearyl ether

10.4 SYNTHESIS GAS

Synthesis gas is the name given to a variety of mixtures of carbon monoxide and hydrogen or nitrogen and hydrogen. It is made from methane from natural gas if the latter is available, as it is in the United States and most of Europe. Countries lacking natural gas (e.g., Japan and Israel) make synthesis gas from naphtha. It may, however, be made from virtually any hydrocarbon (e.g., so-called resid, the residue from petroleum distillation). Indeed, it may be made from almost any carbonaceous material including coal, peat, wood, biomass, agricultural residues, and municipal solid waste.

Coal was an important feedstock prior to 1960. During World War II, it was used in Germany to provide synthesis gas for the manufacture of fuel and chemicals by the Fischer–Tropsch process (Section 12.2). The same technology is applied today in South Africa and makes coal the basis for at least one-half of that country's energy needs. Coal is also gasified in China.

Different applications for synthesis gas require different mixtures. The Fischer–Tropsch reaction and methanol manufacture require $CO{:}H_2 = 1{:}2$; hydroformylation [the oxo process (Section 4.8)] requires $CO{:}H_2 = 1{:}1$ and the Haber process for ammonia requires $N_2{:}H_2 = 1{:}3$ without any carbon monoxide at all. Other organic chemical syntheses require pure hydrogen. Properly adjusted, nonetheless, the basic synthesis gas processes can give all these mixtures.

10.4.1 Steam Reforming of Methane

The most widely used synthesis gas process is the steam reforming of hydrocarbons, with partial oxidation of hydrocarbons as another possibility. Coal-based routes are also of significance and will be described in Section 12.2. The dominant synthesis gas process is the steam reforming of methane.

Before steam reforming can take place, the methane feedstock is desulfurized by passage over a zinc oxide catalyst at 360–400°C. Sulfur levels lower than 2 ppm are required if the nickel steam-reforming catalyst is to have an adequate life. It is then mixed with steam in a molar ratio of between 2.5 and 3.5 of steam per mole of methane and passed over an alkali-promoted nickel catalyst, supported on potassium oxide or alumina. The reaction is carried out at about 800°C and 35 bar; it is endothermic and the heat is supplied externally. The principal reaction is

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad \Delta H_{800^\circ C} = 227 \text{ kJ mol}^{-1}$$

The exit gases contain about 7% unchanged methane plus some carbon dioxide and traces of nitrogen present in the natural gas. The excess steam minimizes coking of the catalyst. The higher the steam:carbon ratio, the higher the CO_2:CO ratio in the products.

$$C + H_2O \longrightarrow CO + H_2$$

$$C + 2H_2O \longrightarrow CO_2 + 2H_2$$

If the synthesis gas is to be used to make ammonia, nitrogen must be added and carbon monoxide removed. This is done by addition of an amount of air calculated to provide a N_2:H_2 ratio of 1:3. The oxygen in the air reacts with some of the carbon monoxide to give carbon dioxide.

$$2CO + O_2 \longrightarrow 2CO_2$$

The gases then pass to a second reforming unit at 370°C, possibly with additional steam. In the presence of an iron oxide catalyst, the water–gas conversion or shift reaction takes place.

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad \Delta H_{370^\circ C} = -38 \text{ kJ mol}^{-1}$$

These reactions are summarized in Figure 10.1.

The product gases contain hydrogen, nitrogen, carbon dioxide, and traces of methane, carbon monoxide, and argon. They are compressed and scrubbed with aqueous ethanolamine and diethanolamine (a variety of other processes is available) to remove

COAL:

$$2C + O_2 \rightleftharpoons 2CO$$
$$C + H_2O \rightleftharpoons CO + H_2$$
$$CO + H_2O \rightleftharpoons H_2 + CO_2 \text{ (SHIFT REACTION)}$$
$$C + CO_2 \rightleftharpoons 2CO \text{ (BOUDOUARD REACTION)}$$
$$C + 2H_2 \rightleftharpoons CH_4$$
$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$

METHANE:

$$CH_4 + 1/2O_2 \rightleftharpoons CO + 2H_2$$
$$CH_4 + H_2O \rightleftharpoons CO + 3H_2$$

NAPHTHA:

$$-CH_2- + 1/2O_2 \rightleftharpoons CO + H_2$$
$$-CH_2- + H_2O \rightleftharpoons CO + 2H_2$$

CARBON FORMATION:

$$2CO \rightleftharpoons C + CO_2$$
$$CO + H_2 \rightleftharpoons C + H_2O$$
$$CH_4 \rightleftharpoons C + 2H_2$$

FIGURE 10.1 Important reactions in synthesis gas formation.

carbon dioxide. Some of the carbon dioxide dissolves in the water—at high pressure the solubility is high—and some reacts with the amine to give an unstable salt. The ethanolamine may then be recovered by steam stripping, which decomposes the salt. A further shift reaction may improve yields, and other processes are employed to reduce carbon monoxide to a very low level. The product is then delivered to an ammonia plant.

10.4.2 Variants of Steam Reforming

If synthesis gas is required for other purposes, the addition of nitrogen is not necessary. The shift reaction will then give CO–H_2 mixtures rich in hydrogen or it will even give pure hydrogen. Alternatively, if carbon monoxide-rich materials are needed, then carbon dioxide may be added at the shift conversion stage so that the equilibrium in the shift reaction is pushed to the left and, instead of carbon monoxide converting water to hydrogen, the reverse occurs.

$$CO_2 + H_2 \longrightarrow CO + H_2O$$

There are many variants to this process. Propane or naphtha may be the feedstock. With propane as the example, the following occurs:

$$C_3H_8 + 3H_2O \longrightarrow 3CO + 7H_2 \quad \Delta H_{800°C} = 552 \text{ kJ mol}^{-1}$$

$$C_3H_8 + 6H_2O \longrightarrow 3CO_2 + 10H_2 \quad \Delta H_{800°C} = 435 \text{ kJ mol}^{-1}$$

If a higher steam/hydrocarbon ratio is used, the product has a higher CO/H_2 ratio than is possible with methane. It is thus less suitable for ammonia. Flexibility is achieved, however, by adjustment with the shift reaction.

In a further application of the steam reforming reaction, methane rather than synthesis gas is produced. It may be obtained fairly readily from any hydrocarbon feedstock that can be vaporized, for example, naphtha. The process is operated at a lower temperature than if synthesis gas is required. Typically, with nonane as an example,

$$C_9H_{20} + 4H_2O \longrightarrow 7CH_4 + 2CO_2.$$

The product is called Substitute Natural Gas (SNG). The process was used in the United Kingdom before North Sea discoveries and is still used in Japan where natural gas is lacking. Various processes are available to give methane from heavier hydrocarbon feedstocks, but the huge discoveries of natural gas in the former Soviet Union in the early 1980s mean that oil is now thought likely to be depleted before natural gas. Hence, interest in SNG from oil has diminished.

10.4.3 Partial Oxidation of Hydrocarbons

A second route to synthesis gas is partial oxidation of carbonaceous materials reacted with steam. If the feedstock can be vaporized, the reactions are carried out simultaneously, but if it is a solid they must be carried out sequentially.

A vaporizable hydrocarbon feedstock (e.g., methane, propane, naphtha) is burned in a flame in the presence of about 35% of the stoichiometric amount of oxygen.

$$CH_4 + O_2 \longrightarrow CO_2 + H_2 \quad \text{Rapid} \quad \Delta H = -318 \text{ kJ mol}^{-1}$$

A little water is also formed by conventional combustion reactions. Excess hydrocarbon can now react.

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CO + 2H_2 \quad \text{Rapid} \quad \Delta H = -36 \text{ kJ mol}^{-1}$$

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \quad \text{Slow} \quad \Delta H = 247 \text{ kJ mol}^{-1}$$

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad \text{Slow} \quad \Delta H = 227 \text{ kJ mol}^{-1}$$

The flame temperature is 1300–1400°C at a pressure of 60–80 bar with a residence time of 2–5 seconds. The rapid initial reactions provide the heat required to drive the subsequent endothermic reactions. These reactions are slower than the initial reactions, however, and, because incomplete combustion is always accompanied by carbon formation, a finely divided carbon is always present in the products and must be removed by washing.

Desulfurization is unnecessary. Sulfur in the feedstock is converted primarily to hydrogen sulfide but also to carbonyl sulfide (COS). Nitrogen compounds end up as elemental nitrogen or ammonia. A plant must be built, however, to produce the pure oxygen for the process. This is generally an economic drawback but confers a slight advantage in ammonia manufacture in that the nitrogen coproduced with the oxygen can be added to the synthesis gas to provide the correct composition for ammonia production. Some of the shift reaction and carbon dioxide removal stages can be avoided. Other variants include combined reforming in which steam reforming and partial oxidation are run in sequence and autothermal reforming where steam reforming and partial oxidation reactions are run simultaneously in a single reactor.

10.4.4 Solid Feedstocks

The two-stage, partial oxidation of coal has been widely used as a route to synthesis gas, and the method could be extended to other carbonaceous feedstocks. A bed of coke or coal is burned in a stream of air until it reaches about 1000°C. The air is then replaced by steam and two coal gasification reactions occur.

$$C + H_2O \longrightarrow CO + H_2 \qquad \Delta H_{1000^\circ C} = 130\ \mathrm{kJ\ mol^{-1}}$$

$$C + 2H_2O \longrightarrow CO_2 + 2H_2 \qquad \Delta H_{1000^\circ C} = 88\ \mathrm{kJ\ mol^{-1}}$$

The product is called water gas because it is made from water plus coke. It is also called blue gas, because it burns with a characteristic blue flame caused by chemiluminescence. It can be converted to synthesis gas by techniques already described.

If air and steam are passed over the coke simultaneously, the product gases are diluted with nitrogen and are known as producer gas or low Btu gas. Producer gas is obsolete in the United States, but is burned *in situ* as a cheap fuel gas in some parts of the world.

Much effort has been expended on the development of gasification processes for coal to produce synthesis gas for chemicals. Most important is the work done by Eastman, based on the Texaco gasifier, which led to a coal-based acetic anhydride process (Section 10.5.2.3).With the discovery of large quantities of gas in the 1980s and 1990s, coal appears even less attractive than it did as a raw material for chemicals.

10.4.5 Hydrogen

Hydrogen is manufactured by steam reforming and partial oxidation, but large amounts are also obtained in the refinery as byproducts of cracking and catalytic reforming reactions (Sections 2.2.1, 2.2.3). Minor sources include coke oven gases, as well as the electrolysis of water, and of sodium chloride (which gives principally sodium hydroxide and chlorine), as well as hydrogen chloride and hydrogen fluoride (to give chlorine and fluorine).

When hydrogen is obtained from synthesis gas or refinery processes, it is purified by washing successively at 180°C and about 20 bar with liquid methane, to remove nitrogen and carbon monoxide, and with liquid propane to remove methane.

About 60% of all hydrogen is used for the production of ammonia. The second largest use is in refinery processes in hydrotreating, hydrocracking (Section 2.2.6), hydrodesulfurization, and toluene hydrodealkylation (Section 8.1). Most of this hydrogen is produced internally in other refinery processes. The Clean Air Act, however, reduced permitted amounts of aromatic hydrocarbons in gasoline, hence less catalytic reforming is now done and less hydrogen is produced. Many refineries have experienced shortages and have found it necessary to build on-purpose hydrogen units. Among organic chemicals made outside the refinery, methanol is the largest consumer of hydrogen. Other applications include the conversion of benzene to cyclohexane (Section 7.2), nitrobenzene to aniline (Section 7.3), and unsaturated fats to saturated or hard fats (Section 13).

10.5 CHEMICALS FROM SYNTHESIS GAS

Ammonia is by far the most important chemical made from synthesis gas and consumes 5% of the world's natural and associated gas production. Even though it is not organic, it is produced from and is used to make organic chemicals. Methanol is the second important chemical from synthesis gas and is the basis for methyl *tert*-butyl ether (Section 5.2.1), formaldehyde, and acetic acid. It consumes about 1% of natural and associated gas production. All except methyl *tert*-butyl ether are described here.

10.5.1 Ammonia and its Derivatives

Ammonia is prepared by the Haber–Bosch process, which requires a synthesis gas of composition N_2:$3H_2$. The mixture is passed over a promoted iron oxide catalyst at about 450°C and 250 bar. Conversions are low, about 10% per pass, requiring a large recycle of unreacted synthesis gas.

Although the process is formally the same as that developed by Haber, the technology has been modified. More active catalysts have reduced the required operating temperature. The main change, however, has been the replacement of reciprocating pumps by centrifugal pumps. Reciprocating pumps operate like bicycle pumps with an in-and-out action and can achieve very high pressures; the early Haber plants operated at 1000 bar. Centrifugal pumps are like giant electric fans and involve only rotary motion. They are cheaper than reciprocating pumps, require less frequent maintenance, and do not require lubrication, so that oil contamination of the catalyst is avoided. They can be driven by turbines operated with the steam generated from waste heat or from the steam-reforming process. Their single drawback is that they are limited to pressures of about 250 bar. Their advantages, however, are so great that it is more economic to operate at this relatively low pressure and tolerate the low conversions.

This new technology has made possible the scaling-up of ammonia plants from the 200 tons/day common in 1960 to 1500–1850 tons/day in the early 2000s. Steam crackers for ethylene also depend on centrifugal pumps, which have made possible impressive scale-up. Another development is the use of microporous polysulfone membranes to separate unreacted hydrogen from the product stream so that it can be recycled without inert contaminants such as argon and without the waste involved in a purge stream (Section 7.1.2.3).

Iron-based catalysts have been used for so long that it seems almost heretical to suggest that they might be replaced. Meanwhile, the engineering company, Kellogg, Brown, and Root have proposed a ruthenium catalyst. At least one plant has been built (in Trinidad). It is said to enable the pressure to be reduced from 150 to 300 bar to 70–105 bar and the inlet–outlet temperature from 370–510 to 350–470°C. Waste heat is used for a synthesis gas reaction, and flue gas nitrogen oxides and carbon dioxide are reduced by 70–75% each.

It seems likely that the Haber–Bosch process will remain the mainstay of nitrogenous fertilizer production for the foreseeable future. There is still a hope for biological nitrogen fixation, whereby nonleguminous plants such as corn, wheat, and oats can be made nitrogen fixing by bacteria created by genetic engineering techniques. Should this objective be achieved, it might provide the basis for a second "Green Revolution" for food production.

About 75% of ammonia production is used for fertilizers, mostly as ammonia and ammonium salts but also, in substantial quantities, in the form of urea. Ammonia reacts with carbon dioxide to give ammonium carbamate, which in turn dehydrates to urea.

$$2NH_3 + CO_2 \longrightarrow \underset{\text{Ammonium carbamate}}{NH_2COONH_4} \xrightarrow{-H_2O} \underset{\text{Urea}}{NH_2CONH_2}$$

Urea contains 46% fixed nitrogen, and 75% of US production is used as fertilizer. Urea plants are always built next to ammonia plants, which supply the raw materials and also have excess heat available.

Urea was first synthesized by Wöhler in 1828, who heated an aqueous solution of ammonium cyanate at ~100°C.

$$\underset{\text{Ammonium cyanate}}{NH_4OCN} \longrightarrow \underset{\text{Urea}}{NH_2CONH_2}$$

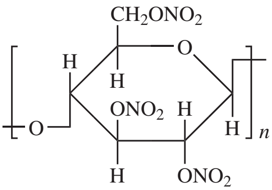
This seminal reaction, in which an inorganic compound was converted to an organic material, proved that organic chemicals, defined in those days as chemicals related to life, were chemicals like any other. The discovery gave rise to the discipline of organic chemistry. It had previously been thought that organic chemicals could only be made by living systems. Indeed, Wöhler defined an organic compound as one associated with life processes. Today the definition is much broader, for organic compounds are simply those that contain carbon.

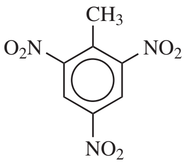
Wöhler's reaction may have commercial application in that nitric oxide, carbon monoxide, and hydrogen have been found to combine at 60°C to give ammonium cyanate.

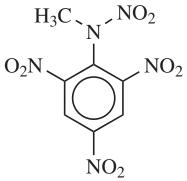
$$2NO + CO + 4H_2 \longrightarrow NH_4OCN + 2H_2O$$

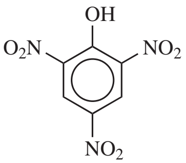
The reaction is catalyzed by a variety of metals including platinum and copper/nickel, although a platinum/rhodium gauze appears to be best. The ammonium cyanate in turn is converted quantitatively to urea, at 100°C. This reaction is not economically feasible as a route to urea because of the cost of NO but it has been considered for removing emissions from automobile exhaust.

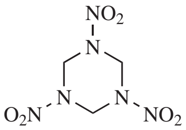
Ammonia may be oxidized to nitric acid, which is used, sometimes mixed with sulfuric acid, to produce a variety of nitro compounds and their derivatives. Most explosives [e.g., cellulose nitrate, TNT (trinitrotoluene), "Tetryl," (2,4,6-trinitrophenylmethylnitramide), picric acid (trinitrophenol), pentaerythritol tetranitrate, "Cyclonite" (cyclotrimethylene trinitramine), nitroglycerol, and ammonium nitrate] are nitro compounds, as are nitromethane, nitroethane, and the nitropropanes (Section 11.1), which are used as propellants, chemical intermediates, and solvents.

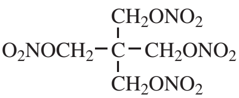

Cellulose nitrate


TNT


Tetryl


Picric acid


Cyclonite



$$O_2NOCH_2-\overset{\displaystyle CH_2ONO_2}{\underset{\displaystyle CH_2ONO_2}{C}}-CH_2ONO_2$$

Pentaerythritol tetranitrate

Nitrobenzene is the precursor of aniline and MDI (Sections 7.3, 7.3.1). Dinitrotoluene is the precursor of toluene diisocyanate (Section 8.3). Nitrocyclohexane was an intermediate in an obsolete caprolactam process (Section 7.2.2), and the most important caprolactam process uses ammonia-based hydroxylamine. Ammonia is important in ammoxidation (Section 4.8) and was involved in the first synthesis of hexamethylene diamine (Section 5.1.1). It is used similarly to convert fatty acids to amides (Section 13.2). It also reacts with both alkyl halides, alcohols, and phenols to give amines (Section 7.3). Chemicals produced from ammonia are shown in Table 10.2.

10.5.1.1 Urea and Melamine Resins

Urea reacts with formaldehyde to give thermoset urea–formaldehyde (U/F) resins. The reactions are complex, involving first of all the formation of methylolurea and *N,N′*-dimethylolurea.

$H_2NCONHCH_2OH$	$OC(NHCH_2OH)_2$
Methylolurea	*N,N′*-Dimethylolurea

These, by a series of condensations that include ring formation, provide thermoset polymers (Section 15.4.1).

TABLE 10.2 Major Chemicals from Ammonia, United States 2000–2001

	Production (billion lb)		Ammonia Content (billion lb)[a]	
	2000	2001	2000	2001
Ammonia (synthetic, anhydrous)	33.61	26.09[b]		
Diammonium phosphate	24.47	22.39	6.30	5.77
Nitric acid	16.96	15.65	4.58	4.22
Ammonium nitrate[c]	15.00	14.20	3.19	3.02
Urea	15.24	14.08	8.64	7.98
Monoammonium phosphate	9.10	8.62	1.35	1.27
Ammonium sulfate[d]	5.74	5.11	1.48	1.32
Nylon resins and fibers	4.29	3.68	–[e]	–[e]
Acrylonitrile	3.35	2.87	1.07	0.92
Caprolactam[f]	1.73	1.59	2.01	1.85
Hydrogen cyanide	1.53	1.50	0.96	0.94
Hexamethylenediamine	1.36	1.17	0.40	0.34
Hydrocyanic acid (liquid, solution)	1.32	1.02	0.83	0.64

Source: Adapted from *Guide to the Business of Chemistry, 2002.*

[a] Assuming 100% yields except where indicated.

[b] This is surprisingly low. Comparison with *Chem. Eng. News* data suggests a figure of ~28 billion lb.

[c] Excluding the ammonia going into the nitric acid.

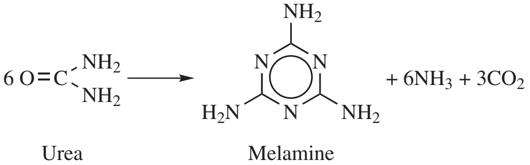
[d] Does not include byproduct ammonium sulfate from caprolactam manufacture.

[e] Not produced directly from ammonia.

[f] Assuming exclusive use of the oxime route and ignoring the ammonia required for the hydroxylamine. About 6.5 billion lb of byproduct ammonium sulfate is produced.

The major use for urea–formaldehyde resins is as a binder for sawdust and wood particles in particle board. They are also used to creaseproof fabrics, to impart wet strength to paper, and, in the form of a foam, as insulation for buildings. There have been questions about the toxicity of residual formaldehyde in such foams. Compression molding of U/F resins gives items such as electrical fittings and toilet seats. Molding powders are invariably formulated with fillers. They are less heat and water resistant than phenol–formaldehyde (P/F) resins but can be fabricated in a range of cheerful colors.

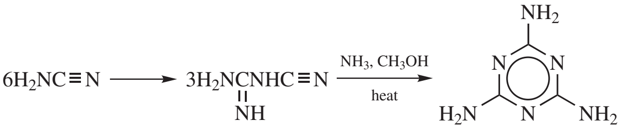
Urea is also the source of melamine, which is made in the United States by a one-step process involving trimerization of molten urea at 400°C with release of ammonia and CO_2, in the presence of an aluminosilicate catalyst. Both low- and high-pressure processes are used and, in the former, cyanic acid HNCO is an intermediate.



An obsolescent process started with calcium carbide from coal and went by way of dicyandiamide. Some plants in Europe still use this process.

$$CaC_2 + N_2 \xrightarrow{CaO} \underset{\text{Calcium cyanamide}}{CaNCN} + C$$

$$CaNCN + 2H_2O \longrightarrow Ca(OH)_2 + H_2NC{\equiv}N$$



Dicyandiamide Melamine

Like urea, melamine reacts with formaldehyde to give complex thermosetting resins. Melamine–formaldehyde (M/F) resins are high quality premium products and are used for dinnerware, the top layer of laminates such as "Formica," and in industrial and decorative coatings, especially for automobiles. They make urethane foams fire retardant. Like the U/F resins, M/F resins are useful for textile and paper treatment, adhesives, and molding powders.

10.5.2 Methanol

Ninety percent of world methanol is based on synthesis gas from natural gas or methane. Seventy-five percent of methanol produced in 2002 was used for chemicals. The remaining 25 percent was used for fuels, particularly for the production of methyl *tert*-butyl ether (Section 5.2.1).

Methanol is made from synthesis gas.

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

Excess hydrogen is added for kinetic reasons, although the CO:H_2 ratio may be as low as 2.02:1. The steam reforming of naphtha, which as indicated earlier, is not widely used in the United States or Western Europe, produces synthesis gas close to the desired composition. The steam reforming of methane or natural gas yields a synthesis gas with a H_2:CO ratio close to 3:1. There are two ways of adjusting the ratio. The first is to purge the excess hydrogen, and the purged gas is normally burned as reformer fuel. The second is to add carbon dioxide from an external source such as an ammonia plant to take up the excess hydrogen.

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

There is recent evidence that the mechanism of the reaction is one in which the carbon monoxide is converted by the shift reaction to carbon dioxide, after which the carbon dioxide reacts with hydrogen as shown above, to yield methanol. A recently announced but uncommercialized process for methanol is based solely on carbon dioxide (see note at the end of this chapter).

Initially, methanol was prepared by BASF by a high-pressure process (320–380°C and 340 bar) with a $ZnO—Cr_2O_3$ catalyst with Zn:Cr ratio of 70:30. In 1972, ICI commercialized a low-pressure process (240–260°C and 50–100 bar), which made use of a copper–zinc catalyst on an alumina support. The energy savings are large but the process requires synthesis gas almost completely free of chlorine and sulfur compounds. There have since been a number of medium pressure processes (100–250 bar) with copper oxide added to the Zn–Cr catalyst system. Techniques for purifying synthesis gas are sufficiently good to have made the ICI process dominant. Although the catalyst is more expensive, the reaction is more selective, giving higher methanol yields and purer product. The major side reaction is the formation of dimethyl ether from methanol. Aldehydes, ketones, esters, and higher alcohols are formed in minute quantities. The methanol is refined by distillation.

At least four new processes are under development for methanol production, none of which has been commercialized. In one process, a homogeneous catalyst, typically ruthenium carbonyl, operates at temperatures as low as 120°C, where the $H_2 + CO/CH_3OH$ equilibrium strongly favors methanol. Intermetallic catalysts have been explored extensively in a second process but thus far have not found commercial application. A barium–copper intermetallic compound makes possible methanol formation at 280°C and 60 bar. A zinc-promoted Raney-copper catalyst also has been shown to have higher activity than the Cu–Zn–alumina catalyst used in the standard low-pressure process.

A liquid-phase methanol process makes use of a copper–zinc catalyst supported on alumina. The reaction can take place at 250°C and 50 bar. The reaction is carried out in an inert liquid such as a hydrocarbon. Once the methanol forms, it is vaporized and purified. The process has been piloted jointly by Eastman Chemical and Air Products who operate a demonstration plant with the CO and H_2 prepared from coal. The possibility of producing methanol by direct oxidation of methane will be discussed in Section 11.1.1.

Various technology licensors are now developing so-called “megamethanol” plants, with capacities of the order of 5000–10000 tonnes/day. These huge plants are intended to maximize economies of scale to allow methanol to be produced at remote locations from low-cost “stranded” gas and still be cheap enough to tolerate shipping costs to developed markets.

Excluding MTBE, ~35% of methanol is converted to formaldehyde. Acetic acid and acetic anhydride (Sections 10.5.2.2, 10.5.2.3) syntheses comprise the second largest use followed by methyl methacrylate (Section 4.10.1) terephthalic acid–dimethyl terephthalate (Section 9.3) methylamines, solvents, and a variety of lower volume uses including dimethyl sulfate and dimethyl carbonate (Section 7.1.2.2). Methanol is also used in the preparation of single-cell protein. Applications in chlorinated methanes (Section 10.2) and certain glycol ethers (Sections. 3.11.6, 4.11) are either banned or declining rapidly.

10.5.2.1 Formaldehyde The major route to formaldehyde is the dehydrogenation–oxidation of methanol. Some producers use pure oxidation over a ferric oxide–molybdenum oxide catalyst. A small amount of formaldehyde is produced by the partial oxidation of lower petroleum hydrocarbons. Proposed methods include the hydrogenation of carbon monoxide, the pyrolysis of formates, and the direct oxidation of methane (Section 11.1).

The dehydrogenation–oxidation process uses a stationary bed silver catalyst and a mixture of methanol vapor and air at approximately atmospheric pressure and 700°C. Some water is added to facilitate methanol conversion and to prevent catalyst deactivation. Less than the stoichiometric amount of oxygen is used. The resulting gases are absorbed in water. It is believed that two gas-phase reactions take place, one involving dehydrogenation and the other oxidation.

$$CH_3OH \rightleftharpoons HCHO + H_2 \quad \Delta H = 20\ \text{kcal mol}^{-1}$$

$$CH_3OH + 0.5H_2 \longrightarrow HCHO + H_2O \quad \Delta H = -38\text{kcal mol}^{-1}$$

The first reaction, like all dehydrogenations, is endothermic and the second is exothermic. Properly carried out, a favorable heat balance results. There is some evidence that a second reaction does not in fact take place as written above but rather that the exothermicity results from the oxidation of some of the methanol to CO_2 and water. Conversions as high as 75% have been reported with net molar yields of 83–92%. The byproduct hydrogen plus traces of formaldehyde can be burned as fuel. The oxidation process uses a ferric oxide–molybdenum oxide catalyst in a ratio of about 1:4. Reaction takes place at 300−400°C with almost quantitative methanol conversion at selectivities above 90%. Compared with the silver-catalyzed process, the lower temperature reduces corrosion problems, and higher formaldehyde concentrations are obtained without distillation. The drawbacks are that the great excess of air means higher capital and energy costs and, because the waste gas contains traces of formaldehyde, it is incombustible and must be specially purified. Consequently, most producers currently prefer silver catalysts.

The gaseous formaldehyde is dissolved in water and, when prepared in this way, always contains 1–2% of methanol, which serves as a stabilizer. Commercial formaldehyde is sold in several forms. Aqueous solutions contain up to 60% formaldehyde (37% is common) as a hydrate or as low molecular weight oxymethylene glycols $H[OCH_2]_nOH$. A second form is as a cyclic trimer called trioxane, and a third is "paraformaldehyde," which forms when water is evaporated from an aqueous solution of formaldehyde. This polymeric form and the oxymethylene glycols are both readily "unzipped" by heat or acid.

Of the 3.5 billion lb/year of formaldehyde produced in the early 2000s in the United States, 16.5% was used for the preparation of phenol–formaldehyde resins (Section 7.1.1). Twenty-four percent was used for urea–formaldehyde resins (Section 10.5.1.1), and a small amount went into melamine–formaldehyde resins (Section 10.5.1.1).

Polyacetal resins (Section 15.2) are polymers of formaldehyde with the recurring unit $-OCH_2-$. They are strong stiff polymers classified as “engineering” plastics, useful for replacing soft metals such as brass in, for example, valves, hose, and tube connectors, as well as in hard metal uses such as machine housings and many structural parts (Section 15.2).

A smaller use for formaldehyde is in the preparation of MDI/PMDI (Section 7.3.1). Formaldehyde combines with acetylene to give 1,4-butynediol, which can be hydrogenated to 1,4-butanediol, and a series of related chemicals (Section 10.3.1). With ammonia it yields hexamethylenetetramine. “Hexa” is an intermediate in the manufacture of RDX, the explosive that replaced TNT in “blockbuster” bombs in both World War II and the Korean War. Its principal use today is as a convenient source of formaldehyde under alkaline conditions for the curing of the B-stage or partially cured phenolic resins (Section 7.1.1) required in the manufacture of plywood or Formica.

Formaldehyde with acetaldehyde yields pentaerythritol (Section 3.11.3). A related material, trimethylolpropane, is made by the condensation of formaldehyde and butyraldehyde (Section 4.12). Similarly, neopentyl glycol results from the condensation of formaldehyde and isobutyraldehyde (Section 4.12).

Nitrilotriacetic acid (Section 10.1) requires formaldehyde. One synthesis of isoprene depends on the condensation of formaldehyde and isobutene (Section 6.2). These miscellaneous uses account for about 15% of formaldehyde consumption. An uncommercialized process for ethylene glycol involves the dimerization of formaldehyde (Section 3.7.2).

10.5.2.2 Acetic Acid

Acetic (ethanoic) acid can be made by a number of routes, the most important of which is Monsanto’s methanol carbonylation process, now owned by BP.

$$CH_3OH + CO \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}$$

This reaction is catalyzed by iodine-promoted rhodium at 200°C and 1–3 bar and gives 99+% selectivity to acetic acid, based on methanol. This high selectivity is exceeded in industrial chemistry only by the reactions in which isobutene is reacted with water or methanol to give *tert*-butanol or methyl *tert*-butyl ether (Sections 5.2.1, 5.2.4).

The Monsanto process followed on the heels of an older BASF process that used cobalt iodide CoI_2 as a catalyst. This synthesis, however, required a temperature of 250°C, a pressure of 60 bar, and gave much lower selectivities than the Monsanto process. Numerous byproducts complicated the purification of the acetic acid.

Both Celanese and BP have improved the Monsanto technology by enabling increased reactor throughputs. The Celanese Acid Optimization (AO) process and the BP Cativa process have doubled or even tripled capacities with the need for only modest capital expenditure. The Cativa process uses an iridium-based catalyst in place of rhodium. The key to both Celanese's and BPs improved acetic acid technology is that the methanol carbonylation reaction is run in the presence of relatively low levels of water, about 4–5 wt%; this is in contrast to the conventional Monsanto process that requires about 14–15 wt%. The water is necessary to ensure that the rhodium catalyst remains in solution. Celanese discovered that adding lithium iodide to the reaction mixture stabilized the rhodium catalyst, while BP found that iridium-based catalysts were effective in a low-water environment. Low water levels reduce energy consumption, decrease carbon monoxide unit consumption, increase reactor productivity, and lower unit capital investment.

Chiyoda in Japan has developed, and is offering for license, an acetic acid process that uses a heterogeneous methanol carbonylation catalyst, composed of rhodium complexed with a polyvinylpyridine resin.

In the United States, about 88% of all acetic acid is made by methanol carbonylation. The remainder is made via butane oxidation, except for a small amount formed as a byproduct from poly(vinyl alcohol) and ethylene-vinyl alcohol copolymer production. In Western Europe, in the early 2000s, about 57% was made by methanol carbonylation, 28% by acetaldehyde oxidation, and 15% from light naphtha (see below).

A method for making acetic acid, which is obsolete in the United States and obsolescent in Western Europe because of methanol carbonylation, is the oxidation of acetaldehyde (Section 3.5). It involves treating a 5–15% acetaldehyde solution in acetic acid with air in the presence of dissolved cobalt or manganese acetates at 50–70°C. As indicated earlier (Section 3.4) methanol carbonylation has been largely responsible for a decline in acetaldehyde production (Section 3.5). In the mid-1990s, Showa Denko commercialized a direct ethylene oxidation process for acetic acid manufacture (Section 3.5). This process avoids the complex chemistry associated with the Wacker process for making acetaldehyde and oxidizes ethylene via a palladium catalyst directly to acetic acid.

Another process is based on liquid oxidation of hydrocarbons—a mixture of propane and *n*-butane in the United States and a light naphtha fraction called primary flash distillate in Europe, especially in the United Kingdom. The process requires large amounts of water and yields a dilute acetic acid solution whose concentration is energy intensive. The oxidation of *n*-butanes takes place at 175°C and 54 bar with a cobalt acetate catalyst. Many byproducts are produced, the major one being methyl ethyl ketone. The oxidation of naphtha takes place at 70–90°C at 40 bar. As might be expected, even more byproducts form than in the oxidation of butane. Important ones are propionic and formic acids. Succinic acid forms in substantial quantity but lacks a market. The hydrocarbon oxidation process makes use of the cheapest raw materials but the separation of the acetic acid is complicated and expensive. Even so, the byproducts have value in their own right and contribute to the economics of the process. Thus the plants have continued to operate into the 2000s.

In 2001, SABIC announced construction of a 30,000 tonne/year plant for the selective catalytic oxidation of ethane to acetic acid. If successful, this technology would represent the second example of a commercially employed alkane activation technology, butane to maleic anhydride having been the first.

Not yet commercialized are processes for making acetic acid by the direct combination of CO and hydrogen. One such process pioneered by Texaco makes use of a bimetallic ruthenium–cobalt system promoted by iodide. Selectivity, however, is far less than with the rhodium catalyzed process.

Of the almost 5 billion lb of acetic acid consumed in the United States in 2002, over 62% is used for the preparation of vinyl acetate (Section 3.5). The 2002 end-use pattern is shown in Figure 10.2. Eleven per cent is used to make cellulose acetate (Section 14.3). A miscellany of commercial acetate esters include butyl, ethyl, *n*-propyl, and isopropyl acetates and consume 8%. However, the largest volume esters are acetates of glycol ethers (Section 3.11.6.2).

About 10% of acetic acid is also used as a solvent in the Amoco process for terephthalic acid (Section 9.3.1). Because much of it is oxidized, continual replacement is necessary. About 6% is converted to acetic anhydride.

Chloroacetic acid production in the United States in 2002 was 92 million lb. It is made by direct chlorination of glacial acetic acid in the presence of red phosphorus:

$$2CH_3COOH + Cl_2 \xrightarrow{P} 2CH_2ClCOOH + HCl$$

About one-third of chloroacetic acid production is converted to thioglycolic acid, a raw material for tin stabilizers for PVC;

$$CH_2ClCOOH + Na^+SH^- \longrightarrow \underset{\text{Thioglycolic acid}}{HSCH_2COOH} + NaCl$$

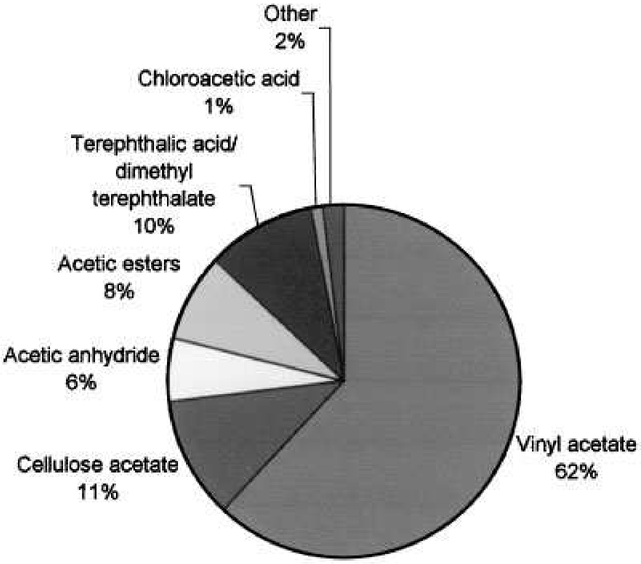
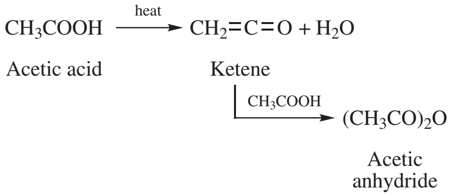


FIGURE 10.2 Acetic acid end-use pattern, United States, 2002.

Another fifth is converted to carboxymethylcellulose (Section 14.3) and the remainder finds application in a number of small volume uses including conversion to glycine and to 2,4-dichlorophenoxyacetic acid, a common herbicide.

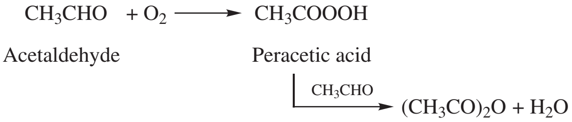
Acetic acid is used in several textile operations including textile dyeing, and in the synthesis of photographic chemicals, rubber chemicals, pharmaceuticals and herbicides. It is also used as a grain fumigant.

10.5.2.3 Acetic Anhydride Acetic anhydride is made by three processes. In one, acetic acid (or acetone, but that is uneconomical) is pyrolyzed to ketene, which in turn reacts with acetic acid. The pyrolysis takes place at 700–800°C in the presence of triethyl phosphate at a very low residence time of 0.25–0.5 seconds. Molar yields are 85–89%.



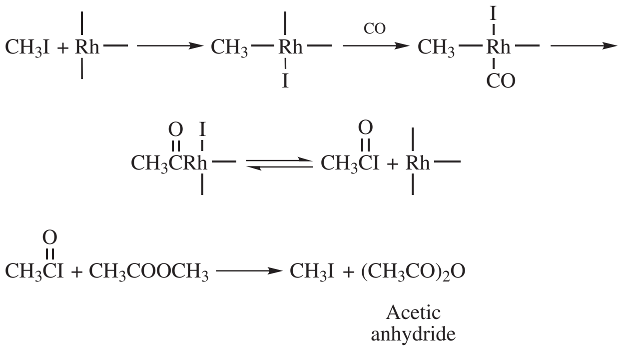
$$CH_3COOH \xrightarrow{\text{heat}} CH_2{=}C{=}O + H_2O \xrightarrow{CH_3COOH} (CH_3CO)_2O$$

The second procedure involves the *in situ* production of peracetic acid from acetaldehyde, which in turn reacts with more acetaldehyde to yield the anhydride. This process is probably not in use. Ethyl acetate may be used as a solvent, and the reaction is catalyzed by a mixture of cobalt and copper acetates. The molar yield of acetic anhydride is about 75%.



$$CH_3CHO + O_2 \longrightarrow CH_3COOOH \xrightarrow{CH_3CHO} (CH_3CO)_2O + H_2O$$

Eastman Chemical working with Halcon have developed a novel process involving the carbonylation of methyl acetate with a catalyst comprising rhodium chloride and chromium hexacarbonyl, $Cr(CO)_6$, in an acetic acid solvent. In one reaction described in a patent (see note at the end of this chapter), β-picoline is a catalyst modifier and methyl iodide is a promoter. The hydrogen/carbon monoxide ratio is important, since increase in the hydrogen content provides a corresponding increase in the production of ethylidene diacetate. This compound is the basis for a proposed process for vinyl acetate (Section 3.5) but is undesirable if high selectivity to the anhydride is desired. Since this reaction is novel, the possible mechanism is of interest. Only the rhodium is shown as the catalyst. In the first steps, acetyl iodide is formed. Reaction of this product with acetate ion yields acetic anhydride.



$$CH_3I + Rh \longrightarrow CH_3{-}\underset{I}{Rh} \xrightarrow{CO} CH_3{-}\overset{I}{\underset{CO}{Rh}} \longrightarrow$$

$$CH_3\overset{O}{\overset{\|}{C}}\overset{I}{Rh} \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}I + Rh$$

$$CH_3\overset{O}{\overset{\|}{C}}I + CH_3COOCH_3 \longrightarrow CH_3I + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

The Eastman/Halcon process is significant not only because of the imaginative chemistry involved but because the synthesis gas (Section 10.4) on which the process depends comes from coal. The Eastman plant in Tennessee is located close to the coal mines, which eliminates expensive transportation costs. The coal is gasified in an Eastman-modified Texaco gasifier operating at a high temperature to provide the synthesis gas with very little of the methane, which is undesirable for chemical operations. The acetic anhydride production is completely synthesis gas based since the carbon monoxide and hydrogen react to form methanol. This in turn esterifies recovered acetic acid (see below) to provide the methyl acetate that is further carbonylated to acetic anhydride.

The acetic anhydride is used by Eastman for the esterification of cellulose to cellulose acetate (Section 14.3). In the process, a mole of acetic acid is released and is recycled, obviating the need for a dedicated acetic acid plant.

$$\text{Coal} + O_2 + H_2O \longrightarrow CO + H_2$$

$$CO + 2H_2 \longrightarrow CH_3OH$$

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O$$

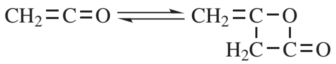
$$CH_3COOCH_3 + CO \longrightarrow \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

$$(CH_3CO)_2O + HO{-}\text{cellulose} \longrightarrow \underset{\text{cellulose acetate}}{CH_3COO{-}\text{cellulose}} + CH_3COOH$$

This is the only modern process in which coal has replaced petroleum. It provides confidence in the belief that coal can be used to manufacture all of the chemicals the world needs, should supplies of petroleum and natural gas be depleted. Full plant cost of the acetic anhydride produced by Eastman is 30% cheaper than the same product produced by conventional techniques. However, the investment for the coal-based process, because of the high cost of the gasifier, is roughly three times that of the investment for the conventional ketene-based process. Thus the use of coal requires a trade-off between high investment and low cost raw material. Also the cost of coal-based chemicals will be increased because of the high cost of transporting coal.

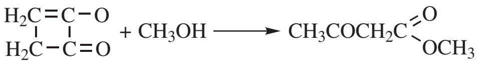
Acetic anhydride's main use is in the production of cellulose acetate. Other uses are small and include the formation of various esters such as acetylsalicylic acid (aspirin) and acetylated amides of which *N*-acetyl-*p*-aminophenol (acetaminophen or paracetamol) is a prime example.

Ketene, the intermediate in one acetic anhydride process, is a powerfully lachrymatory gas with a choking smell. It is invariably used *in situ*. Apart from its role in acetic anhydride production, it can be dimerized over trimethyl phosphate to diketene. Ammonia is added to inhibit the back reaction.



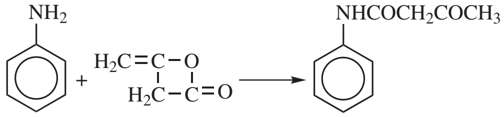
Ketene Diketene

Diketene reacts with methanol and ethanol to give methyl and ethyl acetoacetates.



Methyl acetoacetate

It also reacts with aromatic amines to give acetoacetarylamides. With aniline, acetoacetanilide is produced. This and its homologues are used in the production of azo dyes.



Aniline Acetoacetanilide

10.5.2.4 *Methanol to Gasoline* In addition to the acetic anhydride process described above, there are several additional uses for methanol—conversion to gasoline and olefins, described below, and as a substrate for single cell protein, which is discussed in Section 14.5.

The process for converting methanol to gasoline, known as the Mobil MTG process, has been operated in New Zealand. It is a simple although high-investment process. Like the Fischer–Tropsch process, it starts with the generation of synthesis gas. Methanol is generated by the ICI low pressure process (Section 10.5.2). The methanol is then brought into contact with a fixed bed of the acid form of the zeolite catalyst ZSM-5 (known as HZSM-5, see Section 16.9) at temperatures of the order of 380°C. There is a separation of carbon from oxygen, the former being polymerized into hydrocarbon chains and the latter emerging as water. The same reaction takes place over many acidic catalysts, but there is rapid coking and loss of catalytic activity. The geometrical selectivity of ZSM-5, however, does not allow for the formation of the linked aromatic rings that are the precursors of coke, hence the catalytic activity is maintained.

Water and CO_2 are the only oxygenated products of this highly exothermic reaction. To control the exotherm, the reaction is carried out in two stages. In the first, a dehydration catalyst such as $CuO/\gamma Al_2O_3$ promotes methanol dehydration to dimethyl ether.

$$2CH_3OH \longrightarrow \underset{\text{Dimethyl ether}}{CH_3OCH_3} + H_2O$$

The resulting equilibrium mixture of methanol, water, and dimethyl ether is fed to the second reactor. The dimethyl ether appears to lose water, which diffuses easily out of the zeolite structure, to leave CH_2 radicals. The CH_2 radicals polymerize within the zeolite pore system to give alkanes and aromatic hydrocarbons up to the geometrical selectivity limit (C_{10}) imposed by the pore structure. A mixture of aliphatic and methylated aromatics results with a high octane number. Typical compositions at different temperatures are shown in Table 10.3. The major C_{10} component is durene (2,3,5,6-tetramethylbenzene), a solid that must be removed.

This MTG process without modification would not be suitable for the production of aromatics for the chemical industry unless catalyst changes increased benzene content appreciably. Petroleum's low price during the late 1980s made this process uneconomical until the 1990 Persian Gulf crisis. New Zealand had announced in 1989 that it would divert one-half of the methanol used for the process to the merchant market. The Gulf crisis and increased petroleum prices caused this decision to be reversed, at least temporarily. Subsequently, the plant has operated on a swing basis.

10.5.2.5 Methanol to Olefins

Mobil also found that its MTG catalyst could be modified to make light olefins from methanol but, as it was designed to make

TABLE 10.3 Composition (mol %) of Gasoline from Methanol

Reaction Temperature (°C)	370	538
C_1—C_4 aliphatics	28.84	60.50
C_5+ aliphatics	33.83	3.50
Benzene	0.96	
Toluene	4.69	
Xylenes	12.33	35.90
C_9 Aromatics	12.25	
C_{10} Aromatics	7.10	
C_{11}+Aromatics		0.10
Total aromatics	37.33	36.00

gasoline, it was not ideal. The relatively large pore size in ZSM-5 results in relatively low selectivity to ethylene–propylene. In the mid-1990s, UOP and Norsk Hydro developed a process and catalyst specifically to make light olefins (Table 5.4). Their MTO (methanol-to-olefins) process uses a silica aluminophosphate molecular sieve catalyst, SAPO-34. It has narrower channels and a more controlled distribution of acidic sites than ZSM-5 and gives higher selectivity to ethylene and propylene. Unlike ZSM5, however, SAPO-34 is not physically robust and must be combined with special binders to enable it to withstand the rigors of fluidization. SAPO-34 gives about 78% selectivity to ethylene and propylene combined, on a total hydrocarbon basis. The relative amounts of ethylene and propylene can be altered to meet market demand to some degree by changing reactor severity.

One of the inherent problems of MTO technology is that, as a byproduct of its conversion to CH_2 radicals, methanol loses a molecule of water. Thus, 56% of the reactor output is water and 44% hydrocarbons. The plant must be large enough to cope with the aqueous flow, which increases its capital cost. In a conventional naphtha cracker, about 50% of the total output is ethylene and propylene, whereas in MTO only about 34% of the output is ethylene and propylene.

A variation of this approach is Lurgi's MTP (methanol-to-propylene) process. In MTP, a specially formulated zeolite catalyst is used to push the selectivity toward propylene production which, on a % carbon basis, is about 47% with only 4.6% ethylene. The remainder is 21% butenes, 15% heavier olefins, 8% paraffins, 1.7% naphthenes, and 2.8% aromatics. In 2002, two MTO projects were announced, one in China and one in Nigeria. The economics of MTO processes are only viable if very low cost natural gas is secured. For example, in the Nigerian MTO project, the natural gas is said to be priced at \$0.60/million Btu.

TABLE 10.4 Comparison of Light Olefin Production by Steam Cracking and Methanol to Olefins[a]

	Steam Cracker	Steam Cracker	MTO	MTP
Catalyst	None	None	SAPO[b]-34	Zeolite
Temperature (°C)	850–860	880–900	350–500	420–490
Feedstock	LVN[c]	Ethane	Methanol	Methanol
	Mass balances: tonne/tonne of ethylene + propylene			
Ethylene + propylene	1	1	1	1
Feedstock	1.9	1.2	3.0	3.1
Light products	0.39	0.20	0.07	0.02
C_4+	0.51	0	0.23	0.37
Water	0	0	1.7	1.75

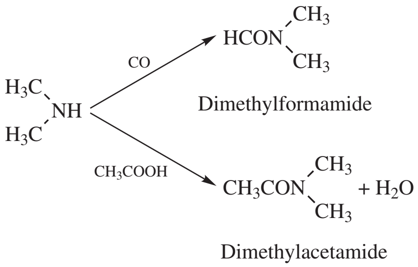
[a] In all cases except with the ethane cracker, the ethylene/propylene ratio can be varied somewhat by varying reaction temperatures and/or residence times.

[b] Silicoaluminophosphate = SAPO.

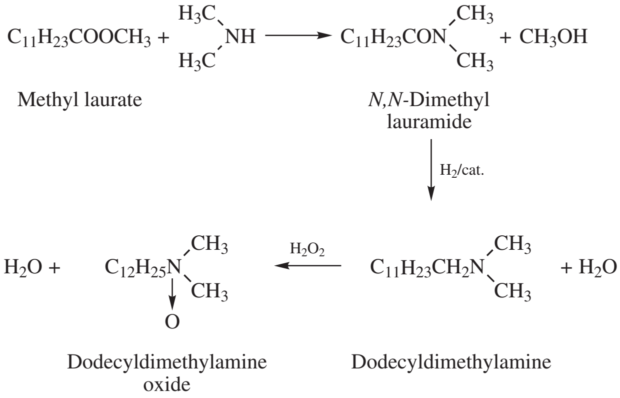
[c] Light virgin naphtha = LVN.

10.5.2.6 Lower Volume and Proposed Uses for Methanol Lower volume uses for methanol include the production of methylamines, glycol ethers, (Sections 3.11.6.2, 4.11.1) dimethyl sulfate, dimethyl carbonate, and methylated phenols. Methylamine, dimethylamine, and trimethylamine are made by the vapor-phase ammonolysis of methanol at 450°C with an alumina gel catalyst. Conversion based on ammonia is 13.5% to primary, 7.5% to secondary, and 10.5% to tertiary amine. The separation of the three products is difficult. Trimethylamine can be separated from the mixture as an ammonia azeotrope. The mono- and diamines may be separated by fractionation. Another method of separation involves removing the dimethylamine, which is the most basic of the three, as the hydrochloride. Extractive distillation is also possible.

Dimethylamine is the product used in largest amount—about 100 million lb/year—but is produced in the smallest amount in the amination reaction. Thus, the methylamine and trimethylamine are recycled without separation. Dimethylamine's largest uses are for conversion to dimethylformamide by carbonylation and to dimethylacetamide by reaction with acetic acid, acetic anhydride, or acetyl chloride. Both are solvents for the spinning of acrylic fibers and serve also as aprotic solvents for synthesis and extractive distillation.

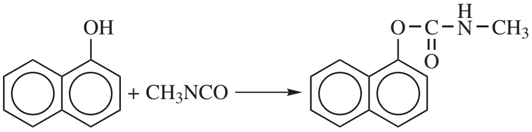


Other applications include the synthesis of dodecyldimethylamine oxide, a detergent ingredient, as shown in the following equations. It is also used for rubber chemicals such as thiuram accelerators, and for conversion to the dimethylamine salt of 2,4-dichlorophenoxyacetic acid, an important herbicide (Section 7.1.6).



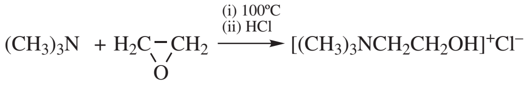
Methylamine and trimethylamine enjoy approximately equal use of about 40 million lb/year. A major application for methylamine is in the synthesis of the insecticide carbaryl. Methylamine reacts with phosgene to give the intermediate, methyl isocyanate, the chemical that gave rise to the Bhopal disaster (Section 17.3.3). The methyl isocyanate, in normal circumstances, reacts with α-naphthol to yield carbaryl.

$$CH_3NH_2 + COCl_2 \longrightarrow \underset{\text{Methyl isocyanate}}{CH_3NCO} + 2HCl$$



α-Naphthol Carbaryl

Trimethylamine's major use is in the synthesis of choline chloride, an important animal feed supplement, by reaction with ethylene oxide.



$$\underset{\text{Trimethylamine}}{(CH_3)_3N} + \underset{\text{Ethylene oxide}}{H_2C{-}CH_2 \ (O)} \xrightarrow[\text{(ii) HCl}]{\text{(i) 100°C}} \underset{\text{Choline chloride or "choline"}}{[(CH_3)_3NCH_2CH_2OH]^+Cl^-}$$

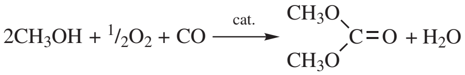
Dimethyl sulfoxide (DMSO), an important aprotic solvent, is manufactured by the oxidation of dimethyl sulfide, which can be obtained either as a byproduct from the Kraft paper pulping process or by the reaction of methanol with hydrogen sulfide, a reaction that also gives methyl mercaptan. The latter vapor-phase reaction takes place at above 300°C and requires a dehydration catalyst. The oxidation to DMSO can be carried out with nitrogen dioxide or, better, with oxygen containing a small amount of nitrogen dioxide. With the former, the reaction takes place at 40–50°C and the product is purified by distillation.

$$CH_3OH + H_2S \xrightarrow{\text{cat.}} \underset{\text{Dimethyl sulfide}}{(CH_3)_2S} + \underset{\text{Methyl mercaptan}}{CH_3SH} + H_2O$$

$$(CH_3)_2S + NO_2 \longrightarrow \underset{\text{DMSO}}{(CH_3)_2SO} + NO$$

$$2NO + O_2 \rightleftharpoons 2NO_2$$

Dimethyl carbonate is made by the oxidative carbonylation of methanol with carbon monoxide and oxygen. These combine in the liquid phase in the presence of a copper-based catalyst to give dimethyl carbonate. The reaction can be carried out continuously at a pressure of about 25 bar with synthesis gas rather than pure CO, which is the only material consumed.

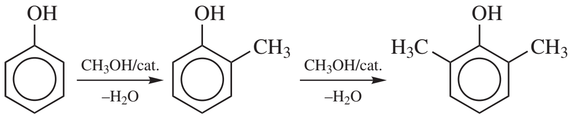


$$2CH_3OH + {}^1/{}_2O_2 + CO \xrightarrow{\text{cat.}} (CH_3O)_2C{=}O + H_2O$$

Dimethyl carbonate

At conversions of 30–35% the yield of dimethyl carbonate is 100% based on methanol and 90–95% based on carbon monoxide. A newer process makes use of a solid copper methoxide with a nitrogen-containing cocatalyst capable of coordination, such as pyridine. Other approaches for making dimethyl carbonate are described in Section 7.1.2.2. Dimethyl carbonate is of current interest because it may be used for alkylations in place of the more corrosive dimethyl sulfate, and because it can replace phosgene in the preparation of isocyanates and carbamates (Section 17.3.4). A General Electric patent describes a synthesis for polycarbonate resins that replaces phosgene with dimethyl carbonate (Section 7.1.2.2). General Electric has constructed two such plants in Japan and Spain. Dimethyl carbonate has also been suggested as an octane improver for gasoline.

Methanol is also an alkylating agent. At 50 bar and a carefully controlled temperature of 300°C, it will alkylate phenol to *o*-cresol or to 2,6-xylenol at about 50 bar over an alumina catalyst. Selectivity is high and only small amounts of ethers or *meta* or *para* alkylated products result. The ratio of *o*-cresol to 2,6-xylenol can be varied by controlling pressure and temperature, but these variations may promote the formation of byproducts such as 2,4-xylenol. The initial and insufficient source of *o*-cresol is coal distillate (Section 12). 2,6-Xylenol is the monomer for an engineering polymer, poly(phenylene oxide).



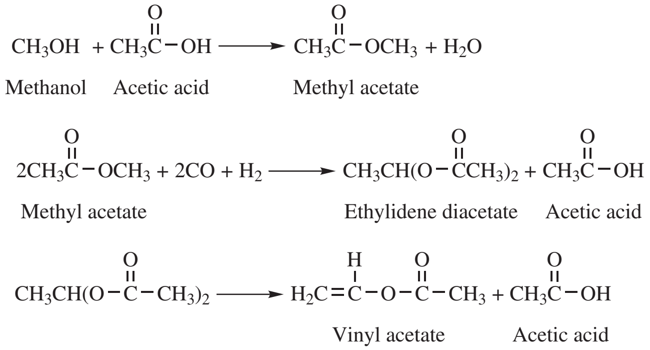
Phenol *o*-Cresol 2,6-Xylenol

10.5.2.7 C_1-Based Development Processes The elaborate chemistry of the olefin and aromatic feedstocks already described provides facile methods for obtaining and using organic compounds from C_2 upward. The great divide is between C_1 compounds and those containing several carbon atoms, and much research was focused on so-called C_1 chemistry in the 1970s and 1980s when methanol was cheap. In the late 1980s, its price increased because of its demand for use in methyl *tert*-butyl ether.

Meanwhile, C_1 chemistry gave rise to a number of processes that merit discussion. The chain reaction between methanol and formaldehyde to yield ethylene glycol was described in Section 3.7.2 and methanol's cracking to olefins in Section 10.5.2.5. Other reactions based on methanol include conversion to aromatics, synthesis of vinyl acetate via methyl acetate, and homologation to ethanol and higher alcohols.

Just as methanol may be cracked to olefins over one set of zeolite catalysts, it may be aromatized over others. One example has already been given for the MTG process (Section 10.5.2.4). The highly methylated aromatics are useful for gasoline but would have to be hydrodealkylated to give the benzene that the organic chemical industry needs. Further catalyst development is required.

Vinyl acetate (Section 3.6) can be prepared from methyl acetate by a process devised by Halcon reminiscent of the Eastman/Halcon acetic anhydride process (Section 10.5.2.3). Methyl acetate reacts with carbon monoxide and hydrogen to give ethylidene diacetate, which on pyrolysis provides vinyl acetate and acetic acid.

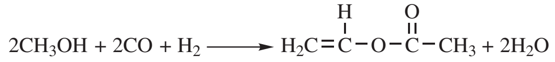


$$CH_3OH + CH_3\overset{\overset{O}{\|}}{C}-OH \longrightarrow CH_3\overset{\overset{O}{\|}}{C}-OCH_3 + H_2O$$

$$2CH_3\overset{\overset{O}{\|}}{C}-OCH_3 + 2CO + H_2 \longrightarrow CH_3CH(O-\overset{\overset{O}{\|}}{C}CH_3)_2 + CH_3\overset{\overset{O}{\|}}{C}-OH$$

$$CH_3CH(O-\overset{\overset{O}{\|}}{C}-CH_3)_2 \longrightarrow H_2C=\overset{\overset{H}{|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3\overset{\overset{O}{\|}}{C}-OH$$

Since the acetic acid is recycled, the net reaction is



$$2CH_3OH + 2CO + H_2 \longrightarrow H_2C=\overset{\overset{H}{|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + 2H_2O$$

The carbonylation in the presence of hydrogen is accomplished with a rhodium chloride catalyst modified with β-picoline and promoted with methyl iodide. Acetic anhydride and acetaldehyde are obtained as byproducts. The economics of the Halcon process seem reasonable although capital investment is considerably higher than for the conventional process.

The homologation of methanol to higher alcohols, which has never been commercialized, is nonetheless of interest as a route to ethanol whose price, conventionally, is several times that of methanol (e.g., in 2001, \$1.55/gallon of ethanol *vs.* \$0.33/gallon of methanol). It also provides a route to higher alcohols conceivably useful as oxygenates to augment octane numbers in unleaded gasoline.

The homologation of methanol to ethanol proceeds with a dicobalt octacarbonyl catalyst.

$$CH_3OH + 2H_2 + CO \longrightarrow CH_3CH_2OH + H_2O$$

At 200 bar and 365°C, 76% conversion and a 40% selectivity to ethanol are obtained. A variety of other catalysts has been tested, including cobalt catalysts with phosphine ligands. A variant of the process involves the reaction of methanol with synthesis gas to give acetaldehyde, which can then be hydrogenated to ethanol.

Typically, higher selectivities result when a reaction is carried out in two steps with the isolation of an intermediate. Many catalysts have been proposed for the preparation of acetaldehyde by this route, based on cobalt, nickel, palladium, ruthenium, and tungsten. In most instances, ligands are required.

The economics of these processes are attractive. Less favorable are the economics associated with either the homologation of methanol to alcohols higher than ethanol or to the production of higher alcohols from synthesis gas directly. Nonetheless, the high selectivity possible for obtaining specific alcohols from synthesis gas is demonstrated by work in which CO and hydrogen are combined to provide 44% selectivity to isobutanol, which may be dehydrated to isobutene for conversion to methyl *tert*-butyl ether. The technology is not practiced because the reaction sequence *n*-butane → isobutene → isobutene, is more economical (Section 5.2.1).

There are several methanol-based routes to ethylene glycol. Until 1968, Du Pont produced ethylene glycol commercially from methanol, formaldehyde, and carbon dioxide. Formaldehyde is carbonylated to give glycolic acid in the presence of a strong acid (Section 3.7.2).

Esterification of the glycolic acid with methanol followed by hydrogenolysis of the ester also yields ethylene glycol (Section 3.7.2). The carbonylation takes place at 200°C and 70–100 bar at high selectivity, as does the esterification reaction. The hydrogenolysis occurs at 200°C and 30 bar with an appropriate catalyst. The released methanol is recycled so that the overall reaction is

$$2H_2 + HCHO + CO \longrightarrow HOCH_2CH_2OH$$

An improvement in this process involves the use of HF in the carbonylation step. Coupled with the development of more active catalysts for the hydrogenolysis (Section 10.3), this could make the Du Pont process attractive once again should low cost synthesis gas from coal or stranded gas become a major feedstock.

10.6 CARBON MONOXIDE CHEMISTRY

Carbon monoxide is the basic C_1 molecule. Much of its chemistry has already been discussed. Current industrial processes for C_1 production are based largely on methane (Sections 10.1–10.5) from natural gas. The other significant C_1 molecules comprise methanol, carbon monoxide, and formaldehyde. Interesting chemistry is in the wings based on these molecules, which are obtainable if necessary from coal.

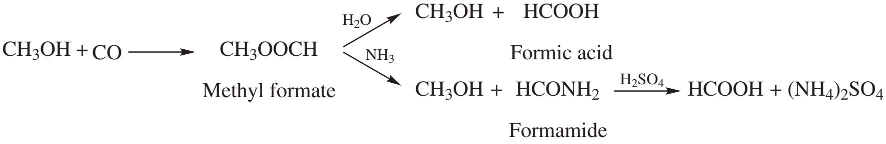
The largest application of C_1 chemistry is the production of methanol (Section 10.4.2). Striking examples of the replacement of classical chemistry by C_1 chemistry are the Monsanto acetic acid process (Section 10.5.2.2.) and the Eastman acetic anhydride process (Section 10.5.2.3). The use of CO in hydroformylation has been discussed under propylene (Section 4.12). The use of CO for the preparation of dimethylformamide and dimethylacetamide was described above (Section 10.5.2.6).

With chlorine, carbon monoxide yields phosgene. The reaction is carried out over activated charcoal at 250°C.

$$CO + Cl_2 \xrightarrow{\text{cat.}} \underset{\text{Phosgene}}{COCl_2}$$

About 85% of United States phosgene is consumed in the production of diisocyanates (Sections 7.3.1, 8.3) and the bulk of the remainder for polycarbonate preparation (Section 7.1.2).

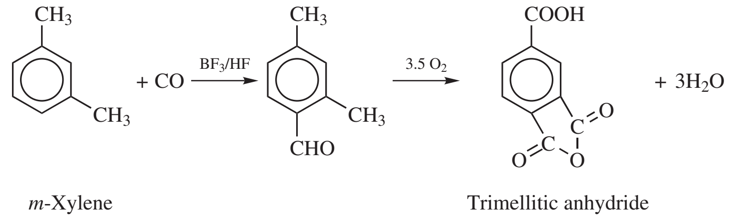
Formic acid is the simplest carboxylic acid. About 60% of global production is by the carbonylation of methanol to methyl formate followed by hydrolysis to formic acid and methanol, which is recycled. An alternative route is by ammonolysis of methyl formate to formamide followed by acidolysis with sulfuric acid to formic acid and ammonium sulfate. Formic acid is also a byproduct in acetic acid production via butane or primary flash distillate oxidation (Section 10.5.2.2).

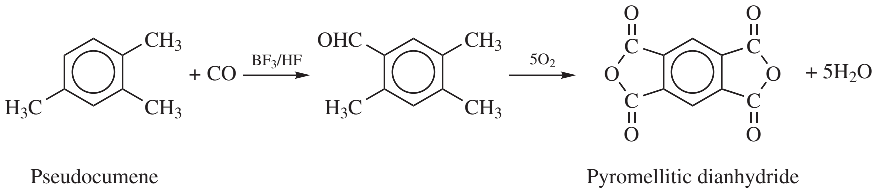


$$CH_3OH + CO \longrightarrow \underset{\text{Methyl formate}}{CH_3OOCH} \xrightarrow{H_2O} CH_3OH + \underset{\text{Formic acid}}{HCOOH}$$

$$CH_3OOCH \xrightarrow{NH_3} CH_3OH + \underset{\text{Formamide}}{HCONH_2} \xrightarrow{H_2SO_4} HCOOH + (NH_4)_2SO_4$$

Mitsubishi Gas Chemical has developed a unique route for making precursors to trimellitic anhydride (TMA) and pyromellitic dianhydride (PMDA). The chemistry is based on the HF/BF_3-catalyzed addition of CO to *m*-xylene and pseudocumene to give the corresponding dimethyl and trimethylbenzaldehydes. These are oxidized to TMA and PMDA.





10.6.1 Proposed Chemistry Based on Carbon Monoxide

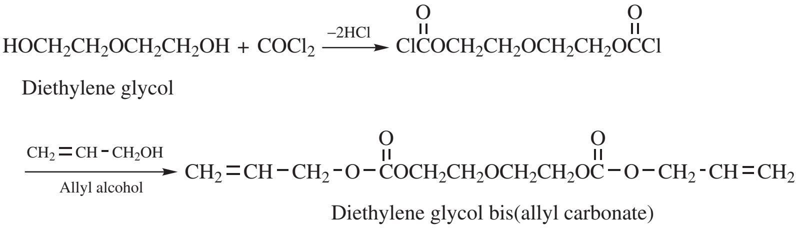
Proposed uses of carbon monoxide in industrial processes have been mentioned throughout this book. In particular, we have described the possibility of making ethylene glycol directly from CO and hydrogen (Section 10.6.1) and non-phosgene routes to isocyanates (Section 7.2.3, 8.4). Much novel carbon monoxide chemistry is associated with glycols, glycol ethers, and glycol carbonates.

Union Carbide has developed two processes that produce ethylene glycol directly from CO and hydrogen. One of the catalysts studied comprises a rhodium cluster with operating conditions of 240°C and 1000–3500 bar. Reactions carried out under such severe conditions tend to have poor selectivity, and the economics of the Carbide process were harmed by the production of appreciable amounts of methanol. A two-step approach involves condensing carbon monoxide and hydrogen with methanol to methyl oxalate (Section 10.6) followed by hydrogenolysis as in the Du Pont process. Neither process was commercialized.

A proposed route to glycol ethers involves the combination of an alcohol with formaldehyde, carbon monoxide, and hydrogen. The reaction takes place at 180 bar and 160°C with a homogeneous catalyst comprising dicobalt octacarbonyl and donor ligands such as diphenyl sulfide and diphenyl oxide.

$$CH_3OH + HCHO + CO \longrightarrow CH_3OCH_2OH + H_2O$$

Diethylene glycol bis(allyl carbonate), also termed allyl diglycol carbonate, is a specialty polycarbonate polymer, whose major use is for molding eye glass lenses by *in situ* polymerization. A classical process involves the reaction of diethylene glycol with phosgene to give a bis(chloroformate) which, on further reaction with allyl alcohol, gives the desired product.



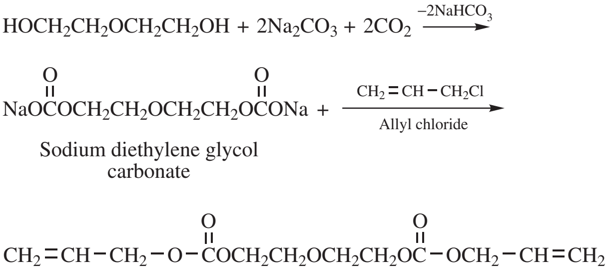
$$HOCH_2CH_2OCH_2CH_2OH + COCl_2 \xrightarrow{-2HCl} Cl\overset{O}{\overset{\|}{C}}OCH_2CH_2OCH_2CH_2O\overset{O}{\overset{\|}{C}}Cl$$

Diethylene glycol

$$\xrightarrow[\text{Allyl alcohol}]{CH_2{=}CH{-}CH_2OH} CH_2{=}CH{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}OCH_2CH_2OCH_2CH_2O\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH{=}CH_2$$

Diethylene glycol bis(allyl carbonate)

An alternative process operated on a pilot plant basis in Japan reacts diethylene glycol and allyl chloride with carbon dioxide in the presence of sodium carbonate. The reaction probably proceeds in two steps.



$$HOCH_2CH_2OCH_2CH_2OH + 2Na_2CO_3 + 2CO_2 \xrightarrow{-2NaHCO_3}$$

$$NaO\overset{O}{\overset{\|}{C}}OCH_2CH_2OCH_2CH_2O\overset{O}{\overset{\|}{C}}ONa + \xrightarrow[\text{Allyl chloride}]{CH_2{=}CH{-}CH_2Cl}$$

Sodium diethylene glycol
carbonate

$$CH_2{=}CH{-}CH_2{-}O{-}\overset{O}{\overset{\|}{C}}OCH_2CH_2OCH_2CH_2O\overset{O}{\overset{\|}{C}}{-}OCH_2{-}CH{=}CH_2$$

The idea of using carbon dioxide instead of phosgene could conceivably be expanded to the preparation of other carbonate polymers.

Carbon monoxide based routes to pelargonic, malonic, phenylacetic, phenylpyruvic, and oxalic acids have been developed but mostly not commercialized. Currently, there are two processes for pelargonic acid, one from natural sources (Section 13.5) and one based on 1-octene (Section 4.12.2), but it may also be made by dimerization of butadiene in the presence of carbon monoxide. The carbonylation is carried out homogeneously with carbon monoxide in alcohol in the presence of a palladium–phosphine complex. Hydrogenation and saponification provide pelargonic acid.

$$2CH_2{=}CH{-}CH{=}CH_2 + CO + ROH \longrightarrow CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2COOR$$

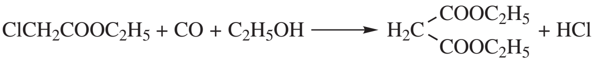
Butadiene

$$\xrightarrow{\substack{\text{(1) Hydrogenation} \\ \text{(2) Saponification}}} CH_3(CH_2)_7COOH + ROH$$

Pelargonic acid

Palladium acetate or palladium acetylacetonate may be used as the source of palladium, with acetonitrile as solvent and methanol as the esterifying agent. The catalyst must be free of halide in order to effect dimerization of the butadiene. If halide is present, the butadiene is also carbonylated to give a five-carbon unsaturated acid.

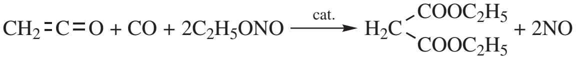
A malonic ester synthesis is based on the reaction of carbon monoxide, alcohol, and ethyl chloroacetate in the presence of cobalt tetracarbonyl at 55°C and 8 bar. The molar yield is 94%. The process is said to be in use in Japan.



$$ClCH_2COOC_2H_5 + CO + C_2H_5OH \longrightarrow H_2C\begin{smallmatrix} \diagup COOC_2H_5 \\ \diagdown COOC_2H_5 \end{smallmatrix} + HCl$$

Ethyl chloroacetate — Diethyl malonate (malonic ester)

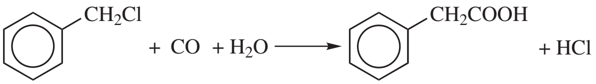
Another carbon monoxide based process for malonic ester involves its interaction with ketene and a nitrous acid ester. The reaction, which makes use of a platinum or platinum salt catalyst, proceeds at 115°C at atmospheric pressure but gives lower yields than the ethyl chloroacetate process.



$$CH_2{=}C{=}O + CO + 2C_2H_5ONO \xrightarrow{\text{cat.}} H_2C\begin{smallmatrix} \diagup COOC_2H_5 \\ \diagdown COOC_2H_5 \end{smallmatrix} + 2NO$$

Ethyl nitrite — Malonic ester

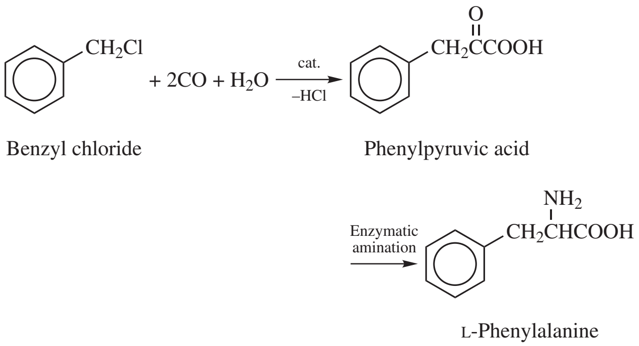
Phenylacetic acid results from the phase-transfer carbonylation of benzyl chloride.



Benzyl chloride — Phenylacetic acid

The aqueous phase comprises 40% aqueous sodium hydroxide solution. The organic phase contains a quaternary ammonium compound and a dicobalt octacarbonyl catalyst. The quaternary ammonium salt transfers the cobalt carbonyl ion $[Co(CO)_4]^-$ from the aqueous phase to the organic phase. The benzyl chloride, which is added continuously, is carbonylated under pressure.

Bis carbonylation of benzyl chloride gives phenylpyruvic acid. The reaction again requires a dicobalt octacarbonyl catalyst and proceeds in the presence of calcium hydroxide at 85°C and 60 bar in a *tert*-butanol–water mixture. Phenylpyruvic acid is formed in a molar yield greater than 90%. Enzymatic amination of this compound yields L-phenylalanine, a key component of the noncaloric sweetener, aspartame.



A Japanese process possibly in use for oxalic acid involves the oxidative coupling of carbon monoxide with an alkyl nitrite.

$$2CO + 2RONO \xrightarrow{Pd} \underset{\text{Oxalic acid ester}}{ROOCCOOR} + 2NO$$

$$2NO + 2ROH + 0.5\ O_2 \longrightarrow 2RONO + H_2O$$

The reaction is carried out homogeneously at 110°C and 60 bar. In a corresponding heterogeneous reaction, palladium on carbon may be used at 120°C and atmospheric pressure. The oxalic acid ester on hydrogenolysis gives ethylene glycol. This process was mentioned earlier as an experimental one explored jointly by Union Carbide and UBE in Japan as a step in the proposed conversion of synthesis gas to ethylene glycol (Section 3.7.2).

α-Olefins (Section 3.3) result when synthesis gas is passed over a zeolite ZSM-5 catalyst impregnated with Fischer–Tropsch catalysts such as iron nitrate. The products have a chain-length distribution of 2–27 carbons, but it is heavily skewed to the C_2–C_5 compounds. It is noteworthy that both odd and even number carbon compounds result. Small concentrations of nonlinear olefins, alcohols, aldehydes, and ketones are also formed (Section 12.2). The process will require much more development before commercialization.

α-Olefins also are formed in the Fischer–Tropsch process as practiced in South Africa. Thus, Sasol has become a dominant supplier of hexene-1 and octene-1, having developed extraction techniques for these products. Subsequently, it devised processes for obtaining higher α-olefins, which are converted to detergent alcohols (Section 3.3.4).

10.7 GAS-TO-LIQUID FUELS

As described in Section 12.2, the Fischer–Tropsch reaction provides a means of converting synthesis gas to liquid hydrocarbons. This reaction was originally intended as a means to convert solid coal to liquid fuels but, in the mid-1990s and continuing into the 2000s, there has been growing recognition that the technology is also a means to convert and "monetize" low cost, "stranded" natural gas to liquid fuels. Stranded gas is gas that has been discovered in remote areas such as southern Chile. Pipelines are the easiest way to transport gas but, the longer the pipeline, the more it costs, and eventually it becomes uneconomic. Liquefied natural gas (LNG) is another option but this method is also capital intensive. Hence, the interest in converting stranded gas to carbon monoxide and hydrogen at the point of origin and hence to transportable liquid fuel by the Fischer–Tropsch reaction. Large companies such as Sasol, ExxonMobil, Conoco, and Shell have developed gas-to-liquids (GTL) process technology. Small entrepreneurial companies such as Rentech and Syntroleum have also developed niche technologies.

10.7.1 Sasol GTL Technology

Sasol's application of Fischer–Tropsch technology dates back to the mid-1950s. Their original plant in Secunda, South Africa employed a fixed-bed reactor and produced 8000 barrels/day of liquid fuels from coal. In 1991, Sasol commercialized what has been called the world's largest synthetic fuel project. This plant, located in Mossel Bay, South Africa, converts not coal but natural gas to gasoline using Sasol's proprietary circulating fluidized-bed reactor (Synthol). Sasol's newest synthetic fuels technology uses a slurry bed reactor. Its design has been simplified; it is easier to fabricate and is less expensive. The reactor consists of a shell with cooling coils in which steam is generated to remove the heat of reaction. Synthesis gas is distributed in the bottom of the reactor and rises through the slurry, which consists of reaction products, predominantly wax. The iron-based catalyst particles are suspended in the slurry. Because of the interaction between the slurry and the gas bubbles, the reactor contents are well mixed permitting accurate temperature control. Sasol is involved in two major projects, one in Qatar and another in Nigeria, where the slurry phase technology will be used to convert gas to liquid fuels.

10.7.2 Shell Middle Distillate Synthesis

The Shell Middle Distillate Synthesis (SMDS) is an example of GTL technology and it is practiced in Malaysia with indigenous gas. It can also be used with associated gas, and a project was underway in Nigeria in the early 2000s to do this, partly to avoid the pollution caused by flaring. Unlike other Fischer–Tropsch technologies that are geared to produce diesel fuel (Section 2.1), SMDS is designed to maximize middle distillates (boiling range 180–400°C), which contain diesel fuel as well as aviation kerosene.

Shell, as indicated above, built a 12,000 barrel/day SMDS plant in Bintulu, Malaysia in 1993. The SMDS process produces synthesis gas from natural gas via noncatalytic partial oxidation (POX). Shell uses a tubular fixed Fischer–Tropsch reactor with a zirconium promoted cobalt catalyst system that is intended to produce high selectivity to paraffin waxes. Wax production is high even in the normal reaction (Table 12.1). Conversion is in excess of 80% in order to maximize the formation of the heavy paraffins or waxes. These waxes are subsequently hydrocracked (Section 2.2.6) to give a maximum yield of diesel fuel along with some naphtha and kerosene. In addition, a solvent fraction and hydrocarbons for detergent feedstock are produced. These are dehydrogenated to olefins for alkylation of benzene. The alkylbenzenes are sulfonated to give detergent intermediates (Section 7.4).

In 1997, an explosion in the Bintulu SMDS plant damaged the air separation unit. After an extensive investigation, Shell concluded that the explosion was unrelated to the core SMDS technology and the plant resumed production in May, 2000.

10.7.3 Other GTL Technologies

ExxonMobil has a large patent portfolio of gas conversion technologies. This research has led to ExxonMobil's Advanced Gas Concept 21st Century (AGC-21) process. It is a three-step process consisting of a fluid-bed POX synthesis gas reactor, a slurry-phase Fischer–Tropsch reactor, and a fixed-bed hydroisomerization unit for product upgrading. This process has not yet been commercialized.

Syntroleum of Tulsa, Oklahoma, has developed a gas-to-liquid fuels technology called the Syntroleum process. Its major innovation is the use of air instead of oxygen in the partial oxidation synthesis gas reaction. In traditional synthesis gas reactors, high gas conversion is achieved by a recycle loop; oxygen is used instead of air in order to avoid a build-up of nitrogen gas in the recycle loop. In the Syntroleum process, a cascade of one-pass reactors is used to achieve high gas conversions and, because there is no recycling, the nitrogen contained in the air is not a problem. The nitrogen gas also serves as an effective heat-transfer agent. One of the most capital intensive steps in synthetic fuels production is the air separation unit for oxygen production. Since the Syntroleum process obviates this step, Syntroleum claims that synfuel production can be economic on a relatively small scale.

ConocoPhillips also have developed a gas-to-liquid fuels process. The synthesis gas technology is based on a low-cost compact partial oxidation, while the Fischer– Tropsch technology is based on a proprietary cobalt catalyst that produces a high proportion of diesel fuel and naphtha. Heavier products are hydrocracked. Another gas-to-liquid fuels technology has been developed by Rentech. The Rentech process is designed to work with all gasification technologies. The Fischer–Tropsch reactor is a slurry bubble design used in conjunction with a proprietary iron-based synthesis catalyst.

NOTES AND REFERENCES

C_1 Chemistry attracted much attention since the early 1980s and *C_1 Molecular Chemistry: An International Journal* was published to focus attention on it. The American Chemical Society published the results of a Symposium, *Industrial Chemicals via C_1 Processes,* D. A. Fahey, Ed., ACS, Washington, DC, 1987. The Japanese Ministry of International Trade and Industry sponsored a 7-year program for C_1 chemistry, some of which was reported in *Progress in C_1 Chemistry in Japan*, Ed., Research Association for C_1 Chemistry, Elsevier, Amsterdam, The Netherlands, 1990. General books about methane include L. H. Clever, *Methane*, Pergamon, Oxford, 1987 and J. C. Murrell, *Methane and Methanol Utilizers*, Plenum, New York, 1992.

Many of the topics in this chapter are covered in *Petrochemical Processes: Vol. 1, Synthesis Gas Derivatives and Major Hydrocarbons; Vol. 2 Major Oxygenated, Chlorinated and Nitrated Derivatives*, Inst. Français du Pétrole Publications, Editions Technip, Paris, 1989.

The potential economic impact of low-cost stranded gas on various C_1-based process technologies is discussed in Nexant Chemsystems' PERP report 99/00S9, Extending the Methane Value Chain (October, 2000).

Section 10.2 We thank Victoria Cook of the Imperial War Museum, London, for the information about Zyklon B. It is difficult to estimate the exact numbers murdered by hydrogen cyanide, and, for further details, we were referred to *Nazi mass murder: a documentary history of the use of poison gas*, E. Kogon, H. Langbein and A. Ruckerl, Ed., Yale University Press, New Haven, CT, 1993.

In this section, we use the systematic rather than the trivial names for the chloromethane. Thus we use chloromethane for methyl chloride, dichloromethane for methylene chloride, trichloromethane for chloroform, and tetrachloromethane for carbon tetrachloride. The technical literature is less consistent and cheerfully mixes terms such as dichloromethane with chloroform.

Among the many books on the problems of fluorocarbons, we note World Health Organization, *Partially Halogenated Chlorofluorocarbons*, WHO, 1992.

Section 10.2.1 For an excellent brief review of silicone properties and uses, the reader, is referred to R. B. Seymour and C. E. Carraher, Jr., *Polymer Chemistry*, 2nd ed., Marcel Dekker, New York, 1988.

Section 10.3 The various production technologies and economics of acetylene production are given in Nexant Chemsystems' PERP report 93S14, Acetylene Manufacture (July, 1996).

Section 10.3.1 Nexant Chemsystems' PERP report 98/99S1, 1,4-Butanediol/THF (August, 1998) provides detailed descriptions of all the commercially employed routes and production economics of 1,4-butanediol and tetrahydrofuran.

Section 10.5.1 The process for converting NO to urea is described in US Patent 3,986,849 (1975) to Val Laboratories.

Section 10.5.2 A number of books have been published on methanol synthesis and possible fuel use including Wu-Hsun Cheng, *Methanol Production and Use*, Dekker, New York, 1994; S. Lee, *Methanol Synthesis Technology*, CRC Press, Boca Raton, FL, 1990 J. H. Perry, *Methanol: Bridge to a Renewable Energy Future*, University Press of America, Lanham, MD, 1990; and J. C. Fahy, *New Prospects for Methanol: Fuel or Chemical?*, Financial Times, London, 1990.

The use of homogeneous catalysis for methanol formation has been described by R. J. Klinger *et al.*, *Exploring Catalytic Methanol Synthesis Using Soluble Metal Oxide Complexes*, Symposium on Chemicals from Syn Gas, Methanol Division of Fuel Chemistry, American Chemical Society, New York, April 1986.

Homogeneous catalysts for methanol formation have been described by E. G. Baglin *et al.*, *Ind. Eng. Chem. Prod. Res.* **20**, 87 (1981).

C. D. Chang's article in *Catal. Rev.*, **25**(1) (1983) was reprinted as *Hydrocarbons from Methanol*, Dekker, New York, 1983.

Promoted Raney-copper catalysts have been described in European Patent Appl. 1,09,702 (October 31, 1983) to Shell.

For methanol formation from carbon dioxide see J. Haggin, *Chem. Eng. News*, March 28, 1994, p. 29 and D. Rotman, *Chem. Week*, March 23, 1994, p. 14.

Nexant Chemsystems' PERP report 98/99-4, Methanol (May, 2000) provides detailed descriptions of conventional methanol processes and emerging megamethanol processes. The impact of low-cost stranded gas on the economics of methanol production is also assessed.

Section 10.5.2.2 The formation of acetic acid from CO and hydrogen has been described by J. F. Knifton, *Hydrocarbon Processing*, 113–117, December (1981).

A comparison of the conventional Monsanto acetic acid process with the Celanese Acid Optimization process is given by M. Gauss *et al.*, *Appl. Homogen. Catal. Org. Compd.*, **1**, 104 (1996).

Chiyoda's acetic process utilizing a resin supported rhodium catalyts is described in US Patents 5,334,755 (August 2, 1994) and 5,364,963 (November 15, 1994) both to Chiyoda.

SABIC's technology for converting ethane directly to acetic acid is described in US Patents 6,087,297 (July 11, 2000), 6,060,421 (May 9, 2000), 6,030,920 (February 29, 2000), 6,028,221 (February 22, 2000), 6,013,597 (January 11, 2000), and 5,907,056 (May 25, 1999) all to Saudi Basic Industries Corporation.

The end-uses of chloroacetic acid were outlined in *Chem. Mkt. Rep.*, May 19, 2003.

Section 10.5.2.3 The Eastman/Halcon process for acetic anhydride is described in West German Patents 2,610,035 (October 3, 1976) and 2,610,036 (September 23, 1976) both to Halcon.

Section 10.5.2.5 The cracking of methanol to olefins has been described in numerous patents and papers, typical of which are US Patent 4,049,573

(September 20, 1977) and US Patents 4,025,571, 4,025,572 (May 24, 1977) to Mobil Oil; B. B. Singh et al. *Chem. Eng. Commun*. **4**, 749 (1980).

UOPs MTO technology based on SAPO-34 catalyst is described in US Patents 5,714,662 (February 3, 1998), 5,774,680 (April 28, 1998), 5,817,906 (October 6, 1998), and 6,049,017 (April 11, 2000) all to UOP.

A process claiming high selectivity to propylene by methanol cracking is described in European Patent Appl. 0,105,591 (April 8, 1984) to Mobil Oil. Lurgi's Methanol to Propylene process is described in European Patents 0 882 692 A1 (December 9, 1998) to Metallgesellschaft AG and 0 448 000 B1 (May 25, 1994 to Sud-Chemie AG and Metallgesellschaft AG and US Patent 5,981,819 (November 9, 1999) to Metallgesellschaft AG.

Section 10.5.2.6 The dimethyl carbonate process using a cuprous chloride catalyst is employed by ENI in Italy. The solid copper catalyst has been developed by Dow and is described in US Patent 4,604,242 (August 5, 1986).

General Electric's process for preparing polycarbonate resins based on dimethyl carbonate is described in US Patent 4,452,968 (June 5, 1984).

Section 10.5.2.7 The conversion of CO and hydrogen to isobutanol is described in European Patent Disclosure 020,810,282 (May 23, 1986) to Union Rheinische Braunkohlen Kraftstoff, AG.

The homologation of methanol is described by B. Juran and R. V. Porcelli, *Hydrocarbon processing*, October 1985, p. 85.

Section 10.6.1 The formation of glycol ethers from carbon monoxide is claimed in US Patent 4,308,403 (December 29, 1981) to Texaco.

The process for preparing diethylene glycol bis(allyl carbonate), in use in Japan, is described in US Patent 4,217,298 (August 12, 1980) to Tokuyama Soda.

The preparation of pelargonic acid from butadiene and CO is described by J. Tsuji et al., *Tetrahedron* **28**, 3721 (1972); W. E. Billoups et al., *Chem. Commun.*, 1067 (1971); and US Patent 4,246,183 (January 20, 1981) to Texaco Development Corp.

The conversion of CO and hydrogen to α-olefins is described in European Patent Appl. 0,037,213 (October 7, 1981) to Mobil.

The carbonylation of benzyl chloride is described in *CHEMTECH* May 1988, p. 317.

The bis(carbonylation) reaction to yield phenylpyruvic acid is described in US Patent 4,492,798 (January, 1985) to Ethyl Corp.

The formation of oxalic acid esters by the coupling of carbon monoxide is described in US Patent 4,229,589 (October 21, 1980) to Ube Industries.

The Val Laboratories process for converting NO to urea is described in US Patent 3,986,849.

Section 10.7 A detailed discussion of the issues and economics surrounding the conversion of stranded natural gas to fuels, chemicals, and plastics can be found in Nexant Chemsystems' multiclient report, *Stranded Gas Utilization* January, 2001.

Section 10.7.3 Syntroleum's GTL technology is described in US Patent 6,172,124 (January 9, 2001). Rentech's GTL technology is described in US Patent 6,534,552 (March 18, 2003).

CHAPTER 11

CHEMICALS FROM ALKANES

Alkanes occur as such in natural gas and petroleum and accordingly are the cheapest raw materials for chemicals. They are the feedstocks for cracking (Sections 2.2.1, 2.2.2) and catalytic reforming (Section 2.2.3). Methane is the main source for synthesis gas (Section 10.4) via steam reforming. The higher alkanes can be subjected to the same process if desired, or the steam reforming process can be redirected to give methane. An important process is pyrolysis of hydrocarbons to carbon black, which is discussed at the end of this chapter.

Apart from pyrolysis, these reactions are endothermic. They are all unselective and take place at high temperatures. There are few examples of alkane functionalization, that is, of the use of alkanes directly for downstream chemicals. The most important are the conversion of *n*-butane to maleic anhydride (Section 5.4), the oxidation of *n*-butane or naphtha to acetic acid (Section 10.5.2.2), the oxidation of isobutane to *tert*-butyl hydroperoxide (Section 4.11), the oxidation of ethylbenzene to ethylbenzene hydroperoxide (Section 4.11) and the chlorination of methane (Section 10.2). Lesser volume uses involve ammoxidation of methane to hydrocyanic acid (Section 10.1), conversion of methane to acetylene (Section 10.3), and nitration of propane. These have largely been discussed.

Any alkane may be nitrated. In practice, only propane is used as feed and from its nitration result nitromethane, nitroethane, and 1- and 2-nitropropane. The nitration takes place at 420°C, and the products are separated by distillation. They are used as additives for gasoline for racing cars, as solvents especially for polycyanoacrylates,

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

and as stabilizers of chlorinated solvents. Du Pont developed a process for the nitration of cyclohexane to nitrocyclohexane as a step in a caprolactam synthesis (Section 7.2.2), but it is not used today.

In the early 1990s a propylene shortage, primarily in Europe, motivated development of processes for the dehydrogenation of propane (Section 2.2.7). *n*-Butane also may be dehydrogenated to butadiene (Section 5) but it is more energy efficient to use *n*-butenes. The dehydrogenation of ethane to ethylene (Section 11.2.2) has not been commercialized. Important in the 1990s was the dehydrogenation of isobutane to isobutene for methyl *tert*-butyl ether (MTBE, Section 5.2).

The functionalization of alkanes is a research goal not only because of the economic advantage of circumventing the cracking process, but also because reserves of methane—and to a lesser extent ethane, propane, and *n*-butane from natural or associated gas—may last longer than those of petroleum. The current route to chemicals from methane is via synthesis gas (Section 10.4) but the reaction is capital and energy intensive. Hence, the aim is to functionalize methane by a direct process.

The strong and equivalent C—H bonds in methane make "bond activation" difficult. Thus the functionalization of methane is a "holy grail" for the chemist. If it can be successfully accomplished, the reward is great, because the chemical industry will have the lowest cost raw material possible. Also, it will not be necessary in the shorter run to make the shift to coal with its inherent ecological problems.

11.1 FUNCTIONALIZATION OF METHANE

Early research on the functionalization of methane yielded only marginal results. On the basis of these efforts, it was easy to predict that chemistry would never be discovered to make methane the chemical industry's basic building block. The 1980s, however, saw major advances in catalysis. Methane functionalization attracted intense research in the 1980s, which accelerated in the 1990s. In the 2000s, however, it became clear that the earlier pessimism was not unfounded and that, despite the progress that had been made, methane functionalization was an elusive goal and depended on catalyst development that could not easily be foreseen.

Three reactions provide the goals. These are the direct oxidation of methane to methanol and/or formaldehyde; the dimerization of methane to ethane, ethylene, or higher hydrocarbons; and the aromatization of methane.

11.1.1 Methane to Methanol and Formaldehyde

The oxidation of methane to methanol and formaldehyde is burdened by the fact that formaldehyde is 21 times more susceptible to oxidation than methane at 670°C. Methanol is even more sensitive to oxidation. Of the scores of patents issued, the one to Hüls is typical. Methane and oxygen are mixed at 300–600°C at a pressure of 400 bar. Residence time is a critical 10^{-3} seconds. Conversions per pass, however, are no greater than 3%. The process is not currently economical because of the high capital investment, which the short residence time and the low-conversion rates necessitate. These negative factors provide the incentives for further research.

Nitrous oxide appears to be a particularly good oxidant for methane and two Japanese patents (see notes at the end of this chapter) claim its use with catalysts such as Mo_3/SiO_2 and V_2O_5 at 450–550°C. A 93% selectivity to formaldehyde was obtained but at a conversion of only 0.5%. At 11% conversion, a 98% selectivity was obtained to a mixture of methanol and formaldehyde. At this latter conversion, the process shows some promise, but its practicality is questionable because the molar ratio of nitrous oxide to methane must be 2:1. Nitrous oxide has historically been an expensive oxidant because it could not be made directly from nitrogen and oxygen and required a roundabout route via ammonium nitrate. Oxygen atoms do not interact with nitrogen because the process, written in spectroscopists' notation:

$$N_2(^1\Sigma_g{}^+) + O(^3P) \longrightarrow N_2O(^1\Sigma_g{}^+)$$

is spin forbidden. What that means is that the nitrogen molecule has no unpaired electrons, and oxygen atoms have two, hence the total electron spin of the products should be two, not zero as in nitrous oxide. The reaction to give two molecules of NO, each of which has one unpaired electron, is far more likely.

In the mid-1990s Mitsui Toatsu developed a route to nitrous oxide via catalytic reaction of oxygen and ammonia. The Mitsui Toatsu catalyst is a copper–manganese oxide ($CuO—MnO_2$).

$$2NH_3 + 2O_2 \longrightarrow N_2O + 3H_2O$$

Solutia, who is pioneering the reaction of benzene with N_2O to yield phenol (Section 7.1), has tried to lower the costs of this route even further by replacing the oxygen with air. Ammonia is still more expensive than nitrogen but not nearly as expensive as ammonium nitrate. Industrial oxidations of alkanes or aromatics with nitrous oxide may become practical in the future.

Typical of more recent work is a Catalytica process in which methane reacts with sulfuric acid to yield methyl hydrogen sulfate CH_3OSO_3H, which can be easily hydrolyzed to methanol and recoverable sulfuric acid. The original catalyst was mercury based, which would cause environmental concerns if used in a large scale process. Catalytica was able to replace this with a platinum complex. At 180°C, selectivity to methanol was 86%. This approach has the potential to lower the cost of methanol production by obviating the need to reform methane to syngas. Before it can be commercialized, however, both reaction rate and yield must be improved.

11.1.2 Dimerization of Methane

The dimerization of methane to ethane and ethylene has been extensively studied. In the Benson process, methane is burned in chlorine in a highly exothermic reaction at an adiabatic flame temperature of 700–1700°C. As might be expected, huge amounts of hydrogen chloride are obtained, which must be reconverted to chlorine or used in some other way. This seriously inhibits commercialization of the process.

Catalytic oxidative coupling of methane has also been explored. Thus it has been shown that lithium-doped magnesium oxide in the presence of oxygen will extract hydrogen from methane to form methyl radicals, which in turn combine to produce ethane and ethylene at 720°C. Conversion is about 38% with a selectivity of about 50%. ARCO has been able to obtain conversions up to 15% with selectivities of 78% to C_2–C_7 compounds, mostly ethane and ethylene. One catalyst described is manganese acetate with sodium promoters. In other work nitrous oxide was used.

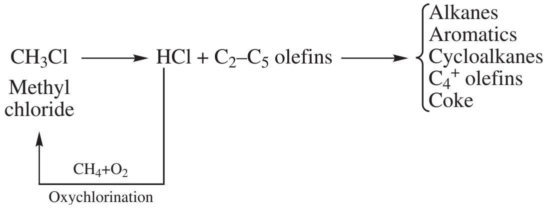
In 1993, the University of Minnesota suggested the feasibility of oxidative coupling of methane to give ethylene at 830°C in the presence of oxygen and samarium oxide Sm_2O_3. Yields of 60% were claimed as opposed to previously achieved values of 25%. The key appears to be the shifting of equilibrium by the rapid removal of oxygen, methane, and ethylene. More recent work from Amoco (now part of BP) improves the oxidative coupling process by integrating the exothermic methane coupling reaction with an endothermic cracking of saturated hydrocarbons in a dual-flow reactor. The heat produced in the methane coupling reactor is transferred through the walls of the reactor tubes to the second cracking zone.

The direct conversion of methane to acetic acid with oxygen, rhodium chloride, and water at 100°C has been accomplished at Pennsylvania State University, although reaction rates are very low.

11.1.3 Aromatization of Methane

The conversion of methane to aromatics has been studied by BP. The aromatization is accomplished in the presence of an oxidant, nitrous oxide, with an acid catalyst, a gallium-doped H-form zeolite. Methane conversion of 39% per pass has been reported with selectivities to aromatics of 19%. Although such results are promising, the economics are doubtful because 1 mol of nitrous oxide is consumed for every two C—H bonds that are broken. Also, additional oxidant is consumed in the undesirable formation of carbon oxides. Either one needs a way of using the oxidant catalytically rather than stoichiometrically, or a cheaper oxidant should be found, or a less expensive method for producing nitrous oxide should be developed (Section 11.1.1).

As mentioned above, methane can be halogenated under mild conditions. In a proposed process for converting methane to gasoline, chloromethane is dehydrohalogenated under conditions such that coupling takes place simultaneously to give C_2–C_5 olefins which, under the conditions of the reaction, recombine to provide gasoline-range paraffins and aromatics. Some olefins are also produced. In the process, hydrogen chloride is evolved and is reused for oxychlorination of the methane:



A report from the University of Minnesota indicates that platinum or rhodium catalysts effect the conversion of methane to synthesis gas (Section 10.4) at ambient temperatures. Selectivity and conversions are reported to be high.

11.2 FUNCTIONALIZATION OF C_2–C_4 ALKANES

The commercialized reactions in which alkanes have been oxidized were listed at the beginning of this chapter. Several interesting processes, not yet commercialized, have been described in the literature.

11.2.1 Oxidation of C_2–C_4 Alkanes

The oxychlorination of ethane to vinyl chloride may be carried out with a metallic silver–manganese catalyst in combination with other compounds such as lanthanum salts, either in the particulate form or impregnated on a zeolite, to provide vinyl chloride at 400°C and atmospheric pressure.

$$CH_3CH_3 + 0.5O_2 + Cl_2 \longrightarrow CH_2{=}CHCl + H_2O + HCl$$

Contact time is 1–2 seconds. Complete conversions can be obtained with selectivity to vinyl chloride as high as 50%. This process, patented by ICI, showed promise and commercialization is predicted by about 2005. An earlier process devised by Lummus using conventional oxychlorination catalysts yielded selectivities of 37% at 28% conversion.

Monsanto studied the oxychlorination of ethane to vinyl chloride in a vapor-phase fluidized bed reactor with a catalyst comprising alumina-supported copper halide and potassium phosphate at 550°C. Ethyl chloride is a byproduct, which can subsequently be oxidatively dehydrogenated to vinyl chloride. Ethylene dichloride byproduct can be cracked by conventional means to vinyl chloride. Conversions of the order of 85–90% based on hydrogen chloride can be achieved with selectivities as high as 87% based on ethylene.

More recent work by European Vinyls Corporation (EVC) has led to promising results. In the EVC process, ethane is catalytically oxychlorinated to vinyl chloride in an integrated multistep process. Because a significant amount of chlorinated hydrocarbons, both saturated and unsaturated, are formed in the primary oxychlorination stage, it is critical to the economics of the process to recycle the byproducts to reduce wasted feedstock. The unsaturated chlorinated byproducts are converted to saturated products by a separate hydrogenation stage and then dehydrochlorinated to vinyl chloride. By recycling the byproducts, a very high overall vinyl chloride yield is achieved. The EVC process operates at low-temperatures relative to earlier attempts at ethane oxychlorination. This is crucial, as high temperatures and a chlorine-containing environment are extremely corrosive, and the metallurgy required to contain such a system is exotic and expensive.

In the mid-1980s, Union Carbide developed the Ethoxene (Section11.2.2) process to produce acetic acid via the catalytic gas-phase oxidation of ethane. The problem was the simultaneous production of substantial quantities of ethylene as well as acetic acid, and development of it seems to have been abandoned. In 2000, SABIC announced its intention to build a pilot plant based on catalytic ethane oxidation using its own proprietary Sabox process, which makes acetic acid in selectivities of up to 60% with little or no ethylene coproduct. This might be an economic source of acetic acid, given the low cost ethane available to SABIC.

The ammoxidation of propane to acrylonitrile has been studied for many years by BP and was targeted for commercialization in the late 1990s. By 2004, plans had still not reached fruition. The reaction is postulated to proceed by way of a propylene intermediate. One proposed catalyst, in an early patent issued to another developer, Monsanto, comprises a mixture of antimony and uranium oxides with a halogen promoter such as methyl bromide. Antimony was a first generation and uranium a second generation catalyst for the ammoxidation of propylene (Section 4.8). Reaction takes place at 500°C to give 71% selectivity at 85% conversion for a yield per pass of 60%. Raw material savings are somewhat eroded by the higher capital costs of the process. Newer patents describe catalysts comprising a mixture of vanadium, antimony, phosphorus, and cobalt as well as bismuth, vanadium, molybdenum, chromium, and zinc. These provide lower yields per pass but may have other advantages. In addition to BP, two Japanese companies, Asahi Chemical and Mitsubishi Chemical, have been active in developing propane ammoxidation processes that can be run in two modes. One mode requires operation at modest per pass propane conversions to maintain high selectivities to acrylonitrile. This requires unreacted propane to be recycled and necessitates the use of oxygen instead of air, because the nitrogen in the air builds up in the recycle loop. The alternative mode is to run at high conversions per pass without recycling the unreacted propane. This route has higher propane consumption but permits the use of air as the oxidant. It remains to be seen which approach, if either, will eventually be commercialized. Catalytic oxidation of propane to acrylic acid is also under development. Promising patents have been awarded to Mitsubishi Chemical, Toagosei, BASF, and Sunoco. No commercialization plans have been announced thus far.

Catalytic oxidation of *n*-butane to maleic anhydride was discussed in Section 5.4. This process, commercialized more than 30 years ago, is still the only transition metal catalyzed alkane activation process to achieve widespread use. A spin-off of this technology are processes to convert *n*-butane to 1,4-butanediol and tetrahydrofuran (Section 5.4). These processes, all proceed via hydrogenolysis of maleic anhydride or maleic acid. As far as the alkane activation component of the process is concerned, they are simply variations on the maleic anhydride technology.

In a reaction analogous to the oxidation of butane to acetic acid, propane or a propane–butane mixture can be oxidized at about 450°C and 20 bar to acetaldehyde and a large number of other oxygenated compounds. The reaction can be conducted either in the liquid or gaseous phase and has been used commercially in the United States. In a related development ICI has oxidized ethane in the presence of hydrogen chloride to acetaldehyde. A silver manganate catalyst, $AgMnO_4$, is used at 360°C. Conversion is 14% and selectivity to acetaldehyde is 71%. Chlorinated byproducts such as methyl and ethyl chloride can be recycled to inhibit their additional production.

11.2.2 Dehydrogenation of C_2–C_4 Alkanes

Dehydrogenation of ethane, propane, or butane to the corresponding olefins is an alternative to steam cracking that requires higher temperatures and greater capital investment. Nonetheless, as the worldwide demand for polypropylene continues to grow, there is concern that conventional sources of propylene will be inadequate. Propane dehydrogenation has been commercialized and is discussed in detail in Section 4.1.

n-Butane is seldom if ever dehydrogenated because of the large energy input required. The dehydrogenation of butenes to butadiene is carried out commercially in the United States (Section 5). A further C_4 dehydrogenation reaction currently in use involves conversion of isobutane to isobutene, the latter being required for MTBE production (Section 5.2.1). The reaction takes place readily, unlike most dehydrogenations, because the tertiary hydrogen is an excellent leaving group. Isobutane is also used as feedstock for propylene oxide (Section 4.11). The isobutane is oxidized with air to *tert*-butyl hydroperoxide, which is used as the source of oxygen in the catalytic epoxidation of propylene to propylene oxide. *tert*-Butanol is a byproduct of this reaction. It can be dehydrated to isobutene for reaction with methanol over acidic ion exchange resins to yield MTBE. Alternatively, the *tert*-butanol can be directly converted to MTBE. This approach to propylene oxide production is not expected to grow, as the future of MTBE is in doubt. Dehydrogenation of isopentane has been used to make isoprene.

Petroleum wax fractions from lubricating oil dewaxing can be dehydrogenated to α-olefins. Hydroformylation (Section 4.12) then gives detergent range alcohols. For example, Sasol in Augusta uses UOPs Pacol process to dehydrogenate paraffins and separates the product olefins from the starting paraffins by UOPs Olex process. These processes could possibly be improved if oxidative dehydrogenation were possible. Thus far, successful processes have not evolved, because the products oxidize more readily than the starting material. Meanwhile, wax cracking has been used in the past in Italy and by Chevron to obtain an *n*-alkane–olefin (not necessarily alpha) mixture used to alkylate benzene to give alkylbenzenes for detergent use. The dehydrogenation of ethane to ethylene is more difficult than that of the higher hydrocarbons. Many companies have worked in this field. Union Carbide, as indicated earlier (Section 11.2) has devised an oxidative dehydrogenation in the vapor phase to produce a mixture of ethylene and acetic acid. The ratio of the two products can be varied from 1:1 to 5:1. The catalyst comprises molybdenum and vanadium doped with niobium, antimony, and one other metal, which can be calcium, magnesium, or bismuth. The reaction takes place at 330–435°C with conversions of about 30% and selectivities as high as 90%. Although this might provide a convenient route to acetic acid without requiring the investment for dedicated plants, the imbalance between ethylene and acetic acid demand (55 *vs*. 4.5 billion lb, in 2002) means that it could never be the sole source of ethylene. If it were, a large surplus of acetic acid would be produced.

11.2.3 Aromatization of C_2–C_4 Alkanes

Since ease of aromatization increases with molecular weight, ethane aromatizes more readily than methane, and propane and butane aromatize more readily than ethane. The dehydrocyclization of alkanes, primarily propane and butane or liquefied petroleum gas (LPG) to aromatics, provides the basis for BPs and UOPs Cyclar process for which a demonstration plant was operated in the early 1990s. In the late 1990s, a plant was built and is operating in Saudi Arabia.

The Cyclar process uses a propane–butane (LPG, Section 2.1) mixture in a reaction maintained at 535°C and 6 bar with a contact time of 14 seconds. Twenty-nine percent conversion with 95% selectivity to aromatics results. The process could be useful as a source of benzene in areas like Saudi Arabia where pyrolysis gasoline (Section 2.2.1) is not available and where very little catalytic reforming (Section 2.2.3) is done. The BTX distribution with propane and butane as feeds is shown in Table 11.1.

The aromatization of ethane takes place with a gallium- or platinum-doped ZSM-5 zeolite catalyst. The shape selective property of the catalyst (cf. Section 8.1, toluene disproportionation) promotes the selective formation of cyclohexane and methylcyclohexane. Dehydrogenation provides benzene and toluene. The inlet temperature is about 700°C. Because the reaction is endothermic, a high input of heat per pound of ethane converted is required. The reaction is carried out at 2 bar and the ethane conversion per pass is about 33%. Of this, 30 mol% is methane and 60% is benzene and toluene. Less than 2% is higher hydrocarbons.

11.3 CARBON BLACK

Many petrochemical processes are seriously hindered by the formation of carbon, which poisons catalysts and blocks furnace tubes. Thermodynamically, alkanes incline toward carbon and hydrogen as the most stable products. The production of carbon from alkanes, including methane, is thus relatively easy.

Carbon black is an amorphous graphite or soot consisting of highly aromatic carbon structures of colloidal size. It is made by partial combustion or combustion plus thermal cracking of hydrocarbons at 1300–1400°C. The feedstock may be an alkane

TABLE 11.1 Aromatics Yield from Aromatization of Propane and Butane (%)

	Propane	Butane
Benzene	32.0	27.9
Toluene	41.1	42.9
Xylenes	18.9	21.8
C_9 and C_{10} Aromatics	8.1	7.4

or olefin or almost any hydrocarbon. Methane was once used widely but is no longer economic. Gas oil and residual oils are now popular especially from sources high in aromatics.

Many grades of carbon black are produced, varying primarily in particle size (between 10 and 500 nm) and surface area but also in other properties important in rubber compounding. About 60% is used in tires to provide abrasion resistance and mechanical strength to the rubber. The remaining 40% goes into other elastomers, printing inks, paints, and plastics.

This mature carbon-black technology has been slightly perturbed by the appearance of nanoparticles, a term generally used to indicate particles with dimensions less than 100 nm, so that traditional carbon blacks overlap with the nanoparticle region. The smallest nanoparticles, only a few nanometers in diameter, contain only a few thousand atoms. These particles are called quantum dots and can possess properties that are entirely different from the bulk materials.

Nanostructured silica–carbon powders of the kind that could be used in tires are made in a so-called turbulent diffusion flame reactor based on a conventional hydrogen–air burner. Hexamethyldisiloxane is fed into the flame and the products collected. Pure silica and composite silica–carbon nanoparticles result from oxidation of hexamethyldisiloxane, $(CH_3)_3Si—O—Si(CH_3)_3$.

The combination of carbon black and silica is more effective in reinforcing rubber than carbon black alone, providing the capability for manufacture of so-called "green tires." As the silica surface is covered with silanol groups, adding an organosilane coupling agent forms a silica network in the rubber. This filler-to-filler network enhances the tire reinforcement and decreases the rolling resistance by up to 24%, while wet traction and tread wear are similar to conventional tires. Fuel consumption is significantly decreased and air and environmental pollution reduced. The problem, of course, is the price. The siloxane starting materials are not cheap and the products market at $2.5–5/lb, compared with typical carbon black prices of $0.40/lb.

Automobile tires now last longer and more automobiles are imported into the United States. Hence, the United States carbon black market has declined from about 3.5 billion lb/year in the early 1970s to about 2.5 billion lb/year in the early 2000s. It nonetheless remains an important chemical and the global market is 12 billion lb/year.

NOTES AND REFERENCES

Nomenclature again: The term alkane is generally preferred to paraffin in the industrial chemical literature. The unsaturated counterpart of an alkane is an alkene, and to be consistent this term should be used. However, the industry overwhelmingly prefers olefin, which, from the point of view of nomenclature, is the unsaturated counterpart of a paraffin. We had little choice in this chapter but to follow the industry practice of using the word olefin but only occasionally the corresponding word paraffin, which is virtually unknown outside textbooks.

A good overview of commercially promising alkane activation technologies is Nexant Chemsystems' multiclient report, *Alkane Activation: Petrochemical Feedstocks of the Future* (June, 1999).

Section 11.1 In addition to the references on methane conversion either to methanol or ethylene, the following, which are but a small sample of the literature available, provide examples of the interest the chemical trade press has taken in this topic. *Chem. Eng. News*, April 10 (1989) p. 5; *ibid.*, July 4 (1988) p. 22; *ibid.*, January 18 (1988) p. 27; *ibid.*, May 9 (1988) p. 45; *ibid.*, September 28 (1987) p. 23; *ibid.*, September 14 (1987) p. 19; *ibid.*, June 1 (1987) p. 22; *Chem. Week*, October 21 (1987) p. 49, *CHEMTECH*, August (1987) p. 501; N. D. Parkyns, *Chem. Brit.* **26**, 841 (1990).

Section 11.1.1 The Catalytica and University of Minnesota work have been reported in *Chem. Eng. News*, January 18 1993, p. 6, *ibid.* October 11 1993, p. 4, and *Science* **262**, 221 (1993). Catalytica's mercury-based catalyst is described in US Patent 5,305,855 (April 26, 1994) and the platinum-based catalyst is described in World Patent 98/50,333 (November 12, 1998).

The Hüls oxidation of methane to methanol is described in German Patent 2,743,113 (1979).

Japanese Patents 189,249-250 (November 27, 1981) to I. Masakazu describe the oxidation of methane with nitrous oxide to methanol and formaldehyde. Mitsui Chemical's catalytic oxidation of ammonia to nitrous oxide is described in US Patent 5,849,257 (December 15, 1998).

Section 11.1.2 For the University of Minnesota work, see reference in Section 11.1.1. The conversion of methane to acetic acid is described in *Chem. Week*, April 20, 1994, p. 8.

The process in which methane is burned in chlorine is described in US Patent 4,199,533 (April 22, 1980) to the University of Southern California.

The lithium-doped magnesium oxide catalyst for methane coupling has been explored by T. Ito and J. Lunsford, *Nature* (*London*) **314**, 25 (1985).

The conversion of methane to gasoline, described in a patent to Atlantic Richfield (US Patent 4,849,751, July 18, 1989), is accomplished by oxidatively coupling methane to convert it to a mixture of ethylene, carbon monoxide, and hydrogen. The mixture is then treated with a dual function catalyst comprising ZSM-5 and an oxide of cobalt, rutheniun, copper, zinc, chromium, or aluminum. The zeolite oligomerizes the ethylene to gasoline-sized molecules whereas the oxide, as in the Fischer–Tropsch reaction (Section 12.2), converts CO and H_2 to gasoline-range molecules. This is a clever approach, typical of what will be needed if methane functionalization is to become practical.

Typical of the ARCO patents that claim methane conversion to higher hydrocarbons, are US Patents 4,443,644-649 (April 17, 1984); US Patents 4,544,784-787 (October 1, 1985); US Patents 4,547,607-64 (October 15, 1985); US Patent 4,499,322 (February 12, 1985); US Patent 4,517,398 (May 14, 1984); US Patent 4,523,049 (June 11, 1985); US Patent 4,523,050 (June 11, 1985); US Patent 4,556,749 (December 3, 1985); US Patent 4,560,821 (December 24, 1985); US Patent 4,568,785 (February 4, 1986); and US Patent 4,554,395 (November 19, 1985).

Section 11.1.3 The conversion of methane to aromatics is described in European Patent Appl. 0,093,543 (November 9, 1983).

The catalyst for the conversion of chloromethane to gasoline-range hydrocarbons comprises zeolites doped with cations such as zinc, gallium, or silver. Reaction takes place at ~325°C and 3 bar.The conversion is described in two International Patent Appl. WO85/02608 (June 20, 1985) and WO85/04863 (November 7, 1985) to British Petroleum.

Section 11.2.1 The ICI process for oxychlorination of ethane is described in two British Patent Appl. (2,095,242A and 2,095,245A) (September 29, 1982). The older Transcat process is claimed in US Patent 3,775,229 (January 19, 1971) to Lummus.

The Monsanto process for vinyl chloride is claimed in US Patent 4,300,005 (November 11, 1981).

The Europeans Vinyls Corporation's ethane to VCM process is described in a series of patents: EP 0 667 844B1 (February 4, 1998), WO 95/07252 (March 16, 1995), WO 95/07251 (March 16, 1995), WO 95/07250 (March 16, 1995), WO 95/07249 (March 16, 1995).

The ICI process for acetaldehyde formation with a silver catalyst is claimed in US Patent 4,415,757 (November 15, 1983).

Standard Oil of Ohio's (BP America) patents describing propane ammoxidation include US Patent 4,873,215 (October 10, 1959) and European Patent Application 0,282,314 (March 10, 1988). An early Monsanto patent is West Germany Patent 2,056,326. Mitsubishi Chemical patents on propane ammoxidation include US Patent 5,750,760 (May 12, 1998) and WO 98/22421 (May 28, 1998). Asahi Kasei patents on this subject include US Patent 5,780,664 (July 14, 1998) and US Patent 5,663,113 (September 2, 1997).

A particulary interesting patent describing propane to acrylic acid technology is BASF's US Patent 6,541,664 (April 1, 2003). The yield to acrolein and acrylic acid combined is 85%.

Section 11.2.2 Carbide's ethane dehydrogenation process is the basis for US Patent 4,524,236 (June 18, 1985) to Union Carbide.

The Cyclar process is described in a number of patents including UK Patent Appl. GB2,082,157A (March 3, 1982); European Patent Appl. 0,202,000 A1 (November 20, 1986); US Patent 4,613,716 (September 23, 1986), and US Patent 4,642,402 (February 10, 1987). All of these patents are held by BP except the last one, issued to UOP, which cooperated with BP on the development.

Wax cracking is described by Weissermehl and Arpe in their definitive text on industrial organic chemistry, cited in Section 0.4.2.

Section 11.2.3 The conversion of ethane to aromatics is described in a Mobil patent (US Patent 4,350,835, September 21, 1982).

Section 11.3 The web provides numerous sources. Political implications are at www.volpe.gov.infosrc. Apart from these, we have drawn on A. M. Thayer, Special Report: Nanotechnology, *Chem. Eng. News*, October 16, 2000; S. E. Pratsinis, Flame aerosol synthesis of ceramic powders, *Prog. Energy Combust. Sci.* 24, 197 (1998);

T. J. Byers and A. A. McNeish, Current advances in tire compounding technology for rolling resistance, paper presented at the Carbon Black World 1997 Conference, San Antonio, TX; and H. K. Kammler and S. E. Pratsinis, Scaling up the production of nanosized SiO_2 particles in a double diffusion flame reactor, *J. Nanoparticle Res.* **1**, 467(1999).

CHAPTER 12

CHEMICALS FROM COAL

We have described the derivation of chemicals from petroleum and natural gas. But between 5 and 10% of organic chemicals come from other sources—coal, fats, oils, and carbohydrates. Historically, these sources are important because it was from them that the modern chemical industry evolved. Their present applications are also significant, particularly for specialty chemicals. Furthermore, because fats, oils, and carbohydrates are renewable resources, they represent an insurance policy for the future.

Coal, although a nonrenewable source of chemicals and energy, occurs on earth in much larger quantities than petroleum and will certainly outlast petroleum reserves by a few hundred years. The reserves to production ratio is six times that for oil and four times that for natural gas. Although seen as polluting and difficult to handle, it still accounts for a quarter of world and US energy consumption. In the European Union, this figure drops to 14.6% but in China it rises to more than 60%. We shall discuss it first, before we turn to the renewable sources.

Coal was important to the chemical industry in the nineteenth and early twentieth centuries. It provided carbide, and hence acetylene (Section 10.3), synthesis gas (Section 10.5), hence ammonia and methanol, petroleum-like fuels, and all the aromatic chemicals contained in coke oven distillate. This distillate still provides some chemicals, although the quantities (about 1.5%, see note at end of this chapter) pale by comparison with those from petrochemicals. The conversion of coal to synthesis gas (Section 10.4) was developed in the nineteenth century as a source of gaseous

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

energy. It was mixed with oil gas (see note to Section 12.2) to increase its calorific content. That coal-based synthesis gas can still provide the basis for chemicals was demonstrated most recently by the Eastman acetic anhydride process (Section 10.5.2.3). Coal-based synthesis gas is also the basis for the Fischer–Tropsch reaction as initially practiced (Section 12.2). It could be used for Substitute Natural Gas (Section 12.5) but this has not been commercialized. The hydrogenation of coal is another approach to converting coal to liquid fuels and conceivably to raw materials for chemicals.

Although there is no interest in the early 2000s in substitute natural gas or coal hydrogenation, the Fischer–Tropsch reaction has come into prominence as a means of converting so-called “stranded” gas to a liquid form for easy transportation (Section 10.7).

After World War II, enthusiasm for coal-based chemicals waned as the cost of petrochemicals dropped. Interest revived in the 1970s at the time of the oil shocks but waned again in the 1980s because the price of petroleum dropped and there were huge discoveries of natural gas around the world especially in the Soviet Union (now the CIS), and the Gulf area, especially Qatar and Indonesia.

12.1 CHEMICALS FROM COKE OVEN DISTILLATE

When coal is heated in the absence of air to a temperature of about 1000°C, coke forms together with a number of liquid and gaseous decomposition products. It is this distillate, also called coal tar, that provided the aromatics and many other chemicals for the early chemical industry. Some of these are shown in Figure 12.1.

The coke is almost pure carbon and is used in steel manufacture which, as it becomes more efficient and processes change, requires less coke. Nonetheless, some coke will always be needed, and therefore the chemical industry will always have available the chemicals that volatilize from the coke ovens. Current global annual production of coal tar is about 20 million tonnes.

A typical coking operation produces 80% coke by weight, 12% coke oven gas, 3% tar, and 1% light oil consisting of crude benzene, toluene, and xylenes as well as over 200 other chemicals. United States production of coal tar in 1998 was 3.2 billion lb, the same order of magnitude as a medium tonnage chemical such as butadiene, but less than one-third of what it was in the 1950. The coal tar is distilled to give four fractions:

1. Light oils, boiling below 200°C. They are called light oils because they float on water. They are crudely fractionated, then agitated with concentrated sulfuric acid to remove olefins. The hydrocarbons are washed with dilute sodium hydroxide and redistilled to give benzene, toluene, xylenes and “solvent naphtha,” a mixture of indene, coumarone and their homologues. This is a powerful solvent especially for coatings containing coal tar and pitch. Treated with a Friedel–Crafts catalyst such as aluminum chloride, it gives coumarone–indene thermoplastic resins, used for cheap floor tiles, varnishes, and adhesives.

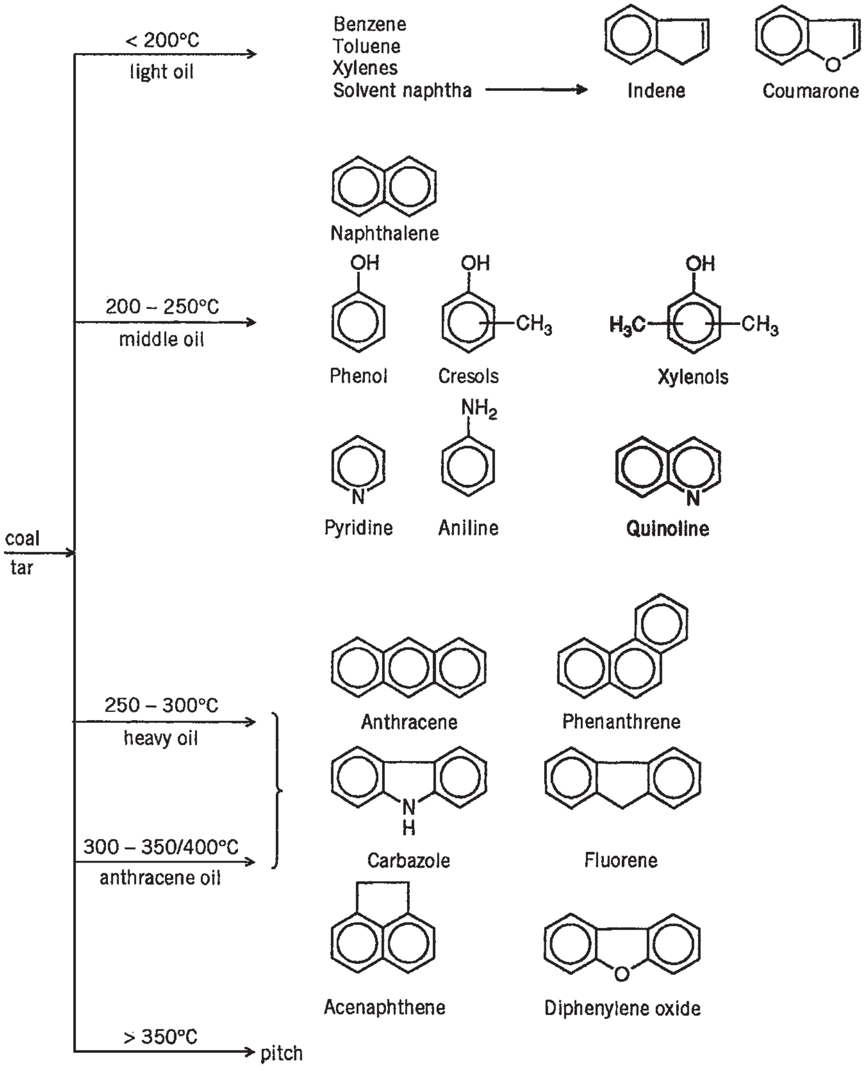


FIGURE 12.1 Coal tar distillation: major and some minor products.

2. The middle oils boil between 200 and 250–270°C. The most abundant chemical is naphthalene and it occurs with phenols, cresols, and pyridines in the tar. It crystallizes when the middle distillate from the tar is allowed to cool and, even in this impure form, is suitable for phthalic anhydride manufacture (Section 9.1.1). Alternatively, it may be purified by sublimation, a somewhat unusual purification process. Extraction of the remaining tar with aqueous sodium hydroxide takes the acidic phenols and cresols into the aqueous layer as phenates and cresylates. They are regenerated with carbon dioxide.

Subsequent extraction of the remaining oil layer with acid gives nitrogen-containing bases, primarily pyridines.

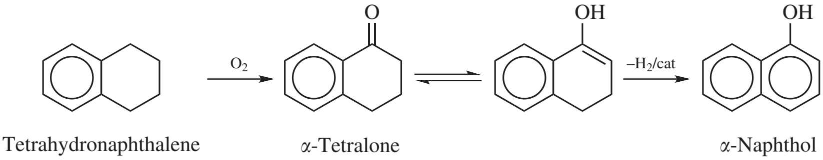
3. Heavy oil comes off between 250 and 300°C if anthracene oil is taken off as a separate fraction, but sometimes they are combined. It is used for wood preservatives generally under the name of creosote or (if the fractions are not separated) anthracene oil.
4. Anthracene oil comes off between 250 and 300–400°C or 350 and 400°C if taken off as a separate fraction. It contains anthracene, phenanthrene, carbazole, and many other compounds in small quantities. It makes up about 1% of coal tar.

Some 60% of the tar remains as a residue called pitch. Its production is driven by the aluminum industry, which thermally polymerizes the pitch to make electrodes for the electrolysis of molten alumina–cryolite mixtures to give aluminum. The generation of each tonne of aluminum consumes 0.45–0.6 tonnes of carbon, which is oxidized to carbon dioxide and monoxide. The use of carbon electrodes rather than an inert metal reduces the voltage required for the electrolysis. By saving electricity in this way the system is acting efficiently as a fuel cell. Other uses for coal tar include roofing sealants and coatings for underground pipelines. The residual tar is used for road building and in paints, primarily to waterproof subsurface structures. These often comprise combinations of the tar with epoxy resins (Section 7.1.2.1). Creosote (heavy oil) is used to preserve telephone poles and railroad ties.

Benzene from coke oven distillate accounted for 3–4% of total benzene production in Europe in the early 2000s, but for only 1–2% in the United States (Section 7). The type and quantity of chemicals in coke oven distillate vary with the type of coal and method of coking. Typically, in the most volatile fraction of coke oven distillate, benzene comprises 70%, toluene 15%, and the xylenes 4%. The remainder consists of alicyclics and aliphatics plus some phenols and cresols.

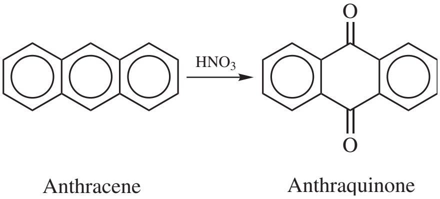
More important in market terms is naphthalene, which is a raw material for phthalic anhydride in competition with *o*-xylene (Section 9.1.1). Until the early 1960s, coke oven distillate was the sole source of naphthalene, but it can now be obtained by catalytic reforming of heavier naphthas. Unfortunately, methylnaphthalenes form, and the methyl groups must be removed by hydrodealkylation if naphthalene itself is desired. This is the same reaction used to convert toluene to benzene (Section 8.1). Annual naphthalene production in the United States in the early 2000s was about 265 million lb. About 15% of the production facilities were petroleum based. The remainder was from naphthalene from coke oven distillate.

Naphthalene can also be hydrogenated mildly to tetrahydronaphthalene (Tetralin) or vigorously to decahydronaphthalene (Decalin). Tetrahydronaphthalene has a number of applications. When there was great interest in the use of coal for chemicals, it was an effective hydrogen donor for coal liquefaction. It is currently used as a source of α-naphthol. Air oxidation gives α-tetralone and catalytic dehydrogenation gives α-naphthol, an important dye intermediate and also the starting material for the insecticide carbaryl (Section 10.5.2.5):



The anthracene and carbazole in anthracene oil are still useful to dyestuffs manufacturers. Anthracene is the starting point for anthraquinone dyes and carbazole gives the Violet 23 shade of a popular chocolate bar wrapper, as well as the light-resistant Hydronblue R dye used in several brands of blue jeans.

Before World War I, anthracene was concentrated sufficiently to enable it to be crystallized and the crude material oxidized to anthraquinone with nitric acid (as it still is) or dichromate.



During the war, the United States was cut off from anthraquinone and developed a synthetic method in which benzene reacted with phthalic anhydride in the presence of a Friedel–Crafts catalyst to give *o*-benzoylbenzoic acid (Section 7.8), which was dehydrated to anthraquinone. The method remained economically preferable to the coal tar extraction route until suspension crystallization techniques were developed in which the anthracene and carbazole were successively precipitated out from copious quantities of high boiling aromatic solvents. Although cheaper than the synthetic route, there were various drawbacks: unwanted products coprecipitated, the use of aromatic organic solvents was environmentally damaging, and the process consumed vast amounts of energy per pound of product.

Rutgers, the only company currently processing coal tar in Germany, brought onstream a new plant for carrying out the separation in 2003 based on new technology. In an industry as traditional as the coal tar industry, this was a major event. The method used relies on engineering innovations that permit melt crystallization at temperatures near 300°C. Liquid feed without solvent is gradually cooled by a series of vertical heat exchanger plates to encourage crystal growth on the surface of the plates. The liquid residue (sooty oil) is drained off. The plates are then heated very slowly enabling the crystals to “sweat away” further impurities. Melting of the remaining crystals produces a fairly pure phenanthrene–anthracene–carbazole mixture, which cannot be separated by crystallization because the compounds form solid solutions. Instead, they are separated by high-temperature vacuum distillation, itself difficult because phenanthrene (at atmospheric pressure) boils at 340°C within a degree of anthracene (bp = 339.9°C) although there is then an appreciable gap before carbazole (bp = 354.75°C) distills.

The quantities of coal tar distillate available are limited by the demand for coke by the steel industry and could not be increased substantially to compensate for a shortage of petrochemical products.

12.2 THE FISCHER–TROPSCH REACTION

The Fischer–Tropsch reaction provides a route from coal to hydrocarbons. When synthesis gas (Section 10.4) at near atmospheric pressure is passed over an iron, nickel, or cobalt catalyst at 150–300°C, a mixture of alkanes and olefins with a broad range of molecular weights is formed. The olefins are formed first and Sasol isolates and sells them (Section 10.6.1). Alternatively, they may be reduced to alkanes. If hydrogen-rich synthesis gas is used, made from naphtha or methane instead of coal, alkanes may be the initial products (Section 10.4).

$$
\begin{aligned}
&n\mathrm{CO} + 2n\mathrm{H_2} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O}\\
&2n\mathrm{CO} + n\mathrm{H_2} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{CO_2}\\
&n\mathrm{CO} + (2n+1)\mathrm{H_2} \longrightarrow \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O}
\end{aligned}
$$

The hydrocarbons are predominantly C_5–C_{11} straight chain, although methane, ethylene, and propylene are also produced together with some higher molecular weight Fischer–Tropsch waxes used for candles. There are also oxygenated compounds such as alcohols and acids. The result is a petroleum-like mixture that can be used both as a fuel and a chemical feedstock. Ruthenium has been proposed as a catalyst for higher molecular weight hydrocarbons. Both fixed- and fluid-bed processes are operated and the products are shown in Table 12.1.

TABLE 12.1 Fischer–Tropsch Products as Obtained at Sasol

Product	Fixed Bed at 220°C (Wt. %)	Fluidized Bed at 325°C (Wt. %)
CH_4	2.0	10
C_2H_4	0.1	4
C_2H_6	1.8	4
C_3H_6	2.7	12
C_3H_8	1.7	2
C_4H_8	3.1	9
C_4H_{10}	1.9	2
C_5–C_{11} (gasoline)	18.0	40
C_{12}–C_{18} (diesel fuel)	14.0	7
C_{19}–C_{23}	7.0	
C_{24}–C_{35} (medium wax)	20.0	4
C_{35}+ (hard wax)	25.0	
Water-soluble nonacid chemicals	3.0	5
Water-soluble acids	0.2	1

The mechanism of the Fischer–Tropsch reaction is complex and has not yet been completely elucidated. It is generally agreed that the above processes are basic. The water gas shift reaction also takes place but requires an iron catalyst.

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Its equilibrium can be directed either way depending on temperature, pressure, and reactant concentrations. Undesirable reactions include the formation of methane, the disproportionation of carbon monoxide to carbon dioxide and carbon, the reaction of hydrogen and carbon monoxide to give carbon and water, the decomposition of methane to hydrogen and carbon and the oxidation of the metal catalyst. Formation of carbon fouls the catalyst. Addition of steam inhibits carbon formation and depresses slightly the yield of methane.

Since the hydrocarbons are straight chain, they have low octane numbers and must be isomerized for use as gasoline or in the alkylation reaction (Section 2.2). On the other hand, the straight-chain structure is ideal for steam cracking and catalytic reforming to provide the olefins and aromatics needed for chemical synthesis.

The process was subject to intensive development between the world wars and was operated successfully on a large scale in Germany during World War II. Currently, Fischer–Tropsch processing is underway in South Africa in three plants. It was by this means that South Africa protected itself in case its racial policies provoked a petroleum boycott. A change of government in the 1990s has obviated this need. Fuel production has continued because the increased cost of oil makes it economical in depreciated plants. The Fischer–Tropsch products are created by growth of carbon chains on an iron-based catalyst and there is no restriction on their size. Thus a range of alkanes of varying molecular weights, many of them useless for gasoline, are produced. Initially, these byproducts were burned as fuel but are now being “mined” for chemicals. The first to be produced were α-olefins in the pentene to octene range.

Pentene-1, while present in C_5 steam cracker streams, is rarely isolated. Sasol’s Fischer–Tropsch “Synthol” stream provides a larger source. The olefins in the Synthol stream are unique in that a large percentage are linear α-olefins with both odd and even numbers of carbon atoms. Ethylene oligomerization, the conventional route to α-olefins, gives only even carbon numbered compounds (Section 3.3.2). Pentene-1 has potential application as a comonomer in linear low-density polyethylene but, because of the historical lack of supply and even now with only a single supplier, adoption of pentene-1 as a comonomer has been very slow. Sasol has been quite successful, however, in taking advantage of their access to low-cost hexene-1 and octene-1 and have quickly become a major supplier of these α-olefins.

The Fischer–Tropsch process does not produce the same balance of products as an oil refinery. When it was operated on a scale to meet South Africa’s gasoline needs, insufficient diesel fuel resulted. Accordingly, additional processing was required, which led to an excess of gasoline. In the early 1990s, this had to be exported at uneconomical international prices. A similar problem afflicted Brazil’s gasohol programme when the replacement of gasoline by ethanol led to a diesel shortage.

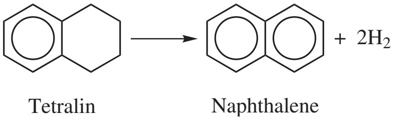
In spite of its superficial virtues, the Fischer–Tropsch process with coal was generally felt to be costly and unreliable in operation. Coal is a solid; consequently reactors were bulky, mechanically complex, and therefore expensive. Utility and maintenance costs were high, and coal had to be dug laboriously out of the ground. However, if one starts with gas rather than coal or coke (Section 10.7), the above objections disappear. Sasol has available offshore gas (Mossgas) that it uses in a small Fischer-Tropsch plant.

An alternative route to gasoline from synthesis gas is the Mobil MTG process described in Section 10.5.2.4. It uses molecular sieve catalysts whose pore size is sufficiently small to control the molecular weight within the C_5–C_{10} range, so that the higher molecular weight alkanes produced in the Fischer–Tropsch synthesis are absent.

12.3 COAL HYDROGENATION

Coal has the approximate empirical formula CH. To convert it to an aliphatic hydrocarbon mixture requires addition of hydrogen. In the Fischer–Tropsch process, this is derived ultimately from water. It is, however, possible to hydrogenate coal directly. This process, called the Bergius process, was operated in Germany in World War II. Coal, lignite, or coal tar was hydrogenated over an iron catalyst at 450°C and 700 bar, and 4 million tonnes of gasoline were synthesized in this way, largely for aviation fuel.

Less drastic conditions could be used for coal hydrogenation if a solvent could be found that would hydrogenate the coal in a liquid–solid phase process. In the hydrogen-donor process, finely powered coal reacts for 1–2 hours with tetralin at about 200°C and 65 bar. The tetralin acts both as a solvent and a hydrogen donor, giving up four hydrogen atoms to form naphthalene.



The hydrogen presumably reacts with free radicals generated by the coal decomposition to stabilize them and prevent further cracking, which would lead to gas formation. Free radical coupling, which leads to coke formation, is also prevented. The naphthalene produced is rehydrogenated to tetralin. The same technique can be used on heavy crude oils and on residues from crude oil distillation. The cheap petroleum of the late 1980s argued against commercialization of this process.

There are thus three routes from coal to petroleum-like fuels. The Fischer–Tropsch and Mobil processes are more attractive than the Bergius process. Whether or not coal ever becomes a raw material for petroleum-like fuels on a world scale depends on the severity of the petroleum shortage, the available of the huge capital investment required, and the feasibility of various other possible sources of energy such as nuclear fission, nuclear fusion or renewables.

12.4 SUBSTITUTE NATURAL GAS (SNG)

Methane made synthetically instead of by extraction from natural gas fields is known as SNG. In the 1960s and 1970s, rapid depletion of methane reserves seemed likely and, in the long term, coal seemed its logical source. So much natural gas has been discovered since then, however, that this prospect has receded. In the long term, however, it may be needed. Today SNG is thought to be produced only in countries such as Japan where natural gas is not available. It is made from petroleum fractions by a lower temperature variant of steam reforming.

$$4C_nH_{2n+2} + (2n - 2)H_2O \longrightarrow (3n + 1)CH_4 + (n - 1)CO_2$$

The Catalytic Rich Gas (CRG) process (450°C, potassium promoted nickel catalyst) and the Gas Recycle Hydrogenator (750°C, no catalyst) are technologies that have been available for many years. The former, together with a variant called the "double methanation process," requires a light naphtha feedstock, whereas the gas recycle hydrogenator can use heavier hydrocarbons.

12.5 SYNTHESIS GAS TECHNOLOGY

Synthesis gas technology was mentioned briefly in Section 10.4.4. In principle, the conversion of coal or coke to synthesis gas is straightforward. The difficulty is one of solids handling. The various processes involve fixed, fluid, and entrained beds. The main processes are summarized in Table 12.2. We shall comment only on the Lurgi process, the slagging gasifier and the Texaco processes.

The supply of steam and oxygen in a molar ratio between 2:1 and 6:1 to a moving bed of coal (replenished at the top with ash that was withdrawn at the bottom to provide effectively a fixed-bed technology) leads to a mixture of hydrogen, carbon monoxide, carbon dioxide, and a little methane plus a mass of clinker (fused ash). The gases can be reformed, but the clinker is difficult to handle in a continuous plant. In the Lurgi process, developed in Germany in 1930s, a high ratio of steam/oxygen was used that kept the temperature down and produced a gas high in methane and low in carbon monoxide plus a fine ash that could be handled in an appropriate grate. The excess steam is expensive and leads to large amounts of dilute but corrosive effluent. It also leads to increased plant size for a given capacity and a low thermal efficiency.

A British Gas process—the Westfield Slagging Gasifier—involves a low steam/oxygen ratio that gives a high proportion of carbon monoxide in the gas plus a slag that, at the high temperatures achieved, can be drawn off as a liquid.

The Texaco process, used by Eastman (Section 10.5.2.3), is a variant of the Koppers–Totzek process and involves an entrained bed. A stream of water carrying pulverized coal meets a stream of oxygen creating a flame at 1400–1600°C, from which an SNG high in carbon monoxide and hydrogen and very low in methane and condensable hydrocarbons can be extracted. This is thermally inefficient because of

TABLE 12.2 Coal Gasification Processes

Process	Main Characteristics
Texaco	Pressurized entrained-bed process involving the use of a watery slurry of powdered coal. Less suitable for lignite. Product gas low in CH_4 and tar-free. Low H_2/CO ratio (~0.7).
Lurgi	Pressurized moving-bed process suitable for noncaking granular coal. Relatively high-steam consumption. Product gas is rich in methane, residual steam, and CO_2 and contains tar, H_2/CO ratio (~1.7).
Koppers–Totzek	Atmospheric entrained-bed process in which powdered coal is used as feed. Suitable for a wide range of coals. Relatively high oxygen consumption. Product gas low in methane, CO_2, and residual steam and free from tar, H_2/CO ratio (~0.5).
Winkler	Atmospheric stationary fluid-bed process suitable for reactive coals (lignite). Moderate O_2 and steam consumption. Moderately pure product gas. Moderate coal conversion. Operates at 800–1100°C.
High-temperature Winkler (Rheinbraun)	Pressurized stationary fluid-bed process suitable for reactive coals (lignite). Higher gasification rates and more complete coal conversion than by Winkler process.
British Gas–Lurgi slagging gasifier	Pressurized moving-bed process primarily for noncaking granular coal. Less steam consumption, smaller reaction volumes and purer product gas than via Lurgi process.
Shell	Pressurized entrained-bed process in which a dry coal powder is used as feed. Suitable for wide range of coals including lignite. High thermal efficiency. Product gas of high purity, comparable to that obtained by Koppers–Totzek.

the high temperature but the product is more suitable for chemicals than the moving bed processes. It cannot be used as SNG without further reforming.

12.6 CALCIUM CARBIDE

The production of acetylene by way of calcium carbide and its uses were discussed in Section 10.3. The process uses energy extravagantly and, at 2001 United States prices, the cost of electricity per pound of acetylene is greater than the total cost of a pound of ethylene. The use of carbide might have become attractive had cheap nighttime electricity become available as a result of nuclear plants operating steadily around the clock. The question mark over the nuclear electricity program suggests that this is now only a remote possibility.

12.7 COAL AND THE ENVIRONMENT

Coal poses social and political as well as technical problems. The cheapest way to mine coal is by open pit or strip mining, which ruins large areas of countryside. On the other hand, traditional underground mining is a dangerous and expensive business that demeans the human spirit. Mechanization of mining and better safety standards have improved the miner's lot from what it was in the nineteenth century, but the situation is far from ideal.

The economic and moral dilemmas are underlined by the virtual closure of Britain's historic mining industry. British coal lies in narrow seams deeply buried. They are uncomfortable and dangerous to work, and the British miners saw themselves as the cream of the manual workers.

Meanwhile, demand for coal has declined. Oil and natural gas have replaced it in many applications, especially now that Britain has its own supplies from the North Sea. Coal is polluting and European Commission legislation on air pollution discriminates against relatively high-sulfur British coal for electricity generation. The possibility of imports of cheap strip-mined coal (much of it produced, say the miners, by sweated child labor in Columbia) has made things worse. The collapse of the British coal industry has led to the disappearance of employment, the fragmentation of historic communities, and the depopulation of whole areas of the country.

Should one applaud the ending of an unpleasant and dangerous industry or mourn the disappearance of employment and community? Either way, the production of coal at a lower social cost may be a problem of crucial importance for future generations.

NOTES AND REFERENCES

The huge classic, *The Chemistry of Coal Utilization*, H. H. Lowry, Ed., originally published in 1945 was reprinted by John Wiley & Sons, Inc., New York, in 1977. For a more succinct background to the industry, see G. J. Pitt and G. R. Millward, *Coal and Modern Coal Processing*, Academic, London, 1979.

The proportion of US organic chemicals coming from coal tar and crudes in the early 1990s can be calculated from *Synthetic Organic Chemicals*, published by USITC and cited in Section 0.4.5. This invaluable source book has now regrettably ceased publication. In 1990, 127 million tonnes of organic chemicals were derived from 52 million tonnes of primary products from petroleum and natural gas and 0.84 million tonnes of coal tar and crudes, from which it appears that coal made up 1.6% of feedstocks. Corresponding 1991 figures were 123, 54, and 0.76 million tonnes respectively, so that the proportion dropped to 1.4%. The 1992 figures, however, are 138, 56, and 2.66 million tonnes suggesting a rise to 4.7%. This is highly unlikely and presumably represents a change of classification.

A major barrier to an extensive coal-based chemical industry would be the amount of coal needed. Bayer estimate at the end of the 1970s that to produce all the organic chemicals then made from petroleum would require an extra 250 million tonnes of coal per year in Western Europe. Total current production of hard coal, lignite, and brown coal, not all suitable for chemicals, is only 400 million tonnes.

Section 12.1 Changes in the coal chemicals field are described by M. McCoy, *Chem. Eng. News*, May 8, 2000, pp. 22–23. The phenanthene–anthracene–carbazole separation is described by C. O'Driscoll, *Chem. Brit.*, April 2003, 56–57. More information is offered by Ali Nikzad of Sulzer Chemtech, e-mail *ali.nikzad@sulzer.com*.

Section 12.2 Coal (town) gas, producer gas, water gas, and synthesis gas are often confused. Coal or town gas is a coproduct of coke oven operation and is high in hydrogen and carbon monoxide. Producer gas was a low Btu gas with a high nitrogen content made by passage of air and steam over coke and is now obsolete. Water gas (or blue gas) is the gas obtained from the passage of steam over coke, when its composition is typically 40% CO, 50% H_2, 5% CO_2, and 5% N_2 and CH_4. A gas with higher H_2/CO ratio is obtained by steam reforming of methane and higher alkanes. For the manufacture of chemicals, a synthesis gas is required with the appropriate CO/H_2 ratio and, to the extent to which this is necessary, water gas is not the same as synthesis gas. Oil gas was obtained in the United States by thermally cracking petroleum distillates. It contained 20–25% ethylene, 13–16% propylene, and some higher olefins and light paraffins. Oil gas was not available in the United Kingdom and synthesis gas was therefore rarely used as a fuel.

A proposed Fischer–Tropsch mechanism involving two simple reactions has been advanced by J. Falpe, *Chem. Eng. News*, October 26, 1981, p. 23.

The Fischer–Tropsch mechanism involving CO dissociation and CO hydrogenation has been elaborated by M. E. Dry, "The Sasol Fischer–Tropsch Process" *Applied Industrial Catalysis*, Vol. 2, Academic Press, New York, 1983.

Catalysts for the Fischer–Tropsch reaction are discussed by R. D. Srivastava, V. U. S. Rao, G. Cinquegrane, and C. J. Stiegel, *Hydrocarbon Processing*, February 1990, p. 59.

A good review of the modern conception of the Fischer–Tropsch reaction has been written by J. Haggin, *Chem. Eng. News*, Aug. 23, 1990, p. 27. See also M. E. Dry, *J. Chem. Technol. Biotechnol.* **77**, 43–50 (2001).

The MTG process led to a flurry of interest in methanol from coal exemplified by several books: E. Supp, *How to Produce Methanol from Coal*, Springer-Verlag, 1990; A. Kasem, *Three Clean Fuels from Coal: Technology & Economics*, facsimile of 1979 edition, Bks demand; H. A. Dirksen, *Pipeline Gas from Coal by Methanation of Synthesis Gas*, Inst. Gas Tech. 1963.

Sasol entered the α-olefins market in 1994. Cf. "α-Olefins: Sasol Inaugurates Plant, Plans Major Expansion," *Chem. Week*, November 16, 1994, p. 19.

Section 12.4 An excellent review of coal gasification before everyone (except Eastman) lost interest is by D. Rooke, *Chem. Eng.*, January 1978, p. 34.

Details of all the gasification technologies are to be found in H. D. Schilling, B. Bonn, and U. Krauss, *Coal Gasification: Existing Processes and New Developments*, Graham and Trotman, 1979 and in E. C. Mangold, *Coal Liquefaction and Gasification Technologies*, Ann Arbor, MI, 1979.

CHAPTER 13

FATS AND OILS

Naturally occurring triglycerides, that is, esters of glycerol with saturated or unsaturated fatty acids, are called oils if they are liquid or fats if they are solid. They may be of animal or vegetable origin. They have the general formula: $ROOCCH_2—CH(OOCR')—CH_2OOCR''$, where R, R′, and R″ are alkyl or alkenyl groups. Usually, more than one fatty acid is present and the triglyceride is said to be "mixed." Some of the fatty acids most commonly found in triglycerides in fats and oils are shown in Table 13.1. They all have even numbers of carbon atoms.

Fats and oils are one of the three major groups of foodstuffs, the others being proteins and carbohydrates. Food is, however, surrounded with a host of cultural attitudes. In southern Europe, oil is widely used for cooking whereas, in northern Europe, solid fats have traditionally been preferred. In the Middle East, a market for butter scarcely exists, whereas in Europe and North America it is an important foodstuff. Therefore ways have been sought by which oils could be hardened to make them culturally acceptable to dwellers in northerly areas. The melting point of a fat or oil is related to the melting points of the fatty acids it contains, and these in turn depend on molecular weight (see the series lauric, myristic, palmitic, stearic), number of double bonds (see the series stearic, oleic, linoleic, linolenic), and the *cis* or *trans* configuration of the double bond (see the series linolenic, α-eleostearic, β-eleostearic). Crystalline structure of the fat also plays a part. To harden a fat or oil, therefore, it is hydrogenated over a nickel catalyst. In partial hydrogenation, *cis* double bonds may isomerize to *trans* double bonds. The

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

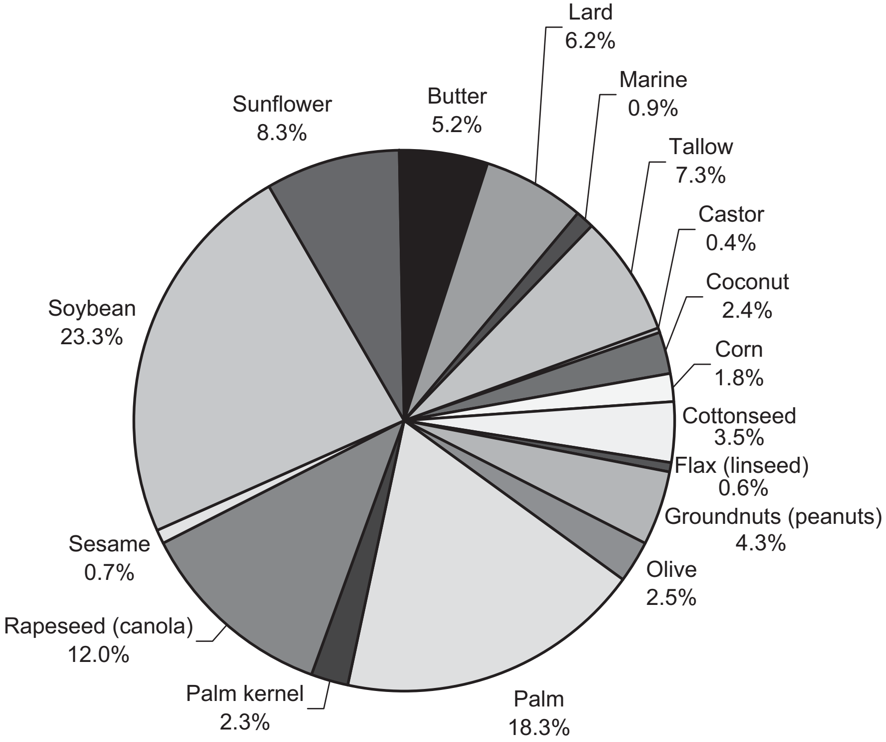


FIGURE 13.1 World production of oils and fats, 2000. (Total production 110.9 million tonnes.)

degree of hardness can be controlled, and fats of any desired consistency can be produced.

The role of fats and oils in cardiovascular disease has been a major area of concern in recent years. European and North American diets are said to be too rich in fats and oils. Saturated fats and fats with *trans* double bonds have been associated with atheroma, and a switch to soft fats containing polyunsaturated side chains has been recommended. Thus a historic trend toward hard fats has been reversed. Opinion now seems to be stressing the virtues of monounsaturated fats, notably olive oil.

World production of fats and oils in 2000 was 110.8 million tonnes (244 billion lb), estimated to reach 135–140 million tonnes by 2010. United States consumption was about 26.9 billion lb (about 105 lb per person). This figure is similar to the production of propylene or benzene. The difference is that propylene and benzene are almost entirely used by the chemical industry, whereas 88% of oils and fats are eaten by humans and another 6% of poorer grade material is made into animal feed. The remaining 6% (about 1.6 billion lb) is used by the oleochemical industry. That is about the same as caprolactam production and rather greater than *o*-xylene production. Thus, in volume terms, oleochemicals are comparable with one fraction of one of the seven major feedstocks.

Figure 13.1 shows world production of the different oils and fats. Four oil crops (soybean, palm, rape, and sunflower) have grown rapidly over the past 35 years compared with traditional oils and fats. They have gone from 26% of world production in 1958 to 62% in the early 2000s. The fastest growing has been palm oil because of excellent merchandising primarily by Malaysia and also by Indonesia. Also, palm oil yields are about 4000 kg/hectare compared with 875 kg/hectare for peanuts, 675 for rapeseed, 355 for coconuts, and 350 for soybeans. Animal fats have only a small share, and production has been static for about 40 years.

Oil producing countries specialize to some extent. Malaysia grows mainly palm oil and is responsible for 51% of world production.. The Philippines grows coconut oil (43% of world production). China (27%), Europe (25%), India (19%), and Canada (15%) grow rapeseed or canola oil. The CIS (25%), Europe (20%), and Argentina (16%) grow sunflower oils, while the United States has 56% of soybean oil production and Argentina another 22%. The United States, China, and the CIS dominate the cottonseed market.

Rapeseed oil containing 90% erucic acid is a new development as is a sunflower oil with 80% oleic acid. Rapeseed as a source of oil is important not only because the oil has a high concentration of unsaturated fatty acids, but also because it can be grown in colder climates than other oilseeds. Thus it is an important crop in Canada and northern Europe. Its importance in Europe, however, reflects the desire of the European Commission to support European farmers and replace imports. It provides few if any economic advantages. At February, 2003 prices, the production cost of palm oil produced in Malaysia and delivered to the United States was \$698/tonne. Soybean oil in the United States cost \$489/tonne and rapeseed oil in Europe \$750/tonne. The market price in the United States was only about \$560/tonne.

The original rapeseed oil contained 40–50% erucic acid, a C_{22} fatty acid with a single double bond, together with so-called glucosinolates, which are toxic compounds inhibiting growth by blocking the capture of iodine by the thyroid gland. Animals (rats, guinea pigs, ducklings, hamsters) fed on a high erucic acid diet concentrated fat in the heart muscle. While there is no evidence that erucic acid has a similar effect on humans, the oil market is geared to edible oils. It was thought prudent to develop a zero erucic acid rapeseed, now called canola oil, and to remove or breed out the glucosinolates. Some high erucic acid oil is still required for industrial needs, and thus a high erucic acid crop is also grown. It is important to prevent cross-pollination of one crop by the other. Rapeseed oil goes into lubricants for diesel engines and erucic acid amide is used as a lubricant in plastics extrusion.

The most important fat or oil in the United States is soybean oil of which about 26 billion lb were produced in 2000. Little of it is used by the chemical industry, which obtains most of its fatty acids (palmitic, stearic, and oleic) from tallow or other animal fats or from tall oil (Section 13.1). The sources of fatty acids for the chemical industry are shown in Table 13.1.

Fats are extracted from the fatty animal tissues in slaughterhouse wastes by rendering. In “dry” rendering, heat alone is use to dry the material and liberate the fat. In “wet” rendering, the fat is liberated by hot water or steam, which is then separated by skimming or centrifuging.

TABLE 13.1 Common Fatty Acids

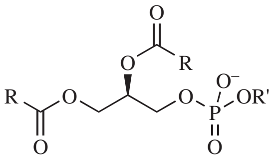
Formula	Trivial Name	Melting Point (°C)	Double-Bond Position and Stereochemistry	Source
$n\text{-}C_{11}H_{23}COOH$	Lauric acid	44.2		Coconut oil, palm kernel oil
$n\text{-}C_{13}H_{27}COOH$	Myristic acid	53.9		Coconut oil, palm kernel oil
$n\text{-}C_{15}H_{31}COOH$	Palmitic acid	63.1		Most vegetable oils and animal fats
$n\text{-}C_{17}H_{35}COOH$	Stearic acid	69.6		Most vegetable oils and animal fats
$n\text{-}C_{17}H_{33}COOH$	Oleic acid[a]	16.0	*cis*-9	Most vegetable oils and animal fats (olives, nuts beans, tall oil)
$n\text{-}C_{17}H_{31}COOH$	Linoleic acid[a]	−9.5	*cis*-9, *cis*-12	Tall oil, most vegetable oils (safflower, sunflower, soy)
$n\text{-}C_{17}H_{29}COOH$	α-Linolenic acid[a]	−11.3	*cis*-9, *cis*-12, *cis*-15	Linseed oil
$n\text{-}C_{17}H_{29}COOH$	γ-Linolenic acid		*cis*-6, *cis*-9, *cis*-12	Evening primrose oil
$n\text{-}C_{17}H_{29}COOH$	α-Eleostearic acid	48.5	*cis*-9, *trans*-11, *trans*-13	Tung oil
$n\text{-}C_{17}H_{29}COOH$	β-Eleostearic acid	71.5	*trans*-9, *trans*-11, *trans*-13	Tung oil
$n\text{-}C_{17}H_{32}(OH)COOH$	Ricinoleic acid[a]	5.0	*cis*-9	Castor oil
$n\text{-}C_{19}H_{29}COOH$	Eicosapentaenoic acid		*cis*-5, *cis*-8, *cis*-11, *cis*-14, *cis*-17	Fish oil
$n\text{-}C_{19}H_{29}COOH$	Arachidonic acid	−49.5	*cis*-5, *cis*-8, *cis*-11, *cis*-14	Animal fats and organs
$n\text{-}C_{21}H_{41}COOH$	Erucic acid	33.5	*cis*-13	Rapeseed (canola) oil
$n\text{-}C_{21}H_{31}COOH$	Docosahexaenoic acid	22.6	*cis*-4, *cis*-7, *cis*-10, *cis*-13, *cis*-16, *cis*-19	Fish oil

[a] Oleic acid: $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$; Linoleic acid: $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$; Linolenic acid: $CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$; Ricinoleic acid: $CH_3(CH_2)_4CH_2CH(OH)CH_2CH{=}CH(CH_2)_7COOH$.

Oils are extracted either by pressing (expression) or by solvent extraction. Expression, for example, of peanuts, used to leave about 6% of the oil in the so-called oil cake, but modern presses leave only 3–5%. Nonetheless, solvent extraction may be preferred because it leaves less than 1%. Soybean oil is invariably solvent extracted, usually with hexane. The soybeans are heat-treated and then mechanically pressed to flakes. The flakes are solvent extracted (leached) with hexane, which is subsequently stripped off and recycled.

The modern trend is the use of supercritical carbon dioxide for solvent extraction of food and personal products. For example, it is used for high cost products such as decaffeinated coffee and essential oils for the perfume industry. It was suggested as an attractive process for edible oils because it would avoid the traces of hexane contamination, but thus far the expense of the capital equipment has deterred the industry.

Once the oil has been extracted, it is subjected to a series of purification processes: degumming, refining, bleaching, deodorization and possibly fractionation by melting point, and hydrogenation. In the degumming process, phospholipids are removed by washing the oil with hot water or dilute acid. They precipitate and are removed as a sludge and vacuum dried. Alternatively, they are removed during the alkali refining treatment. The sludge contains four phosphatides, which are esters of phosphatidic acid. These are 1,2-diglycerides with a phosphoric acid group on the third carbon, and the phosphoric acid group is in turn esterified with choline, ethanolamine or serine. If the structure is written



and R = stearic, palmitic, or oleic, then if R′ = $CH_2CH_2N^+(CH_3)_2$, the compound is called lecithin or phosphatidylcholine, if R′ = $CH_2CH_2NH_2$ it is cephalin or phosphatidylethanolamine, and if R′ = $CH_2CH(NH_2)COOH$ it is phosphatidylserine. The trade lecithin is a mixture of all three plus minor components. It is used as a cationic surfactant in foods and specialty chemicals. For example, it is added to chocolate to prevent "blushing" and to soft margarine to stabilize the emulsion. There is some clinical evidence that phosphatidylserine enhances memory in elderly persons suffering from memory loss.

Vegetable oils usually contain free fatty acids resulting from enzymatic decomposition. If the oils are to be used as foodstuffs, these are removed by alkali treatment in a so-called refining process. The sodium salts of the fatty acids are separated. They are called soapstocks or "foots." The free fatty acids are regenerated by acidification. Associated with them are small quantities of tocopherols, which may be converted to vitamin E, and small amounts of sterols, including stigmasterol, which can be converted to cortisone (see note at the end of this chapter). The major source of tocopherols and sterols, however, are the deodorizer distillates mentioned below.

The bleaching process decolorizes the oil by adsorption rather than by oxidation, which is the mode of action of conventional bleaches. The colored material is adsorbed on bentonite or montmorillonite clays. The oil may then be fractionated by melting point to extract a particular range of triglycerides, or it may be hydrogenated.

Hydrogenation is carried out over a nickel catalyst and "hardens" the oil, that is, it raises the melting point. Margarine is a typical product. The hardening process involves reduction of double bonds, *cis–trans* isomerization and shifting of double bonds along the chain.

Deodorization involves removal of the strong flavor associated with vegetable oils. It depends on a combination of high vacuum (0.004–0.008 bar) and high temperature (240–260°C) for 15–40 minutes and is a variant of vacuum steam distillation, which removes undesirable volatiles while not damaging the triglycerides. A distillate results (deodorizer distillate) containing odor bodies together with small amounts of two valuable products. One is a mixture of tocopherols, the precursor of vitamin E and thus the source of natural vitamin E. The other is a sterol mixture containing stigmasterol and sitosterols. Stigmasterol is the major raw material in the United States for cortisone.

13.1 FATTY ACIDS

Worldwide, fatty acid production was about 5.7 billion lb in 2000. The United States accounted for about 1.0 billion lb and the Pacific rim for another 2.7 billion lb.

Oils and fats are saponified to glycerol and soap, the sodium salt of fatty acids, by treatment with alkali (Fig. 13.2) when soap is the desired end-product. "Splitting"—continuous noncatalytic hydrolysis at high temperature and pressure—is more widely used in both the United States and Europe to obtain free fatty acids. In smaller plants, continuous autoclave splitting is used in the presence of oxide catalysts such as zinc oxide, and very small operations may use batch processes with so-called Twitchell catalysts, which are combinations of sulfuric and sulfonic acids.

The separation of saturated from unsaturated acids, if required, is normally effected by cumbersome crystallizations. A somewhat less efficient but simpler process for separating fatty acids, primarily from tallow, is known as hydrophilization. An aqueous solution of a wetting agent is slurried with a crystallized fatty acid mixture. The higher melting stearic acid crystals are wetted preferentially and are sufficiently solubilized by the wetting agent to transfer into the aqueous phase. The aqueous layer is separated from the oleic acid by centrifugation. Heating melts the stearic acid, which separates from the water and is easily isolated.

The enzymatic hydrolysis of fats has been extensively studied but a practical process that proceeds at an acceptable rate has not yet been devised. Another source of the vegetable oil fatty acids used by the chemical industry is "foots" or soapstocks (see above).

The lower molecular weight acids, lauric and myristic, come from coconut and palm kernel oils. Palmitic and stearic acids are found in most oils and fats, tallow being the most important. Oleic acid is a component of animal fats and a major constituent of many vegetable oils. Its ozonolysis gives azelaic and pelargonic acids

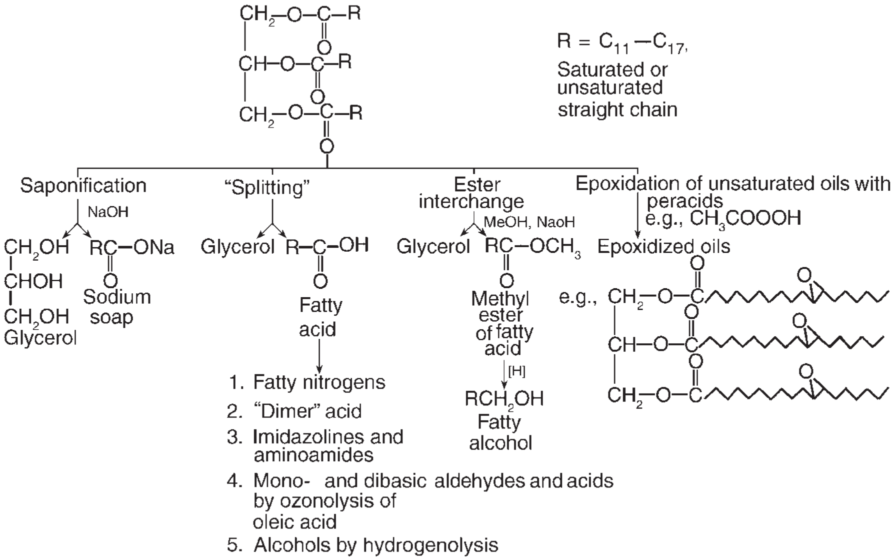
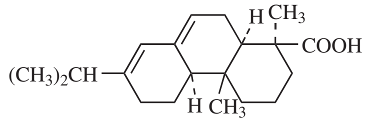


FIGURE 13.2 Chemical reactions of oils and fats.

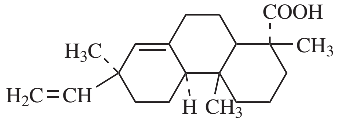
(Section 13.5). 12-Hydroxyoleic (ricinoleic acid) with its OH is an oddity found in castor oil. Erucic acid (see above) is found in rapeseed oil from plants where it has not been removed by breeding.

Linoleic acid is found in many vegetable oils, particularly linseed and safflower oil. Nonetheless, it is largely obtained from tall oil, which became important after World War II. Tall *oil* is a misnomer because oils are triglycerides by definition and tall oil is a mixture of rosin and fatty acids. It is a byproduct of the pulping of southern pine for paper manufacture. Southern pine is converted to pulp by the Kraft process, in which sodium hydroxide is used to separate the desired cellulosic fibers from the undesired lignins (polymers of phenylpropane monomers containing OH and OCH_3 groups), rosins, fatty acids, and other materials in the wood. The fatty acids, mainly oleic and linoleic, end up as their sodium salts in a smelly black liquid. Acidification gives rosin and fatty acids (mainly oleic and linoleic), which may be separated by distillation.

Rosin is a complex mixture of about 90% acids, related to partially hydrogenated phenanthrene, and 10% neutral matter. Of the rosin acids, 90%, including pimaric acid, are isomeric with abietic acid and the remainder with dihydro- and dehydroabietic acids in which one or both the double bonds have been reduced.



Abietic acid



Pimaric acid

The rosin is famous for its use on violin bows, but far larger quantities are formulated into paints and varnishes. As its sodium salt, it is the important size in paper manufacture, and this is its major use.

The fatty acids with more than 18 carbon atoms are found in fish oils. They are of current interest because they are the precursors in the body of the prostaglandins, leukotrienes, thromboxanes, and prostacyclins. They are "essential," that is, they cannot be synthesized by the body and must be obtained in diet.

Evening primrose oil is advertised as being rich in the important C_{18} fatty acid, γ-linolenic acid, an isomer of the α-linolenic acid from tall oil. The seeds of the evening primrose fall when ripe, that is, over a long period. As a result, commercial harvesting gives only about 5% recovery, so that the oil would be impossibly expensive. The active ingredient can be manufactured by fermentation using fungi of the class *Phycomycetes*. For example, species of *Mucor* can be grown on a glucose-containing medium in large fermenters (about 220 cubic meters), and an oil containing 7% γ-linolenic acid (GLA) recovered from the fungal mycelium. Another useful species is *Phycomyces blakesleeanus*, its oil also containing large quantities of β-carotene.

In Russia, Japan, and China, impure petrochemical-based fatty acids with mixtures of odd and even numbers of carbon atoms have been produced by oxidation of petroleum wax. The products are generally regarded as inferior.

A large proportion of fatty acid production goes into soaps. Domestic soap is merely the sodium salt of the mixture of fatty acids obtained by hydrolysis of fats or oils. In practice, the fat or triglyceride is treated with sodium hydroxide to yield the sodium salt (or soap) and glycerol. The process is called saponification. The major components are sodium stearate and palmitate. Soap is used also used as a lubricant in rubber and polymer processing.

The reaction of soap with hydrochloric acid to yield sodium chloride and a fatty acid mixture called stearine was discovered by Chevreul in 1823. In the nineteenth century, until the advent of cheap paraffin wax, it was the principal material used in household candles. Unlike the traditional tallow, there was no glycerol moiety in its structure. Thus it did not give acrolein, a powerful lachrymator, on combustion. It is still blended with paraffin wax in some candle formulations to improve the melting properties of the wax. Only in countries such as Denmark and Sweden, whose fishing industries produce a surplus of cheap stearine, is it still a major component of candles. Paraffin candles dominate the world market, which has passed its nadir and is again growing. This is partly due to fashion in developed countries but also to the frequent interruptions in electricity supply in developing countries, where the inhabitants are no longer content to sit in the dark. Paraffin wax comes from the heavier petroleum fractions, and ceresin or microcrystalline waxes from the same source are used in US candles. These are branched-chain paraffins, and consequently must be blended with an antioxidant to prevent oxidation at the tertiary carbon atoms. Fischer–Tropsch waxes are made in South Africa (Section 12.2) and in Shell's Middle Distillate Synthesis (Section 12.3). They are probably the reason why Shell's process is profitable. The waxes of higher molecular weight are used throughout the world for the fashionable long, thin candles, while the fraction equivalent to paraffin wax is used in the larger domestic market.

Salts of fatty acids are used as stabilizers for PVC. These are the laurates or stearates of metals such as lead, barium, calcium, strontium, and zinc. Metal salts of cobalt, lead, manganese, calcium, and zirconium can be added to unsaturated oils to accelerate their oxidation and are thus used as so-called driers in oil-based paints. Metal soaps (e.g., those based on lithium) are also used to thicken lubricating oils to yield greases. Free fatty acids may be components of automobile lubricating oil formulations. The sucrose esters of fatty acids are said to have advantages over traditional oils and fats in lubricant formulations. (Section 14.1). Microbial conversion of fatty acids gives mono-, di-, and trihydroxy derivatives that are said to have antimicrobial, medical, and industrial properties, but applications are still in the exploratory stage.

13.2 FATTY NITROGEN COMPOUNDS

Fatty acids may be converted into a large number of fatty nitrogen compounds of which the fatty amines, including quaternary amines, are the most important. Some of these are shown in Figure 13.3. They find many applications in industry as surface active agents. The worldwide market for fatty amines in 2000 was about 1.2 billion lb with the United States consuming about 400 million lb.

In Figure 13.3, the route to fatty nitrogen compounds starts with fatty acids in which the alkyl group may contain 7–17 carbon atoms. Normally it is saturated, although derivatives based on oleic and erucic acids are also produced. Treatment

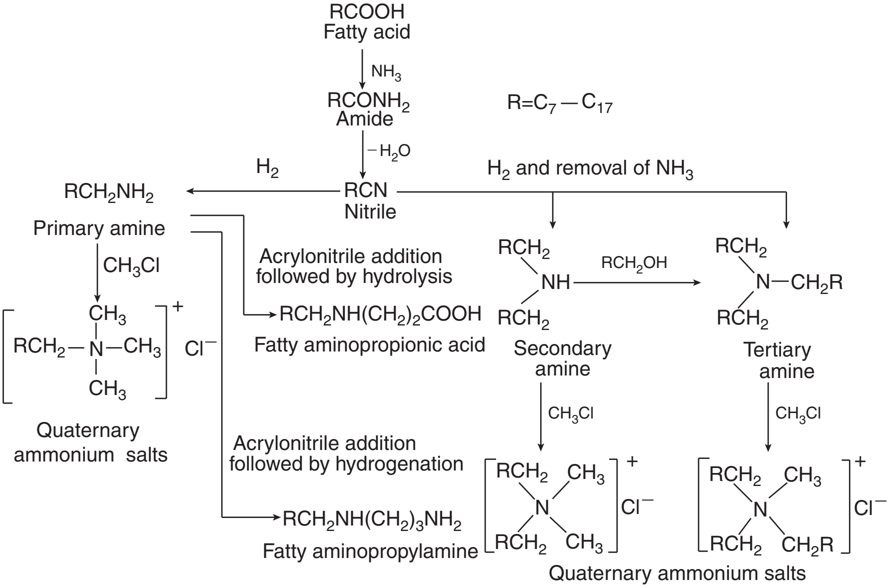


FIGURE 13.3 Fatty nitrogen chemistry.

with ammonia converts the fatty acid to a nitrile through successive dehydrations of the ammonium salt and the amide, neither of which need be isolated. This chemistry was observed earlier in the classic synthesis of hexamethylenediamine (Section 5.1.2). Amides, however, are articles of commerce and are used as a parting agent or slip agent to prevent plastic from adhering to the die during extrusion. The nitrile in turn may be reduced to a primary, secondary, or tertiary amine. Conditions for primary amine formation require that ammonia be present to suppress secondary amine formation. Conversely, when the secondary amine is the desired product, ammonia must be removed continuously from the reaction mixture. The tertiary amine may also be prepared by hydrogenation with removal of ammonia. It is better prepared, however, by the interaction of a di-(long-chain alkyl) amine with an alcohol. The primary, secondary, and tertiary amines may be quaternized with methyl chloride or sulfate.

The most important use for distearyldimethylammonium chloride is as a textile softener for home laundering. It must be added during the last rinse, otherwise it will precipitate on contact with anionic detergents. Although still widely used, it is believed to present some ecological problems. Substitutes are certain ethoxylates (Section 3.7), which are nonionic and can be included as part of the detergent formulation.

Distearyldimethylammonium chloride and related quaternaries also react with bentonite clays to modify them, so that they are dispersible in organic solvents. As such they are the basis for high-performance greases, which result when the organoclay is dispersed in mineral oil. These organoclays are also widely used in oil-based paints to impart thixotropy.

An application for long-chain quaternary alkylammonium compounds is in phase-transfer catalysis (Section 16.10). A related application is liquid ion exchange used primarily in the extraction of uranium ore. Uranium is leached with sulfuric acid to give the complex anion $[UO_2(SO_4)_2]^{2-}$. A trifatty amine in which the fatty groups contain 8–10 carbon atoms is converted to a sulfate as shown in Eq. 1 and this organic-soluble salt, dissolved in kerosene, is mixed with the aqueous leach liquor containing the uranium anion. On vigorous stirring, ion exchange takes place between the sulfate ion of the trifatty amine salt and the uranium-containing anion so that the latter is transferred to the organic solution, whereas the sulfate is transferred to the aqueous layer (Eq. 2). Thus the uranium, which was present in the aqueous phase at a concentration of considerably less than 1%, is not only concentrated in the organic phase but is separated from numerous impurities. It can be removed from the organic phase by stripping with an alkali (Eq. 3), which converts it into so-called "yellow cake." The trifatty amine is recycled.

1. Salt formation.

$$2R_3N_{\text{kerosene}} + H_2SO_{4.\text{aqueous}} \rightleftharpoons [(R_3NH)_2{}^+SO_4{}^{2-}]_{\text{kerosene}}$$

2. Liquid ion exchange.

$$[(R_3NH)_2{}^+SO_4{}^{2-}]_{\text{kerosene}} + [UO_2(SO_4)_2]^{2-}_{\text{aqueous}} \rightleftharpoons [(R_3NH)_2{}^+[UO_2(SO_4)_2]^{2-}_{\text{kerosene}} + SO^{2-}_{4\text{aqueous}}$$

3. Stripping.

$$[(R_3NH)_2{}^+[UO_2(SO_4)_2]^{2-}]_{\text{kerosene}} + 2Na_2CO_3 \rightleftharpoons$$
$$2R_3N_{\text{kerosene}} + [UO_2(SO_4)_2]^{2-}_{\text{aqueous}} + 2Na^+ + H_2O + CO_2$$

Figure 13.3 shows another reaction sequence for primary amines. They may react with acrylonitrile to give a fatty aminopropionitrile. This in turn can be reduced to a fatty aminopropylamine or hydrolyzed to a fatty aminopropionic acid. Each of these compounds varies in degree of surface activity, and it is this variation that accounts for their specific applications. For example, the diamine is used as a corrosion inhibitor and the amino acid is an amphoteric detergent.

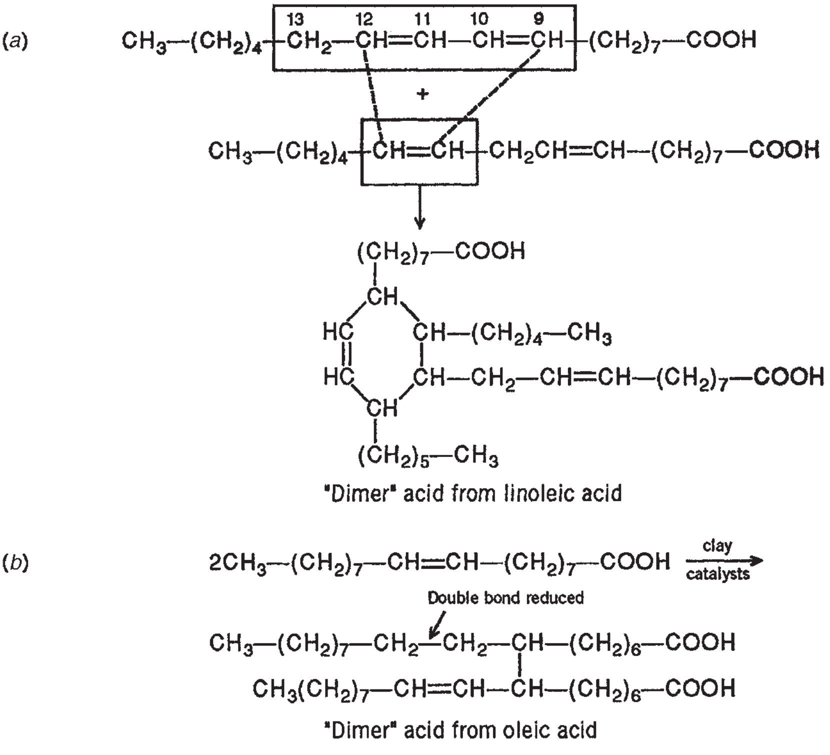
In addition to the foregoing simple reactions, fatty acids undergo a number of more complicated reactions of chemical interest, although the tonnages involved are trivial compared with petroleum and natural gas derivatives. Many of the products, however, are not accessible from petrochemical sources. An example is "dimer acid," produced at a level of 275 million lb/year worldwide. United States demand in 2001 was 115 million lb.

13.3 "DIMER" ACID

The dimerization of linoleic acid is shown in Figure 13.4*a*. Natural linoleic acid has double bonds in the 9,12-positions (Table 13.1) but, when heated, it isomerizes to the conjugated 10,12, or 9,11 structures. In Figure 13.4*a*, the 9,11 acid is shown. This diene may then undergo a Diels–Alder reaction with another molecule of the original 9,12-acid or either of the conjugated isomers. The figure shows the reaction with the 9,12-acid to give a typical Diels–Alder adduct—a cyclohexane with four side chains, two of which contain carbonyl groups.

The conjugation reaction can go in two ways, and the products can react with either of the double bonds in the 9,12-; 10,12- or 9,11-acids. Furthermore addition may be head-to-head or head-to-tail. The figure shows head-to-head addition. In all, 24 different products are possible. An added complication is that the double bonds can be *cis* or *trans*. Although most naturally occurring double bonds, including those in linoleic acid, are *cis*, some *trans* double bonds form at the temperature of the reaction. Whether they are *cis* or *trans*, however, markedly affects the kinetics of the reaction.

Linoleic acid is scarcer and more expensive than oleic acid and it was desirable to find a way to dimerize the cheaper oleic acid which, with its one double bond, will not undergo the Diels–Alder reaction. It will, however, dimerize over a natural acid clay catalyst (e.g., a montmorillonite), known as a "pillared clay." Such a clay consists of layers separated by ions, such as metal ions, which function as "pillars." Large organic molecules can undergo reactions in the spaces between the layers. Oleic acid dimerizes as shown in Figure 13.4*b*. This is one of the relatively rare examples in organic chemistry of an intermolecular dehydrogenation. For it to proceed, the hydrogen must react immediately when it is produced, and here it hydrogenates the double bond. Other examples are benzene/ammonia (Section 7.3) and methane/ammonia (Section 10.1).



(The bond forms in many of the possible positions, and one double bond is reduced, as shown)

FIGURE 13.4 “Dimer” acid.

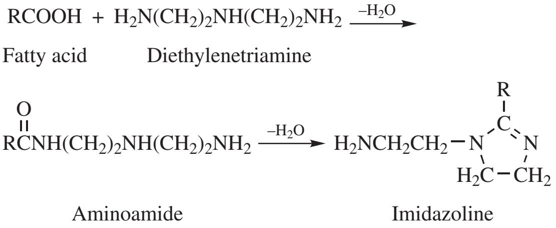
The product from oleic acid is also known as “dimer acid,” and many different chemical structures are present, although all contain 36 carbon atoms and two carboxyl groups. These dibasic acids are used in the production of specialty polyamide oligomers (Versamids) with unusual adhesive and coating properties. For example, when reacted with ethylenediamine, an alcohol-soluble oligomer results that adheres to polyethylene, and which is therefore useful as a vehicle for printing inks for polyethylene film. The alcohol solubility is necessary since stronger solvents such as aromatic hydrocarbons dissolve the natural rubber printing rolls.

When dimer acid reacts with diethylenetriamine, triethylenetetramine, or higher polyalkylene amines, an amino-containing polyamide oligomer results. It is an important coreactant for epoxy resins for adhesives and particularly for maintenance paint for metals. The amino-containing resin imparts corrosion resistance by reacting chemically with the metal oxide surface (e.g., ferric oxide) that is invariably the top layer of iron exposed to air. The chemical reaction is salt formation that takes place between the acidic hydrated amine groups and the basic hydrated metal oxides.

An interesting specialty use involves the substitution of dimer acid esters, such as the di-(2-ethylhexyl) ester, for lubricating oil in two-cycle outboard engines in lakes in Switzerland that were being polluted by petroleum engine oil discharged from motor boats.

13.4 AMINOAMIDES AND IMIDAZOLINES

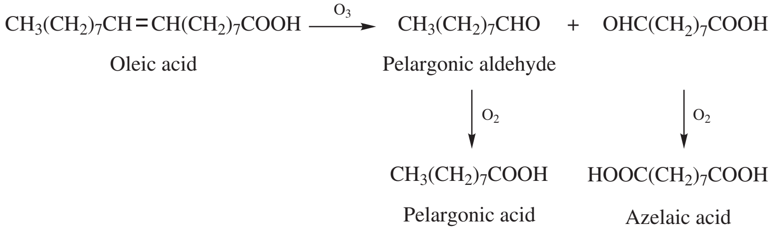
A small volume application for fatty acids involves their conversion to aminoamides and imidazolines. In some applications such as flotation and corrosion inhibition, they compete with the fatty nitrogen compounds discussed in Section 3.2. A fatty acid will react with a polyamine such as diethylenetriamine to give an aminoamide, a molecule of water being eliminated. Further dehydration leads to cyclization. Imidazolines have many of the properties of the fatty nitrogen compounds already described.



If quaternized with methyl chloride or sulfate, they are useful as textile softeners, like the fatty quaternaries already discussed (Section 13.2). Their main use is as corrosion inhibitors, particularly in petroleum applications. They are also used as asphalt emulsifiers and antistrippants. An asphalt emulsifier is an emulsifying agent that brings particles of liquid asphalt and water into close proximity to provide a convenient means for laying down a layer of asphalt on a road bed. An asphalt antistrippant causes asphalt to adhere to the rock or aggregate with which it is frequently mixed in road construction. The antistrippant is particularly useful if he road is wet. It functions by adsorbing onto the surface of the rock, which is usually silica. Adsorption is so strong that water on the surface of the rock is replaced. The fatty tails point away from the surface of the rock and are solvated by the asphalt. In this way, aminoamides and imidazolines facilitate the bonding between the asphalt and the rock.

13.5 AZELAIC, PELARGONIC, AND PETROSELINIC ACIDS

Oleic acid may be cleaved at the double bond by treatment with ozone from an electrical discharge. Intermediate aldehydes form that can be oxidized to acids *in situ*.



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow{O_3} CH_3(CH_2)_7CHO + OHC(CH_2)_7COOH$$

$$CH_3(CH_2)_7CHO \xrightarrow{O_2} CH_3(CH_2)_7COOH \qquad OHC(CH_2)_7COOH \xrightarrow{O_2} HOOC(CH_2)_7COOH$$

A petrochemical-based pelargonic acid process has been developed by Celanese, and thus once more petrochemicals have encroached on natural products. The Celanese process involves the linear hydroformylation of 1-octene, followed by oxidation of the resulting aldehyde (Section 4.12.2).

Both azelaic and pelargonic acids are raw materials for specialty polymers and polyesters for synthetic lubricants. Thus a typical first generation synthetic automotive lubricant useful at very low temperatures is the diisodecyl or ditridecyl ester of azelaic acid. The pelargonic acid also finds its way into synthetic lubricants by way of pentaerythritol pelargonate (Section 3.11.3). However, the most important material of this type today is the trimer of 1-decene (Section 3.3). A lubricant used in automobiles is actually a mixture of all three. In comparison with petroleum lubricants they are said to provide greater lubricity, better engine protection, and lower gasoline consumption. They are also easier to recycle. They may be blended with oil derived hydrocarbons, which reduces the cost but increases the difficulty of recycling.

Odd number carbon atom acids are rare in nature and in industrial chemistry. Azelaic and pelargonic are the most accessible. It appears that odd number carbon acids are often more surface active than are those with an even number.

In an effort to find natural products to compete with petrochemicals, some effort is being invested in the production of seed oils from *umbelliferae* (e.g., coriander). Their seeds are rich in petroselinic acid, an isomer of oleic acid with a *cis*-6 double bond. Ozonolysis followed by oxidation gives adipic and lauric acids, products with larger markets than azelaic and pelargonic acids but adipic acid is more readily available from petrochemical sources (Section 7.2.1).

$$CH_3(CH_2)_{10}CH{=}CH(CH_2)_4COOH \xrightarrow[(2)\ O_2]{(1)\ O_3} CH_3(CH_2)_{10}COOH + HOOC(CH_2)_4COOH$$

Petroselenic acid Lauric acid Adipic acid

13.6 FATTY ALCOHOLS

Fats and oils may easily be "split" to fatty acids and glycerol (Section 13.1). They can also be converted to fatty alcohols and glycerol by hydrogenolysis (Fig. 13.2). Because the fatty acid groups have mixed chain lengths, a mixture of fatty alcohols results. The hydrogenolysis was originally carried out with sodium in ethanol—the Bouveault–Blanc reaction—but hydrogen and a copper chromite catalyst at high pressures are now used. The products differ in that the latter method hydrogenates all the double bonds in the fatty alcohol, whereas the Bouveault–Blanc procedure leaves them intact. A proprietary chromite catalyst, however, is said to preserve the double bonds.

In practice it is easier to convert the fatty acid in the triglyceride to its methyl ester by alcoholysis with methanol and then to subject the methyl ester to hydrogenolysis. Most vegetable oil-based alcohols are made in this way.

While esters undergo hydrogenolysis to fatty alcohols fairly easily, reduction of a fatty acid to a fatty alcohol is more difficult. A clever procedure that brings it about involves a copper chromite catalyst (as above) in a slurry in fatty alcohol. The small amount of alcohol esterifies some of the fatty acid, the hydrogenolysis catalyst serving also as an esterification catalyst. The ester undergoes hydrogenolysis (Fig. 13.5) to yield a fatty alcohol, which esterifies more of the fatty acid to yield an ester for further hydrogenolysis. Thus, even though the feed is fatty acid, an ester forms *in situ* for the hydrogenolysis. Since this is a high molecular weight ester, it reacts more slowly than a methyl ester, but the process is still useful industrially.

The hydrogenolysis of the methyl or of fatty acids takes place at 250–300°C and 200–300 bar. Catalysts that cause lower molecular weight esters to undergo hydrogenolysis at considerably milder conditions such as 5–25 bar have been described (Section 3.7.2). Conceivably modifications of these catalysts could be used for the hydrogenolysis of fatty acid esters under less strenuous conditions.

Fatty alcohols as well as α-olefins may also be obtained from ethylene oligomerization by use of aluminum trialkyls (Section 3.3.2) or by the Shell SHOP process (Section 3.3.4). Here again petrochemicals have made an impact on traditional processes, but the vegetable oil based routes, used primarily by Henkel in Germany and Proctor and Gamble in the United States, are competitive, at least when vegetable oil prices are low. Together, the two processes accounted for 980 million lb of alcohols in the United States in 2000. Worldwide demand was 1615 million lb.

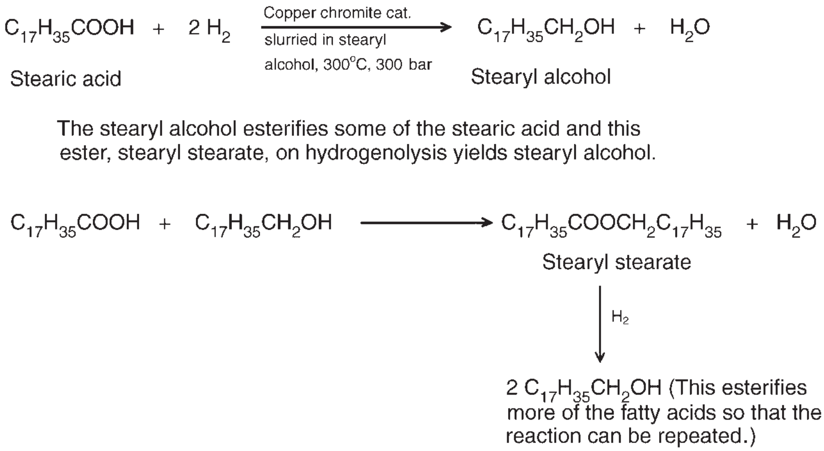
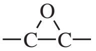


FIGURE 13.5 Hydrogenolysis of fatty acids.

The possibility of using triglycerides directly in a hydrogenolysis reaction has long been discussed but never achieved commercially. The proposed catalyst is copper chromite in the form of lumps, and the reaction is run at 180–250°C at pressures as high as 280 bar.

The special role now occupied by straight-chain primary alcohols in detergent technology results not only from the excellent detergent properties of their derivatives but also because products based on them biodegrade more quickly than compounds containing a benzene ring. Furthermore, degradation of benzene ring containing detergents eventually leads to phenols, and these are toxic to fish. This has been hotly contested by the manufacturers of alkylbenzene sulfonates who maintain that their products are completely biodegradable.

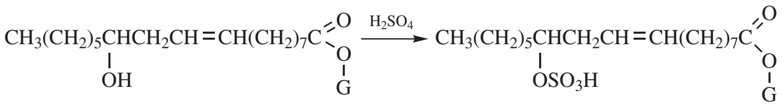
13.7 EPOXIDIZED OILS

Unsaturated fats and oils can be epoxidized so that some of the double bonds are replaced by  groups. These compounds are added to PVC often together with metal soaps to prevent degradation by light and heat.

Epoxidized oils are also secondary plasticizers, that is, they add their softening power to that of any plasticizer that softens PVC when used on its own. Epoxidation of fatty acid esters such as butyl or hexyl oleate or “tallate” gives a primary PVC plasticizer (see note at end of this chapter). Such materials are widely used in the United States where soybean oil is produced on a large scale. In 2001, 70–80 thousand tonnes of epoxidized soya oils were produced in the United States, representing about 7.5% of total plasticizer production. In Western Europe, on the other hand, epoxidized oils are normally used only for their stabilizing properties (see note at the end of this chapter).

13.8 RICINOLEIC ACID

Ricinoleic acid, with its OH group, is found as its triglyceride only in castor oil. Well over 100 million lb of castor oil are consumed yearly in the United States, the largest application being in paints and varnishes. Dehydration of the acid gives an isomer of linoleic acid that can be used in nonyellowing protective coating formulations. Castor oil itself may also be dehydrated to give a useful drying oil and it may be sulfated to give Turkey Red oil, a textile dye leveler. It is also used as a polyol (three hydroxyls per molecule of oil) in polyurethane production.



$$CH_3(CH_2)_5\underset{OH}{CH}CH_2CH{=}CH(CH_2)_7C(=O)OG \xrightarrow{H_2SO_4} CH_3(CH_2)_5\underset{OSO_3H}{CH}CH_2CH{=}CH(CH_2)_7C(=O)OG$$

G = glycerol nucleus

Turkey red oil

High-temperature cleavage of ricinoleic acid at 275°C with concentrated aqueous sodium hydroxide gives 2-octanol and sodium sebacate.

$$\underset{\text{Ricinoleic acid}}{CH_3(CH_2)_5CHOHCH_2CH{=}CH(CH_2)_7COOH} \xrightarrow{NaOH}$$

$$\underset{\text{2-Octanol}}{CH_3(CH_2)_5CHOHCH_3} + \underset{\text{Sodium sebacate}}{NaOOC(CH_2)_8COONa}$$

2-Octanol was an important foam depressor prior to the advent of the silicones. Sebacic acid condenses with hexamethylenediamine to give the specialty polyamide, nylon 6,10. Its dioctyl ester is an excellent PVC plasticizer, but its properties rarely justify its high price.

Thus far, castor oil has been the only source of sebacic acid, although a Japanese process has been described for the electrodimerization of 2 mol of adipic acid with elimination of two molecules of carbon dioxide.

Dry distillation of the sodium or calcium salt of ricinoleic acid at 500°C breaks the carbon chain between the eleventh and twelfth carbon atoms to yield *n*-heptaldehyde and undecylenic acid (Fig. 13.6). The heptaldehyde may be reduced to *n*-heptanol, which is an acceptable plasticizer alcohol. The undecylenic acid is treated with hydrobromic acid in the presence of peroxide so that it will add "anti-Markovnikov." Replacement of the bromine with an amino group gives ω-aminoundecanoic acid (the real reason for the process), which can then be polymerized to nylon 11. Nylon 11 is used in highly specialized formulations and never became a tonnage product.

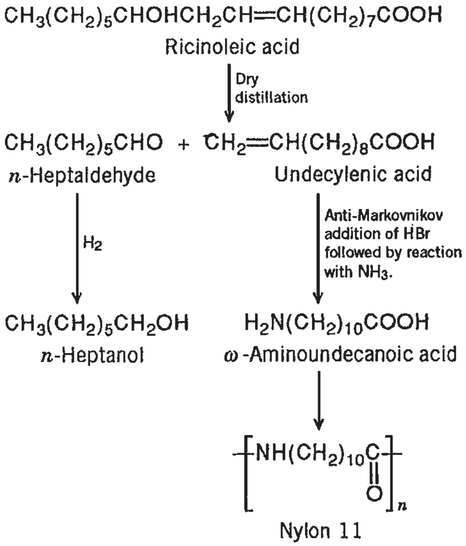


FIGURE 13.6 Nylon 11 from castor oil.

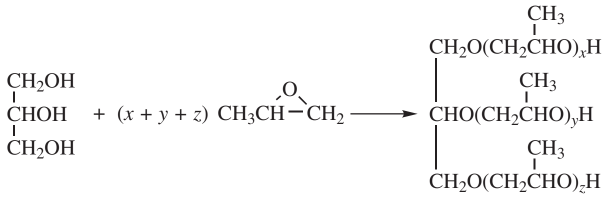
Undecylenic acid, as its zinc salt, is a fungicide effective against *tinea pedis* or athlete's foot.

13.9 GLYCEROL

We have already described the production of glycerol from fats and oils (Section 13.1) and from propylene by way of allyl chloride (Section 4.14.2). Its major uses are in the formulation of cosmetics, toiletries, foods, and beverages for its moisturizing, lubricating, and softening characteristics. It is also a humectant in tobacco and serves as a plasticizer for cellophane. United States production of refined glycerol in 2001 was 385 million lb.

Dynamite is glyceryl trinitrate (nitroglycerin) adsorbed on wood pulp. The compound is also used as a coronary vasodilator for *angina pectoris.* It is delivered either as a sublingual tablet or a transdermal patch. Although it has been used for at least a century, its mode of action via the blood's nitric oxide pathways has only recently been discovered. Glycerol competes with other polyols such as pentaerythritol and sorbitol as a raw material for alkyd resins (Section 9.1.1) and for polyethers for polyurethanes (Section 7.3.1).

Glycerol's most important chemical use is in alkyd resins and to a lesser extent in unsaturated polyester resins. Alkyds are condensates of glycerol or pentaerythritol (Section 3.11.3) with phthalic anhydride (Section 9.1.1) and fatty acids. They are the major vehicles for oil-based paints, but their use is declining because of the trend toward solvent-free coatings. When reacted with propylene oxide, glycerol yields a coreactant that gives polyurethane resins (Section 7.3.1) with isocyanates. Trimethylolpropane is usually preferred to glycerol in this application.



Glycerol monoesters, for example, the monooleate and the monostearate, are used as nonionic surfactants especially in the food industry. Triacetin (glyceryl triacetate) is an antifungal used against athlete's foot, a fixative in perfumery and a plasticizer for the cellulose acetate filter tips in cigarettes.

13.10 ALCOHOLYSIS OF FATS AND OILS

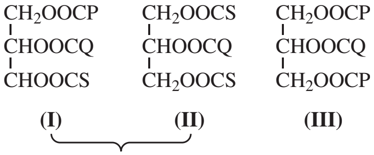
One of the most important commercial reactions of fats and oils is ester interchange or alcoholysis. Mono- and diglycerides for food emulsifiers are made this way—by

Eastman, for example. If a triglyceride is heated with a polyol such as glycerol or pentaerythritol in the presence of a suitable catalyst such as sodium methoxide, mixed partial esters are obtained. The partial esters may then be reacted with a dibasic acid or its precursor to give an oil modified alkyd resin (see note at the end of this chapter). If the partial esters are reacted with toluene diisocyanate, oil modified urethanes are obtained. The mixture of mono- and diglycerides is also widely used in food emulsifiers

13.10.1 Cocoa Butter

Transesterification of triglycerides has a significant application in the production of synthetic cocoa butter. As a general rule, triglycerides from animal sources (fats) are solid at room temperature while fish and vegetable oil triglycerides are liquid. Cocoa butter is unique in being the only solid vegetable triglyceride. It is pressed from cocoa beans that have been harvested and fermented so that the pulp can be drained.

Cocoa butter consists of triglycerides that are mixed esters of palmitic acid ($C_{15}H_{31}COOH$), oleic acid ($C_{17}H_{33}COOH$), and stearic acid ($C_{17}H_{35}COOH$). Only the oleic acid contains a double bond, hence the high-melting point. If the alkyl residues are represented as P, Q, and S, respectively, then the main triglycerides in cocoa butter are **(I)** and **(II)** below.



$$\underbrace{\begin{array}{l} CH_2OOCP \\ | \\ CHOOCQ \\ | \\ CHOOCS \end{array}\quad \begin{array}{l} CH_2OOCS \\ | \\ CHOOCQ \\ | \\ CH_2OOCS \end{array}}_{\text{Cocoa butter}} \quad \underbrace{\begin{array}{l} CH_2OOCP \\ | \\ CHOOCQ \\ | \\ CH_2OOCP \end{array}}_{\text{Palm oil}}$$

(I) **(II)** **(III)**

Cocoa butter Palm oil

Nature, in her wisdom, has not provided the correct ratio of cocoa to cocoa butter in the cocoa bean, for there is not enough butter to turn all the cocoa solids into chocolate. Surplus cocoa solids may be sold on their own as the base for beverages or blended with alternative fats to give a low grade chocolate which, in some countries, cannot even be sold under the name of chocolate.

The substitute fats have two limitations. They lack the volatile flavor constituents of cocoa butter and they have the wrong melting characteristics. Cocoa butter melts over a range and becomes completely liquid just below the temperature of the mouth, hence a high-quality chocolate will “melt in the mouth” in a satisfying way.

Cocoa butter is expensive but palm oil, which resembles it in structure, is cheap and readily available. Unilever devised a process in which a mixture of palm oil and stearic acid was treated with a 1,3-specific lipase immobilized on kieselguhr. The solvent was *n*-hexane saturated with water. The tiny amount of water that dissolves in hexane means that appreciable overall hydrolysis does not take place. The processes of hydrolysis and reesterification take place at 313°C over a few hours.

Unfortunately, it was not possible to reproduce the flavour constituents of cocoa butter and this, together with labeling regulations, means that the process is currently being used only in a few countries on a small scale. If the flavor constituents could be synthesized, the situation might change. The potential market is huge. World production of cocoa butter is about 1.5 million tonnes compared with about 16 million tonnes of soybean oil and 6 million tonnes of butter. The British are the world's top chocolate eaters. In 2001, they had net imports of 30,000 tonnes of cocoa butter and ate 9.37 kg of chocolate per person compared with a mere 5.42 kg/person in the United States.

13.11 THE FUTURE OF FAT AND OIL CHEMISTRY

Although fat and oil chemistry is mature, several developments have reawakened interest. On the health side, there is the growing problem of obesity and excessive fat intake. On the pharmaceutical side, there is the physiological role played by fatty acids, and the use of oily fish and fish oils as diet supplements (Section 13.1). Arachidonic acid, 5,8,11,14-eicosatetraenoic acid, has been shown to be the progenitor of the prostaglandins, remarkable chemicals with multiple physiological functions that occur in minute quantities in the body. Among other functions, good and bad, two of them cause inflammation. Their formation is inhibited by aspirin and this accounts for that drug's efficiency. In addition, there is interest in fat substitutes, biodegradable surfactants, and fuels and lubricants.

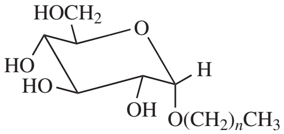
13.11.1 Non-Caloric Fat-Like Substances

There is a huge market for nonnutritive substances that function like fats for those who feel themselves to be overweight. Proctor and Gamble developed a fully esterified fatty acid ester of sucrose called "Olestra." It was said to have the mouth feel, taste, and cooking and baking functionality of triglyceride fats. The product was made by an ester interchange reaction between sucrose, dissolved in water and surfactant, with fatty acid methyl esters. Apparently, esters from several oils are useful, but the patents stress the highly unsaturated safflower oil.

The methyl esters were prepared by an alcoholysis reaction between safflower oil and methanol. The coproduct was glycerol and, had the product been a success, it might have led to a 50% world oversupply of glycerol. The problem, however, did not arise. Olestra was commercialized initially in a brand of potato chips. It turned out to deplete oil-soluble vitamins, which had to be replaced in diet or added to the product itself. Its lubricating properties, and the fact that it was not broken down in the digestive system meant that, in some consumers, it led to anal leakage. The consumer response was poor and Proctor and Gamble have sold the operation. It is, however, still available in low calorie potato chips.

13.11.2 Alkyl Polyglycosides

A family of nonionic surfactants for detergents, commercialized by both Henkel and Air Liquide in the early 1990s, are called alkyl polyglycosides and are the first important fatty acid derivatives with an acetal linkage. They comprise acetals of a mixture of mono- and disaccharides of glucose, from which an acetal or glucoside has been formed with a fatty alcohol with 10–14 carbon atoms. The formula for a product from glucose and an alcohol where $n = 9$–13 is



The use of the term glycoside indicates that sugars other than glucose may be involved. The preferred process for manufacture appears to involve two steps. In the first, the sugar reacts with *n*-butanol in the presence of weak acid to form an acetal. In the second, this intermediate reacts with a C_{10}–C_{14} fatty alcohol mixture to give the glucoside surfactant, with the release of the *n*-butanol for recycle.

The products are biodegradable and are said to be "green" since the sugar portion comes from corn starch and the fatty alcohols from coconut or palm kernel oil. The products are being targetted for shampoos and specialties such as cosmetics, as well as for laundry and dishwashing detergents.

These products are related to the sugar esters—C_{12} to C_{18} partial fatty acid esters of sucrose—which have been popular in Japan as nonionic rapidly biodegradable surfactants for many years. In 1995, Proctor and Gamble announced that it was replacing a portion of the alkylbenzene sulfonate in heavy duty detergents with a sugar-based surfactant.

13.11.3 Fatty Acid-Based Fuels and Lubricants

Concern about biodegradability, pollution, and depletion of nonrenewable resources has led to the development of fuels and lubricants based on fats and oils. Thus in the early 1990s "biodiesel" fuels emerged. These consisted of methyl esters of animal or vegetable oils such as rapeseed, sunflower, or tallow compounded with additives similar to those used for petroleum-based diesel fuel. The triglyceride-based products, unlike their petroleum-based counterparts, are free of sulfur. On combustion they are said to produce less smoke, less hydrocarbons, and less carbon monoxide. Nitrogen oxides emission, however, is not reduced. The interest in biodiesel fuels has also increased because they burn more cleanly.

Although non-polluting biodegradable fuels that burn more cleanly are attractive, there are two problems. The first is how to dispose of coproduct glycerol, particularly since it appears that methyl esters made by methanolysis of fats will be the primary materials. The second problem is one of supply. In 2000, the world produced about 111 million tonnes of fats and oils, of which 88% was used for human food. Correspondingly, the United States alone used about 90 million tonnes of diesel fuel in 1992. It is therefore doubtful that oil and fat production can be increased to the point that will allow it to gain more than a niche market as a diesel fuel replacement. However, in areas in the world with a high ecological sensitivity, dimer acid esters (Section 13.3) have been used as fuel in two-cycle engines. Introduced in the early

1990s were oils for two-cycle engines based simply on esters of acids. These were intended as fuels for engines for lawnmowers, outboard motor boats and for engines for motor cycles, to replace the normal smog-producing motor oil–gasoline mixture. The problem with the motor oil–gasoline is well demonstrated in Bangkok, where two-cycle engines on motorcycles contribute to a serious smog problem. This is an example of a niche market for fatty-based fuels. They compete with a combination of gasoline with polybutenes (Section 5.2.3) and mixtures of propane and butane (LPG; Section 2.1). The latter are actually in use in Bangkok today, an infrastructure having been developed for LPG distribution.

Of potential importance is the use of biodegradable fatty materials as lubricants. The lubricity of fatty materials is well established, and our ancestors used tallow on the moving parts of their chariots in 1400 BC. Esters with lubricant properties have been know since World War II and synthetic lubricants for automobiles today may contain pentaerythritol tetraesters (Section 3.5) and esters of dibasic acids such as the di-(2-ethylhexyl) ester of azelaic acid (Section 13.5). Such compounds become much more biodegradable in the form of their fatty acid counterparts, and such materials are being proposed for use in automobiles, and as metal working lubricants, turbine oils, hydraulic fluids, and functional fluids generally.

NOTES AND REFERENCES

The classic work on the chemistry of fats and oils is *Bailey's Industrial Oil and Fat Products*, 5th ed., Y. H. Hui, Ed., John Wiley & Sons, Inc., New York, 1996, in five volumes. Another authoritative book is R. D. O'Brien, *Fats and Oils: Formulating and Processing for Applications*, Basle: Technomic Publishing, 1997. It aims especially to illustrate problem solving in processing and products. A conference on agriculture as a source of raw materials is reported in *Progress in New Crops*, J. Janick, Ed., Alexandria, VA, ASHS Press, 1997. A review of the oleochemicals industry was published by Nexant/Chemsystems, White Plains, New York in 2001. There is an excellent although old series of articles on oleochemistry in a special issue of the *J. Oil Chemists' Society*, February, 1984. See also G. Hoffman, *Chemistry and Technology of Edible Oils and Fats and their High Fat Products*, Academic, New York, 1989; D. M. Small, *The Physical Chemistry of Lipids: Handbook of Lipid Research*, Plenum, New York, 1986, *Developments in Oils and Fats*, R. J. Hamilton, Ed., Blackie, London, 1994; and F. D. Gunstone and F. A. Norris, *Lipids in Foods: Chemistry, Biochemistry and Technology*, Pergamon, Oxford, 1983, on which we have drawn. Developments in the oleochemical market are surveyed in Gunstone, F. D., *Oils and Fats go to Market*, *Chem. Brit.* **26**, 569 (1990).

Other statistics on the world oil market come from *Fats and Oils, Oilcakes and Meals*, 1994, Basic Foodstuffs Service, Commodities and Trade Division, FAO, United Nations, Rome. Problems with erucic acid and glucosinolates are dealt with in P. N. Maheshwari, D. W. Stanley, and J. I. Gray, *J. Food Protection* **44**, 459 (1981) and J. M. Concon, *Food Toxicology*, Dekker, New York, 1987, Part A, pp. 352ff and 422ff.

H. B. Patterson has written three authoritative books on oil processing—*Hydrogenation of Fats and Oils*, Appied Science, New York, 1983, *Handling and Storage of Oilseeds, Oils, Fats and Meal*, Elsevier, Amsterdam, The Netherlands, 1989, and *Bleaching and Purifying Fats and Oils*, American Oil Chemists' Society, Chicago, IL, 1993.

Section 13 The oil prices came from the then current *Chem. Mkt. Rep.*

Section 13.1 A volume devoted to fatty acid chemistry, E. H. Pryde, Ed., is *Fatty Acids*, American Oil Chemists' Society, Chicago, IL, 1979, reprinted 1985. See also the various articles in *Applewhite*, cited in the note to Section 13.11.

Information and statistics about fatty acids may be obtained from the Fatty Acids Producers' Council, 475 Park Ave. So., New York, 10016.

The role of fats and oils in cardiovascular disease is discussed in innumerable articles including S. Sanders, *Chem. Ind.* 426 (1990), and J. Beare-Rogers, *Chem. Ind.* 131 (1995).

The extraction of oils with supercritical carbon dioxide is discussed by J. M. Snyder, J. P. Friedrich, and D. Christiansen *J. Am. Oil Chem. Soc.* **61**, 1851 (1984) and G. R. List and J. P. Friedrich, *J. Am. Oil Chem. Soc.* **66**, 98 (1989).

Stigmasterol is one of the few naturally occurring sterols with an unsaturated side chain. The double bond makes possible side chain cleavage and, with subsequent chemical reactions, transformation to progesterone. This in turn is converted to cortisone. A key step is the enzymatic insertion of oxygen in the 11-position. See *Pharmaceutical Chemicals in Perspective*, B. G. Reuben and H. A. Wittcoff, John Wiley & Sons, New York, 1989, p. 325.

The hydrophilization process is described by J. C. Stein, *J. Am. Oil Chem. Soc.* **45**, 471 (1968).

Bioconversion of fatty acids is discussed in *Chem. Mkt. Rep.*, September 30, 2002.

Section 13.2 The use of trifatty amines in solvent extraction operations has been described by J. E. House, *J. Am. Oil Chem. Soc.* **61**(2), 357 (1984).

Organoclay technology has been described by W. S. Mardis, and *J. Am. Oil Chem. Soc.* **61**(2), 382 (1984).

Developments such as a high erucic acid oil are described by L. H. Princen and J. A. Rothfus, *J. Am. Oil Chem. Soc.* **61**(2), 281 (1984).

Section 13.6 The process for converting triglycerides to fatty alcohols by a one-step hydrogenolysis has been described in European Patent 334,118 (September 27, 1982) to Henkel.

Section 13.7 Isooctyl "tallate" is an isooctyl ester of tall oil fatty acids, predominantly a mixture of oleic and linoleic acids (Fig. 13.1). Plasticizers are discussed in detail in H. A. Wittcoff and B. G. Reuben, *Perspective*, Part II, cited in Section 0.4.2. The epoxidized oils stabilize PVC by mopping up free chlorine radicals that would otherwise cause the PVC chain to "unzip" in a free radical chain reaction. Market data on epoxidized soybean oil are confused. The last reliable figures from the US Bureau of the census show 62,383 tonnes production in 1991 as 7.5% of the total US plasticizer market. S. F. Thames and T. P. Schuman in R. D. O'Brien, *op. cit.* quote a world figure of 6.25% (100 billion lb) of the plasticizer market in 1996, but even if the figure refers to the plasticizer market not that for epoxidized soybean oil, it is still ridiculously large. The United States is said to have consumed 55,000 tonnes of soybean oil in plasticizers in 1996 so, assuming modest growth, our figure of 70–80 thousand tonnes looks reasonable.

Section 13.10 Oil-modified alkyds are discussed in more detail in H. A. Wittcoff and B. G. Reuben, *Perspective*, Part II, cited in Section 0.4.2*; see* Section 5.6.

Section 13.10.1 The cocoa butter transesterification is described in *Catalysis at Surfaces*, I. M. Campbell, cited in Chapter 16. More details are given in A. R. McRae, *Biochem. Soc., Trans.* **17**, 1146 (1989). The field is reviewed in J. L. Harwood, *Cocoa Butter: Food of the Gods?*, *Chem. Ind.* October 21, 1991, p. 753. The figures for UK chocolate consumption come from government and trade sources. Figures obtained by other official sources asking a sample of consumers to keep diaries of what they ate gave consumption about one-tenth of the actual figures, indicating that consumers regard chocolate as sinful.

Section 13.11 For a brief discussion of the arachidonic acid cascade and the functions of prostaglandins, see *Pharmaceutical Chemicals in Perspective*, cited above.

An excellent review of the use of enzymes for fatty chemical reactions has been authored by C. Wandrey, *"Biochemical Engineering for Oleochemicals,"* in Proceedings, World Conference on *"Oleochemicals into the 21st Century,"* T. H. Applewhite, Ed., American Oil Chemical Society, Champaign, IL, 1991.

Section 13.11.1 J. Spinner's article, entitled *"Olestra Update"* is found in *Applewhite*, cited in the note for Section 13.11.

Section 13.11.2 Alkyl polyglycoside development is described in by P. Lorenz, *Problem Solving with New Fatty Alcohol Derivatives*, in *Applewhite*, cited in the note for Section 13.11.

Section 13.11.3 Biodegradable lubricants are the subject of articles by H. Kohashi, *Application of Fatty Acid esters for Lubricating Oil* and L. Bogaerts, *Esters: Performance Oleochemicals for Food & Industrial Usage* in *Applewhite*, cited in the note for Section 13.11.

CHAPTER 14

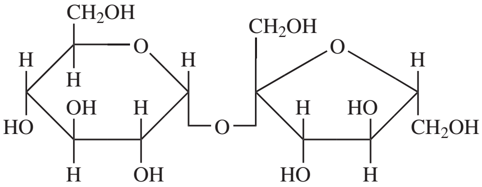
CARBOHYDRATES

Carbohydrate sources for chemicals may be subdivided into four main groups: sugars, starch, cellulose, and the so-called carbohydrate gums. In addition, there are miscellaneous sources such as the pentosans found in agricultural wastes from which furfural is made. We consider each of these as a source of chemicals. Fermentation processes are mainly carried out on carbohydrate substrates, so they too have been included briefly in this chapter.

14.1 SUGARS AND SORBITOL

For the chemist, the term sugar covers a multitude of mono-, di-, and trisaccharides composed of pentose and hexose units. In ordinary speech, however, it generally means sucrose. Sucrose is a major constituent of diet, and the average citizen of a developed country consumes approximately 40 kg—about two-thirds of his/her body weight—annually. It is the purest crystalline organic substance to be sold in quantity to the general public, routinely reaching 99.96% purity on an anhydrous basis.

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9



Sucrose

Sucrose is extracted from sugar cane, which is a member of the grass family, or sugar beet, which is a root crop. The cane is chopped and crushed and juice extracted sometimes with the aid of water or weak juice. The residue—bagasse—is a fairly pure cellulose and is either burned as fuel to make the sugar refinery self-sufficient for energy or converted to paper or hardboard. One tonne of bagasse at 51% solids provides the same amount of energy as a barrel of oil.

The juice is purified, clarified, and concentrated from about 85% water to 40% water in triple or quadruple effect evaporators, to conserve energy. Vacuum evaporation supersaturates the liquid, and seeding precipitates sugar crystals, leaving blackstrap molasses. This is used as cattle feed, as a substrate for fermentation to produce citric acid, for rum making, and for other fermentations. In chemical terms, the extraction of sugar beet is similar, although both processes are far more complicated than is indicated above.

World production and consumption of sugar are indicated in Figure 14.1. The European Union, India, and Brazil are the largest producers and consumers, the first growing sugar beet and the other two sugar cane. The European Union, Cuba, Australia, Thailand, and Brazil are the major exporters, and the CIS, the European Union, Japan, Indonesia and the United States are the major importers. The appearance of the European Union in both lists is a consequence of its bizarre system of subsidies.

There are few chemical uses for sucrose. Sucrose octaacetate is used as a denaturant in ethanol. The acetate, isobutyrate, and octabenzoate are used as plasticizers. The mono and difatty acid esters are surfactants, and sucrose polyether polyols may be used in polyurethane formulations. The bacteria *Leuconostoc mesenteroides* and *Lactobacteriacae dextranicum* convert sucrose to dextran, a polysaccharide consisting of a backbone of D-glucose units linked predominantly α-D($1 \rightarrow 6$). This is used as a plasma volume expander for transfusion for problems such as burns where there is a drastic loss of body fluids. Dextran competes with “natural” materials such as fresh frozen blood plasma and albumen, and with degraded gelatin and hydroxyethyl starch. In the past, the “natural” products have been preferred where available, but with the current anxiety about infected blood, dextran is likely to benefit.

D-Glucose, known as dextrose, is manufactured on a large scale from corn starch, which is hydrolyzed by a mixture of acid and the enzyme glucoamylase, producing a syrup of high nutritive value but not as sweet tasting as sucrose. Yields per acre of corn are so much higher than those of sugar cane that sweeteners obtained in this way are in principle cheaper than sucrose.

D-Fructose is isomeric with D-glucose but is sweeter, and therefore offers the opportunity for a reduced calorie diet without sacrificing “sweetness.” It is produced

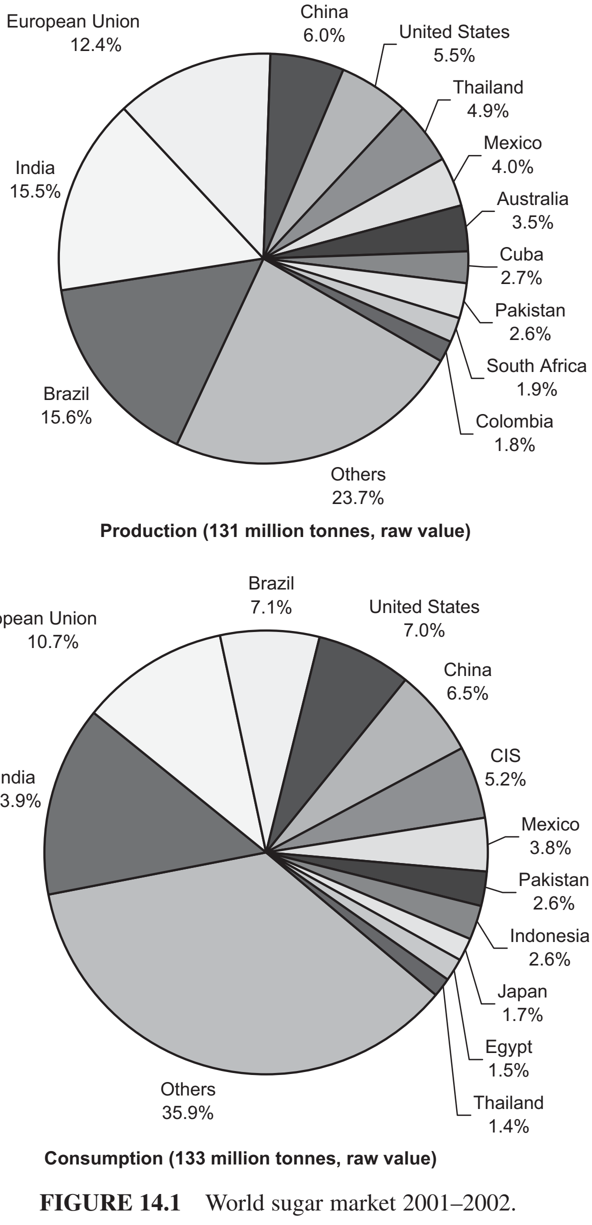
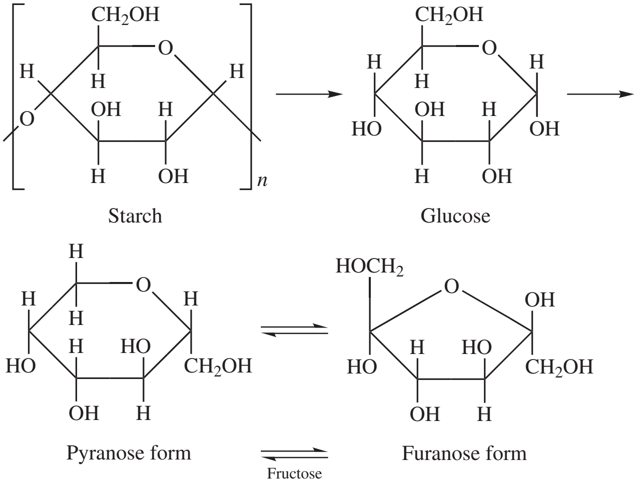


FIGURE 14.1 World sugar market 2001–2002.

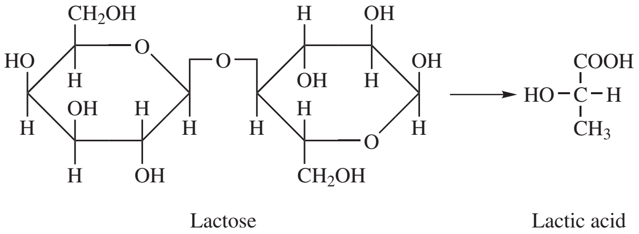
by the action of three enzymes on starch. The first is an immobilized amylase that degrades the starch to lower molecular weight polymers; the second is an immobilized amyloglucosidase that converts these oligomers to glucose; and the third is an isomerase that changes the glucose to fructose. The isomerase may be adsorbed on an insoluble carrier or fixed within the cellular microorganism in which it occurs.



Crystalline D-fructose is more hygroscopic than dextrose and requires special packaging. Hence, it is usually used as a syrup (high fructose corn syrup) in soft drinks, confectionery and foodstuffs.

Sweeteners based on corn make up about 40% of the United States sweetener market. High-fructose syrup production started in 1967, and by 1980 had overtaken the per capita consumption of glucose. In Western Europe, pressure from the sugar farmers has prevented the use of high fructose syrup within the European Community.

Lactose is the only other sugar available in large quantities. It is extracted from waste skim milk and is used as an acidulant in foods, in cheese production, in printing and dyeing, and in leather production. Fermentation of whey, lactose, sucrose, or glucose with *Bacillus acid lacti* or related *Lactobacilli* gives lactic acid:



Lactic acid is the monomer for a polymer, poly(lactic acid) or polylactate, which provides a biodegradable plastic (Section 17.3.11).

Glucose may be oxidized to gluconic acid, reduced to sorbitol, and lactonized to α-methylglucoside as shown in Figure 14.2. Gluconic acid is primarily used as a food additive, and α-methylglucoside has been of some interest in alkyd resins. Surfactants based on glucose and fatty alcohols are described in Section 13.11.2.

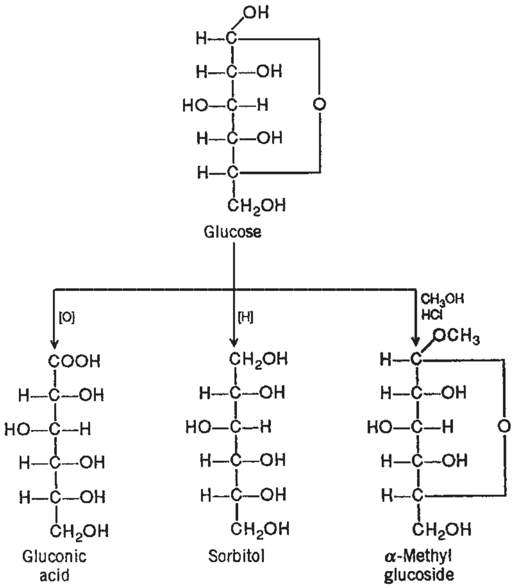
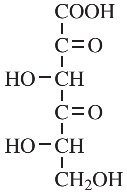


FIGURE 14.2 Reactions of glucose.

Sorbitol is the starting material for the classic synthesis of vitamin C (ascorbic acid) shown in Figure 14.3. The crucial stage is the second, and it is an early example of the use of biotechnology to supplement the synthetic skills of the chemist. Conversion of D-sorbitol to L-sorbose would present a formidable problem in organic chemistry. The appropriate bacterium, *Acetobacter suboxydans*, selectively oxidizes the hydroxyl group on the C2 of sorbitol, making feasible the remainder of the synthesis.

A biotechnological synthesis of ascorbic acid was announced in 1988 by Genencor International and Eastman Chemical. Glucose is converted to 2-keto-L-gulonic acid (see Fig. 14.3) in two steps as compared to five steps in the traditional process. In the first step, an organism such as *Erwinia herbicola* converts glucose to 2,4-diketo-L-gulonic acid:



$$\begin{array}{rl} & COOH \\ & | \\ & C{=}O \\ & | \\ HO- & CH \\ & | \\ & C{=}O \\ & | \\ HO- & CH \\ & | \\ & CH_2OH \end{array}$$

In the second step, the diketo compound is converted to 2-keto-L-gulonic acid using a *Corynebacterium*.

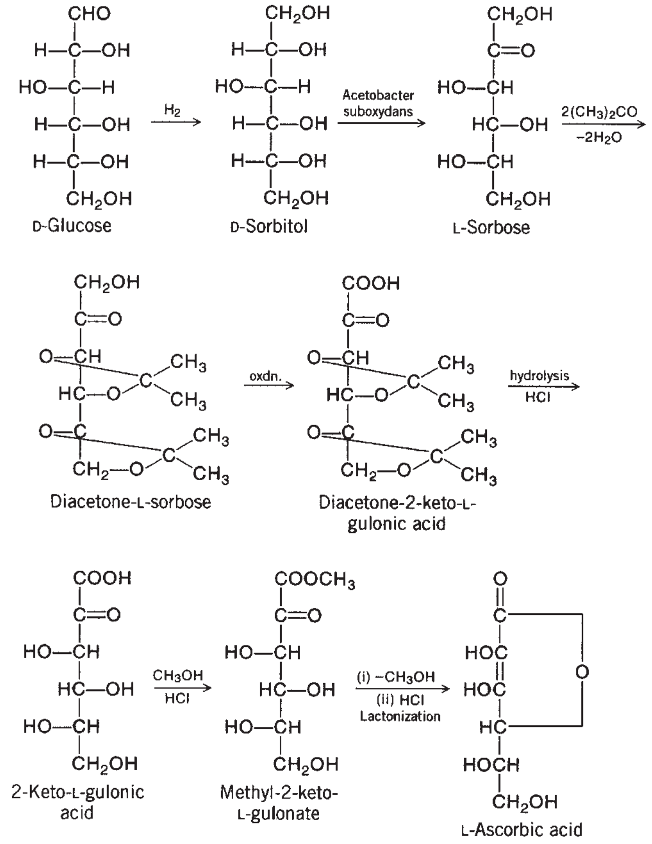


FIGURE 14.3 Synthesis of vitamin C (ascorbic acid).

Sorbitol is also the source of a range of surfactants—the sorbitan esters and ethoxylated sorbitan esters (Fig. 14.4). These have been marketed for about 40 years. Sorbitol is simultaneously dehydrated and esterified with stearic, palmitic, lauric, or oleic acid, to give mono- or trisubstituted sorbitan esters. A mixture of esters is obtained in both cases, and the hydroxyls are esterified more or less randomly. The sorbitol can also lose another molecule of water to give isosorbide, which remains in the reaction mixture and is also esterified. Sorbitan esters are often water insoluble but are used as solubilizers in the oil phase and are also approved for human consumption. Hence, they are used as emulsifiers in drinks, cosmetics, pharmaceuticals and foods. The most widely known trade name is “Span,” and a range of compounds is available depending on the esterifying groups.

Treatment of the sorbitan esters with ethylene oxide leads to an ethoxylation–transesterification process in which all four of the hydroxyls originally present in the sorbitan are ethoxylated and one or three fatty acid groups migrate to esterify some

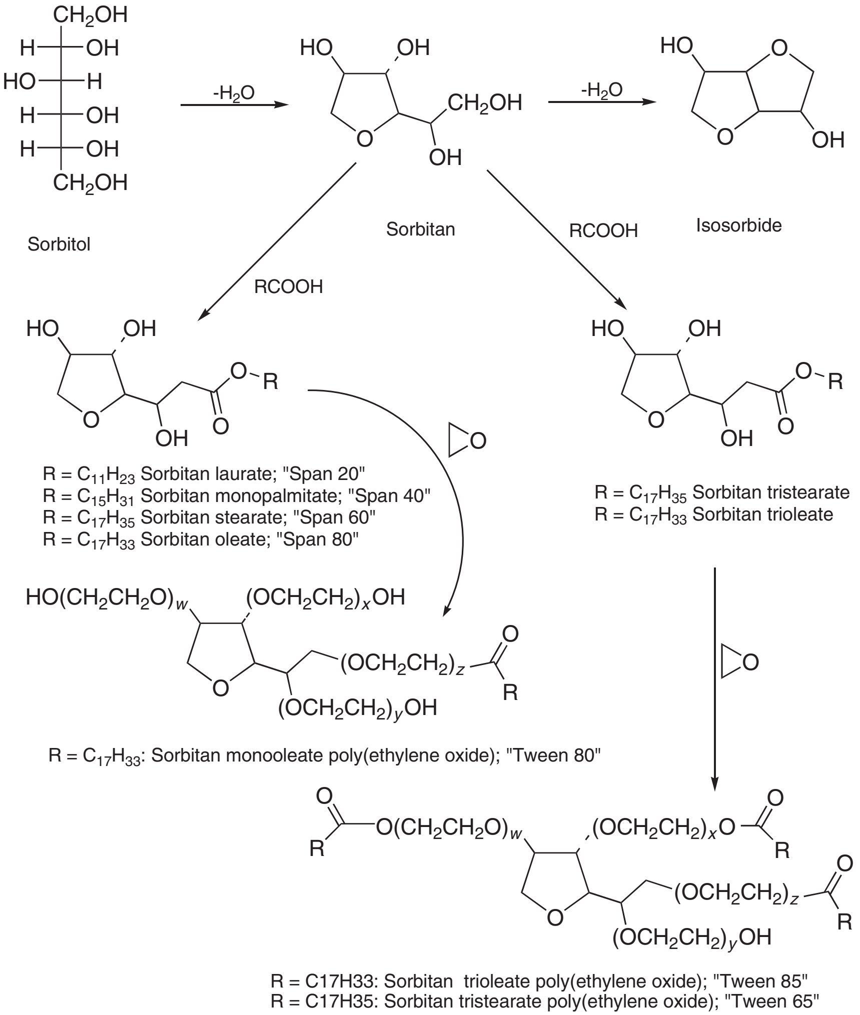


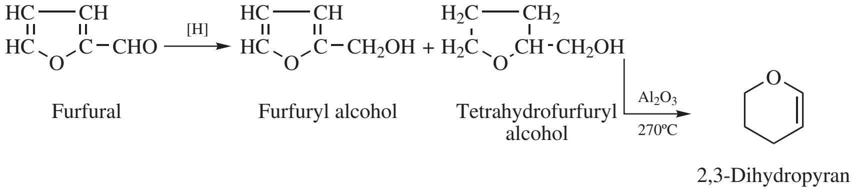
FIGURE 14.4 Sorbitan esters and ethoxylated derivatives ($w + x + y + z \approx 20$).

of the terminal hydroxyls. Again, the positions of the fatty acid residues are more or less random, and the positions shown in the figure are only illustrative. The ethoxylated derivatives are water soluble and are known as polysorbates or by the trade name “Tweens.” They are used as industrial emulsifiers, antistatic agents, fiber lubricants, and solubilizers. For example, Tween 60, an ethoxylated monostearate, is used to stabilize “synthetic” whipped cream, the stearate having less flavor than the oleate. Sorbitol is also used as a diluent in nonnutritive sweeteners, for example, mixed with aspartame to provide bulk, so that consumers can sprinkle teaspoonfuls of sweetener on their breakfast cereal instead of having to measure out a tiny quantity of pure aspartame.

14.1.1 Furfural

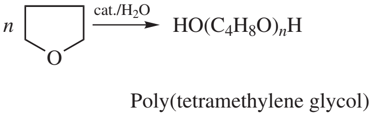
Oat hulls, corn cobs, sugar cane stalks, wood, and many other vegetable wastes contain polymers (pentosans) of pentose sugars such as arabinose. On dehydration with hydrochloric or sulfuric acid, furfural is produced. Furfural is used as a selective solvent in petroleum refining and has been used in the extractive distillation of butadiene to separate it from other C_4 olefins (Section 5.1). With phenol it gives phenol–furfuraldehyde resins, which are used to impregnate abrasive wheel and brake linings.

Reduction of furfural gives furfuryl alcohol and tetrahydrofurfuryl alcohol, and the latter can be dehydrated and its ring expanded by passage over an alumina catalyst at 270°C. The product is 2,3-dihydropyran. The largest use for furfural in the United States is for conversion to furfuryl alcohol, which in turn undergoes an acid-catalyzed condensation polymerization to yield resins useful as binders in the preparation of foundry cores for molding.



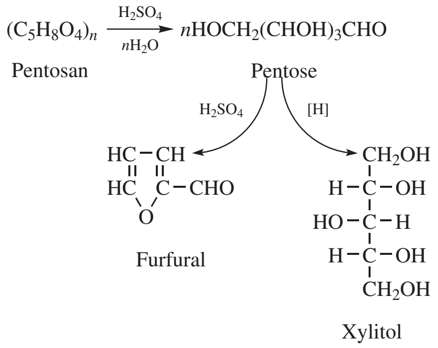
Tetrahydrofuran is made by the decarbonylation of furfural with a zinc–chromium–molybdenum catalyst followed by hydrogenation. It is also made by the dehydration of 1,4-butanediol (Section 10.3.1) and by the hydrogenation and hydrogenolysis of maleic anhydride or maleic esters. These are by far the largest sources, the furfural route accounting for less than 10% of US production.

Like ethylene and propylene oxides, THF can be oligomerized to a polyether with hydroxyl end groups. The polymer is called poly(tetramethylene glycol) and is a component of the elastomeric fiber, Spandex (Section 5.4).



Until 2001 there was a single major producer of furfural in the United States, Penn Specialties, who acquired the technology from Great Lakes Chemical, who in turn acquired it from the Quaker Oats Company, who pioneered it. About six tonnes of corn cobs, or other vegetable wastes are required for every tonne of liquid product, so collection of feedstock involves high labor costs, and Penn has since gone bankrupt.

Another development that bears on furfural is the interest in the sugar alcohol, xylitol, as an ingredient in chewing gum, candy, and sweet cereals to prevent dental caries. Xylitol, like furfural, is derived from pentosans. It is produced in a plant in Finland. A similar plant that was planned for the United States was never built.



14.2 STARCH

Starch is one of the most important chemical products of the vegetable kingdom and is found in practically all plant tissues, especially in seeds (e.g., wheat and rice) and tubers (e.g., potatoes). Commercial starch in the United States is extracted chiefly from corn and to a lesser degree from wheat. In Europe, potatoes are an important source.

The use of corn as a source of starch is only one of an extensive range of uses. It is primarily used in foodstuffs. Its protein, known as gluten, is used in various food formulations. Corn oil is one of the several important cooking oils. Meanwhile, starch itself has a value chain shown in Figure 14.5. About half the starch produced in the United States is hydrolyzed with hydrochloric acid to glucose or partially hydrolyzed to starch–glucose syrups that can be sold as such or isomerized to fructose (Section 14.1). Its conversion to sorbitol, sorbitol derivatives, and vitamin C have already been described. Starch-derived glucose is a substrate to produce, by fermentation, lactic acid, hence poly(lactic acid) (Section 17.3.11), and 1,3-propanediol (Section 14.5), hence poly(trimethylene terephthalate).

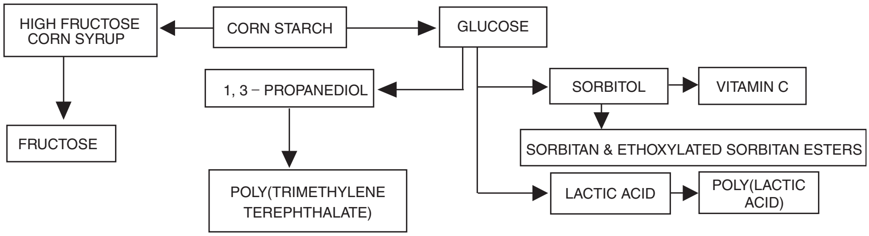
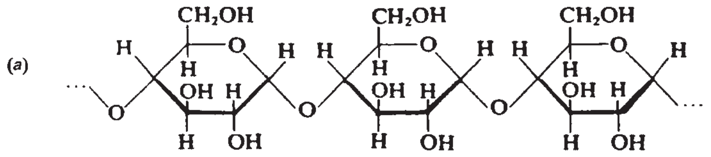
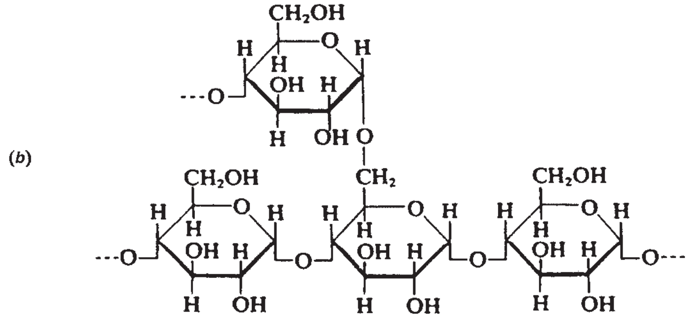


FIGURE 14.5 The corn starch value chain.

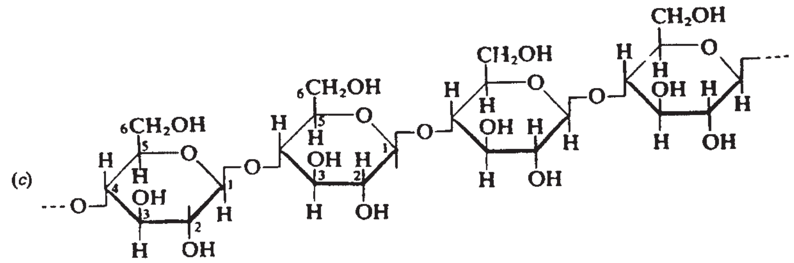
Chemically, starch comprises two distinct polymers of α-D-glucopyranoside. The linear polymer, amylose, is composed of several hundred glucose units connected by α-D-(1 → 4) glucosidic linkages (Fig. 14.6*a*). The branched-chain polymer, amylopectin (Fig. 14.6*b*), is of much higher molecular weight and contains between



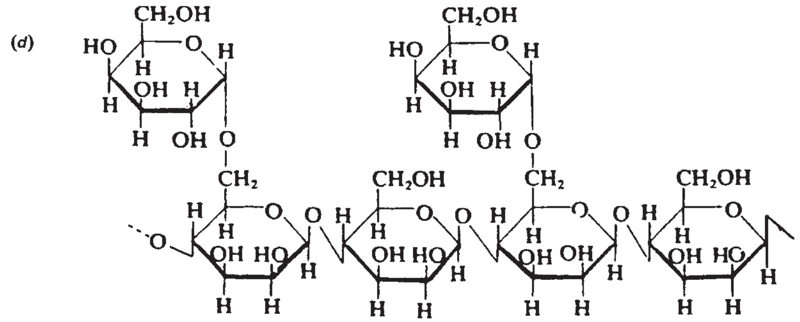
Part of amylose molecule showing α-D-(1→4)-glucosidic linkages



Part of amylopectin molecule showing chain branching and 1→6 bonds



Part of cellulose molecule showing β-D-(1→4)-glucosidic linkages



Part of guar gum molecule, showing chains of mannose units with pendant galactose units

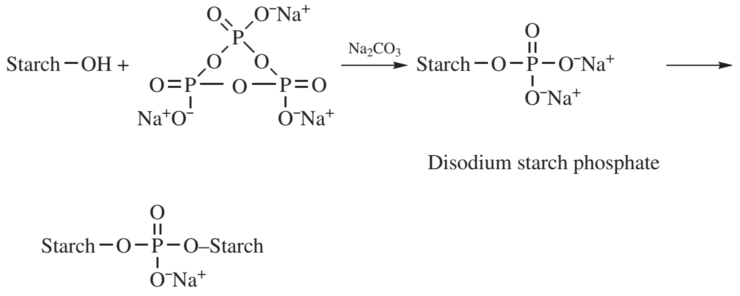
FIGURE 14.6 Starch, cellulose, and guar structures.

10,000 and 100,000 glucose units. The segments between the branched points contains about 25 glucose units joined as in amylose while the branched points are linked by α-D-(1 → 6) bonds. Most cereal starches contain about 75% amylopectin and 25% amylose.

Because amylose has straight chains, its molecules can approach each other within molecular range to form hydrogen bonds. This interaction is so strong that amylose can scarcely be dispersed in water. Amylopectin, on the other hand, has branched chains that have more difficulty in approaching each other, and it is therefore readily dispersed.

If starch, which is an amylose–amylopectin mixture, is dispersed in water, a gel results that forms a "skin" on standing. The skin is a result of hydrogen bonding. So-called waxy starches, such as waxy maize starch, which arose from genetic experimentation, are very high in amylopectin, and consequently they form gels that do not "skin."

Amylose is prevented from skinning if it is converted into a derivative such as the phosphate. Phosphorus oxychloride or sodium trimetaphosphate are the reagents. Only a small number of phosphate groups per polymer molecule are required to interfere with the hydrogen bonding. Consequently, starch phosphates are widely used as thickeners in the food industry and in other situations where a stable, high viscosity starch paste is required.



Disodium starch phosphate

Starch dihydrogen pyrophosphate

Other cross-linking agents for starch are also approved by the FDA, the most widely used being epichlorohydrin and linear mixed anhydrides of acetic and di- or tribasic carboxylic acids.

Starch is used in adhesives and as a size in textiles and paper manufacture. Sizing is a method for altering the surface properties of paper fibers. For example, many grades of paper are coated with an aqueous suspension of pigments (such as clay) with adhesives (such as starch) to provide a smoother surface, control the penetration of inks, and generally improve the paper's appearance. Dextrinized or degraded starch is used as an adhesive.

Starch acetates are made from starch and acetic anhydride, the extent of acetylation being measured by the degree of substitution (DS). This is the number of hydroxyl groups per glucose unit that are esterified. Total substitution therefore represents a DS of 3. Starch acetates are used in the food, paper, and textile industries.

Hydroxyethylstarch, made by the action of ethylene oxide on starch, is used in paper coating and sizing, because it disperses more easily than starch itself and provides a dispersion of better clarity. Starch may also be reacted with cationic reagents such as dimethylaminoethyl chloride to give "cationic starch," which is used to impart greater strength to paper products. Acrylonitrile may be polymerized onto a starch polymer with the aid of a ceric sulfate catalyst to give a graft copolymer which, on partial hydrolysis of the nitrile groups, is capable of absorbing large amounts of water (Section 4.7).

There are many other chemically modified starches that find specialized uses in the food industry but which are outside the scope of this book, and the reader is referred to sources quoted at the end of this chapter.

14.3 CELLULOSE

Cellulose is the primary substance of which the walls of vegetable cells are constructed. It occurs in plants, wood, and natural fibers, usually combined with other substances such as lignin, hemicellulose, pectin, fatty acids, and rosin. It accounts for about 30% of all vegetable matter. It may be represented by the formula $(C_6H_{10}O_5)_n$.

Cellulose is a linear polymer composed largely of glucose residues in the form of anhydroglucopyranose joined together by β-glucosidic linkages (Fig. 14.6*c*). The β-linkages make the cellulose molecule very stiff compared with amylose, which has α-glucosidic linkages. It also makes cellulose more difficult to hydrolyze than starch. It is this difficulty that makes cellulose indigestible by humans. Accordingly, one of its uses is in diet foods, providing bulk and satiety but not calories. Had nature not insisted on β-linkages, a vast source of nutrition would be available to humans. On the other hand, cellulose with α-linkages would not be stiff and would not possess the structural properties it has in wood or the strength it has in textiles. Cows and other ruminants have digestive systems containing organisms with enzymes that hydrolyze cellulose, and they are therefore able to use grass and similar materials for food.

Cellulose may be obtained from wood or derived in very high purity from cotton linters. The majority of production is used in paper manufacture. In the manufacture of the pulp used in cheap paper, the wood fibers are simply pulped mechanically. In the premium chemical pulp, lignins, fatty acids, and rosins are first removed by sodium hydroxide treatment.

Cellulose also has a range of chemical uses. Cellulose derivatives (Fig. 14.7) may be water soluble like methylcellulose, hydroxyethylcellulose, or sodium carboxymethylcellulose, or water insoluble like the cellulose esters and ethylcellulose.

Methylcellulose, sodium carboxymethylcellulose, and hydroxyethylcellulose are all thickening agents and form protective colloids. For example, they are used in water-based latex paints to produce desirable flow and viscosity and to help stabilize the emulsion and pigment dispersions. Protective colloids affect the washability, brushability, rheological properties, and color acceptance of a paint. The same properties make them useful in foods such as ice cream and in inks and adhesives.

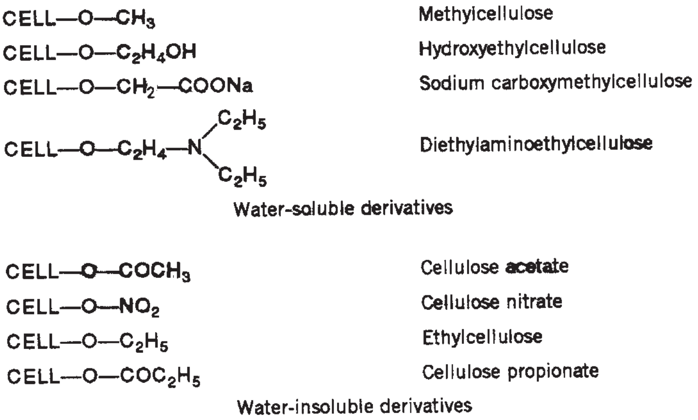


FIGURE 14.7 Cellulose derivatives. (Cellulose is represented as CELL-OH.)

Methylcellulose is also used as a base for paper coatings since it is a good film former. Hydroxyethylcellulose is an adhesive and a binder in woven fabrics. Sodium carboxymethylcellulose (CMC) has a major use as a soil suspending agent in detergents, for if it were not present the dirt would tend to redeposit on the articles being washed. Instead, the CMC forms a protective colloid and holds it in suspension. CMC is used in textile sizing, paper coating, and in oil well drilling mud, a material that helps to bring to the surface the dirt and rock particles dislodged by the drill. Diethylaminoethylcellulose is a cationic material useful in cotton finishing.

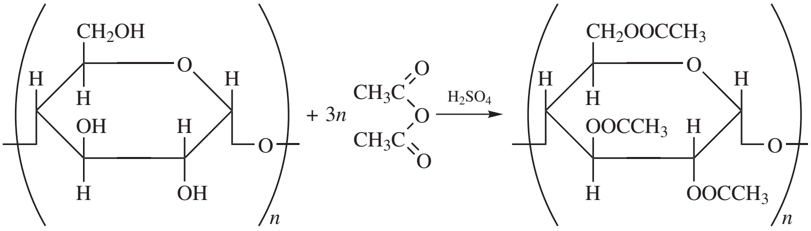
Sodium carboxymethylcellulose is made by spraying powdered cellulose first with sodium hydroxide solution and then with chloroacetic acid. The product contains some sodium chloride, which is removed by washing if food grade material is required. The commonest grade has a degree of substitution of 0.7 (0.7 hydroxyls substituted per glucose unit).

$$\underset{\text{Cellulose}}{\text{Cell}-\text{OH}} + \text{NaOH} \longrightarrow \text{Cell}-\text{ONa}$$

$$\text{Cell}-\text{ONa} + \underset{\text{Sodium chloroacetate}}{\text{ClCH}_2\text{COONa}} \longrightarrow \underset{\text{Carboxymethyl cellulose}}{\text{Cell}-\text{OCH}_2\text{COONa}}$$

Its most important use is as an antisoil redeposition agent in detergents. As such, it prevents soil from redepositing on the textile surface once the surfactant has removed it. It is also used as a thickening agent in diet and other foods, where a higher viscosity is seen as desirable.

Cellulose triacetate is made by the action of equal quantities of acetic anhydride and glacial acetic acid on "chemical cotton," a form of cellulose obtained by purification and conversion of cotton linters. All three hydroxyl groups in each glucose unit are acetylated.



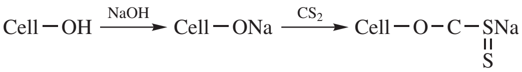
Cellulose

Cellulose triacetate

Cellulose acetate is obtained by partial hydrolysis of cellulose triacetate with water and a small amount of acetic and sulfuric acids. Addition of a large excess of water at the appropriate stage stops the hydrolysis and precipitates the acetate (with an average of two acetyls per glucose unit) as flakes. Cellulose acetate and triacetate may be used as plastics molding materials or spun into fibers and used for textiles. Cellulose triacetate is more difficult to process than the acetate but can be heat-set to give wash-and-wear fabrics. The largest use, however, for cellulose acetate is for cigarette filters. Cellulose propionate, acetate-propionate, and acetate-butyrate are also used as plastics materials and for films and lacquers. Ethylcellulose is useful in coatings and some plastics applications.

Cellulose nitrate or nitrocellulose was an early explosive (guncotton), as well as a plastic (celluloid), and surface coating (lacquer) both for wood and metal. Thus it was the first material used for coating automobiles by assembly-line procedures, its rapid drying making semiautomated production possible. It is also used in plastic moldings and film, and for fabric coating. Cellulose nitrate coated fabric was widely used for airplane wings in the early days of aviation. As the basis for lacquers for furniture, it has largely been displaced by "melamine precatalyst" formulations. It is obtained by nitration of cellulose, about two nitro groups per glucose unit being introduced.

In addition to chemical conversion, cellulose may be altered physically or "regenerated." Two processes are used, both of which start with highly purified cellulose from wood pulp. The products are known as viscose rayon and cuprammonium rayon. Viscose rayon is produced by conversion of the cellulose into the soluble xanthate. It is first "ripened" with concentrated sodium hydroxide and then treated with carbon disulfide:



$$\text{Cell}-\text{OH} \xrightarrow{\text{NaOH}} \text{Cell}-\text{ONa} \xrightarrow{\text{CS}_2} \text{Cell}-\text{O}-\text{C}-\underset{\overset{\|}{\text{S}}}{\text{S}}\text{Na}$$

Cellulose

Cellulose xanthate

Each glucose unit is derivatized with an average of 0.5–0.6 xanthate groups. The solution is known as "viscose." It is extruded through a spinerette—a metal disk with many tiny holes—into an acid coagulating bath that regenerates the cellulose as a fiber. The fibers are washed and spun, that is, oriented by stretching. The carbon disulfide is also regenerated and is recycled. The xanthation serves to solubilize the cellulose into a form from which it can readily be regenerated. During the regeneration, additional hydrogen bonds form, thus increasing strength.

The premium cuprammonium rayon is made by dissolution of cotton linters or wood pulp in ammoniacal copper oxide. The solution is extruded through spinnerettes into an acid bath in the same way as viscose. Cuprammonium rayon is chemically similar to viscose rayon but gives a finer yarn that is used in sheer fabrics.

Less vigorous treatment at the pulping stage leads to higher molecular weight cellulose, which yields so-called polynosic rayon with longer, finer fibers, and high wet strength.

Cellophane film is also made from viscose solution, but the cellulose is regenerated in sheet form instead of fibers. It has high-moisture transmission and is lacquered with a waterproofing agent, traditionally cellulose nitrate, which also imparts heat sealing capability. Poly(vinylidene chloride) is now widely used for this purpose. Cellophane is still a major packaging film for decorative items such as flowers and candy boxes, despite the advent of plastic films such as polyethylene, Saran, and oriented polypropylene.

Cellulose sponges are also made from xanthate, which is cast into blocks together with sodium sulfate crystals of various sizes. The xanthate is decomposed to regenerate cellulose, and when the sulfate is washed out it leaves holes in the sponge. Recovery of sodium sulfate is a major part of the operation. Of course, in all processes involving cellulose xanthate the carbon disulfide is recovered and recycled.

The strength properties of cellulose, and to a degree its ability to hydrogen bond, make it useful for the formation of paper and nonwoven fabrics. For paper, cellulose is "beaten" or "pulped" until very finely divided particles result. Glassine is prepared from particles so finely divided that it is translucent. Opaque papers result from less finely divided particles. The wet and dry strength, bulk density, water and oil resistance, and gas permeability of paper are properties that can be modified either by adding chemicals to the pulp or by coating the finished sheet. Urea–formaldehyde and melamine–formaldehyde resins increase wet strength. Starch and rosin soap are widely used for sizing.

Nonwoven fabrics result when rayon is chopped into very fine particles known as fibrils and converted to sheets by various processes including (with the aid of a bonding agent such as an acrylate) the paper-making process.

14.4 GUMS

Gums, like starch and cellulose, are carbohydrate polymers. They differ from them in that the monomeric unit may be a sugar other than glucose, and the chemical configuration and the way in which the units are joined are different.

The molecular weight of gums is usually between 200,000 and 300,000, that is, about 1500 monomer units. Guar (Fig. 14.6*d*) is a typical gum. It consists of a chain of mannose units joined by 1,4-glycosidic linkages, and attached to every other mannose unit is a pendant galactose unit.

The main gums and their origins are shown in Table 14.1. Each gum has characteristic properties slightly different from other gums. Frequently, the commercially important differences lie in the rheological properties of the dispersions of the gums in water. Gums may be chemically modified just as cellulose is, and the most useful derivatives are carboxymethyl, hydroxypropyl, and dimethylaminoethyl gums.

TABLE 14.1 Natural Gums

Source	Examples
Plant seeds	Guar gum, locust bean gum
Seaweed extracts	Alginates, carrageenan, agar
Tree exudates	Gum arabic, karaya gum, gum tragacanth
Citrus fruits	Pectin
Animal skin and bones	Gelatin
Fermentation	Xanthan gum

The applications of gums are wide. Guar gum is the most important and may be considered typical. It has many times the thickening power of starches and may be used in combination with them. Its derivatives are useful as flocculents for precipitating mineral slimes and as a suspending agent for ammonium nitrate that not only leads to a much cheaper explosive than dynamite or nitroglycerin but also to one that is more effective, because it assumes the shape of the cavity where the blast is to start.

Carboxymethylguar gum is an anionic material useful as a print gum paste. This means that it serves as a binder for a pigment used to impart color and design to cloth. In contrast, diethylaminoethylguar gum is cationic and is used in paper manufacture. It is a particularly effective flocculent of “fines,” the very fine cellulose particles in the paper matrix, onto which it adsorbs. By helping to retain the “fines,” it increases the yield of product and, since fewer “fines” are in the water that drains from the machine, the pollution problem is diminished. Guar itself strengthens the paper by hydrogen bonding to the fibers and helping them achieve a linear rather than a random configuration.

Xanthan is an unusual gum in that it is obtained not from animals or plants but by fermentation of carbohydrates with a bacterium, *Xanthamonus campestris.* The gum is a complex glucose polymer, and its aqueous solutions are unusually stable, showing unchanged viscosity over broad temperature, salt concentration, and pH ranges. The product is therefore used to thicken oven cleaners based on strong alkali as well as the acid solutions used as metal cleaners. Differently formulated, it is a component of low-calorie salad dressings. Its largest use is as a component of oil well drilling mud that must contain saline water. Its largest potential use is in so-called enhanced oil recovery where it thickens the water used to “push” oil, unobtainable in any other way, through the dense, oil-bearing rock formation. Unlike other gums such as guar, xanthan does not adhere to surfaces. If it did, it would deposit as a film on the rock surface and lose its thickening power.

14.5 FERMENTATION AND BIOTECHNOLOGY

When supplied with suitable nutrients, single-cell microorganisms, yeasts, molds, fungi, algae, bacteria including the important antibiotic-producing *Actinomycetes*, thrive and multiply. As they do so, various waste products of their metabolisms accumulate. The microorganisms can tolerate only low concentrations of their own wastes. Nonetheless, under certain circumstances, these wastes, which can be either intra- or extracellular, can be concentrated and used. The process is known as microbial conversion or fermentation, and it occurs as a result of the catalytic action of various enzymes produced by the microorganisms on the nutrient or substrate. Thus fermentation can also be brought about by pure enzymes or portions of cells that contain enzymes such as mitochondria.

The substrate is usually but not always a carbohydrate In the past, there was interest in the use of gas oil (Section 2.1) or other petroleum hydrocarbon substrates for the production of single-cell protein for both human and animal food. Much of the development work was done in the days of seemingly abundant petroleum with ammonia added as a nitrogen source. An ICI methanol-based plant, opened in 1979, survives. In the presence of aqueous nutrient salt solutions containing inorganic sulfur, phosphorus, and nitrogen, a variety of *Pseudomonas* will grow to give a bacterial culture, where the dried cells contain up to 81% protein. This is supplemented by various essential amino acids that are underrepresented in single cell protein and used as animal feed.

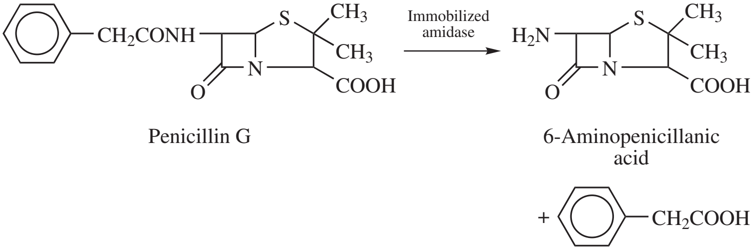
ICI built a plant in partnership with the baking company, Rank, Hovis, McDougal, to grow the fungus *Fusarium graminearum* in a continuous airlift fermenter. This mycoprotein—a relation of the mushroom—can be processed to yield a proteinaceous food with the fibrous texture of meat. The product is known as “Quorn” and is marketed especially to vegetarians and those aiming at a high fibre, low saturated fat diet. The joint company, Marlow Foods, passed to AstraZeneca when ICI broke up and was bought in 2003 by Montagu Private Equity. A joint venture of Phillips Petroleum and Petrofina also produced specialty proteins for human consumption, but the plant was sold to Monsanto in the late 1990s.

In the United States, inexpensive soy protein is available, and there is little incentive for the development of other sources. Soybean production is also being expanded in Brazil, and there should be adequate supplies of vegetable protein in the western hemisphere for the foreseeable future. On the other hand, there are many protein-short countries in the world where fermentation protein might be helpful, and there is believed to be a plant in the CIS.

Fermentation is used in the chemical industry only when an economical chemical process is not available. Its largest volume application is in sewage treatment, where obnoxious amines and sulfur compounds in the sewage are oxidized to nitrates and sulfates. Other wastes are anaerobically digested to methane or aerobically oxidized. The next largest application is the production of alcoholic beverages, where the product can either be consumed in dilute form (beer and wine) or concentrated by distillation (whisky, brandy, gin, vodka).

Fermentation reactions are usually selective and take place under mild conditions. “Waste heat” from power stations, refineries, and factories can easily be used as an energy source if one is required. On the other hand, nutrients are frequently expensive, reactions are slow, and the product is so dilute that huge tank capacities are required. Unless the product precipitates (e.g., single-cell protein), its isolation can be tedious and expensive. If the fermentation is aerobic, mass transfer of oxygen to the required site demands intricate engineering. Contrary to popular opinion, fermentation processes are not ecologically friendly. In general, they produce large volumes of waste water and mycelium with a high biochemical oxygen demand, which must be treated before discharge into a waterway. Nonetheless, there are products for which fermentation methods are uniquely suitable.

Antibiotics are an example. Practically all antibiotics—penicillins, cephalosporins, macrolides, tetracyclines—are made by fermentation. Penicillin is made by fermentation of a corn-steep liquor substrate (a cheap form of sucrose) with *Penicillium chrysogenum* (see note at end of this chapter). For the production of semisynthetic penicillins, such as amoxycillin, the penicillin from this first stage is then cleaved to 6-aminopenicillanic acid with an immobilized amidase (Section 16.8).



Penicillin G

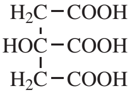
6-Aminopenicillanic acid

Phenylacetic acid

Penicillin has been synthesized in the laboratory but the process would be hopelessly uneconomic compared with the biotechnological route.

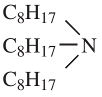
Lactic (Sections 14.1, 17.3.11) and citric acids are made by fermentation. Citric acid has a structure that makes economical chemical synthesis difficult. It is obtained by growing *Aspergillus niger* on a molasses, starch, or hydrocarbon substrate.

One method for separation of the acid from the fermentation broth is unique. The mixture is shaken with a trioctylamine–lauric acid "couple" in an organic solvent. The citric acid displaces the lauric acid from the acid–base couple and enters the organic phase leaving the impurities behind. After phase separation, the organic phase is shaken with hot water. The entropy of the phase transfer is such that, at the higher temperature, the process is reversed and the citric acid returns to the aqueous phase from which it can simply be extracted (see note at end of this chapter).



$$\begin{array}{r}H_2C-COOH\\ |\\ HOC-COOH\\ |\\ H_2C-COOH\end{array}$$

Citric acid



$$(C_8H_{17})_3N$$

Trioctylamine

$CH_3(CH_2)_{10}COOH$

Lauric acid

Other noteworthy fermentation processes include the Weizmann process, which gives acetone, ethanol, and *n*-butanol by fermentation of corn with *Bacillus clostridium acetobutylicum* (this was important in World War I and afterwards, but is now obsolete); the production of evening primrose oil (Section 13.1); the use of an immobilized cell to hydrolyze acrylonitrile to acrylamide (Section 4.14.3); the production of vitamin C (Section 14.1); the 11-hydroxylation of progesterone in the synthesis of cortisone (see note at the end of this chapter); and the production of synthetic cocoa butter (Section 13.10.1).

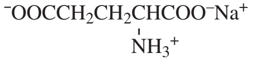
A route to hydroquinone from glucose has been reported but not yet commercialized (see note at end of this chapter). Potentially of great interest is Du Pont's plans to make

1,3-propanediol by fermentation of corn-derived glucose with a genetically modified organism. This is the raw material for the new polyester poly(trimethylene terephthalate). The success of this process could lead to effort to devise other fermentation-based processes starting with renewable raw materials rather than petroleum.

14.5.1 Amino Acids

The synthesis of L-amino acids by fermentation has been pioneered largely in Japan. Production of every essential amino acid by fermentation is now possible. Because demand is small, many of them are still being made by chemical methods followed by resolution of the resulting DL-racemate. The most important amino acids made by fermentation are L-glutamic acid, L-lysine, and L-aspartic acid.

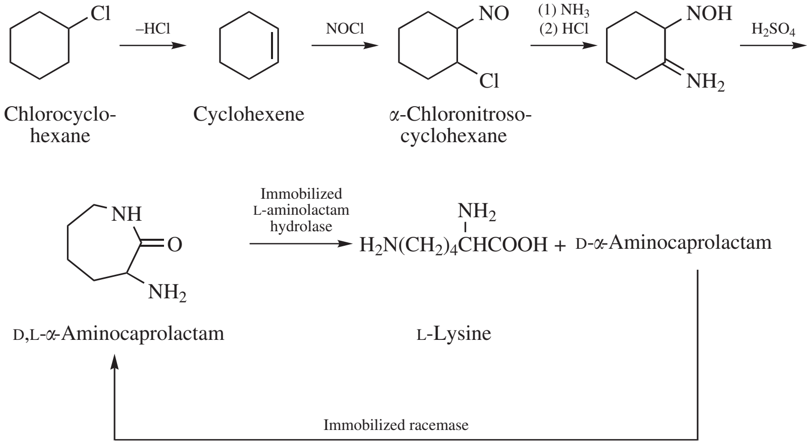
L-Glutamic acid is produced by fermentation of glucose or sucrose from molasses or other sugar refinery wastes. The bacterium is *Micrococcus glutamicus*, and nitrogen is supplied in the form of ammonia. Monosodium glutamate is used as a flavor enhancer in prepared foods, such as packaged soups. Only the L form enhances flavor. Monosodium glutamate is also widely used in Southeast Asia and in Chinese restaurants throughout the world. Excessive doses can lead to *Kwok's disease*, the so-called *Chinese restaurant syndrome.*



$$^{-}OOCCH_2CH_2\underset{\underset{NH_3^+}{|}}{C}HCOO^{-}Na^{+}$$

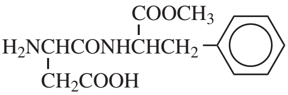
Monosodium glutamate

Lysine was originally manufactured by Du Pont, who used a conventional synthetic route followed by classical resolution of the D and L isomers. It was also isolated from blood meal by General Mills Chemicals. The L form resulted, obviating the need for the tedious resolution. These methods were displaced by fermentation routes based on *Clostridium glutamicum* and ammonium acetate or carbohydrate/ammonia substrates. Toray then developed a new route based on the nitrosyl chloride chemistry and the chlorocyclohexane byproduct from its caprolactam synthesis (Section 7.2.2).



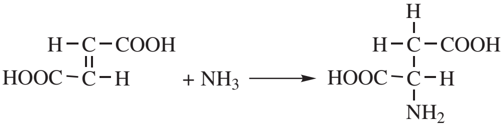
Only the L-α-aminocaprolactam is attacked by the L-hydrolase so that only L-lysine is produced. The D-α-aminocaprolactam is racemized to a D,L mixture for reuse with the aid of a second immobilized enzyme.

L-Aspartic acid is an amino acid with wide uses in the food and pharmaceutical industries. Its significance on a tonnage scale arises because it is a starting material for the nonnutritive sweetener, Aspartame.



Aspartame

The enzyme *aspartase* promotes the addition of ammonia across the double bond of fumaric acid to give the DL form of aspartic acid:



$$\begin{array}{c} \text{H}-\text{C}-\text{COOH} \\ \| \\ \text{HOOC}-\text{C}-\text{H} \end{array} + \text{NH}_3 \longrightarrow \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{COOH} \\ | \\ \text{HOOC}-\text{C}-\text{H} \\ | \\ \text{NH}_2 \end{array}$$

Fumaric acid DL-Aspartic acid

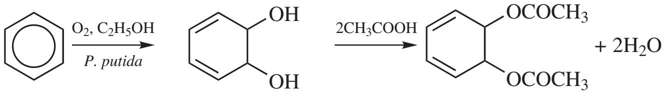
Microbial strains of *Escherichia coli* with high *aspartase* activity are immobilized in a κ-carrageenan gel cross-linked with glutaraldehyde and hexamethylenediamine and operate at a temperature of 38°C. κ-Carrageenan is a gel-forming mixture of sulfated polysaccharides extracted from red seaweed.

DL-amino acid mixtures in general may be resolved by use of immobilized enzymes. If a racemic mixture is acetylated and passed over an immobilized L-acylase, the acetyl group is hydrolyzed from the L-amino acid but the D-amino acid remains unchanged. The mixture may then be separated by crystallization.

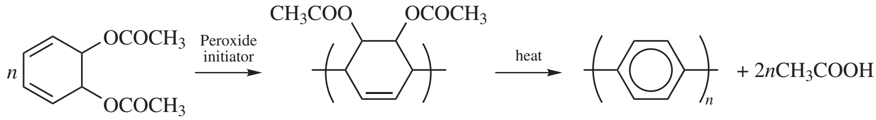
14.5.2 Polymers

A fermentation route to nylon 6,6 is described in Section 7.2.1. The production of xanthan gum (Section 14.4), which has a molecular weight of more than a million, is an example of the production of polymers by fermentation but the product does not have the physical properties generally associated with polymers.

ICI developed a route to a biodegradable polyester copolymer of γ-hydroxybutyric and γ-hydroxyvaleric acids, which was later sold to Monsanto and then to Metabolix, discussed further in Section 17.3.11. ICI also developed a fermentation route to poly-*p*-phenylene. This polymer has excellent high-temperature resistance and hydrolytic stability but is highly intractable with no known solvent, and it can be molded only at high temperatures and pressures. ICI found a strain of *Pseudomonas putida* that would convert benzene to benzene *cis*-glycol when supplied with benzene and ethanol in the absence of oxygen. Esterification with acetic acid leads to a diester, which is polymerized with a free radical initiator. The intermediate polymer is not aromatic. It can be solubilized and is converted into fibers and supported or unsupported film. Heating volatilizes the solvent and completes the polymerization to polyphenylene *in situ*. The acetic acid is regenerated for recycle. This ingenious process was never commercialized.



Benzene *cis*-glycol



Poly–*p*–phenylene

14.5.3 Proteins by Recombinant DNA Technology

The revolution in biotechnology over the past two decades has made possible the manufacture of almost any protein by recombinant DNA technology. Large scale single-cell protein production has already been mentioned in Section 14.5. The technique by which protein-producing genes are spliced into single-cell organisms is altogether remarkable. Insulin, interferon, a range of blood clotting factors for hemophiliacs, human growth hormone, bovine growth hormone, and a range of vaccines are already on the market. Organisms have already been cloned to produce others should it become economic. We can scarcely conclude this section on fermentation without mention of this development.

Implications for the heavy chemical industry, however, are less dramatic. The largest volume genetically engineered protein on the market is insulin, which sold in the mid-1990s for about \$50–60/g (\$23,000–\$27,000/lb). Annual production is measured in pounds rather than tonnes. The adaptation of these methods to bulk proteins presents a whole series of new problems and will not happen for a long time. On the other hand, genetically modified organisms are being used to make non-proteins such as polyalkanoates such as poly(lactic acid) (Section 17.3.11).

14.5.4 A Fermentation Scenario

Discussion of fermentation, however, raises the question as to whether the chemical industry could survive were supplies of oil and natural gas depleted. In terms of technology, the answer is encouraging. In between the world wars, fermentation was a major route to organic chemicals, providing ethanol, *n*-butanol, and acetone as feedstocks. Production was expensive and tonnages were low. Today reaction pathways exist by which most modern organic chemicals and polymers could be made from these feedstocks more efficiently than they were 60–80 years ago. Thus ethanol can be dehydrated to ethylene. Ethylene can be dimerized to 2-butene, and the metathesis reaction (Section 2.2.9) then permits the production of two molecules of propylene from one each of ethylene and 2-butene. Thus C_2, C_3, and C_4 olefins basic to the chemical industry can be produced via fermentation but currently at an uneconomic cost. This question is discussed in Section 14.5.5.

Methane is produced by anaerobic fermentation of sewage sludge and of organic wastes generally. About 75% of the calorific value of sludge can be recovered in this way, which sounds impressive but in fact serves mainly to make sewage plants independent of outside sources of power. In India and China, biomass fermentation processes are well developed and are used in rural areas to generate heating and cooking gas from accumulated biomass wastes. The so-called biogas makes an important contribution to an improved lifestyle in these regions.

It is estimated that biomass (which includes residues of the forest industry, corn cobs, oat hulls, and various plants) could supply $5–10 \times 10^{15}$ Btu (~5000–10,000 terajoules) of fuel and chemicals by the year 2020. This would amount to 5–10% of present US energy consumption.

In summary, therefore, fermentation is currently valuable to do what the chemist cannot do, such as antibiotic and L-amino acid production, and steps in vitamin C and cortisone synthesis. It can provide energy via methane and has been the basis since biblical and classical times of bread and alcoholic beverages. At a cost, it can provide ethanol, which can be dehydrated to ethylene, on which a lion’s share of the chemical industry is based. How much energy, food, or ethylene will be produced by fermentation, however, depends on economics which, in spite of some exceptions, tend to favor petrochemicals. Wider use of fermentation will depend on the seriousness of shortages and the alternative routes devised to alleviate them.

14.5.5 Can Ethanol be Justified as a Fuel?

Ethanol is thought to be valuable as a fuel and, in the 1980s in Brazil, cars were designed that ran entirely on ethanol. Brazilian ethanol production in 1975 was 320 million liters rising to 12 billion in 1986. In 1994 legislation required 22% anhydrous alcohol to be added to gasoline, and production rose to 14 billion liters, one-third being anhydrous.

In the United States, ethanol is used as an octane improver in gasoline as well as methyl-*tert*-butyl ether, which was the preferred replacement for lead tetraalkyls when their use in gasoline was forbidden. The banning of lead was followed by the Clean Air Act, which specified the use of oxygenates to cause the gasoline, and particularly the aromatic fraction, to burn more cleanly. With the discovery that MTBE leaked into groundwater, fermentation ethanol from corn starch has been recommended as a replacement. This requires a huge subsidy, but the fundamental question arises as to whether ethanol is actually a renewable energy source. Does its production use more nonrenewable fossil fuel energy than is produced when it is burned?

The production process starts with the farmers raising corn. They use agrochemicals (pesticides, herbicides, insecticides, etc.) and gasoline-powered tractors. The corn must then be harvested and the starch extracted in a complex process called wet milling. It must then be subjected to batch fermentation to give a dilute aqueous solution of ethanol and then distilled. Straightforward distillation gives an ethanol azeotrope containing 4.4% water—too much for fuel use. On the other hand, farmers are not set up to carry out the fermentation nor operate the azeotropic distillation with benzene on a farm scale, especially since benzene is toxic. Instead, their corn is purchased by companies like Archer–Daniels–Midlands who extract the starch, etc., and who get more than 80% of the subsidy. The shipping of the corn and the complex distillation are energy intensive. Corn growing increases degradation of agricultural land. Pimental (see note at the end of this chapter) has calculated that about 72% more fossil fuel energy is required to produce a tonne of ethanol than is contained in the ethanol.

In addition, ethanol has a much lower octane number than MTBE and raises the volatility of gasoline to which it is added. Batch processes are less energy efficient than continuous processes and there is the problem of disposing of the waste water (about 6 tonnes/tonne of ethanol) as well as the biomass. Thus the wisdom of using subsidized ethanol either as an oxygenate or as a pure fuel is doubtful. Furthermore, if all the corn, wheat, and other crops grown by world farmers were converted to ethanol, it would still give only 6–7% of the energy equivalent of present world oil production.

This gloomy conclusion could only be reversed by a number of breakthroughs. Work is in progress to develop cellulases that would enable the cellulosics in wood, grasses, and agricultural wastes to be broken down into sugars that could then be fermented, but the cost of the enzymes is currently $150/tonne of ethanol compared with the $33 required to make the process remotely feasible. A method of separating ethanol that did not involve distillation is also required. For example, a membrane that would transmit ethanol but not water could be used in a cross-flow system provided it had high enough transmission. A continuous rather than a batch fermentation process would be valuable, and work has also been done on this. The fact remains that bioethanol is still a long way from showing a positive energy balance, let alone economic feasibility.

NOTES AND REFERENCES

Section 14.1 Statistics on sugar come from *Sugar: World Markets and Trade*, US Dept. of Agriculture, Foreign Agricultural Service, Circular Series FS-2-02, Washington DC, 2002. We are indebted to Les Chislett, late of BP Chemicals, for details of Span and Tween manufacture.

Section 14.2 R. L. Whistler, J. N. BeMiller, and E. F. Paschall, *Starch: Chemistry and Technology*, 2nd ed., Academic, Orlando FL, 1984, is the classic book on starch, the earlier edition having appeared in 1965. The immobilization of enzymes for high-fructose syrup is dealt with in this volume by N. E. Lloyd and W. J. Nelson, *Glucose and Fructose Containing Sweeteners from Starch*, p. 635. See also T. Galliard, *Starch: Properties and Potential*, SCI Critical Reports on Applied Chemistry, Vol. 13, John Wiley & Sons, Inc., New York, 1987.

The biosynthesis of 1,3-propanediol is described in numerous patents including US Patents 6,013,494 (2000), 6,428,767 (2002), 6,136,576 (2000), 6,468,773 (2002) and US Patent Appls. 20,020,177,197A1(2002), and 20,030,040,091A1(2003).

Section 14.3 Cellulose makes up ~50% of wood together with 25% of lignin (phenylpropane polymers) and 25% of hemicelluloses (carbohydrate polymers built up from molecules of simple sugars). Wood is thus a source of such polymers. In prehistoric times, it was a precursor of coal and oil. In principle, therefore, it should be possible to obtain chemicals from wood. In practice, it has proved even more difficult than getting them from oil. Two rather old articles describing what can be done are by I. S. Goldstein, *AIChemE Symp. Ser.* **74**, 11 (1978), and in a paper *Chemicals from Wood: Outlook for the Future* to the 8th World Forestry Congress, Jakarta, Indonesia, October, 1978.

Section 14.4 A third edition of R. L. Whistler and J. N. BeMiller, *Industrial Gums, Polysaccharides and their Derivatives*, Academic, San Diego, CA, 1993 has become the standard work on the subject.

Section 14.5 A relatively recent account of the Weizmann process together with a scholarly account of developments in biotechnology to the present day appears in R. Bud, *The Uses of Life: A History of Biotechnology*, Cambridge University Press, Cambridge, UK, 1993.

The production of single-cell protein is described in N. Calder, "Food from Gas Oil," *New Scientist* **36**, 468 (1967). BP produces an educational publication on the topic of single-cell protein. Quorn is discussed in M. G. Wiebe, G. D. Robson, B. Gunliffe, A. J. P. Trinci, S. G. Oliver, *Biotechnology and Bioengineering*, **40**, 1181 (1992).

The pharmaceutical processes mentioned here are described in more detail in our book *Pharmaceutical Chemicals in Perspective* cited in Section 0.4.2. Some of the immobilized enzyme processes are taken from Ian Campbell's book on catalysis cited in Chapter 16.

The Miles citric acid process is described by A. M. Baniel, European Patent 49,429 (1982), A. M. Baniel, R. Blumberg, and K. Hajdu, US Patent, 4,275,234 (1981) and J. E. Alter and R. Blumberg, US Patent 4,251,671 (1981).

The biotechnological route to hydroquinone and benzoquinone was reported in *Chem. Eng. News*, December 14, 1992.

Section 14.5.2 The poly-*p*-phenylene process is described in European Patent Application 0,076,606A1 (April 13, 1983) to ICI. See also S. C. Taylor, Paper presented at BIOTECH '86, Online Publications, Pinner, UK, 1986.

Section 14.5.5 The energy balance for ethanol fuels is calculated by D. Pimentel in *Encyclopedia of Physical Science and Technology*, 3rd ed., Vol. 2, pp. 159–171, Academic Press, San Diego, CA. The question of cellulase development is considered briefly in A. M. Thayer, "Biocatalysis," *Chem. Eng. News*, May 21, 2001, pp. 27–34.

CHAPTER 15

HOW POLYMERS ARE MADE

The polymer industry stands out above all others as a consumer of heavy organic chemicals, and it converts these to the products called plastics, fibers, elastomers, adhesives, and surface coatings. The terms polymer and resin are used synonymously in the chemical industry, but the terms plastics, elastomers, and fibers have specific meanings, and it is incorrect to refer to all synthetic polymers as plastics. A plastic is a material that is formed or fabricated from a polymer, usually by causing it to flow under pressure. Thus if a polymer is molded, extruded, cast, machined, or foamed to a particular shape, which may include both supported and unsupported film, the polymer can be described as a plastic. Often a plastic contains pigments and additives such as antioxidants, plasticizers, and stabilizers. Fibers and elastomers are defined in Section 15.6.

This chapter includes some of the chemistry of individual polymer manufacture but is intended more as a broad description of how to synthesize a polymer, how to influence its properties, and how these properties relate to end uses that affect everyone's daily lives.

In 2002, the US polymer industry produced about 112 billion lb of polymers. Table 15.1 gives figures for 2001. These can be compared with the output of the US organic chemical and polymer industry of about 550 billion lb.

The latter figure refers to chemicals actually isolated before being subjected to another reaction. Thus we might conclude that the polymer industry consumes only about one-fifth of the chemical industry output. Such a conclusion ignores an important element of double counting implicit in the statistics. If 1 billion lb of ethylene

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

TABLE 15.1 US Polymer Production (2000 and 2001)

	Million lb	
Polymer Use	2000	2001
Plastics	84,865	79,857
Fibers	10,995	9,355
Elastomers	2,215	2,195
Coatings	1,281[a]	1,266[a]
Adhesives	5,000	5,000
Total	98,500	89,100

Source: Guide to the Business of Chemistry, 2002, and *Chem. Eng. News*, June 24, 2002. The figures are arrived at by adding published data, but various important materials do not appear. The plastics and fibers figures are accurate, the adhesives figure, although estimated, is likely to be close to the correct value. Total elastomers are likely to be ~10 million lb and coatings ~6 million lb, and the published information underestimates them.

[a] Millions of gallons.

and 3 billion lb of benzene are produced from naphtha and react together to give about 4 billion lb of ethylbenzene, which is then dehydrogenated to a like amount of styrene, which in turn is polymerized to almost 4 billion lb of polystyrene, then the production statistics will record 16 billion lb of chemicals. It is difficult to eliminate this element of double counting altogether, but one estimate is that the 87 billion lb of polymers consume about 216 billion lb of chemicals (about 48% of the total of all chemicals produced). To that should be added such materials as solvents for surface coatings, plasticizers for PVC, as well as many compounding and processing aids. Thus we can say with confidence that the polymer industry consumes well over one-half of the tonnage output of the organic chemical industry.

Polymers may be subdivided into two categories: thermoplastic and thermosetting. Thermoplastics soften or melt when heated and will dissolve in suitable solvents. They consist of long-chain molecules often without any branching (e.g., high-density polyethylene). Even if there is branching (e.g., low-density polyethylene) the polymer may still be two dimensional. Thermoplastics may be used in the five main applications of polymers (plastics, fibers, elastomers, coatings, and adhesives) as shown in Table 15.2. These are discussed further in Section 15.6.

Thermosets decompose on pyrolysis and are infusible and insoluble. They have elaborately cross-linked three-dimensional structures and are used for plastics, elastomers (lightly cross-linked), coatings, and adhesives but not fibers. Fibers require unbranched linear molecules that can be suitably oriented by stretching during the spinning and drawing processes in order to achieve high tensile strength.

Table 15.3 shows the sales of polymers for plastics applications in the United States in 2000 and 2001 (an unusually bad year). If we add together low, linear low, and high-density polyethylenes, then polyethylene emerges as the most important plastic worldwide.

Sales of thermoplastics for plastics applications are about five times those of thermosets in spite of the fact that thermosets, especially urea–formaldehyde and

TABLE 15.2 Major Applications of Polymers

Plastics
Extruded products
Low-density and linear low-density polyethylene
Poly(vinyl chloride)
Polystyrene and styrene copolymers (e.g., styrene acrylonitrile)
High-density polyethylene
Poly(ethylene terephthalate)
Polypropylene
Acrylonitrile–butadiene–styrene copolymers
Cellulose acetate
Cellulose acetate butyrate
Molded products
Polystyrene and styrene copolymers
High-density polyethylene
Polypropylene
Low-density and linear low-density polyethylene
Poly(vinyl chloride)
Phenolics
Polyacetals
Urea–formaldehyde
Melamine–formaldehyde
Acrylics
Cellulose acetate
Cellulose acetate butyrate
Film and Sheet
Low-density and linear low-density polyethylene
Poly(vinyl chloride)
Regenerated cellulose (cellophane)
Acrylics
Poly(ethylene terephthalate)
Polypropylene
High-density polyethylene
Foams
Polyurethane
Polystyrene
Many others
Fibers
Poly(ethylene terephthalate)
Nylon (polyamides)
Aramids
Polyacrylonitrile copolymers
Polypropylene
Rayon
Cellulose acetate
Glass

TABLE 15.2 (*Continued*)

Elastomers
Styrene–butadiene rubber
Polyisoprene
Ethylene–propylene copolymers and ethylene-propylene-diene monomer
Polybutadiene
Butadiene–acrylonitrile copolymers
Silicone
Sulfochlorinated polyethylene
Styrene–butadiene–styrene thermoplastic rubber
Coatings
Paper and Textile applications
Low-density polyethylene
Polystyrene and styrene copolymers
Poly(vinyl chloride)
Poly(vinyl acetate) and copolymers especially with acrylics
Urea–formaldehyde
Melamine–formaldehyde
Conventional coatings
Alkyds
Oils
Acrylics
Poly(vinyl acetate)
Poly(vinyl chloride)
Epoxies
Cellulose acetate
Cellulose acetate butyrate
Urea–formaldehyde
Urethanes
Polystyrene and styrene copolymers
Unsaturated polyesters
Adhesives
Laminating
Phenol–formaldehyde
Urea–formaldehyde
Melamine–formaldehyde
Conventional
Phenol–formaldehyde
Urea–formaldehyde
Melamine–formaldehyde
Poly(vinyl acetate)
Epoxies
Cyanoacrylate

TABLE 15.3 US Production of Selected Polymers (2000 and 2001)

Polymer	Production (million lb)	
	2000	2001
Thermoplastic resins	**89,970**	**83,489**
Polyethylene (low density)	7,575	6,940
Polyethylene (linear low density)	7,951	7,630
Polyethylene (high density)	13,968	12,479
Poly(vinyl chloride) and copolymers	14,442	14,259
Polystyrene	6,844	6,114
Expanded polystyrene	987	938
Acrylonitrile–butadiene–styrene	1,459	1,218
Polypropylene	15,739	15,934
Thermoplastic polyurethanes	6,373	5,418
Thermoplastic polyesters (PET, PBT)[a]	5,140	5,520
Polyamide, nylon type	1,281	1,039
Thermoplastic poly(vinyl alcohol)	350	340
Polycarbonate	1,620	1,550
Other engineering polymers (inc. nylon)	1,383	1,310
Poly(methyl methacrylate)[b]	1,558	n.a.
Poly(vinyl acetate)[b]	3,300	2,800
Thermosetting resins	**14,585**	**14,272**
Phenol–formaldehyde	4,353	4,362
Unsaturated polyester	1,770	1,710
Urea-formaldehyde	2,853	2,750
Epoxy	693	610
Melamine–formaldehyde	316	290
Polyurethane(c)	4,600	4,550
Synthetic fibers	**10,610**	**9,003**
Acrylics and modacrylics	339	302
Nylon	2,606	2,199
Olefin (polypropylene)	3,221	2,953
Polyester	3,830	3,082
Cellulose acetate and rayon	345	230
Other	269	237
Elastomers	**2,156**	**1,975**
Styrene–butadiene rubber	874	782
Polybutadiene	605	562
Ethylene–propylene/EPDM	349	310
Nitrile	89	83
Polychloroprene	64	58
Butyl	175	180

Sources: *Chem. Eng. News*, June 24, 2002, p. 42. Guide to the Business of Chemistry. American Plastics Council, Production and Sales of Thermosetting and Thermoplastic Resins, 2002. The total figures for thermosets, fibers, and elastomers are reasonably consistent within the statistics; our figure for total thermoplastics is higher because we have included a number of polymers omitted in the statistics.

[a] Poly(ethylene terephthalate) and poly(butylene terephthalate).

[b] Estimated.

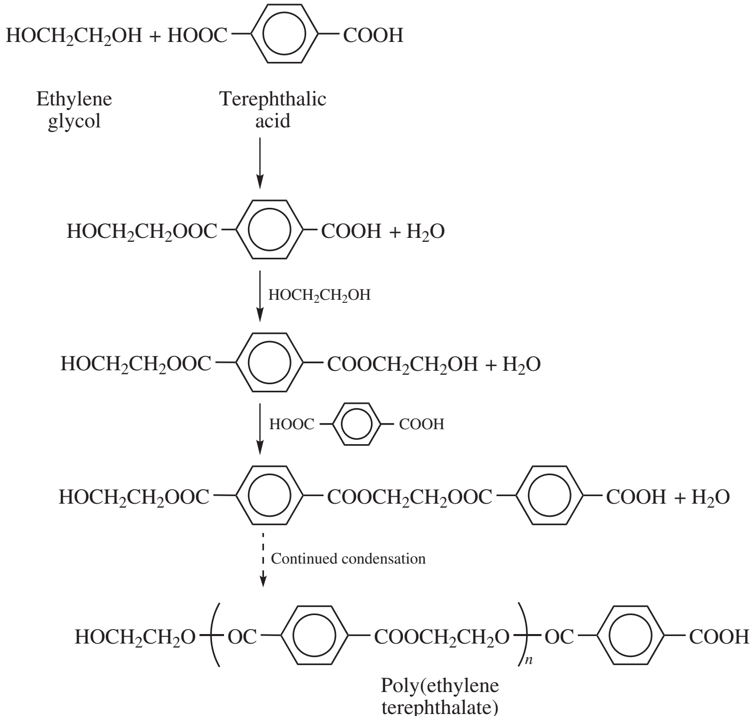
[c] Includes isocyanates and polyether polyols.

phenol–formaldehyde resins, have been produced commercially for much longer than any of the thermoplastics. The thermosets have been unable to share more extensively in the phenomenal growth of plastics because they are difficult to process and do not lend themselves to the high-production speeds that can be achieved, for example, by modern injection molding machines. Methods of processing plastics are summarized in the notes.

15.1 POLYMERIZATION

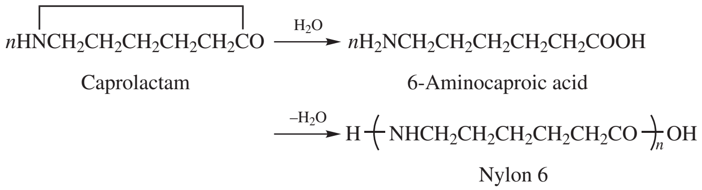
Before considering polymer properties, we shall describe how molecules link together to form polymers. There are two types of polymerization: addition or chain growth (also called simply chain), polymerization and condensation, or step growth (also called simply step) polymerization. The terms chain and step are more accurate than the older terms, addition and condensation. Chain growth polymerization often involves monomers containing a carbon–carbon double bond, although cyclic ethers such as ethylene and propylene oxides, and aldehydes such as formaldehyde polymerize in this way. Chain growth polymerization is characterized by the fact that the intermediates in the process (free radicals, ions, or metal complexes) are transient and cannot be isolated.

Step growth polymerization occurs because of reactions between molecules containing functional groups, for example, the reaction between a glycol and a dibasic acid to give a polyester.



The low molecular weight intermediates are called oligomers, a term also used for the low molecular weight products obtained by chain-growth polymerization. In the polyesterification shown here, an oligomer can have two terminal hydroxyl groups, two terminal carboxyls, or one of each. The hydroxyls can react further with terephthalic acid and the carboxyls further with ethylene glycol. Alternatively, two oligomers can condense. The continuation of these reactions, familiar from simple esterification chemistry, leads to the final polymer. The step-growth or condensation reactions can be stopped at any time, and low molecular weight polyesters (terminated by hydroxyl or carboxyl groups) isolated. Step-growth polymerization, as opposed to chain growth polymerization, is therefore defined as a polymerization in which the intermediates can be isolated.

Usually a small molecule such as water is given off, but this is not always so. In the polymerization of the cyclic monomer caprolactam, for example, both functional groups are in the same molecule, and there is no byproduct. Indeed, 1 mol of water is needed to start the polymerization by hydrolyzing the caprolactam to 6-aminocaproic acid. Each molecule of the latter that self-condenses does indeed give off a molecule of water, but it is needed to hydrolyze more caprolactam to 6-aminocaproic acid. Because no small molecule is given off, the reaction reaches an equilibrium in which about 10% of the caprolactam remains unreacted. The monomer and oligomers (see below) that are always present must be removed by washing with water. This polymerization is carried out under the same conditions that are used to produce nylon from two bifunctional reagents and is clearly a step growth reaction.



$$n\overline{\mathrm{HNCH_2CH_2CH_2CH_2CH_2CO}} \xrightarrow{H_2O} n\mathrm{H_2NCH_2CH_2CH_2CH_2CH_2COOH} \xrightarrow{-H_2O} \mathrm{H}\left(\mathrm{NHCH_2CH_2CH_2CH_2CH_2CO}\right)_n\mathrm{OH}$$

Caprolactam

6-Aminocaproic acid

Nylon 6

Caprolactam can also be polymerized by a chain mechanism using ionic initiators. Figure 15.1 demonstrates the ionic polymerization of caprolactam with sodium methoxide as the initiator. Ionic polymerization is discussed in greater detail in Section 15.3.6.

15.2 FUNCTIONALITY

Functionality is a measure of the number of linkages one monomer may form with another. A monomer that, when polymerized, may join with two other monomers is termed bifunctional. If it may join with three or more molecules, it is tri- or polyfunctional. Glycols and dibasic acids are clearly bifunctional. Similarly 6-aminocaproic acid, the reaction product of water and caprolactam, is bifunctional because it contains a carboxyl and an amino group. The functionality rules state that if bifunctional molecules react, only a linear polymer will result (Fig. 15.2*a*). If a trifunctional monomer (Y in Fig. 15.2*b*) is added, chain branching can occur (see note at the end of this chapter). If there is enough of it, an elaborate three-dimensional network can result. If some of the

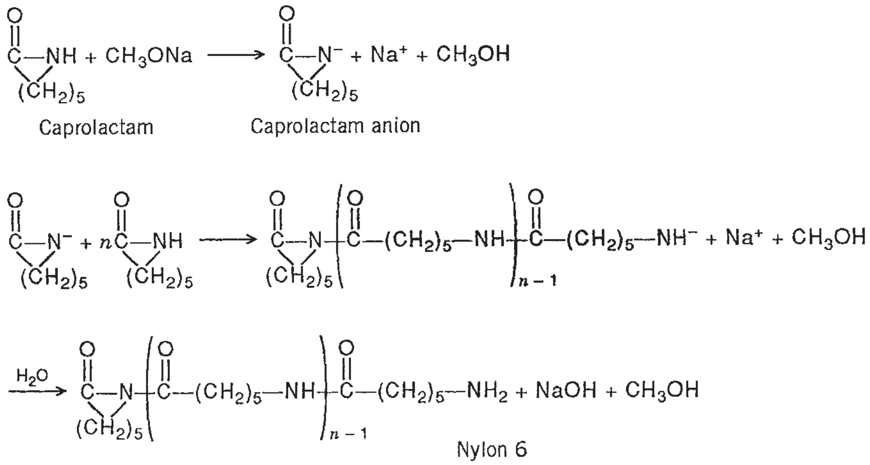


FIGURE 15.1 Ionic polymerization of caprolactam.

chains attached to the Y groups in Figure 15.2*c* are thought of as coming off at right angles to the plane of the paper, some concept of the three-dimensional structure can be gained. A cross-linked polymer of this kind is essentially one huge molecule.

Glycerol has a functionality of three and if condensed with a dibasic acid can give the multifunctional oligomers shown below. Cross-linked polymers soon become insoluble and infusible as their molecular weights increase. The cross-linking may lead to excellent strength characteristics, but the infusibility and insolubility mean that such

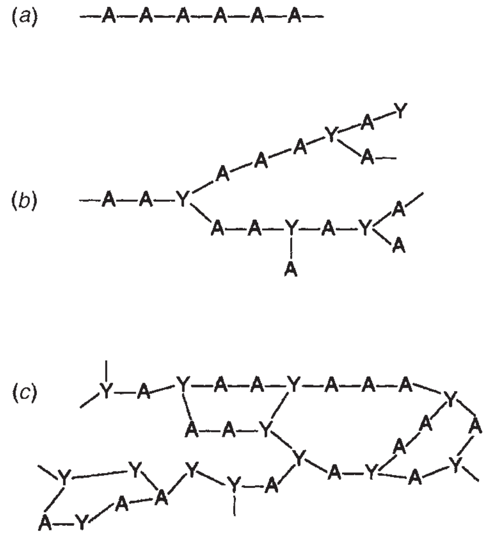
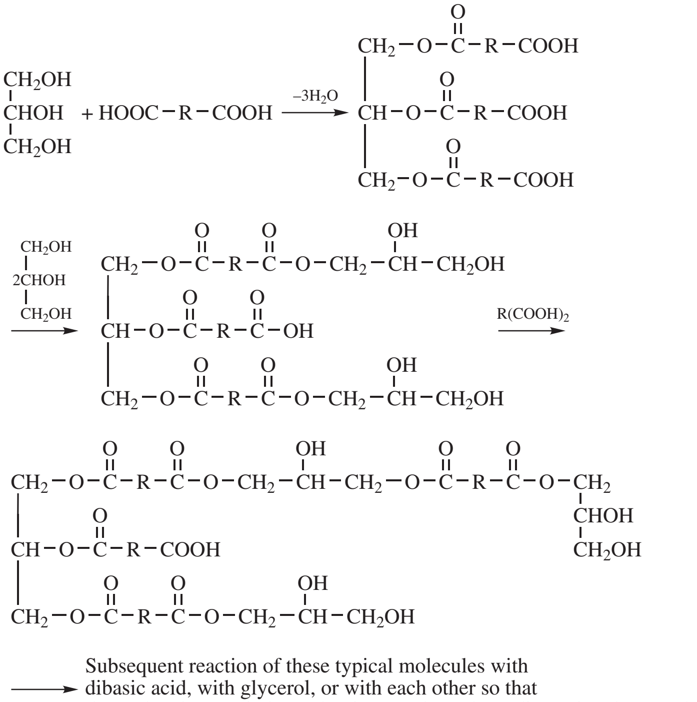


FIGURE 15.2 Linear, branched, and cross-linked structures.

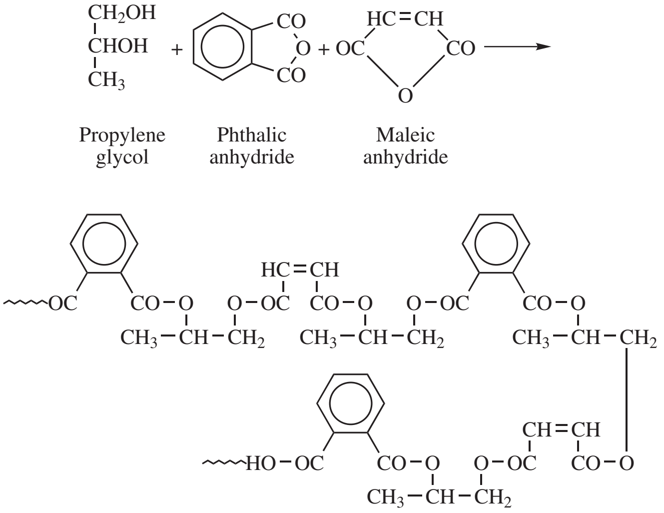
polymers are difficult to convert into shapes. The chemistry of thermoset polymers produced by step-growth polymerization is further discussed in Section 15.4.



Subsequent reaction of these typical molecules with dibasic acid, with glycerol, or with each other so that the molecules are tied together in a random, three-dimensional network

The ethylenic double bond so important in chain-growth polymerization has a functionality of two even though the organic chemist would regard the double bond as a single functional entity. However, the ability of the extra electron pair of the ethylenic linkage to enter into the formation of two bonds makes it bifunctional. Thus ethylene polymerizes to form a linear thermoplastic polymer. The double bond in propylene contributes a functionality of two, but propylene also possesses allylic hydrogens that are activated by peroxide initiators so that a cross-linked structure results. Thus propylene has a functionality greater than 2 toward peroxide catalysts. On the other hand, Ziegler–Natta catalysts do not activate the allylic hydrogens. Propylene shows a functionality of two toward them, and a linear polymer results. This chemistry is harnessed in some ethylene–propylene rubbers. A linear ethylene–propylene copolymer is made with a Ziegler–Natta catalyst. It may then be cross-linked with a peroxide catalyst (Section 3.2.5).

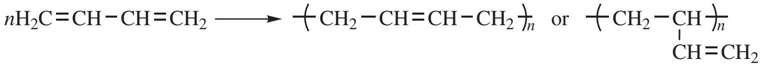
In the production of unsaturated polyester resins, a linear liquid oligomer is made by step-growth polymerization, typically of propylene glycol with phthalic and maleic anhydrides. Each of these reagents exhibits functionalities of two in an esterification reaction. The maleic anhydride, however, has a double bond that can undergo chain-growth polymerization. Thus subsequent treatment of the unsaturated polyester with styrene and a peroxide catalyst leads to a solid, infusible thermoset copolymer in which polyester chains are cross-linked by polystyrene chains. The maleic anhydride has a functionality of 2 in both the step- and chain-growth polymerizations. In chain-growth polymerization, cross-linking results because the unsaturated polyester with its multiple double bonds has a functionality much greater than 2.



Unsaturated polyester

The fact that monomers exhibit different functionalities toward different reagents and polymerization techniques provides a means by which an initial polymerization can give a linear polymer that can subsequently be cross-linked by a different technique. Further examples of this are given in Section 15.4.

Conjugated structures, such as those in butadiene, are considered to have a functionality of only 2. When they polymerize, linear polymers are formed that still contain double bonds.



$$n\mathrm{H_2C{=}CH{-}CH{=}CH_2} \longrightarrow \left(\mathrm{CH_2{-}CH{=}CH{-}CH_2}\right)_n \text{ or } \left(\mathrm{CH_2{-}\underset{\underset{\textstyle CH{=}CH_2}{|}}{CH}}\right)_n$$

Butadiene 1,4-Polybutadiene 1,2-Polybutadiene

These can subsequently react to form a cross-linked polymer but, in the initial polymerization, butadiene is bifunctional.

Pyromellitic dianhydride has a functionality of 2 when reacted with diamines, and linear polyimides result as shown in Figure 15.3. On the other hand, this anhydride reacts with water to form a tetracarboxylic acid that has a functionality of four when reacted with compounds containing hydroxyl groups.

The functionality of a molecule is not always obvious. The situation with a double bond has already been discussed. Formaldehyde has a functionality of 2 and will polymerize to the common laboratory reagent, paraformaldehyde:

$$\mathrm{nHCHO} \longrightarrow \left(\mathrm{OCH_2}\right)_n$$

Although very high molecular weights can be obtained, the product is of little commercial value because it “unzips” easily to regenerate formaldehyde. This can be prevented and practical polymers obtained by acetylation of the hydroxyl end groups. Alternatively a formaldehyde–ethylene glycol copolymer is made and is then subjected to conditions that would normally degrade it. The formaldehyde groups at the end of the chains “peel off” until an ethylene glycol unit is encountered. Depolymerization ceases, and a stable polymer molecule with hydroxyethyl end groups is left with the following structure:

$$\mathrm{HOCH_2{-}CH_2{-}O(CH_2O)_{\mathit{n}}CH_2{-}CH_2OH}$$

Formaldehyde polymers are known as polyacetals. Aldehydes in general can be polymerized anionically or cationically (Section 15.3.6) to give polymers with a $\sim\!\sim\mathrm{C{-}O{-}C{-}O{-}C{-}O}\sim\!\sim$ backbone.

15.3 STEP- AND CHAIN-GROWTH POLYMERIZATIONS

Step-growth polymerization can be described as a simple chemical reaction carried out repeatedly. Polyesterification, for example, is bought about by the same catalysts as esterification reactions, and the equilibrium is pushed to the ester side of the equation by removal of the byproduct water either by simple distillation or as an azeotrope. A major difference between a simple condensation reaction and a polycondensation is that the high molecular weight of the polymer product increases the viscosity of the reaction mixture if the polymer is soluble in it; if not, it precipitates. To solve the viscosity problem, the reaction may be carried out in a solvent, a technique that is particularly useful if the polymer is to be used in a surface coating that requires solvent. More often the engineer is called on to devise equipment with powerful stirrers that can accommodate viscous masses.

In the production of many thermoset polymers, polymerization is interrupted at an early stage before cross-linking starts. The product is still fusible and soluble and is known as a “B-stage” polymer. *In situ* curing, usually with the aid of heat and a catalyst, is relied upon to build up molecular weight and achieve the cross-linked state. Phenolics are often used as B-stage polymers (Section 15.4). In polyimide formation an intermediate chemical species, an “amic” acid, is formed (Fig. 15.3). This is soluble, albeit in very strong solvents such as dimethylformamide. The solution can, however, be laid down as a film and then heated further to achieve polyimide formation. Polyimides are linear as Figure 15.3 indicates but are almost intractable because of their insolubility and rigidity.

The molecular weight and tendency to gel of a polycondensation polymer may be controlled by addition of a monofunctional compound known as a “chain stopper.”

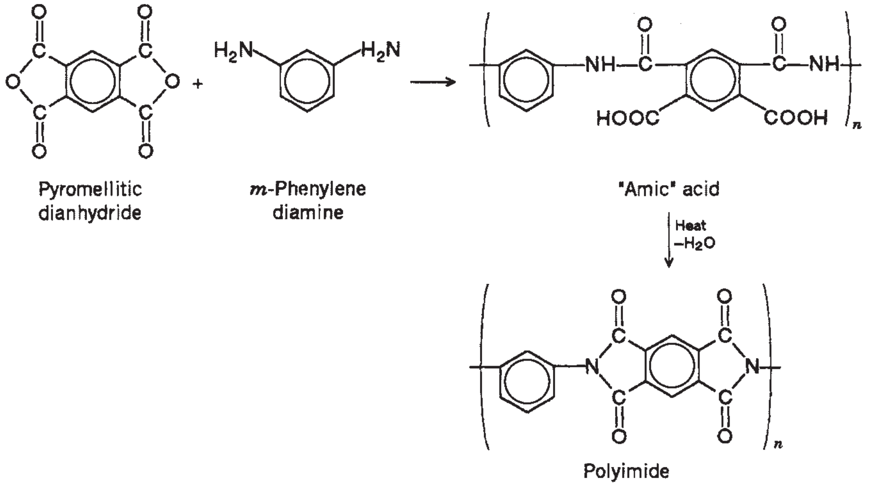


FIGURE 15.3 Polyimide synthesis.

In the production of polymeric plasticizers such as poly(ethylene glycol)adipate, for example, butanol is used as a chain stopper. Chain stoppers are also important in the production of alkyds (Section 9.1).

Chain-growth polymerization proceeds rapidly by way of transient intermediates to give the final polymer. We can write an overall equation,

$$n\mathrm{CH_2{=}CHX} \longrightarrow \left(\mathrm{CH_2{=}CHX}\right)_n$$

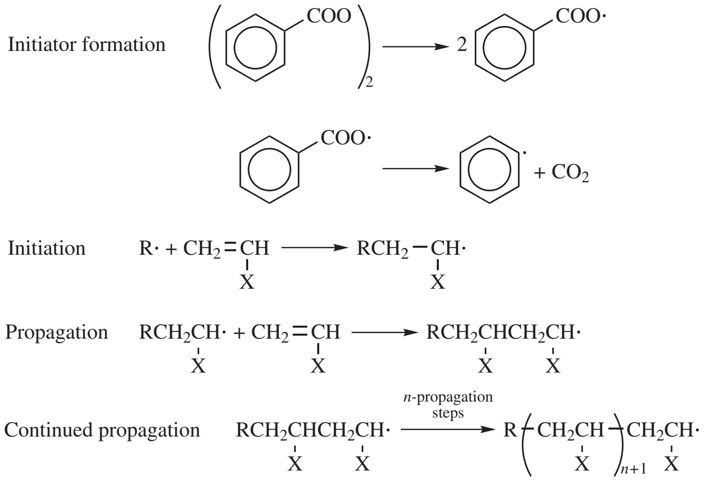
but it provides no indication of the reaction mechanism. Polymerization is started by a chain initiator that converts a molecule of monomer into a free radical or an ion or else by a catalyst that converts the monomer to a metal complex. The free radicals or ions then undergo so-called propagation reactions that build up the polymer chain. In the case of metal complex catalysis, often referred to as Ziegler–Natta catalysis, the propagation takes place on the surface of the metal complex catalyst. Finally, there must be a chain-termination step in which the transient intermediate, now a polymer chain, is stabilized.

In chain-growth polymerization, repeating units are added one at a time, as opposed to step-growth polymerization where oligomers may condense with one another. Propagation and termination steps are very rapid. Once a chain is initiated, monomer units add on to the growing chain quickly, and the molecular weight of that unit builds up in a fraction of a second. Consequently, the monomer concentration decreases steadily throughout the reaction. Prolonged reaction time has little effect on molecular weight but does provide higher yields. At any given time, the reaction mixture contains unchanged reactant and "fully grown" polymer chains but a very low concentration of growing chains. The growing chains cannot readily be separated from the reaction mixture.

In step-growth polymerization (Section15.1) the monomer does not decrease steadily in concentration; rather it disappears early in the reaction because of the ready formation of low molecular weight oligomers. The molecular weight of a given polymer chain increases continually throughout the reaction, and thus long reaction times build up the molecular weight. After the early stages of the reaction, there is neither much reactant nor a great deal of "fully grown" polymer present. Instead there is a wide distribution of slowly growing oligomers. If desired this distribution can be calculated and the separate oligomers isolated from the reaction mixture.

15.3.1 Free Radical Polymerization

Free radical polymerization is initiated by free radicals from compounds such as benzoyl peroxide which, on heating, decomposes to give benzoylperoxy radicals, some of which eliminate carbon dioxide to give phenyl radicals. One of the free radicals then adds on to a molecule of monomer such as ethylene, vinyl chloride, or styrene to convert that monomer to a radical. Initiation is now complete, and the initiating free radical is incorporated into one end of a polymer chain. Its concentration in a high molecular weight polymer is so small that it does not affect final properties. The radical now reacts with another molecule of monomer to give a larger free radical, and this chain propagation process continues until the chain is terminated.



Initiation $R\cdot + CH_2{=}\underset{X}{CH} \longrightarrow RCH_2{-}\underset{X}{CH}\cdot$

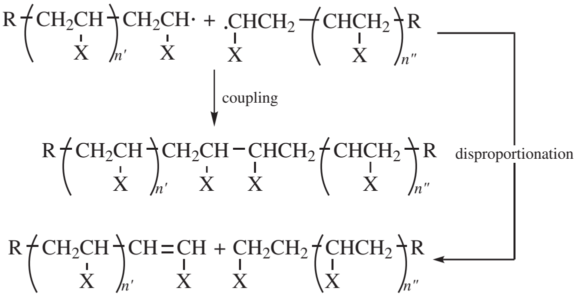
Propagation $RCH_2\underset{X}{CH}\cdot + CH_2{=}\underset{X}{CH} \longrightarrow RCH_2\underset{X}{CH}CH_2\underset{X}{CH}\cdot$

Continued propagation $RCH_2\underset{X}{CH}CH_2\underset{X}{CH}\cdot \xrightarrow{n\text{-propagation steps}} R\left(CH_2\underset{X}{CH}\right)_{n+1}CH_2\underset{X}{CH}\cdot$

Termination Radical coupling
Disproportionation
Chain transfer (termination or branching, Section 15.3.2)

The most important free radical initiators are benzoyl peroxide, dicumyl peroxide, dialkyl peroxides (especially methyl ethyl ketone peroxide, used for unsaturated polyester resins, and di-*tert*-butyl peroxide) and peroxyesters of the general formula R—CO—O—O—R.

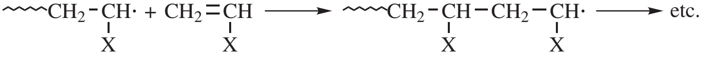
What can stop the chain? The three possible processes are called coupling, disproportionation, and chain transfer. Coupling occurs when two growing free radicals collide head to head to form a single stable molecule with a molecular weight equal to the sum of the individual molecular weights. In the disproportionation reaction two radicals again meet, but this time a proton transfers from one to the other to give two stable molecules, one saturated and the other with a terminal double bond. Above 60°C polystyrene terminates predominantly by coupling, whereas poly(methyl methacrylate) terminates entirely by disproportionation. At lower temperatures, both processes occur.



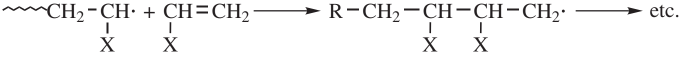
Chain transfer can cause either termination or branching. It is discussed in Section 15.3.2.

Because propagation reactions in chain-growth polymerizations is very fast, polymerizations can and sometimes do become explosive. Termination steps occur rarely relative to the propagation reaction, not because they are slow but because the concentrations of free radicals are normally so low that encounters between them are rare.

In the polymerization of ethylene, it makes no difference which end of the molecule is attacked by the free radical. With unsymmetrical monomers such as vinyl chloride or styrene, however, there could be head-to-tail propagation (Eq. **1**), head-to-head propagation, or completely random addition. In the head-to-head case, the side chain or heteroatom X would sometimes occur on adjacent carbon atoms (Eq. **2**).



$$\sim\sim CH_2-\underset{X}{CH}\cdot + CH_2=\underset{X}{CH} \longrightarrow \sim\sim CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}\cdot \longrightarrow \text{etc.} \quad (1)$$



$$\sim\sim CH_2-\underset{X}{CH}\cdot + \underset{X}{CH}=CH_2 \longrightarrow R-CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2\cdot \longrightarrow \text{etc.} \quad (2)$$

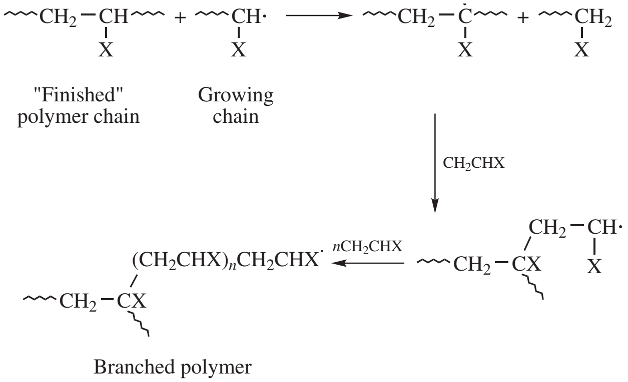
Head-to-head propagation rarely occurs because the unpaired electron in the free radical prefers to locate itself on the —CHX end of the monomer molecule where it has a better opportunity to delocalize. The free radical is thus more stable. Head-to-tail polymerization is the norm, and only an occasional monomer molecule slips in the "wrong way." Termination by coupling, of course, creates a head-to-head structure.

The relative rates of the initiation, propagation, and termination processes are reflected in the key property of molecular weight on which many of the other properties of the polymer depend. If the rate of initiation is high, for example, then the concentration of free radicals at any given moment will be high, and they will stand a good chance of colliding and coupling or disproportionating. A high initiation rate will therefore lead to a low molecular weight polymer.

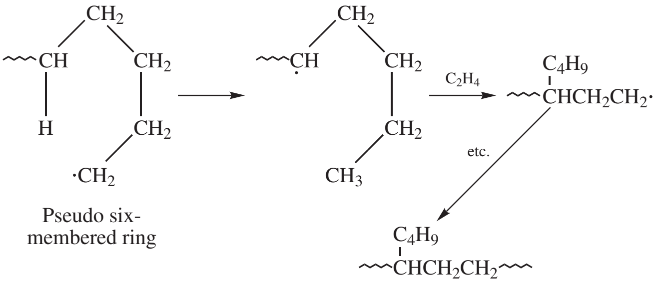
For a high molecular weight polymer, a low initiation rate is required together with a high propagation rate. We might also say a low termination rate, but, because termination steps have no activation energy, they occur on every collision and are diffusion controlled. The termination rate is decreased by increase in viscosity or decrease of concentration in a system. If propagation and termination steps have comparable rates, a polymer will not result. A propagation rate thousands of times the termination rate is required, and the molecular weight is in fact a function of the ratio of propagation to termination rates.

15.3.2 Chain Transfer

Another factor that affects molecular weight is chain transfer. A growing polymer radical may extract a hydrogen atom from a finished polymer chain. This "finished" polymer chain now becomes a radical and starts to grow again. If the hydrogen atom is extracted from the end of the chain, the new chain simply continues to grow linearly. But if, as is more probable statistically, the hydrogen atom is extracted from the body of the chain, then further propagation occurs at right angles to the original polymer chain and a branch forms.



Branching can have a marked effect on polymer properties. It can keep polymer molecules from achieving molecular nearness to each other, and hence reduce cohesive forces between them. Correspondingly, branching makes it harder for polymer crystals to form (Section 15.5.1). The following equation shows how branching takes place in polyethylene.



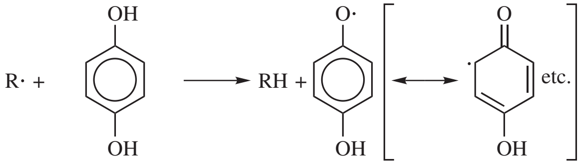
A growing polymer molecule with a free radical end can bend to form a pseudo six-membered ring that facilitates the transfer of the free radical site from the end of the chain to a carbon atom within the chain. The chain then starts to grow from this new site with the net result that the branch has four carbon atoms. Low-density polyethylene is indeed characterized by C_4 branches.

Chain transfer can occur not only to another polymer chain but also to a molecule of monomer. The new radical will then propagate in the usual way. If this happens often, a low molecular weight polymer will form.

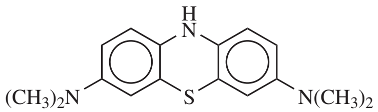
Chain transfer is undesirable except when it is used intentionally to limit molecular weight. It can be controlled by addition of chain-transfer agents. These are materials from which hydrogen atoms can readily be abstracted. If a growing radical is liable to extract a hydrogen atom, it will do so preferentially from the chain-transfer agent rather than from another polymer molecule. The problem of branching will thus be avoided but not that of reduced molecular weight. Dodecyl mercaptan is used as a chain-transfer agent in low-density polyethylene and rubber polymerizations. When it loses a hydrogen atom, a stable disulfide forms. The formation of a stable compound after loss of a proton is a key characteristic of a chain-transfer agent.

$$\underset{\text{Dodecyl mercaptan}}{C_{12}H_{25}SH} \longrightarrow 2H + \underset{\text{Dodecyl disulfide}}{C_{12}H_{25}S{-}SC_{12}H_{25}}$$

Phenols may be used similarly because they give up their phenolic hydrogen readily and the resulting phenoxy radical is relatively stable and does not add to the monomer.



During storage, monomers are sometimes stabilized with polyhydric phenols (e.g., hydroquinone and *tert*-butylcatechol) or aromatic amines (e.g., methylene blue) so that they do not polymerize spontaneously.



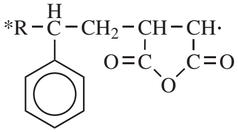
Methylene blue

Hydroquinone is ineffective in the absence of oxygen, so its mode of action is probably more complicated than suggested here. If a free radical should appear in the monomer, it immediately accepts a proton from the inhibitor and is “squelched.” To polymerize the monomer, the inhibitor must be removed, usually by distillation.

15.3.3 Copolymerization

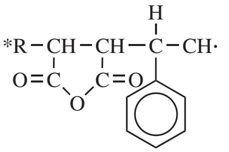
Discussion of propagation rates leads to the topic of copolymerization. Copolymers are made from two or more monomers and are of four kinds: regular, random, block, and graft. In regular copolymers, the monomer units alternate in the chain (—A—B—A—B—A—B—A—B—); in random copolymers they follow each other indiscriminately (—A—A—B—A—B—B—A—B—). Block copolymers (Section 15.3.8) consist of a group of one polymerized monomer followed by a group of the other (—A—A —A—A—B—B—B—B—), and graft copolymers result when a polymer chain of one monomer is grafted on to an existing polymer backbone (Section 15.3.9):

Occasionally a step-growth copolymer is regular. An example is based on maleic anhydride and styrene. Maleic anhydride will not homopolymerize but reacts rapidly in a polymerization reaction with another monomer. Thus one styrene monomer will react with a maleic anhydride monomer. The resulting free radical,



*R = Initiator residue

has a choice of reacting further with another styrene molecule or with another maleic anhydride. It chooses the styrene because the maleic anhydride will not react with itself. The free radical,



chooses a maleic anhydride monomer because the reaction rate between styrene and maleic anhydride is much greater than between styrene–styrene. In this way a completely regular copolymer, $\sim\!\sim\!\sim \mathrm{S}\text{—}\mathrm{MA}\text{—}\mathrm{S}\text{—}\mathrm{MA}\text{—}\mathrm{S} \sim\!\sim\!\sim$, is obtained.

In the random copolymer, the monomer units are not in an orderly sequence. To form a random copolymer, the two monomers must react with themselves at a rate comparable to that at which they react with each other. If the propagation rates differ widely, the first polymer molecules to be formed will consist almost entirely of the fast reacting monomer and, when all of it is used up, the slow reacting material will polymerize to give a polymer consisting almost entirely of the slow reacting material. The possible propagation reactions are as follows. It is the relative rates of these processes that decide whether a random copolymer, two homopolymers, or something in between is obtained.

$$\sim\!\sim\!\sim \mathrm{A}\cdot + \mathrm{A} \longrightarrow \sim\!\sim\!\sim \mathrm{A}{-}\mathrm{A}\cdot$$

$$\sim\!\sim\!\sim \mathrm{A}\cdot + \mathrm{B} \longrightarrow \sim\!\sim\!\sim \mathrm{A}{-}\mathrm{B}\cdot$$

$$\sim\!\sim\!\sim \mathrm{B}\cdot + \mathrm{B} \longrightarrow \sim\!\sim\!\sim \mathrm{B}{-}\mathrm{B}\cdot$$

$$\sim\!\sim\!\sim \mathrm{B}\cdot + \mathrm{A} \longrightarrow \sim\!\sim\!\sim \mathrm{B}{-}\mathrm{A}\cdot$$

Copolymerization serves several functions. First, a copolymerizing monomer may be included to plasticize the polymer, that is, to make it softer. Because vinyl acetate gives too brittle a film for water-borne paints, it may be copolymerized with 2-ethylhexyl acrylate. Second, the copolymerizing monomer may insert functional groups. In unsaturated polyesters (Section 4.6) the maleic anhydride provides double bonds that may subsequently be cross-linked by chain-growth polymerization. In elastomers, a comonomer with two double bonds is almost always used. One double bond engages in chain-growth polymerization, and the other remains intact on each recurring unit so that sites for "vulcanization" or cross-linking with sulfur are present. Thus butyl rubber is a copolymer of isobutene with a small amount of isoprene.

Finally, copolymerization can be used to reduce crystallinity (Section 15.5.1). Low-density polyethylene is about 50% crystalline. By making a copolymer with propylene, this crystallinity is destroyed, and a polymer results that becomes an elastomer on cross-linking.

Copolymerization plays an important role in the synthesis of linear low-density polyethylene (LLDPE). High-density polyethylene (HDPE) (Section 3.1.3) requires mild conditions for manufacture whereas low-density polyethylene (LDPE) requires severe conditions such as 1200 bar and 200°C. Chemists learned how to make a polymer whose properties approximate those of LDPE simply by making a copolymer of HDPE, under the mild conditions HDPE requires, using the comonomers 1-butene, 1-hexene, or 1-octene in concentrations of 6–8% (Section 3.1.4). These destroy some of the crystallinity of HDPE, which is above 90%, lowering it to about 50%, which is the crystallinity of LDPE. The LLDPE has greater tensile strength than LDPE because its branches (cf. Fig. 15.2*b*) are all the same length—2 carbons if 1-butene is used, 4-carbons if 1-hexene is used, and 6-carbons if 1-octene is used. Because of its lesser energy requirements, LLDPE production has grown rapidly, although this economic advantage is partially offset because the C_6 and C_8 comonomers are more expensive than ethylene.

15.3.4 Molecular Weight

We have referred several times to the molecular weight of a polymer, which is not as simple a concept as it sounds. Since the chains in a sample of polymer do not all have the same number of recurring units, the molecular weight of a polymer is always an average. A broad molecular weight distribution is often desirable, for oligomers may serve as lubricants during processing and as plasticizers thereafter.

The molecular weight of polymers is commonly expressed in two ways: by number average $\bar{M}_n$ and by weight average $\bar{M}_w$. The number average is obtained by adding the molecular weights of all the molecules and dividing by the number of molecules. If we have n_1 molecules of molecular weight M_1, n_2 of molecular weight M_2, and n_x of molecular weight M_x then

$$\bar{M}_n = \frac{n_1M_1 + n_2M_2 + \cdots + n_xM_x + \cdots}{n_1 + n_2 + \cdots + n_x \cdots}$$

The weight average, on the other hand, is calculated according to the weight of all the molecules at each molecular weight. Let w_1 be the weight (in molecular weight units) of molecules of molecular weight M_1, w_2 the weight of molecules of molecular weight M_2, and so on, then

$$\bar{M}_w = \frac{w_1M_1 + w_2M_2 + \cdots + w_xM_x + \cdots}{w_1 + w_2 + w_3}$$

But the total weight of all molecules with molecular weight w_1 is M_1n_1, so we can substitute $w_1 = M_1n_1$, $w_2 = M_2n_2$, $w_x = M_xn_x$, and so on in the above equation, hence

$$\bar{M}_w = \frac{n_1M_1^2 + n_2M_2^2 + \cdots + n_xM_x^2 + \cdots}{n_1M_1 + n_2M_2 + \cdots + n_xM_x + \cdots}$$

$\bar{M}_n$ tells us where most of the polymer molecules are relative to the molecular weight distribution. On the other hand, $\bar{M}_w$ tells us where most of the weight is regardless of the molecular weight distribution. Because $\bar{M}_w$ is biased toward molecules with higher molecular weight, it will be larger than $\bar{M}_n$.

As an example consider three persons, two weighing 100 lb and one weighing 200 lb. Their number average weight is (100 + 100 + 200)/3 = 133 $^1/_3$ lb, but their weight average is $(100^2 + 100^2 + 200^2)/(100 + 100 + 200) = 150$ lb. In the first instance, we can consider that a person was selected at random; in the second, that a pound of weight was selected at random. The second selection (weight average) will naturally lead to a higher result because the pound of weight will tend to be selected from the heavier persons.

Both $\bar{M}_w$ and $\bar{M}_n$ provide a narrow view of molecular weight. Their ratio, $\bar{M}_w/\bar{M}_n$, is called the molecular weight distribution and is a measure of the spread. If $\bar{M}_w/\bar{M}_n = 1$ then all the molecules have the same molecular weight, and as the distribution of molecular weights becomes wider this ratio increases.

Boiling point elevation, freezing point depression, osmotic pressure, and end-group analysis give number average molecular weight; light scattering and sedimentation methods give weight averages. Viscosity measurements give a value somewhere between the two.

The molecular weight profile of a polymer can be determined only by fractionation. Cumbersome solvent precipitation techniques give numerous fractions, and the molecular weight of each is determined. The fractions must be so narrow that for each of them $\bar{M}_w/\bar{M}_n$ is effectively unity.

15.3.5 Polymerization Procedures

Chain-growth polymerizations, whether initiated by free radicals as we have already described, or by ions or metal complexes as we describe later, are carried out by four different procedures—bulk, solution, suspension, and emulsion polymerizations.

In bulk polymerization, the monomer and the initiator are combined in a vessel and heated to the proper temperature. This procedure, although the simplest, is not always the best. The polymer that forms may dissolve in the monomer to give a viscous mass, and heat transfer becomes difficult. Heat cannot escape, and the polymer may char or develop voids. If the exotherm gets out of hand, the system may explode.

Even so, the polymerization of ethylene by the high-pressure method is a bulk polymerization and is one of the polymerizations carried out on the largest scale. Fortunately, the polymer does not dissolve in the monomer. Instead it collects in the bottom of the reactor and is drawn off. The exotherm still presents a problem, and the strictest possible control of temperature and heat transfer is necessary to prevent problems. The polymerization of methyl methacrylate to “Lucite” (Plexiglas, Perspex) is also carried out in bulk.

Fluid-bed processes are essentially bulk polymerizations and represent one way to handle the exotherm. They have become popular because they provide an economical way to make standard grades of high-density polyethylene, LLDPE (Section 3.1.4), and polypropylene. The fluid-bed comprises small particles of the preformed resin, fluidized by inert gas. The gaseous monomer and catalyst are injected into the fluid bed and the polymer forms around the nuclei provided by the particles of preformed resin. Conversion is only 2%, but ethylene is easily recycled.

The other polymerization procedures are all designed to solve the problem of heat transfer. In solution polymerization, the reaction is carried out in a solvent that acts as a heat sink and also reduces the viscosity of the reaction mixture. The snags with solution polymerization are first, it is frequently difficult to remove the last traces of solvent from the polymer, and second, the solvent participates in chain-transfer reactions so that low molecular weight polymers result. Solution polymerization is useful if the product is to be used in solvent. Solvent-based poly(vinyl acetate) adhesive is an example. Slurry polymerization is a variant of solvent polymerization and is used for the important polymerizations of ethylene to high-density (low-pressure) polyethylene in one version of the Phillips process (Section 15.3.11) and for propylene to polypropylene. A small amount of solvent is combined with the monomer and catalyst in the reactor. The solvent forms a slurry with the catalyst and aids in its distribution throughout the reaction mixture. At the same time it helps to remove exotherm. Initially, it was necessary to separate the catalyst by a cumbersome process. This has led to the development of catalysts that separate more readily. Also, catalysts are now available that give such high yields, and thus are present in such low concentrations, that they can be left in the polymer without affecting its properties.

In suspension polymerization, the monomer and catalyst are suspended as droplets in a continuous phase such as water. These droplets have a high surface/volume ratio so heat transfer to the water is rapid. The droplets are maintained in suspension by continuous agitation and also, if necessary, by addition of a water-soluble polymer such as methylcellulose that increases viscosity of the water. Finely divided inorganic materials such as clay, talc, aluminum oxide, and magnesium carbonate have a similar stabilizing effect on the suspension. The need to remove these materials is one of the disadvantages associated with their use. Poly(vinyl chloride) is frequently made by suspension polymerization.

The final procedure is emulsion polymerization, a technique that was developed as part of the synthetic rubber program during World War II. The products are particularly useful for the formulation of water-based paints. As its name implies, it uses an emulsifying agent, usually various kinds of soap. In solution, these form micelles in which the nonpolar hydrophobic ends of the soap molecules point inward, and the polar hydrophilic groups point outward and interact with the water. If monomer is added, it is absorbed into the micelle to give a stable emulsion particle. If more monomer is added than can be absorbed in the micelles, a separate monomer droplet phase may form that is also stabilized by the soap molecules, the droplets being a micrometer or more in diameter.

A water soluble composite initiator called a "redox" catalyst is then added. This consists of a mixture of a reducing agent and an oxidizing agent. An example is ferrous ammonium sulfate and hydrogen peroxide. In the absence of monomer, the former would reduce the latter in a two-stage process:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^{\cdot} + OH^{-}$$

$$Fe^{2+} + OH^{\cdot} \longrightarrow Fe^{3+} + OH^{-}$$

If monomer is present, however, the hydroxyl free radical can initiate polymerization. Other redox systems include benzoyl peroxide–ferrous ammonium sulfate, hydrogen peroxide–dodecyl mercaptan, and potassium persulfate–potassium thiosulfate, which gives radical ions:

$$\underset{\text{Persulfate ion}}{S_2O_8^{2-}} + \underset{\text{Thiosulfate ion}}{S_2O_3^{2-}} \longrightarrow SO_4^{2-} + SO_4^{\dot{-}} + S_2O_3^{\dot{-}}$$

These polymerizations must be carried out with rigorous exclusion of oxygen, which is an inhibitor for these reactions, although it is an initiator for low density polyethylene production.

The free radicals diffuse into the micelles, and polymerization takes place within them. Diffusion into the droplets also occurs but, since they have a far lower surface/volume ratio than the micelles, virtually none of the polymerization takes place within them. As polymer is formed, the micelles grow by diffusion of monomer from the droplets into the micelles. Rather than providing a site for polymerization, the droplets serve as reservoirs for monomer that will later react in the micelles.

Polymerization within a micelle may take as long as 10 seconds. Very high molecular weights are produced, higher than by any of the three other procedures. The product is a latex, a dispersion of solid particles in water, which is frequently a desirable form for a polymer. For example, poly(vinyl acetate) or polyacrylate latices are used as such for "emulsion" paints. On the other hand, if solid polymer is required, the dispersion must be broken and the polymer precipitated.

There are two important differences between emulsion and suspension polymerization. In emulsion polymerization the catalyst or initiator is in the aqueous phase, not dissolved in the monomer. Also, particles produced are at least an order of magnitude smaller than those obtained from suspension polymerization.

15.3.6 Ionic Polymerization

Free radical initiation is the most widely used way to produce polymers (Fig. 15.4). A second method involves initiation by ions, either anions or cations. Table 15.4 provides a list of ionic initiators useful for polymerization. In Table 15.5 there is a list of monomers and an indication of whether they can be polymerized anionically or cationically. Many of them can be polymerized also by free radicals and by the metal complex catalysts discussed later. Ethylene may by polymerized cationically and also with the aid of free radicals. Propylene, however, has allylic hydrogens on the methyl group, which terminate or transfer the chains terminators (Section 15.3) and any attempt at free radical polymerization leads to low molecular weight cross-linked structures.

As a general rule, monomers containing electron-withdrawing groups are more easily polymerized anionically, whereas those with electron-donating groups are more easily polymerized cationically. Nonetheless styrene, which contains the electron-withdrawing phenyl group, may be polymerized both anionically and cationically and, for that matter, by free radicals. Cationic polymerization of styrene, however, yields low molecular weight polymers.

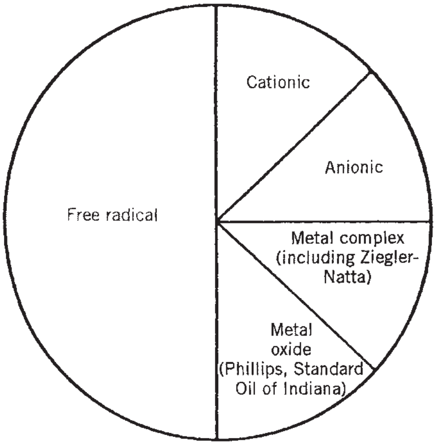
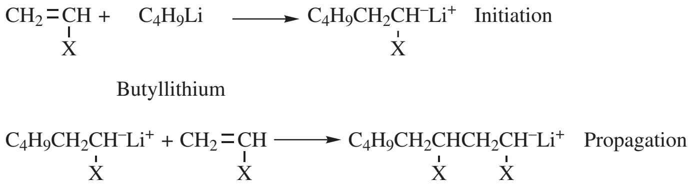


FIGURE 15.4 Methods of polymerization: use distribution (%).

Ionic polymerization is usually unsuitable for the preparation of copolymers. The reason is that the differences in the stabilities of organic ions are much greater than those between the corresponding radicals. It represents a serious limitation to ionic polymerization. An exception is block copolymers (Section 15.3.8), which may be prepared by ionic polymerization because the monomers are added successively not simultaneously.

The initiation step in anionic polymerization is the production of an anion from the monomer by a strong base. This is shown in the equation that follows where butyllithium is the initiator. Butyllithium and other anionic initiators such as sodium or potassium amides in liquid ammonia, or sodium cyanide in dimethylformamide are expensive and not recoverable. Consequently, this procedure is used only where there is no cheaper method of polymerization available and when the value of the product justifies the high initiator cost.

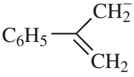


$$\mathrm{CH_2{=}\underset{\displaystyle X}{\underset{|}{C}}H} + \underset{\text{Butyllithium}}{\mathrm{C_4H_9Li}} \longrightarrow \mathrm{C_4H_9CH_2\underset{\displaystyle X}{\underset{|}{C}}H^{-}Li^{+}} \quad \text{Initiation}$$

$$\mathrm{C_4H_9CH_2\underset{\displaystyle X}{\underset{|}{C}}H^{-}Li^{+}} + \mathrm{CH_2{=}\underset{\displaystyle X}{\underset{|}{C}}H} \longrightarrow \mathrm{C_4H_9CH_2\underset{\displaystyle X}{\underset{|}{C}}HCH_2\underset{\displaystyle X}{\underset{|}{C}}H^{-}Li^{+}} \quad \text{Propagation}$$

The propagation step in anionic polymerization is formally similar to that in free radical polymerization (Section 15.3.1), but actually there are differences. Ions like to be solvated, and the solvating power of the polymerization medium may affect the propagation rate. Also, an ion is always associated with a counterion of opposite

TABLE 15.4 Ionic Initiators

Initiators	Sample Monomers[a]
Cationic Types	
Lewis acids	
BF_3 (with H_2O, ROH, ROR)	1, 2
$AlCl_3$, $AlBr_3$ (with H_2O, ROH, RX)	2, 3
$SnCl_4$ (with H_2O)	3
$TiCl_4$	4
$FeCl_3$ (with HCl)	3
I_2 (with Zn halides)	10
Brønsted acids	
H_2SO_4	3 (low mol wt.), 4
$KHSO_4$	
HF	3
$HClO_4$	
Cl_3COOH	5
Active salts	
$(C_6H_5)_3C^+BF_4^-$ $(C_6H_5)_3C^+SbCl_6^-$	3
$C_2H_5O^+BF_4^-$	3, 4
$Ti(OR)_4$	
Anionic Types	
Free metals[b] Na K in toluene, naphthalene, liquid ammonia etc.	3, 6, 7
Bases and salts	
KNH_2, $NaNH_2$	3, 6
$Ar_2N^-K^+$	8
NaCN	
$NaOCH_3$	3
RLi, RK, RNa R may be $C_4H_9^-$, $(C_6H_5)_3C^-$, $C_6H_5CH_2^-$,  $C_6H_5{-}C(=CH_2)CH_2^-$	9

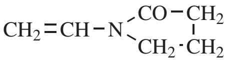
[a] 1 = 2-butene; 2 = isobutene; 3 = styrene; 4 = propylene; 5 = isopropenylbenzene; 6 = butadiene; 7 = stilbene; 8 = 2-cyano-1,3-butadiene; 9 = acrylonitrile; 10 = vinyl ethers.

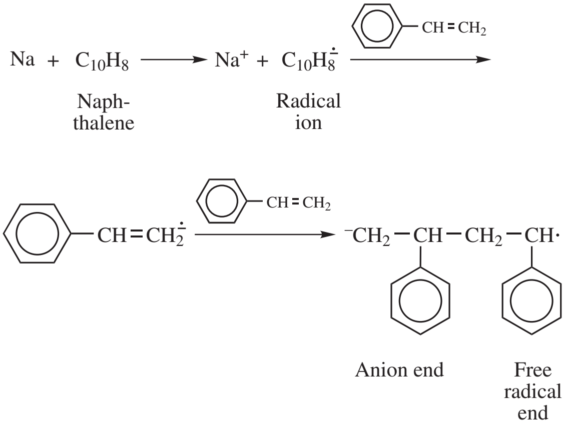
[b] Operate by way of production of radical anions and subsequent reaction of these to actual initiating anions.

charge, which in the above equation is Li^+. This counterion may be completely dissociated from the negative ion or it may be associated with it as an ion pair, and this too can affect the course of propagation.

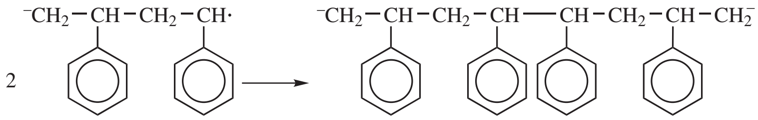
The use of anionic initiation leads to a radical ion that can propagate at both ends of the polymer chain. If styrene is treated with sodium in naphthalene, the sodium first transfers an electron to the naphthalene, which in turn transfers it to the styrene. The styrene has become an anion with an odd number of electrons, that is, it is also a free radical and is called a radical ion. It will combine with more monomer to give a chain with an anionic end and a free radical end.

TABLE 15.5 Methods of Polymerizing Monomers

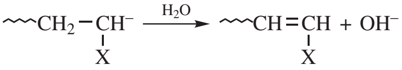
Monomer		Polymerization Mechanism			
		Anionic	Cationic	Free Radical	Metal Oxide or Coordination Catalyst
$CH_2{=}CH_2$	Ethylene		+	+	+
$CH_2{=}CHCH_3$	Propylene		+		+
$CH_2{=}C(CH_3)_2$	Isobutene		+		
$CH_2{=}CH{-}CH{=}CH_2$	Butadiene	+		+	+
$CH_2{=}C(CH_3)CH{=}CH_2$	Isoprene	+		+	+
$CH_2{=}CHC_6H_5$	Styrene	+	+	+	+
$CH_2{=}CHNO_2$	Nitroethylene	+			
$CH_2{=}CHOR$	Vinyl ethers		+		+
 $CH_2{=}CH{-}N\begin{matrix}CO-CH_2\\ CH_2-CH_2\end{matrix}$	*N*-Vinylpyrrolidone		+	+	
$CH_2{=}C(CH_3)COOCH_3$	Methyl methacrylate	+		+	+
$CH_2{=}C(CN)COOCH_3$	Methyl α-cyanoacrylate	+		+	
$CH_2{=}CHCN$	Acrylonitrile	+		+	



This species could conceivably add monomer from the two ends by different mechanisms. More likely, because the charge is sufficiently delocalized, two of the radical ends couple to give a divalent anion that propagates from both ends by an ionic mechanism:



Chain termination is more complicated than it is for free radical polymerization, where it takes place by way of coupling or disproportionation (Section 15.3). Neither of these is possible because two negative ions cannot easily come together. The reluctance of ionic chains to terminate leads to the so-called “living” polymers (Section 15.3.7). Termination may result because of proton transfer from solvent, weak acid, polymer, or monomer. Thus water will quench an anionically initiated polymer. Proton transfer is not true destruction of transient species, and termination only occurs if the new species is too weak to propagate.

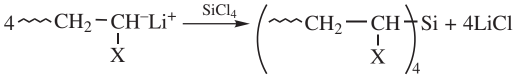


$$\sim\!\!\sim CH_2-\underset{X}{CH^-} \xrightarrow{H_2O} \sim\!\!\sim CH=\underset{X}{CH} + OH^-$$

Termination

The recombination of a chain with its counterion or the transfer of a hydrogen to give terminal unsaturation, frequent in cationic polymerization (see below), is unlikely in anionic systems. For example, if the counterion is Na^+, the transfer to it of H^- is improbable.

Termination can be brought about by a cation-generating small molecule such as silicon tetrachloride. Four chains can terminate at the silicon atom, so the molecular weight of the polymer has been quadrupled, and it has a "star" shape.

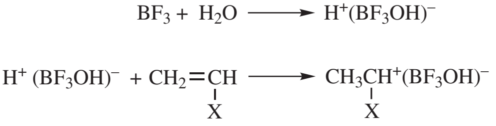


$$4\sim\!\sim\!\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}{}^{-}\mathrm{Li}^{+}\xrightarrow{\mathrm{SiCl_4}}\left(\sim\!\sim\!\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}\right)_4\mathrm{Si}+4\mathrm{LiCl}$$

Termination

For a "three-armed star-shaped" polymer, a terminating agent such as 1,3,5-tris (chloromethyl) benzene may be used. This unique aspect of ionic termination has no counterpart with free radicals. The radial block polymer is much less viscous than a linear polymer of similar molecular weight, and it is more soluble simply because its shape provides more opportunities for solvation. Thus it couples the benefits of very high molecular weight with easier handling properties. In some respects, it is the halfway stage between linear polymers and the dendritic polymers discussed in Section 15.4.4.

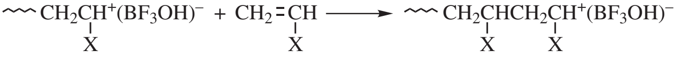
An alternative procedure for preparing a star-shaped polymer is to start with multifunctional initiators such as $C(CH_2C_6H_4Li)_4$. An initiator for a three-armed star-shaped polymer is the alkoxide of triethanolamine, $N(CH_2CH_2ONa)_3$. Ionic polymerization may also be cationic. Table 15.5 shows which monomers may be polymerized cationically. Initiation is by proton donors such as conventional acids and Lewis acids, and these give rise to carbonium ions. Boron trifluoride in water is typical of a Lewis acid.



$$\mathrm{BF_3}+\mathrm{H_2O}\longrightarrow \mathrm{H^+(BF_3OH)^-}$$

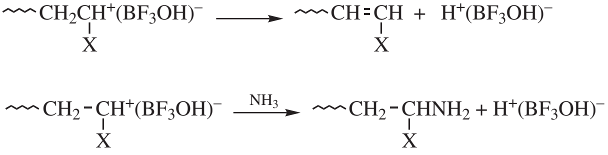
$$\mathrm{H^+\,(BF_3OH)^-}+\mathrm{CH_2}{=}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}\longrightarrow \mathrm{CH_3}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}{}^{+}\mathrm{(BF_3OH)^-}$$

Initiation



$$\sim\!\sim\!\sim\mathrm{CH_2}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}{}^{+}\mathrm{(BF_3OH)^-}+\mathrm{CH_2}{=}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}\longrightarrow\sim\!\sim\!\sim\mathrm{CH_2}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{C}}\mathrm{HCH_2}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}{}^{+}\mathrm{(BF_3OH)^-}$$

Propagation



$$\sim\!\sim\!\sim\mathrm{CH_2}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}{}^{+}\mathrm{(BF_3OH)^-}\longrightarrow\sim\!\sim\!\sim\mathrm{CH}{=}\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}+\mathrm{H^+(BF_3OH)^-}$$

$$\sim\!\sim\!\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{X}}}{\mathrm{CH}}{}^{+}\mathrm{(BF_3OH)^-}\xrightarrow{\mathrm{NH_3}}\sim\!\sim\!\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{X}}}{\mathrm{C}}\mathrm{HNH_2}+\mathrm{H^+(BF_3OH)^-}$$

Termination

Propagation occurs as in anionic polymerization, and termination occurs when a proton is transferred back to the counterion leaving a polymer molecule with terminal unsaturation. Unlike anionic polymerization, the initiator is regenerated and can go on to generate other chains or even to attack the solvent. Termination can also be brought about by addition of a small molecule such as ammonia, and a polymer with an amine end group is formed. Again the initiator is regenerated.

It is only by way of ionic polymerization that functional end groups can be attached to polymer molecules. With anionic polymer molecules that grow in two directions, as described, CO_2 yields carboxyl groups; ammonia will provide amine end groups; potassium isocyanate, isocyanate end groups; and HCl, chlorine end groups. If the molecular weight of a polymer is very high, the effect of these end groups is negligible. On the other hand, if the ratio of initiator to monomer is such that the number of recurring units is low, an oligomer is obtained. This termination procedure provides an elegant method for the manufacture of bifunctional compounds such as dibasic acids and diisocyanates. But, as so often happens, elegance and expense go together. One mole of expensive initiator is required for every mole of bifunctional compound produced.

15.3.7 Living Polymers

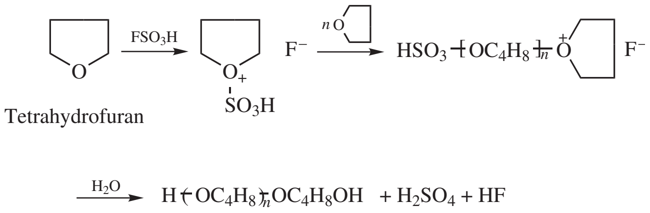
Living polymers are an important ramification of ionic polymerization. The polymer theory that has been outlined so far was developed between 1935 and 1950. The importance of initiation and propagation reactions was recognized, but no one worried very much about termination. It was understood that termination was more difficult in ionic than free radical polymerization because the charges on the growing chains repelled one another, but it was assumed that termination would come about somehow or other.

Eventually, it was realized that it did not have to occur at all. If styrene is polymerized ionically with sodium naphthalide in tetrahydrofuran solution, and care is taken not to introduce agents that terminate chains, a polymer is formed whose chain length can be estimated from the viscosity of the polystyrene solution. The ends of the chains are unterminated, and the polymer is described as “living.” If further styrene is added, weeks or even months later, there will be a marked increase in viscosity showing that the polymer chains have started to grow again once they are supplied with fresh monomer.

15.3.8 Block Copolymers

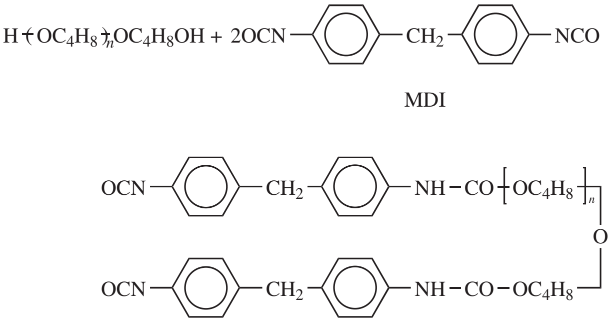
Instead of styrene, in the above example, some other monomer such as isoprene may be added to the living polymer, and a copolymer results. Copolymers can be achieved by other means (Section 15.3.3), but they are usually random. With the living polymer technique, the copolymer is ordered, consisting of a chain of X molecules followed by a chain of Y molecules. If desired a further set of X molecules or of any other monomer can be added. Such materials are called block copolymers.

Block copolymers can also be made by condensation techniques. Spandex is an elastomeric fiber whose use over the last three decades into the early 2000s has grown at a rapid rate. It comprises a block polymer in which there is a flexible block comprising poly(tetramethylene ether) made by oligomerizing tetrahydrofuran to obtain a hydroxyl-terminated polyether.



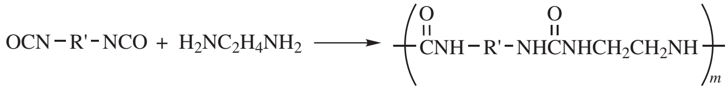
Poly(tetramethylene ether)

Reaction of 2 mol of the polyether with one of methylene diphenyldiisocyanate (MDI, Section 7.3.1) yields an isocyanate-terminated prepolymer. The fluorosulfonic acid, because it presents ecological problems, is being replaced by solid acid catalysts.



MDI adduct or prepolymer

The prepolymer, on reaction with ethylenediamine, yields a copolymer with a hard polyurea block adjacent to the soft polyether block. Elasticity is contributed by crimping.



$$\text{OCN}-\text{R}'-\text{NCO} + \text{H}_2\text{NC}_2\text{H}_4\text{NH}_2 \longrightarrow \left(\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NH}-\text{R}'-\text{NH}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{NHCH}_2\text{CH}_2\text{NH}\right)_m$$

Prepolymer Spandex

Condensation reactions can be used to prepare block polymers only if the reactions take place at low temperatures. At high temperatures, existing bonds in many polymers break and reform to provide random distribution and thus a random copolymer.

Block copolymers have industrial applications, especially in the formation of so-called thermoplastic elastomers. The two blocks may be insoluble in one another and thus tend to repel each other. They will, however, tend to associate with similar blocks in other polymer molecules. This is illustrated in Figure 15.5 for a styrene–butadiene–styrene block copolymer. It is quite different from the common free radical polymerized styrene–butadiene rubber, which is a random copolymer. Polybutadiene is a flexible rubbery material; polystyrene is hard and brittle. Furthermore,

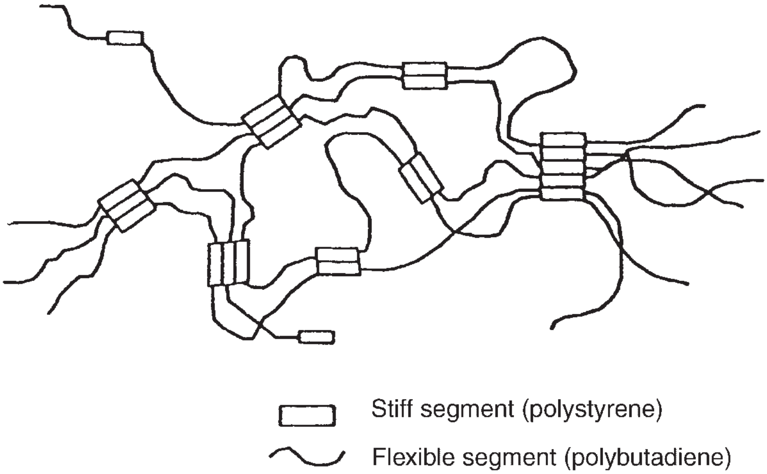


FIGURE 15.5 Block copolymer: styrene–butadiene–styrene.

polystyrene is highly insoluble in polybutadiene. The polystyrene blocks therefore associate with other polystyrene blocks with which they are more compatible, and physical bonding, that is, Van der Waals forces, results. Although these forces are not very strong, they nonetheless give an element of cross-linking so that the polymer at room temperature has many of the properties of a cross-linked material. At higher temperatures, however, the weakness of the forces dissociates the "cross-links" so that the polymer can be processed as if it were a simple thermoplastic.

The useful range of temperature for a block copolymer is determined by the glass transition temperature of the blocks that constitute it. The glass transition temperature is a property of amorphous polymers and is discussed in more detail in Section 15.5.2. At this stage it is sufficient to say that, if an amorphous polymer is melted and then allowed to cool, it will cease to be soft, pliable, and plasticizing at its precise T_g and become hard, rigid, and glassy.

If the styrene–butadiene–styrene block copolymer (e.g., Shell's Kraton) is to be an elastomer it must be used above T_g for polybutadiene. Equally, if it is to retain physical cross-linking it must be used below T_g for polystyrene. By varying the flexible and rigid blocks other thermoplastic elastomers result, some of which are now articles of commerce. Two are of interest because of their high service temperatures. One is a block copolymer of poly(tetramethylene ether) with hydroxyl end groups, obtained from tetrahydrofuran, and poly(butylene terephthalate) from terephthalic acid and 1,4-butanediol (Du Pont's "Hytrel"). Its service temperature ranges from -50 to 150°C, appreciably higher than that for the styrene–butadiene–styrene copolymer. The other is a block copolymer of polypropylene as the soft segment with a hard segment comprising fully cured ethylene–propylene–diene–monomer (EPDM) rubber (Section 5.1). This is Monsanto's "Santoprene" and has a service temperature of -50 to 135°C. High-temperature properties are also obtained by Shell in a hydrogenated version of styrene–isoprene–styrene.

Polymers of this sort have found application in rubber footwear, in rubber soles for shoes, as asphalt modifiers and in both solvent-based and hot melt adhesives.

15.3.9 Graft Copolymers

Chains are usually grafted onto a polymer backbone by creation of a free radical site along the backbone, which initiates growth of a polymer chain. Less often the backbone possesses functional groups, and chains can be condensed onto it.

An example of graft copolymerization is the production of high-impact polystyrene. Polystyrene is a useful low-cost plastic. Unfortunately, it is brittle, and under stress it tends to craze or stress crack. These defects are alleviated by graft copolymerization, although the grafted polymer is no longer transparent. Polybutadiene is dissolved to the extent of 5–10% in monomeric styrene and an initiator added. Because polybutadiene readily undergoes chain transfer, polystyrene chains grow on the polybutadiene backbone, and an impact resistant graft copolymer results (Section 5.1.1).

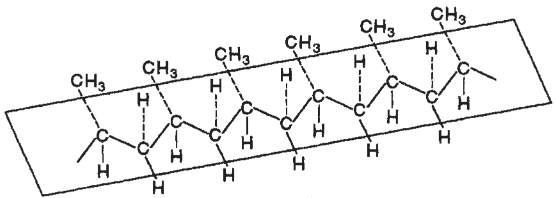
Polyacrylonitrile chains can be grafted onto a starch backbone with the aid of a ceric sulfate initiator or ionizing radiation from a cobalt 60 source. Typically, three chains of acrylonitrile, each with a molecular weight of about 800,000, graft onto each starch molecule. The graft copolymer has markedly different properties from starch itself and is able to absorb as much as 1000 times its own weight of water (Section 4.3).

15.3.10 Metal Complex Catalysts

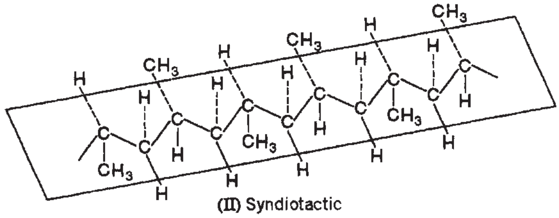
The third method to bring about chain-growth polymerization is by the use of metal complex catalysts. Karl Ziegler, who spent World War II at the Kaiser Wilhelm Institute in Germany trying to find ways to oligomerize small molecules into gasoline, found that titanium tetrachloride or titanium trichloride combined with an alkyl aluminum catalyzes the polymerization of ethylene. The two components of the catalyst form a solid complex, a proposed structure for which is shown on page 493. Ziegler found that his catalyst produced a high molecular weight linear crystalline polyethylene without any of the chain branching or oxygen bridges obtained in the high-pressure free radical polymerization. It was stronger and denser than the conventional material. The conditions required—about atmospheric pressure and 60°C—were astonishingly mild. Ziegler offered his discovery to ICI in the United Kingdom at a remarkably low price. But ICI was heavily committed to its own high-pressure process and was not interested. Other companies did license his process throughout the world, but a competing process developed by Phillips Petroleum in the United States proved to have advantages (Section 15.3.11) and initially was more widely used. Thus Ziegler's contribution, which attracted well-earned attention throughout the scientific world, did not find its greatest application in polyethylene manufacture.

In 1955, about three years after Ziegler's breakthrough, the Italian chemist, Giulio Natta, who was working for the Italian chemical giant, Montecatini, tried the new catalyst system on propylene. It does not take great scientific intuition to realize that if a catalyst works on ethylene it might also work on propylene. This, however, had not been so with free radical polymerization. The allylic hydrogens on propylene were labile and easily displaced, so that several free radical sites developed on the monomer and growing polymer. A useless, low molecular weight, cross-linked polymer was obtained. With Ziegler catalysts, however, the propylene polymerized smoothly to a high molecular weight linear polymer, and in addition—and this was the dramatic thing that won Ziegler and Natta a Nobel prize—the polymer was stereoregular. Few discoveries in organic chemistry have created as much interest or excitement.

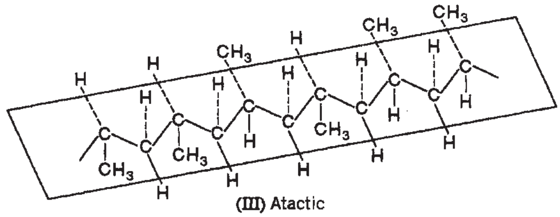
A stereoregular polymer may be defined as one in which the substituent groups are oriented regularly in space. Structure (**I**) of Figure 15.6 shows such a polymer with a substituent, CH_3, in a regular formation. The carbon atom on which the substituent occurs is asymmetric, that is, four different groups are attached to it. It had long been recognized that polymers could contain asymmetric carbon atoms; indeed, natural rubber was just such a polymer. But Natta was the first person to synthesize such a polymer in which all the asymmetric carbons had the same orientation. This polymer is said to be isotactic because all the substituents are similarly placed. Another type of stereoregularity is shown in structure (**II**) of Figure 15.6 in which the substituents point alternately forward and backward. Such polymers are said to be syndiotactic. Low temperatures favor formation of syndiotactic structures, but they are difficult to synthesize with Ziegler–Natta catalysts. They can more easily be made with metallocenes (Section 15.13.12). The conventional nonstereoregular polymers [Fig. 15.6(**III**)] have their substituents placed randomly and are said to be atactic.



(I) Isotactic



(II) Syndiotactic



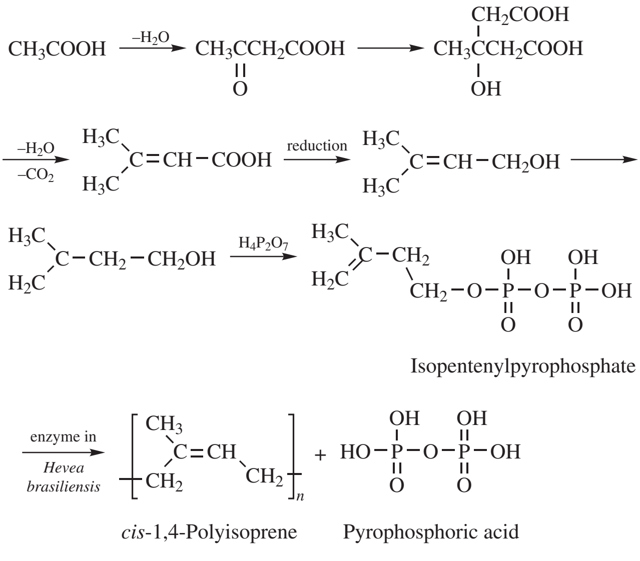
(III) Atactic

FIGURE 15.6 Stereoregular and atactic polymers.

The discovery of Ziegler–Natta catalysis meant that almost overnight a procedure had become available for polymerization of unsaturated compounds that could not be polymerized by way of free radicals. The method was versatile and offered scope for further research. There are many transition metal salts besides the titanium trichloride and tetrachloride that Ziegler used and an equally large number of organometallic compounds with which to combine them. The adding of ligands increased the possibilities for influencing results. Since Ziegler's discovery hundreds of combinations and thousands of ratios of constituents have been evaluated. Polymer chemists today have power to achieve practically any molecular configuration they think will give them the properties they are seeking. It is this versatility that makes Ziegler–Natta catalysis such a powerful tool. Metal oxide catalysis (Section 15.3.11), so important for ethylene polymerization, does not have this versatility.

It is illustrated by the polymerization of butadiene. Polybutadiene may have either a 1,2 or a 1,4 configuration (Fig. 15.7). The 1,4 polymer has a double bond, and the chain structure can be *cis* or *trans*. The 1,2 polymer has vinyl side chains, and these can be arranged in atactic, isotactic, or syndiotactic configurations. Thus five different polybutadienes exist, and all of them have been synthesized with the aid of Ziegler–Natta catalysts. The structure are shown in Figure 15.7.

The stereospecificity of Ziegler catalysts has allowed chemists to do what nature can do with its highly specific enzymes. Nature is able to synthesize optically active compounds, sterically complex antibiotic molecules, and also stereoregular polymers. Natural *hevea* rubber is *cis*-1,4-polyisoprene while *trans*-1,4-polyisoprene is the nonelastomeric *balata* or *gutta percha*. In the syntheses of *hevea* rubber in nature, every step is catalyzed by an enzyme. The starting material is acetic acid, a material manipulated with particular ease by nature as is illustrated by its various metabolic pathways in the body. The final step is the polymerization of the monomer, isopentenyl pyrophosphate, which nature prefers over isoprene, by a polymerase present in the rubber plant.



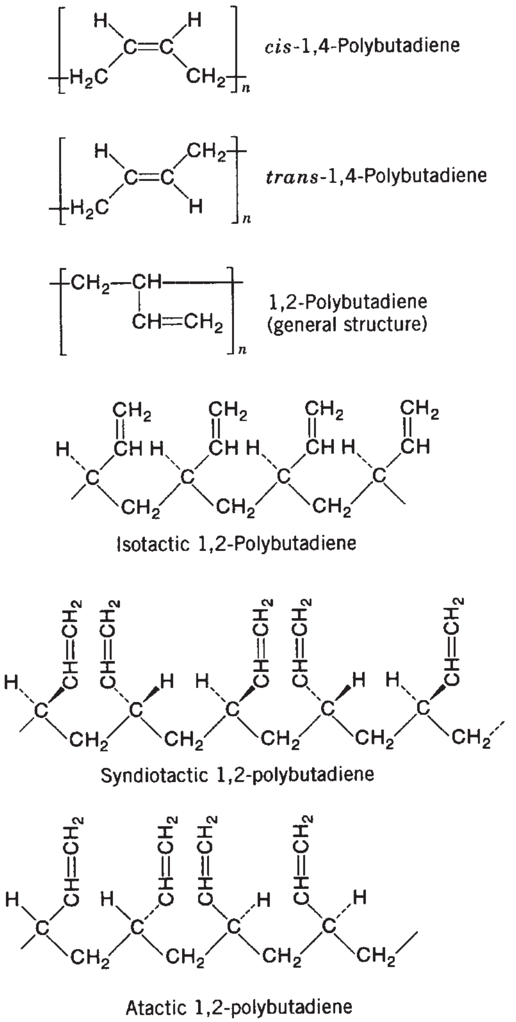
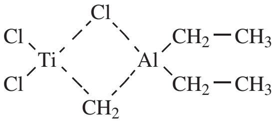


FIGURE 15.7 The isomeric polybutadienes.

With Ziegler–Natta catalysis, scientists can duplicate nature's precision and produce materials that are similar to either *hevea* rubber or *gutta percha*. Thus the chemical industry can and does produce "synthetic natural rubber." It is not quite the same as natural rubber, because end groups and molecular weight distribution differ. Hence, it is almost but not quite as resilient. Equally significant on the plane of ideas is that Ziegler–Natta catalysis enables chemists to mimic nature by making stereoregular polymers. It is satisfying too that Ziegler catalysis works, as does nature, at moderate temperatures and pressures compared with, for example, the formidable 1200 bar and 200°C required for traditional low-density polyethylene synthesis.

What causes stereospecificity? How do Ziegler–Natta catalysts work? It is known that polymerization takes place at active sites on the catalyst surface. The catalyst is an electron deficient solid complex of an aluminum alkyl and a titanium halide, the alkyl group on the titanium atom coming from the alkyl aluminum portion of the catalyst. This is one of several possible structures.



The electron deficiency occurs between the titanium–carbon and carbon–aluminum bonds. Titanium has an octahedral configuration with one ligand vacancy, as shown in Figure 15.8*a*, and a monomer (e.g., propylene) may become π-bonded to the titanium at the vacancy as in (*b*). It is then inserted into the chain as in (*c*) with the regeneration of the vacant orbital with a different orientation (*d*). Continued addition would lead to a syndiotactic polymer and, to give an isotactic polymer, the chain must migrate back to the original site (*e*). The ligand vacancy again exists so that the same progression can happen all over again, and another propylene molecule can be incorporated into the alkyl chain. This is the propagation step, and the polymer chain grows by successive insertion of monomer units at the surface of the titanium complex catalyst.

The system is heterogeneous, and the catalyst is insoluble in the monomer and in the solvent. The insertion of monomer molecules takes place at the solid–liquid interface, and the polymer chain grows from the insoluble catalyst into the solvent. It is the solvating effect of the solvent on the polymer that attracts the chain away from the catalyst surface and into the solvent and allows further monomer to have access to the titanium atom. Some homogeneous metal-catalyzed polymerizations using ligands can also be carried out.

The mild conditions in the use of Ziegler–Natta catalysis are not only a bonus but also a prerequisite for it. At higher temperatures bonds around the catalyst would tend to break and reform, and stereospecificity would be lost. The mild conditions also insure linear polymers and eliminate the branching that is characteristic of free radical initiation. Furthermore, the linear chains can get very near to each other, which gives them high cohesive strength and crystallinity and confers certain desirable properties discussed in Section 15.5.1.

15.3.11 Metal Oxide Catalysts

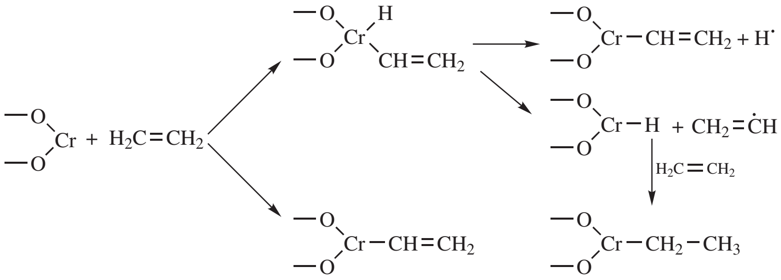
Before Ziegler discovered his catalyst, studies on supported metal oxide catalysts were underway. Researchers for Standard Oil of Indiana developed a molybdenum oxide catalyst supported on silica or alumina that gives high-density polyethylene.

Their discovery predated Ziegler's but they did not exploit it because a consultant's evaluation was negative. The consultant, interested in making film, could see no virtue in a stiff, structural-like polymer. The conventional wisdom associated with this story is that it is not enough to invent. One must also recognize the importance of the invention.

Another oxide catalyst system, chromic oxide on silica or alumina, was developed almost concurrently with Ziegler's catalyst by Phillips Petroleum. With it, polymers can be obtained of higher molecular weight than those obtained by the Ziegler method, and these tend to be intractable. For example, it is difficult to remove them from the kettle. More tractable polymers result when hydrogen and about 1% of a comonomer, 1-butene, is included. The hydrogen controls molecular weight by serving as a chain stopper, which can be regarded as a chain-transfer agent (Section 15.3.2). The comonomer controls density. The reaction takes place in a hydrocarbon solvent at 100°C and 40 bar.

Chromic oxide is the most active catalyst, although oxides of Ti, Zr, Ge, and Th are also effective. The best supports are silica or aluminosilicates with low alumina contents. It is important that they have low mechanical strength to permit the breakup of the catalyst particles during polymerization.

X-ray studies suggest that the catalytically active species is Cr(II) and that the polymerization centers contain isolated chromium moieties. Polymerization is initiated by the formation of chromium–carbon bonds on the surface of the catalyst to give a chromium alkyl. The oxidative addition of ethylene to a divalent chromium ion with vacant coordination positions may take place by one of the following mechanisms:



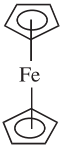
Propagation probably occurs as in Ziegler–Natta catalysis by the sequential insertion of ethylene molecules into the chromium–carbon bond.

The mechanism of metal oxide catalysis is less well established than that of Ziegler–Natta catalysis. Theoretical interest, perhaps unjustifiably, is less, because neither the Standard Oil of Indiana nor the Phillips process can be used to make polypropylene (see note at the end of this chapter).

15.3.12 Metallocene and Other Single-Site Catalysts

Metallocene-based single site and constrained geometry catalysts are the latest development in the design of "tailored" polymers. In the 1930s, ethylene was first polymerized industrially to low-density polyethylene at high pressures with free radical initiators, then in the 1950s to high-density polyethylene at much lower pressures with metal oxide and Ziegler–Natta catalysts. In the 1980s, addition of α-olefin comonomers to Ziegler polyethylene provided linear low-density polyethylene at low pressures, which inhibited growth of the high-pressure process. It might have seemed as if the possibilities had been exhausted, but technology moves inexorably. In 1991, Exxon opened a plant for production of polyethylenes based on so-called metallocene single-site catalysts, and Dow opened a plant based on constrained geometry single-site catalysts in 1993. These innovations have caused great excitement.

Metallocenes are organometallic coordination compounds in which transition metals are sandwiched between cyclopentadienyl rings. The first metallocene was ferrocene (**IV**). Its rings are capable of free rotation and are parallel to one another. Compounds of catalytic interest are discussed below.

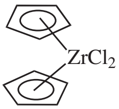


(IV) Ferrocene

The key difference between metallocene catalysts and the conventional Ziegler–Natta catalysts is that Ziegler–Natta catalysts are heterogeneous and have many nonidentical active sites, only some of which are stereospecific. Metallocene catalysts, on the other hand, are homogeneous or supported and have a single active polymerization site. As a result, polymers made with them are effectively a single molecular species, having a very narrow molecular weight distribution. Comonomers are taken up in a uniform manner, and their distribution within the polymer chains will be similar. This narrow distribution provides polymers with lower crystallinity, greater clarity, lower heat seal temperatures, and better resistance to extraction. In foodstuffs, extraction of even tiny amounts of low molecular weight polymers adds unpleasant taste and odor. Because metallocene polymers have very low amounts of such low molecular weight materials, they add less taste and odor.

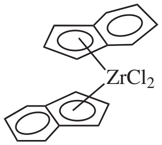
The drawback of the narrow distribution is that ease of processing is diminished. Lower molecular weight polymers act as plasticizers for the processing of the higher molecular weight material. This problem is overcome in three ways. First, addition of conventional Ziegler–Natta catalysts to metallocenes or use of two different metallocene catalysts can give broad or bimodal molecular weight distributions. Second, a controlled amount of long-chain branching can be arranged to give narrow molecular weight distribution branched polymers that are more readily processed. Third, low molecular weight polymer, still with a narrow molecular weight distribution, can be added to the formulation.

The metallocenes of catalytic interest are those of the group 4b metals, titanium, zirconium, and hafnium. Compound (**V**) is a typical zirconocene. Metallocene rings are not necessarily parallel and they may be substituted. The cyclopentadienyl ring can be part of a condensed ring system such as fluorene or indene (**VI**), and the cyclopentadienyl rings may be joined by silyl or alkylene bridges (**VII**, **VIII**). Such metallocenes do not allow ring rotation and restrict access to the metal. By definition, metallocenes contain two cyclopentadienyl rings but monocyclopentadienyl compounds of transition metals are sometimes also included in the term.



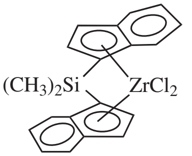
Bicyclopentadienyl zirconium dichloride

V



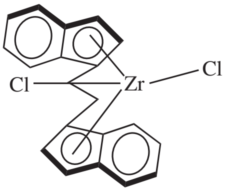
Bi-indenyl zirconium dichloride

VI



Silyl-bridged zirconocene

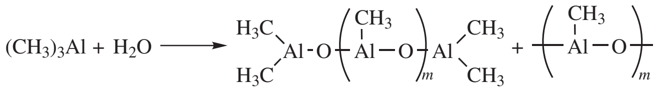
VII



Alkylene-bridged zirconocene

VIII

Metallocene catalysts are of low activity unless used with a cocatalyst, usually a methylaluminoxane, but sometimes an ionic activator. Methylaluminoxanes, in turn, are linear or cyclic polymers formed when trimethylaluminum reacts with water:

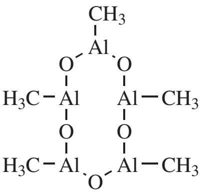


Linear

Cyclic

$m = 4–20$

An example of a cyclic methylaluminoxane with five mesomer units is



A simple example of a single-site catalyst suitable for polymerization of ethylene is the reaction product of the zirconocene (**V**) and a methylaluminoxane. Compound (**VIII**)

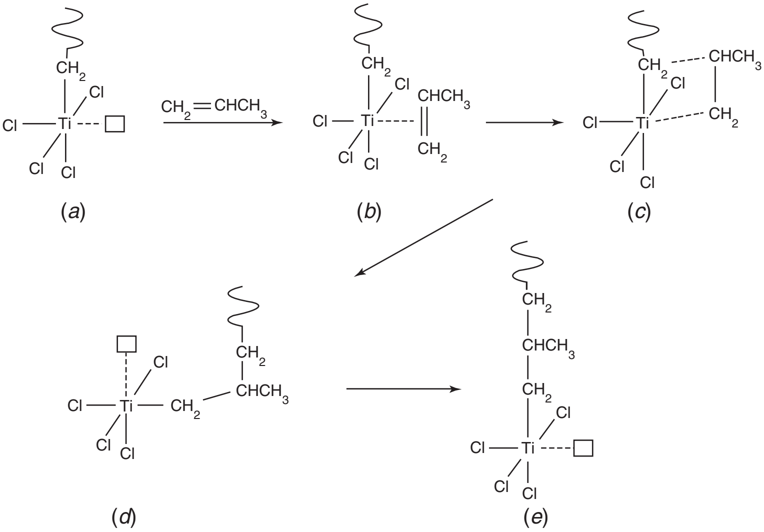
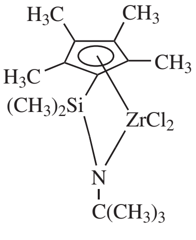


FIGURE 15.8 Mechanism of Ziegler–Natta polymerization.

is also used with methylaluminoxane and (**V**) is used with the ionic activator $C_6H_5N^+(CH_3)_2B^-(C_6H_5)_4$. The mechanism of the polymerization process is similar to that of conventional Ziegler–Natta polymerization. The monomer π bonds to the metal atom and then inserts into the growing polymer chain, as was shown in Section 15.3.10. The activities of the metallocenes with cocatalysts is high. A proprietary metallocene (1 g) is claimed to generate 4000 lb of polypropylene, a ratio of 1.8 million : 1.

The most advanced group of metallocene catalysts are the constrained geometry catalysts. These are based on a constrained geometry ligand attached to a transition metal catalyst center. A group 4b transition metal is bonded to a cyclopentadiene ring and the ring and a heteroatom are bonded to both by a suitable bridge. An example suitable for ethylene copolymers is (**IX**).



(*t*-butylamino)dimethyl(tetramethyl-η^5-cyclopentadienyl)silane-zirconium dichloride (**IX**)

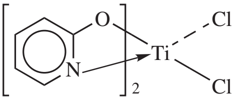
The cyclopentadienyl–zirconium–nitrogen bond angle is said to be less than 115°, and the metal is therefore more open for monomer and comonomer insertion.

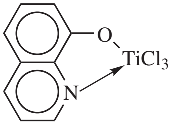
It permits the use of higher olefins such as octene, vinylcyclohexene and even styrene as comonomers and also allows polymer molecules with terminal unsaturation to act as comonomers to give long-chain branching. The branching permits easier processing, as mentioned above.

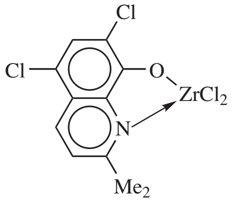
The ethylene–styrene copolymers prepared via constrained geometry catalysts are “pseudorandom.” After incorporation of one bulky styrene unit, the active site becomes crowded and at least one unit of ethylene must be added before there is again room for a styrene. Thus the polymer is not iso- or syndiotactic but all the phenyl groups in the polymer are separated by at least two methylene groups. The product is amorphous (unlike conventional Ziegler–Natta polymers) and elastomeric. The ethylene-1-octene polymer is also elastomeric.

15.3.12.1 Single-Site Nonmetallocene Catalysts

In addition to metallocene-based polyolefin catalysts, other single-site nonmetallocene catalysts have been under development by a number of polyolefin producers. Equistar has introduced nonmetallocene materials based on titanium or zirconium atoms with quinolinol or pyridinol ligands:

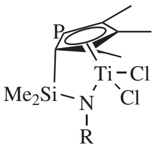




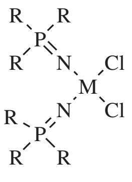


Nova has developed new families of single site non-metallocene catalysts based on phospholes and phosphinimine ligands. A wide range of high density and linear low-density polyethylenes can be tailored by use of these high-activity catalysts in conjunction with Nova’s Advanced Sclairtech reactor technology.

Phosphole Catalysts

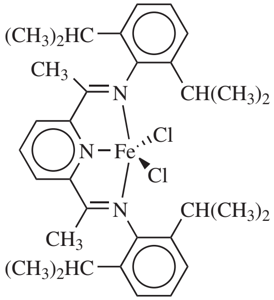


Phosphinimine Catalysts

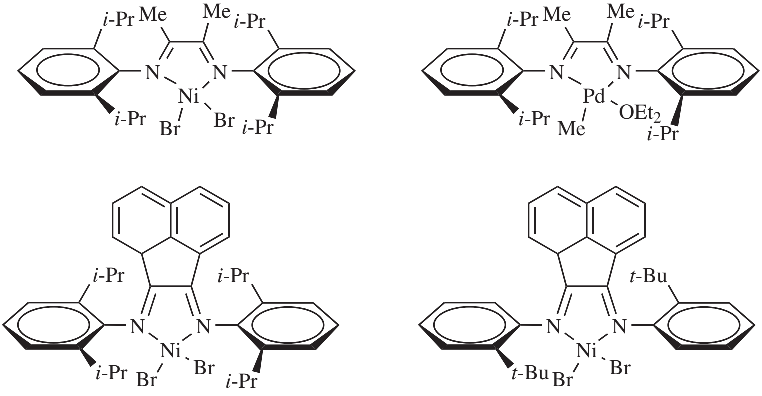


15.3.12.2 Late Transition Metal Catalysts

All the single-site catalysts discussed so far have been based on early transition metals such as titanium and zirconium. In 1996 DuPont, working in collaboration with the University of North Carolina, developed single-site polyolefin catalysts based on the late transition metals, nickel, and palladium. This work was subsequently extended to catalysts based on iron and cobalt. Independently, a team composed of BP and Imperial College, London, has also developed novel iron and cobalt polymerization catalysts. These highly active catalysts have tridentate pyridine and bisimine ligands in which the bisimine ligands are bulky substituted arylamines.



Pyridylbisimine complexes



alpha-Bisimine Complexes *(i*-Pr = isopropyl; *t*-Bu = *tert*-butyl)

The bulky substituents are believed to retard the rate of chain transfer and are key to the high molecular weight polymers that can be made using these catalysts. The cobalt compounds generally exhibit an activity that is an order of magnitude lower than the iron analogues. Late transition metal single-site coordination catalysts bring the promise of a range of polymer structures, from the highly branched low-density structures afforded by nickel and palladium systems to the highly linear high-density products from iron and cobalt catalysts. Perhaps the most exciting property of these late transition metal catalysts is that they are not sensitive to trace amounts of water or other polar compounds, a negative characteristic of classical Ziegler–Natta catalysts. This feature allows these late transition metal catalysts to carry out copolymerizations of ethylene with such polar monomers as methyl acrylate.

15.3.12.3 Commercial Prospects Commercial acceptance of metallocene-based resins was at an early stage in the early 2000s. Exxon is offering a range of ethylene copolymers with propylene, butene, and hexene. Dow is offering a range of ethylene-1-octene copolymers. The methylaluminoxane cocatalyst is particularly expensive and metallocene-based products sell at a premium into the food packaging, personal care, and medical markets. Their biggest use was for bags for shipping bananas because the film was puncture proof.

Single-site resins are the fastest growing sector of the United States LLDPE market, albeit from a very small base, now that leading film fabricators have fully approved commercial product lines containing these resins. In addition, a major driving force is the technology push from the increasing number of polyolefin producers developing single-site catalysts and the increasing number of collaborations and licensing agreements between technology developers. In 2002, there were seven polyolefin producers in North America with commercial and developmental single-site product lines using solution, gas-phase, and slurry processes.

Applications that single-site grades are targeting are varied and include film use for food packaging, multi-ply packaging, and heavy duty sacks. Added value for the film producer comes from improved film sealability, clarity, and toughness. Metallocene medium-density polyethylene blow molding grades have been introduced for making small personal care and cosmetic bottles. This grade of resin offers high gloss, comparable to that of polypropylene, plus greater flexibility than competing glossy HDPEs. Metallocene LLDPE resins are also finding use in extrusion coating of paperboard. Compared with conventional LDPE, LLDPE and ethylene–vinyl acetate extrusion coating resins, the metallocene resin has a much higher peel strength.

Metallocene polypropylene was introduced into the United States markets in 1996 and continues to be used for only niche applications. It is mostly being used to develop new products as opposed to replacing existing demand for conventional polypropylene. To date, metallocene polypropylene has largely been targeted to non-woven fiber and specialty injection molding applications. Syndiotactic polypropylene is available in quantity for the first time but, owing to its high cost, is still in market development. Atactic polypropylene for such applications as adhesives and bitumens is planned.

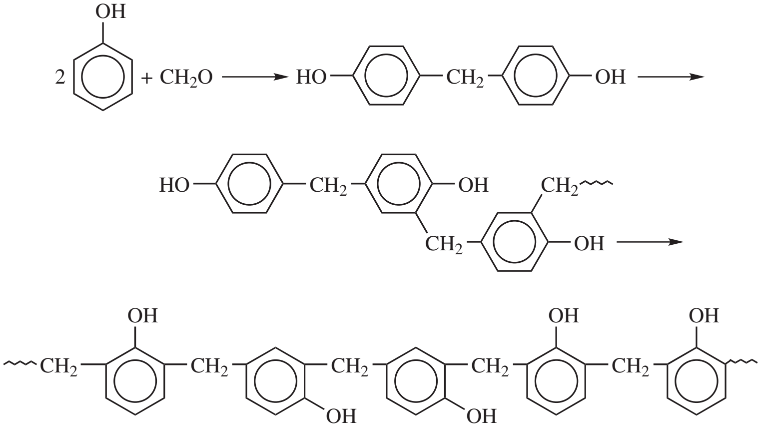
Unlike LLDPE, single-site HDPE is finding very slow market penetration. Producers are striving to find niche film applications. Demand for metallocene HDPE is expected to accelerate once low-cost, gas-phase, single reactor, bimodal high molecular weight film grades are commercialized.

Resins based on metallocene and other single-site catalysts are unlikely to make serious inroads into the markets for the large tonnage commodity polymers in the near future. It is evident, nonetheless, that the fine tuning of polymer properties by variation of polymerization technique offers almost limitless possibilities. The discovery of Ziegler–Natta catalysis was merely the first step along the road.

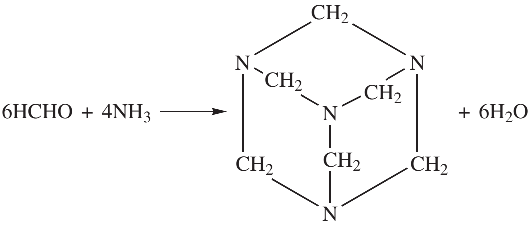
15.4 EXAMPLES OF STEP POLYMERIZATION

15.4.1 Phenoplasts and Aminoplasts

There are two types of phenolic resins (phenoplasts), known as novolacs and resoles. Both are made by step polymerization. Novolacs are made by condensing excess phenol with formaldehyde in the presence of an acid catalyst. Fusible polymers result with the phenol rings joined by methylene bridges but no free methylol groups. They are linear thermoplastic resins that may be stored or sold in that form. Cross-linking via the formation and condensation of free methylol groups is brought about by heat in the presence of a curing agent that provides more formaldehyde under alkaline conditions. An example is hexamethylenetetramine (Section 10.5.2.1), a condensate of formaldehyde and ammonia, the latter providing the alkaline conditions. The products are called two-stage resins.



Typical novolac structure



Hexamethylene
tetramine **X**

Resoles are made with an alkaline catalyst and sufficient formaldehyde to allow for cross-linking. The initial stage is the production of the simplest methylolphenols, saligenin and homosaligenin, followed by trimethylolphenols. The methylolphenols condense to give di- and trimethylolphenols, and then low molecular weight linear polymers called resoles, which contain occasional oxygen bridges. These are the A-stage resin and are thermoplastic and soluble in organic solvents. If left to go to

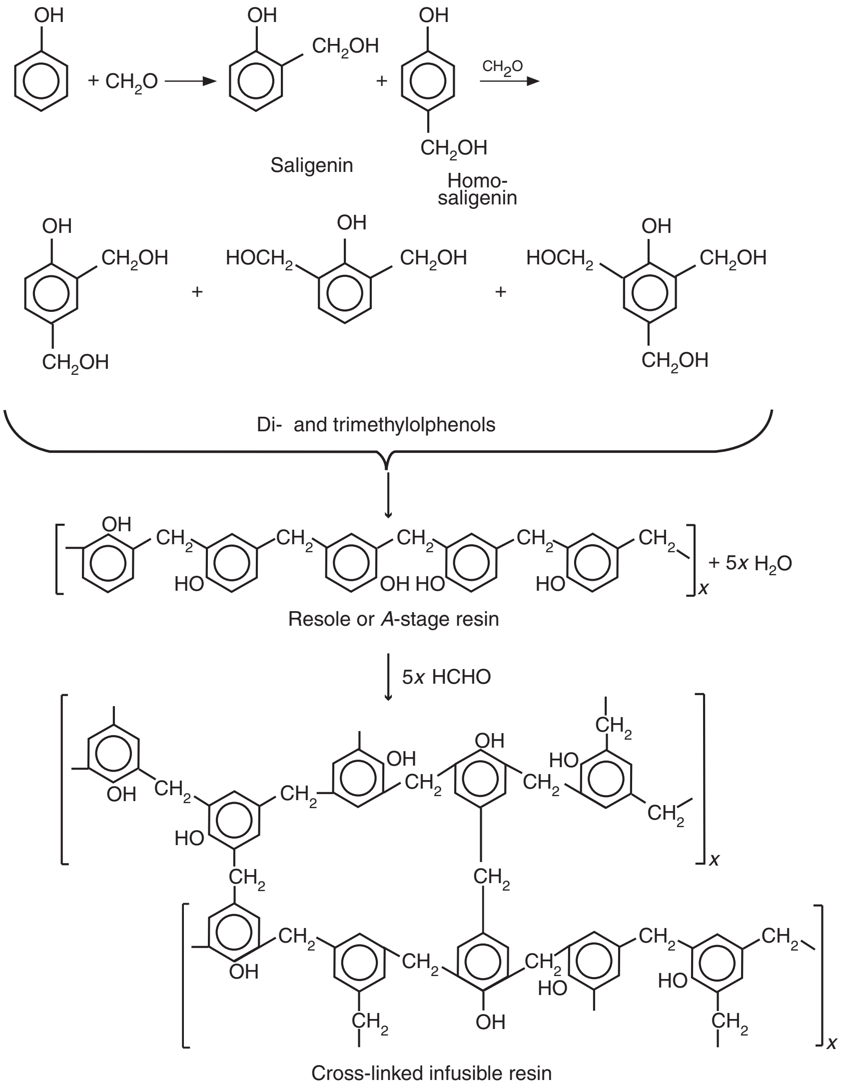
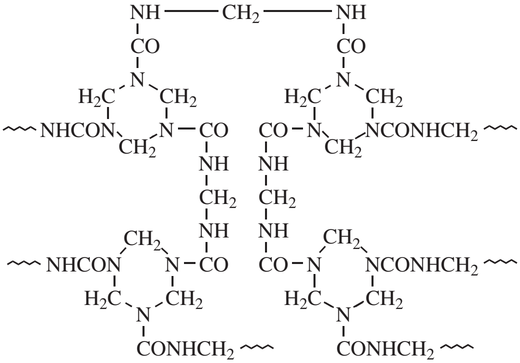


FIGURE 15.9 Formation of resoles and cross-linked phenolic resins.

completion, the process would give a cross-linked structure in one operation (a “one-stage” resin). However, the reaction is stopped at a so-called B-stage before cross-linking occurs. At that stage the polymer is nearly insoluble but still fusible under heat and pressure. It still contains free methylol groups. The resin has sufficient shelf life for use in compounds for automotive and electrical applications. Cross-linking is brought about by further heating and pressure, which causes the free methylol groups to condense. Typical structures are shown in Figure 15.9.

In these reactions the formaldehyde shows a functionality of two while the phenol has three active sites—two positions *ortho* and one *para* to the hydroxyl group. Only two of them are used in novolac formation because of the scarcity of formaldehyde. Thermoplastic phenolics useful for the preparation of varnishes result from the condensation of formaldehyde with *p*-substituted phenols.

Urea will also give cross-linked resins with formaldehyde (aminoplasts) under slightly alkaline conditions (Section 10.5.1.1). Methylolureas are formed first. There follows a series of condensations that include ring formation, and the product is a complex thermoset polymer of poorly defined structure of which the following may be typical.



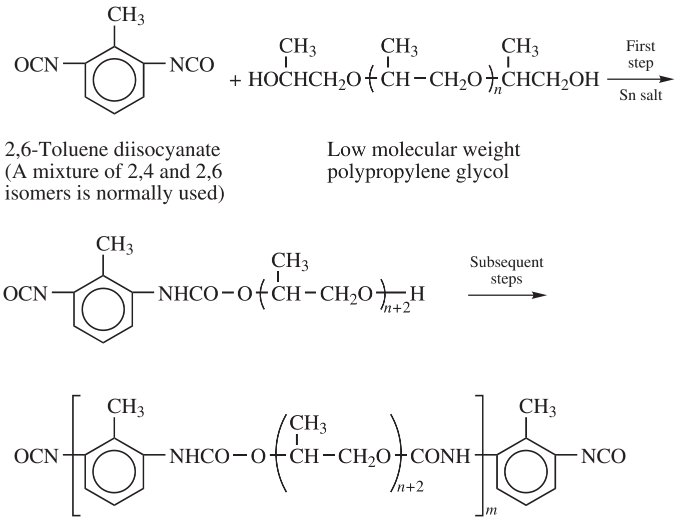
Cross-linked urea–formaldehyde

Urea has a functionality of four in urea–formaldehyde resins, corresponding to the four labile hydrogen atoms. Melamine (Section 10.5.1.1) with three amino groups and six labile hydrogens has a functionality of six, and it too will form thermoset resins with formaldehyde—the so-called melamine-formaldehyde.

15.4.2 Polyurethanes

Polyurethanes result from the reaction of di- or polyisocyanates with di- or polyols. They can be manufactured by a one-step process in which the main reactants are mixed with catalysts, fillers, reinforcing and coloring agents, blowing agents and minor constituents, and placed in a mold to give the final product. Alternatively, a two-step process is employed in which a relatively high molecular weight prepolymer is assembled first. It is then reacted with a low molecular weight diamine or diol to give two- or three-dimensional higher molecular weight polyurethanes. An example is MDI prepolymer, described in Section 15.3.8. The two-step process is the basis of RIM technology (Section 7.3.1) and also avoids the handling of toxic isocyanates during shipment and final processing.

If a diol undergoes step polymerization with a diisocyanate, a linear thermoplastic polyurethane is obtained because both monomers are bifunctional.

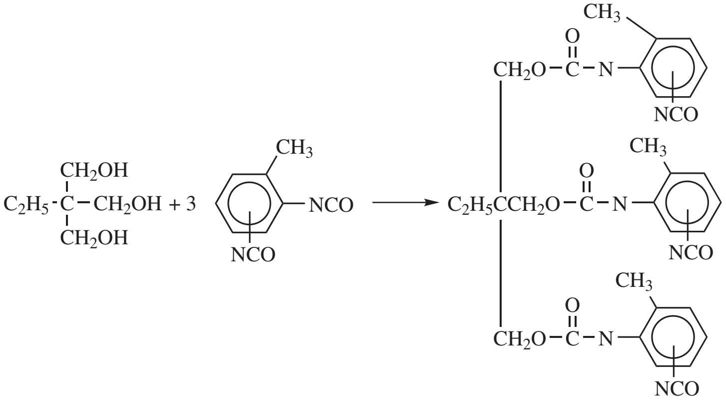


2,6-Toluene diisocyanate (A mixture of 2,4 and 2,6 isomers is normally used)

Low molecular weight polypropylene glycol

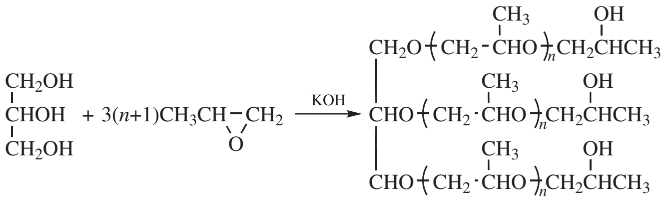
Thermoplastic polyurethane

Poly(propylene glycol) is a bifunctional oligomer synthesized from propylene oxide (Section 4.7.1). To obtain the more useful cross-linked polyurethanes, trifunctional reagents are required. Sometimes toluene diisocyanate (TDI) is converted to a trifunctional reactant by reaction with trimethylolpropane. The new reagent has the advantage of being considerably less toxic than TDI because of its lower vapor pressure. Alternatively, trifunctional hydroxyl compounds may be made by reaction of propylene oxide with glycerol or trimethylolpropane.



Trimethylol-propane

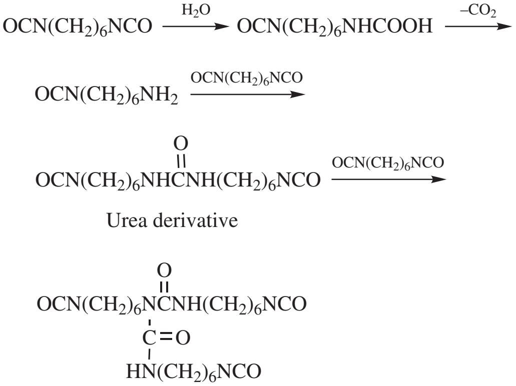
Toluene diisocyanate (mixture of 2,4 and 2,6 isomers)



Glycerol Propylene oxide

Castor oil (Section 13.1) is a naturally occurring triglyceride that contains three hydroxyl groups and is another useful starting material.

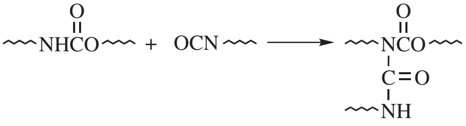
Toluene diisocyanate is the raw material for about 60% of polyurethanes. MDI, which is 4,4′-diphenylmethane diisocyanate and oligomers of it, is second in importance. The presence of the trimer and tetramer in the product mixture means that the product has a functionality greater than 2. The aliphatic isocyanate HMDI, hexamethylene diisocyanate, $OCN(CH_2)_6$ NCO, leads to coatings with good color retention and weathering properties. It is toxic and is used in the form of a trimer with a biuret structure. A biuret forms from the interaction of an isocyanate group with a urea. It exemplifies a second type of linkage found in polyurethanes. The HMDI biuret trimer forms as follows:



$$OCN(CH_2)_6NCO \xrightarrow{H_2O} OCN(CH_2)_6NHCOOH \xrightarrow{-CO_2} OCN(CH_2)_6NH_2 \xrightarrow{OCN(CH_2)_6NCO} \underset{\text{Urea derivative}}{OCN(CH_2)_6NH\overset{\overset{O}{\|}}{C}NH(CH_2)_6NCO} \xrightarrow{OCN(CH_2)_6NCO} OCN(CH_2)_6\underset{\underset{HN(CH_2)_6NCO}{\overset{|}{C=O}}}{\overset{|}{N}}\overset{\overset{O}{\|}}{C}NH(CH_2)_6NCO$$

Biuret trimer

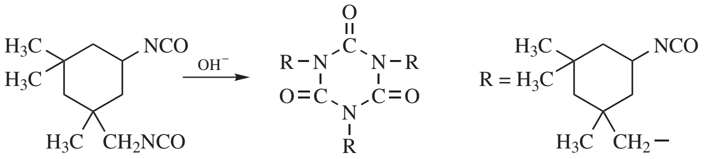
A third linkage, found in polyurethane foams, is the allophonate group, which forms from the interaction of an isocyanate with a urethane linkage.



$$\sim NH\overset{\overset{O}{\|}}{C}O\sim \; + \; OCN\sim \longrightarrow \sim\underset{\underset{\sim NH}{\overset{|}{C=O}}}{\overset{|}{N}}\overset{\overset{O}{\|}}{C}O\sim$$

Urethane Isocyanate Allophonate

Still another form in which isocyanates are used is as isocyanurates. These are isocyanate trimers and have an advantage over biurets in being more stable. A typical isocyanurate is the trimer of 3-isocyanatomethyl-3,5′,5-trimethylcyclohexyl isocyanate, trivially known as “isophorone diisocyanate” (**XI**) (Section 4.6.2). The conversion to trimer (**XII**) takes place in the presence of a basic catalyst.



3-Isocyanatomethyl-3,5,5'-trimethylcyclohexyl isocyanate, "Isophorone diisocyanate"

XI

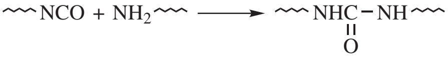
Isocyanurate trimer of isophorone diisocyanate

XII

In the formation of polyurethane foams, carbon dioxide for foaming may be produced by the addition of water, which gives a carbamate, which in turn decomposes to an amine and CO_2:

$$\sim\!\sim NCO + H_2O \xrightarrow[\text{amine}]{\text{Tertiary}} \underset{\text{Carbamate}}{\left[\sim\!\sim NHCOOH\right]} \longrightarrow \underset{\text{Amine}}{\sim\!\sim NH_2} + \underset{\text{Carbon dioxide}}{CO_2\uparrow}$$

This method, however, is an expensive way to obtain a gas for foaming, and specialized foaming agents are used. When water is added, urea linkages form by the condensation of the amine with more isocyanate:



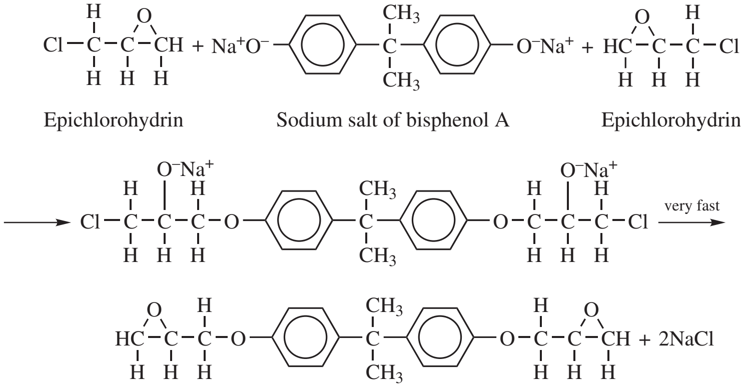
$$\sim\!\sim NCO + NH_2\sim\!\sim \longrightarrow \sim\!\sim NH\underset{\underset{O}{\|}}{C}-NH\sim\!\sim$$

Polyurethane foams contain both these and biuret linkages.

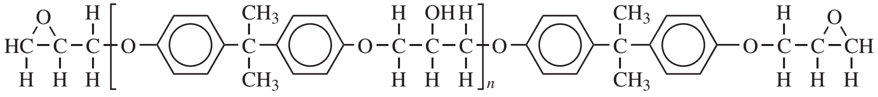
15.4.3 Epoxy Resins

The curing of epoxy resins is interesting because functionality is generated in the course of the reaction.

Epoxy resins are typically condensates of bisphenol A with epichlorohydrin. If a large excess of epichlorohydrin is used, a simple molecule results from the condensation of 2 mol of epichlorohydrin with 1 mol of bisphenol A.

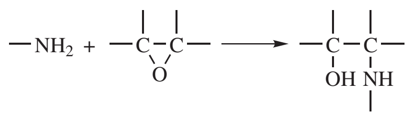


If the reactants are close to equimolar, on the other hand, a low molecular weight polymer (**XIII**) is formed where *n* is between 1 and 4. In either case the terminal groups are epoxy groups.

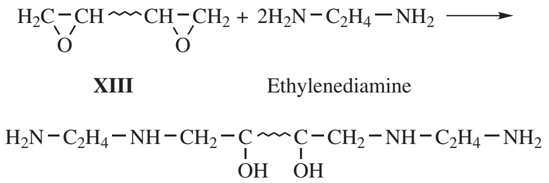


XIII

The epoxy groups will react with di- or multifunctional amines such as ethylenediamine or diethylenetriamine to give a cross-linked resin. When one of the primary amine groups reacts with an epoxy group a hydroxyl group and a secondary amine group are generated (**XIV**). Both of these groups can react further with epoxy groups in principle, although the hydroxyl group will react only at high temperatures. The aliphatic amine groups react at room temperature, and if two molecules of ethylene diamine react with one polymer molecule of epoxy resin a molecule (**XV**) is generated with four amine groups—two primary and two secondary. The new polymer has four amine groups with six active hydrogens, each of which can react with more epoxy resin, and thus the conditions for cross-linking have been established.

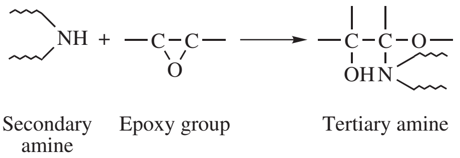


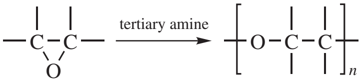
(**XIV**)



XV

The interaction of the secondary amine group with an epoxy group generates a tertiary amine. Tertiary amines are catalysts for the self-polymerization of epoxy groups to polyethers, so yet another polymerization mechanism comes into play and is shown in the following equation. This polymerization is chain growth, whereas the polymer formation resulting from the condensation of amine and epoxy groups is step growth.





15.4.4 Dendritic and Hyperbranched Polymers

Dendritic polymers are a special class of macromolecules and their production represents the ultimate in step-growth polymerization, in that each step is carried out separately. A linear polymer consists of long chains of monomer, sometimes coiled and tangled, sometimes ordered laterally in a crystalline domain. A dendrimer, on the other hand, consists of molecular chains branching out from a common center, and there is no entanglement between them. The first dendrimer was synthesized by Vögtle in 1978 and is typical. It involves a Michael condensation of acrylonitrile to primary amine groups, for example, aniline (**XVI**). The initial reaction (Fig. 15.10) gives a dicyano compound (**XVII**), and these groups are reduced to amine groups (**XVIII**). The Michael condensation is repeated to give four cyano groups; reduction gives four amino groups, and so on, until a spherical polymer molecule is obtained with amine groups at its surface. The starting molecule is said to be the zero generation dendrimer. Structure (**XVII**) is said to be first generation, (**XIX**) is second generation, (**XXI**) is third generation, and so on, until the terminating generation. The molecular weights of dendrimers increase exponentially with the number of generations. The molecular weights of the zeroth, first, second, third, and fourth generation poly(propylenimines) are, respectively, 93, 209, 437, 893, and 1805 daltons. The molecular weight of dendrimers is limited by steric factors, that is, overcrowding at the molecule surface. This is called the starburst effect. Molecular weight can also be limited by the use of terminating reagents that have no further functional groups to react. They may have other properties instead. Figure 15.11 shows a fifth generation poly(propylenimine) with butylenediamine at its core and with 64 strongly fluorescent dansyl units at its periphery. This method of making dendrimers is called divergent. Convergent polymerization is also possible, where one starts with the groups that are to appear at the surface and links them backward to the inner-unit and finally to a central core molecule. Either method requires polymerization to be brought about step by step as each successive generation is added. Monomers are prevented from undergoing more than a single step in the polymerization process by

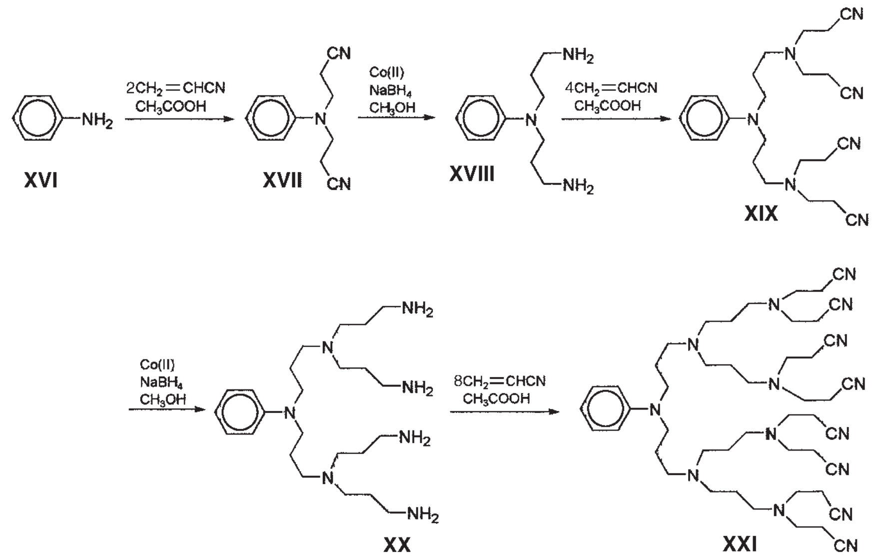


FIGURE 15.10 Vögtle's synthesis of poly(propylenimine).

requiring a change in functional groups, as occurs with the conversion of cyanide to amine groups in Figure 15.10. A consequence is that dendrimers are inevitably expensive to make, although the automatic synthetic methods devised for protein synthesis and combinatorial chemistry can be invoked. If functional groups were not changed, then unbridled polymerization would take place to give less regular but still highly branched polymers known as hyperbranched polymers. These share some of the characteristics of dendrimers and are much easier to make. Their closeness to dendrimers is measured by their molecular weight distribution (Section 15.3.4). Dendrimers have a distribution of unity. The second generation hyperbranched polymer shown in Figure 15.12 is made from 1,3,5-benzenetricarboxylic acid (**XXII**) at its core, an aminodicarboxylic acid as monomer (dendrone) (**XXIII**) and diethylamine as capping agent. A molecular weight distribution of 1.2 is claimed.

Dendrimers and hyperbranched polymers differ from linear polymers in their properties. Some of these are shown in Table 15.6. As with radial block polymers (Section 15.3.6) viscosities are lower because there is no tangling of chains, and solubilities are higher because of the number of sites for solvation. Crystallinity is low because there is no scope for alignment of polymer chains or interaction between them, and reactivity is high unless terminating agents have blocked the surface of the dendrimer. The spherical structure combined with the lack of polarity means that dielectric constants are often less than 2 compared with 4–6 for most linear polymers.

The synthesis of dendrimers and hyperbranched molecules is a fascinating extension of polymer technology. Dendrimers are at present in the situation that lasers were roundabout 1960, that is, they are answers in search of a problem. There are potential medicinal applications in drug delivery systems, in which the drug is loosely bonded

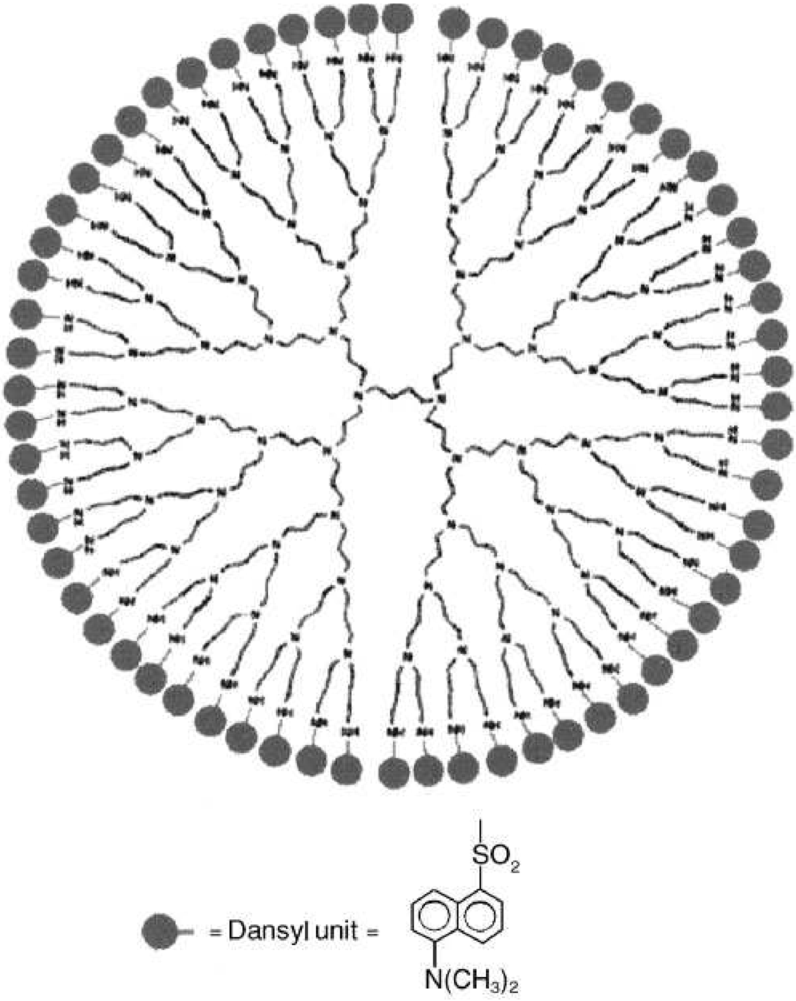


FIGURE 15.11 A fifth generation poly(propylenimine) dendrimer with 64 strongly fluorescent dansyl units at its periphery. *Source:* V. Balzani in M. Freemantle, *Chem. Eng. News* **77.** No. 44, 1 November 1999, p. 27.

to the dendrimer so that it can be released by heating, enzyme action, or photochemically. The dendrimer itself can be made water soluble, for example, by surface carboxyl groups, while still retaining a water soluble drug. Additional functional groups can be attached that will bond to the target organ. Poly(amidoamine) dendrimers (PAMAM) are transvection agents that are effective in transferring genetic materials into the cell. They also have potential application as immunodiagnostic agents.

Polyether dendrimer films can occlude metal ions, and functional groups on the surface of dendrimers can be arranged to detect organic compounds selectively. Dendrimers made by the convergent method can be made unsymmetrical with

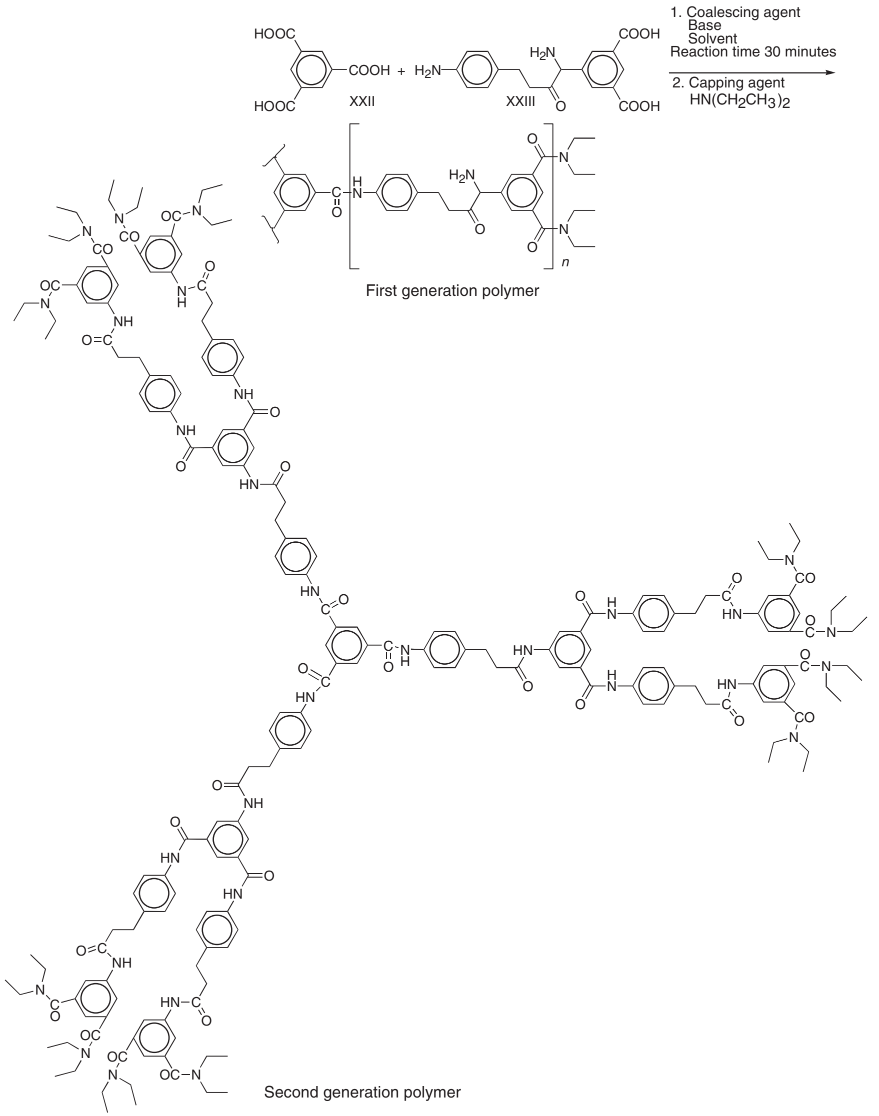


FIGURE 15.12 Second generation hyperbranched polymer from 1,3,5-benzenetricarboxylic acid and an aminodicarboxylic acid dendrone.

hydrophilic groups at one side and hydrophobic groups at the other, and these will form monolayers at interfaces. Large dendrimers can behave as single-molecule micelles.

There is empty space within dendrimers in the form of voids and channels, and these offer the possibility of catalytic reactions similar to those brought about within zeolites. Dendrimers provide unique catalytic environments both at their surface and in the cavities. They can provide a microenvironment for molecular reactions and

TABLE 15.6 Properties of Linear Polymers and Dendrimers

	Linear Polymers	Dendrimers
Shape	Random coil	Spherical
Viscosity	High	Low
Solubility	Low	High
Crystallinity	Depends on polymer	Low
Reactivity	Low	High
Compatibility	Low	High
Compressibility	High	Low
Structural control	Low	Very high
Dielectric constant	Typically 4–6 (polyethylene = 2.26)	Ultra low, <2

nanoscale reactor sites for catalysis. Dendrimers can have many light absorbing groups at their peripheries and can therefore harvest successive quanta of light, as occurs in photosynthesis. This energy can transform into chemical energy for reactions or electric current, or it can be converted to monochromatic light. A laser dye has been placed in the dendritic core and the system acts like an optical amplifier. Another potential application is the use of the dendrimer as a host for polymerization, which can occur in the cavities of the dendrimer, thereby avoiding termination with other polymerization chains. Finally, dendrimers have ultralow dielectric constants, which could lead to breakthroughs in semiconductor performance.

15.5 POLYMER PROPERTIES

In Section 5.4.4, we described how monomers were converted to polymers, bifunctional monomers leading to linear thermoplastic resins and polyfunctional monomers providing cross-linked thermosetting resins. Only one property, average molecular weight, has been mentioned. Molecular weight and mechanical strength are related since strength increases rapidly between 50 and 500 monomer units. Further increases in molecular weight have little effect. In this section, we describe additional properties of polymers and discuss the factors that give them the properties that make them useful: high viscosity, tensile strength, and toughness.

15.5.1 Crystallinity

Crystallinity is the key factor governing polymer properties. An easy way to visualize it is to regard crystallinity as a situation in which the polymer chains fit into an imaginary pipe. That is, they align themselves in bundles with a high lateral order, and the chains lie side by side. To do this they must be linear, not coiled, and there must not be bulky groups or branching to prevent the polymer chains from achieving molecular nearness.

There is an analogy, although not an exact one, with the crystallization of nonpolymeric materials like sodium chloride or *n*-hexane, where the ions or molecules must fit into a crystal lattice. With polymers, however, it is long-chain molecules, not ions or small molecules, that must fit, and the structure into which they fit is not a lattice but an imaginary cylindrical tube. Figure 15.13 attempts to illustrate this concept and shows how the chains may line up in an ordered fashion. It is, however, unlikely that all the chains in a polymer or even all of a single chain will be able to enter into the ordered structure of complete crystallinity, although nylon and high-density polyethylene come close. Usually, the ordered regions are small (microcrystalline) and are scattered through the polymer that is otherwise amorphous. Where the polymer is crystalline, it is platelike and of uniform thickness. Emanating from these crystalline regions are the sections of the chains that are not incorporated into the crystal lattice. They form the amorphous part of the polymer and may actually coil back over the crystalline platelets. Thus one can legitimately talk of the degree of crystallinity of a polymer. Some polymers are almost totally crystalline, others almost totally amorphous. Even a single polymeric substance can exist with a range of crystallinities depending on how it was made and processed.

Two factors govern the tendency of a polymer to crystallize. One is the ease with which the polymer chains will pack into a "crystal," and the other is the magnitude of the attractive forces between neighboring molecules of the polymer. The first of these means that crystalline polymers are more likely to form from chains that do not

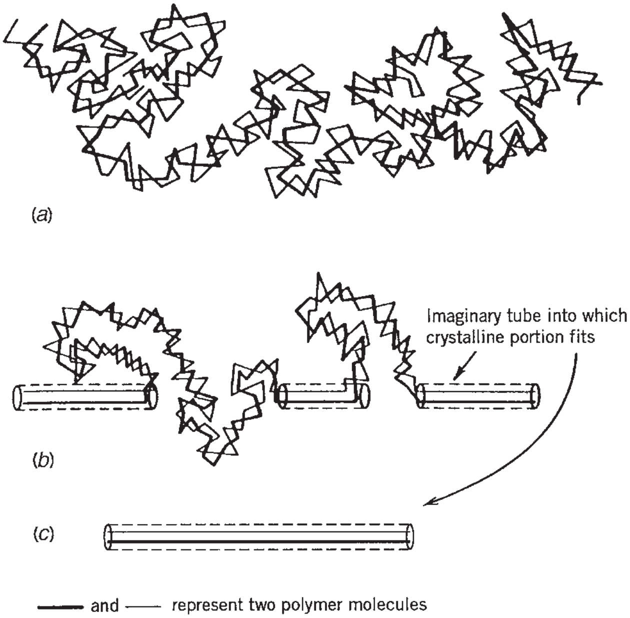


FIGURE 15.13 Polymer crystallization: (*a*) Noncrystalline; (*b*) partially crystalline; and (*c*) completely crystalline.

have bulky substituents, and where there is not a great deal of branching. Poly(ethylene terephthalate) is without bulky side chains and is crystalline after orientation, that is, after the fibers are drawn. The rigid benzene ring makes the polymer chains stiff and unwilling to coil.

Isotactic polymers made by Ziegler–Natta polymerization are also highly crystalline unless, as in *p*-substituted polystyrenes, a bulky group keeps the polymer chains apart. Polystyrene, polymerized as it normally is by peroxide catalysis, is an example of an amorphous polymer. Isotactic polystyrene made by Ziegler–Natta catalysis, however, is highly crystalline with better properties between its glass transition temperature (~80°C) and its crystalline melting point (~240°C). Its commercialization was inhibited because it crystallizes very slowly, and therefore changes its properties after processing. However, metallocene catalysts (Section 15.3.12) were thought to have made possible a syndiotactic form with a high-melting point that would function as an engineering polymer, that is, one that would replace metals. Dow discovered various difficulties and aborted their development effort.

Other amorphous polymers are exemplified by poly(methyl methacrylate) and polycarbonates. The latter are condensates of bisphenol A and phosgene (Section 7.1.2.2). The pendant groups on the methacrylate polymer are bulky, and the two phenyl groups in the polycarbonate are not coplanar. Thus crystal formation is obstructed. Most copolymers have little crystallinity because their structures are nonlinear.

In general, crystalline polymers are opaque because light is reflected or scattered at the boundaries between the microcrystalline and amorphous regions. Amorphous polymers are transparent and glasslike. Two exceptions should be noted. If a crystalline polymer is biaxially oriented, that is, stretched simultaneously in two directions, as in drawn poly(ethylene terephthalate) (Mylar) sheet, then the whole sheet is in effect a single crystal and is transparent. Furthermore, in a few polymers, the most important of which is the polymer from 4-methyl-1-pentene, the refractive index of the crystal is identical with that of the amorphous region. No light scattering occurs at boundaries, and the crystalline polymer is clear and transparent.

The second factor leading to crystallization is the forces of attraction between neighboring molecules. These comprise hydrogen bonding, which is the strongest, and the various kinds of van der Waals forces, dipole–dipole forces, dipole-induced dipole forces, and London dispersion forces. They vary in strength from about 1–2 kcal mol^{-1} (5–10 kJ mol^{-1}) per unit of polymer chain in elastomers to 5–10 kcal mol^{-1} (20–40 kJ mol^{-1}) in fibers. London forces are weak, whereas the others can be quite high. Cellulose and nylon provide examples of hydrogen bonding, PVC, and polyacrylonitrile of dipole–dipole interaction, and polyethylene of London forces.

We can extend the analogy between crystallization of *n*-hexane and polyethylene. As *n*-hexane is cooled, the thermal motion of the molecules decreases until it can no longer overcome the forces of attraction between them. Accordingly the molecules pack into the orientation of lowest energy, that is, the crystal lattice, and the sample solidifies or crystallizes.

The molecules of polyethylene are hundreds of times larger than those of hexane. Although the intermolecular forces between the $\text{—CH}_2\text{—}$ units are about the same in the two molecules, the total force per molecule in the polymer will be much higher. Furthermore, the polyethylene chains will not have the freedom of movement of hexane molecules. Instead they will be wriggling and coiling. There is little chance that one of them will ever be fully extended. The chains will also become entangled with one another, which will hinder molecular motion. Molten polymers are viscous both because of chain entanglement and intermolecular forces. The latter factor is negligible at high temperatures, and viscosity under these conditions is due largely to chain entanglement.

When the temperature of molten polyethylene is reduced, molecular motion diminishes as it does in hexane. Eventually, there will be a tendency for the chains to pack into a crystal lattice. In order to do this they will need to be extended and not coiled, but the chance of a chain being fully extended is small. There will, however, be large portions of polymer chains that are extended. These will pack into an ordered crystal lattice and provide the microcrystalline regions, while the tangled, coiled portions will form the disordered amorphous regions seen in Figure 15.13.

In block copolymers (Section 15.3.8), it is possible to create a block that is highly crystalline together with one that is amorphous to obtain a final copolymer with special properties.

Crystalline polymers tend to have greater mechanical strength and higher melting point than amorphous polymers. Because the chains in the crystalline regions are closely packed, they would also be expected to have higher densities, and this too is observed. For example, low-density polyethylene has a tensile strength (Section 15.5.4) of 2000–2500 psi (140–175 kg cm^{-2}), a softening point of 85–87°C, and a specific gravity of 0.91–0.93. High-density polyethylene, on the other hand, has a tensile strength of 3500–5500 psi (245–385 kg cm^{-2}), a softening point of 127°C, and a specific gravity of 0.94–0.97.

The degree of crystallinity of a polymer is measured by X-ray diffraction by the same technique used for single crystals. High-density polyethylene may have as much as 90% crystallinity; the low-density material has only ~55%, which is still high considering the extent of chain branching in the polymer. It occurs because the lengths of polymer chain between the branches are capable of getting close enough to other chains for crystallization to take place.

Crystallinity is also related to orientation. If one slowly flexes a wide rubber band, an appreciable amount of heat is generated, which can be felt if the band is touched to the lips. This results from the friction of one polymer molecule rubbing against another as the stretching action causes them to align. Before it is stretched, the rubber band is largely amorphous. The alignment on stretching is tantamount to crystallization, which also causes the translucent rubber band to become opaque. Orientation of the polymer has caused it to crystallize. The heat generated can therefore also be thought of as heat of crystallization. The degree of crystallinity that can be induced in an elastomer by stretching can reach 30% (Fig. 15.14).

The orientation or crystallization of polymer molecules by stretching or drawing is an important step in the processing of polymers for use as textile fibers. When nylon and polyesters are manufactured they have low crystallinity. The stretching or drawing of the fibers causes the polymer molecules to line up or crystallize to give the longitudinal strength required in fibers.

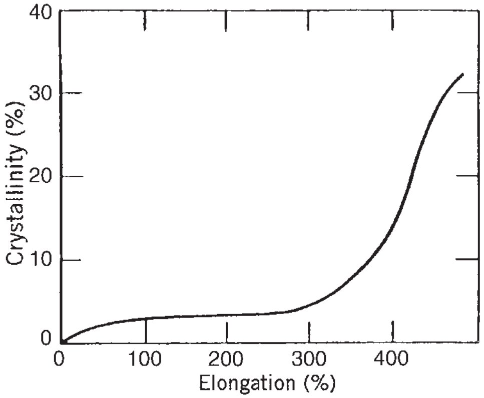


FIGURE 15.14 Crystallization of cured rubber by stretching.

A difference between fibers and rubbers is that the latter have much greater "elastic memory" and do not remain stretched and crystalline. In other words, it is hard to stretch them beyond their limit of crystallinity. The reason is that rubber is lightly cross-linked, and these cross-links tend to pull the rubber molecules back to their original configuration. In addition, stretching is a disorder–order transition, and the entropy decreases. The return to the unstretched state is favored by the corresponding entropy increase. In nylon, the "cross-linking" takes the form of hydrogen bonds that break and reform as the fiber is stretched. Indeed, stretching orients the molecule so that more hydrogen bonds are formed than are broken. Consequently, the elastic memory is quickly exceeded on stretching.

15.5.2 Glass Transition Temperature, Crystalline Melting Point, and Softening Temperature

If an amorphous material such as polystyrene is melted and then allowed to cool, it does not solidify sharply. First, it goes from a viscous liquid to a rubbery solid, then to a leathery solid. Finally, when all of the molecules have lost their thermal "wriggling" motions, it becomes a glassy solid, recognizably polystyrene. The last change is a sharp one, and the temperature at which it occurs is called the glass transition temperature (T_g) of the polymer. Obviously, it has a bearing on the properties of the polymer at the service temperature at which it is to be used. A polymer that is a soft, leathery material above its T_g. may be a hard, brittle, amorphous one below the T_g.

T_g is associated primarily with amorphous polymers, although crystalline polymers also have a T_g, because all polymers have amorphous regions between the microcrystalline regions.

If a crystalline polymer is used above the T_g of the amorphous regions, the latter will be flexible, and the polymer will be tough. If the temperature is below the T_g, however, the amorphous regions will be glassy and the polymer brittle. A similar situation for block copolymers is described in Section 15.3.8.

TABLE 15.7 Typical T_g and T_m Values for Polymers

	Temperature (°C)	
	T_g	T_m
cis-Polybutadiene	−101	4
cis-Polyisoprene	−73	29
trans-Polyisoprene	−58	70
Linear polyethylene	−70 to −20	132
Polypropylene	−16	170
trans-1,4-Polybutadiene	−9	139
Nylon 6,6	47	235
Poly(methyl methacrylate)	49	155
Poly(vinyl chloride)	70	140
Polystyrene	94	227
Polycarbonate	152	267
Cellulose triacetate	111	300
Poly(tetrafluoroethylene)	135	327

The temperature at which a molten polymer changes from a viscous liquid to a microcrystalline solid is called the crystalline melting point, T_m, of the polymer. If the solid polymer is partly crystalline, the change is accompanied by sudden changes in density, refractive index, heat capacity, transparency, and similar properties. It is analogous to the melting point of a nonpolymeric chemical compound, but is not as sharp, and melting and freezing take place over a small range. The value of T_m depends on chain structure, intermolecular forces, and chain entanglement.

The softening point is an arbitrary measure of the temperature at which a polymer reaches a certain specified softness. It is of great importance as the upper service temperature of a polymer but has little significance on the molecular level.

Table 15.7 indicates typical values for T_g and T_m for various polymers. T_g is about half to two-thirds of T_m for most polymers if the temperatures are in degrees absolute. Deviations from this may be due to unusual molecular weight distributions, chain stiffness, and symmetry. These values, unlike the melting points of pure organic compounds, can be considered only "typical." T_g may vary with the molecular weight of the polymer, its method of preparation, its end-group distribution, and with the degree of crystallinity in a given polymer sample. For a completely unoriented material T_g will be very low. When the material is oriented or converted to a crystalline state, T_g increases. T_g for poly(ethylene terephthalate) may vary from −80 to 180°C.

15.5.3 Molecular Cohesion

Molecular cohesion is the average force between the repeating units of a polymer chain and its neighbors. The forces are van der Waal's forces or hydrogen bonds. Their magnitude can be calculated from cohesive energy density (see note at the end of this chapter).

Hydrogen bonds contribute most to molecular cohesion. Dipole–dipole forces contribute less, and London dispersion forces the least. The strength of the molecular interactions diminishes rapidly, actually with the sixth power of the distance between the molecules. Thus bulky amorphous polymers have relatively low intermolecular forces, whereas those in crystalline polymers are much higher because the molecules are much closer together.

15.5.4 Stress–Strain Diagrams

Many of the quoted properties of polymers are derived from stress–strain diagrams. These are graphs of the deformation in a polymer sample (expressed as percent of elongation) produced by a particular applied stress [a tension expressed as pounds per square inch (psi), grams per square centimeter, or meganewtons per square meter]. Such diagrams can be generated quickly from a given polymer sample of controlled size in a testing laboratory. For reproducibility, a standard sample and rate of extension must be used. An example (for a hard, tough plastic) is shown in Figure 15.15.

In the initial stages of the extension, the stress–strain diagram is linear. That is to say the material obeys Hooke's law, and stress is proportional to strain. The gradient or slope of this straight section is called the initial modulus of elasticity and is

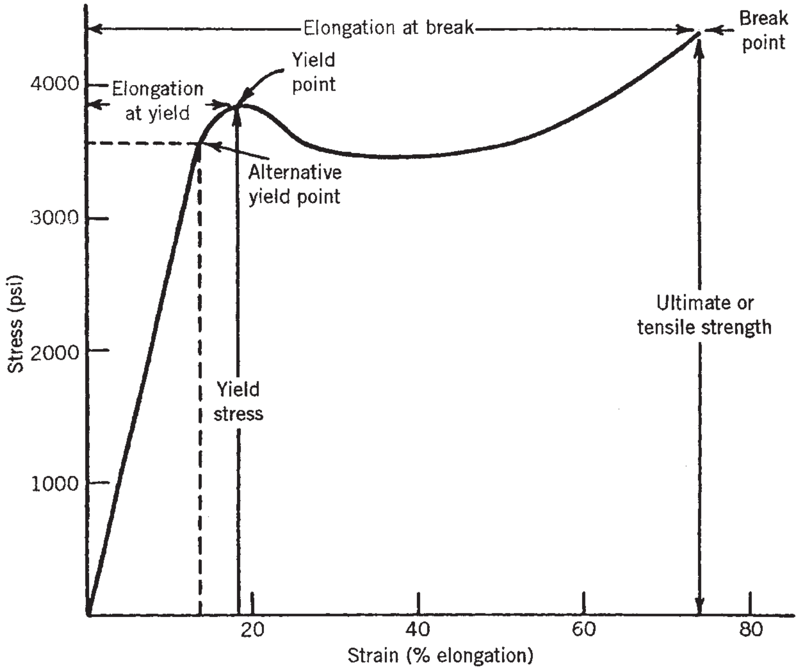


FIGURE 15.15 Stress–strain diagram.

a measure of the stiffness of the material (Young's modulus). If the applied stress is removed at this stage, the polymer will return to its initial length. After a certain stress the graph ceases to be linear, and the extension is nonreversible; that is, a permanent deformation is produced. The yield point is defined as the maximum in the stress–strain curve, as shown in the diagram, and has an elongation at yield and a yield stress associated with it. Some authorities define the yield point as the point at which deformation becomes irreversible, that is, at which Hooke's law ceases to be obeyed. Because many polymers do not obey Hooke's law, the modulus is frequently expressed as pounds per square inch of tensile strength at a given degree of elongation such as 2%, which is called the 2% modulus. Some elastomers are better described by a 100 or 300% modulus.

After the yield point the plastic stretches relatively easily and, after stiffening a little toward the end, it breaks, and the curve comes to an abrupt end. The break point has associated with it an elongation at break or upper limit of extensibility and an ultimate tensile strength. The area under the curve up to the break point may be measured and is called the work-to-break. The tensile strength is the strength required to pull the polymer apart, and the work-to-break is a measure of the ability of the polymer to resist not only tension or "pulling apart," but also other stresses such as bending, compression, impact, and twisting.

Figure 15.16 shows the type of stress–strain diagrams obtained for fibers, thermoplastics, and elastomers. Fibers, because they have been oriented, have high tensile strength and modulus and resist elongation. The work-to-break is small, although the polymer is strong and resists "pulling apart." The elastomer, on the other hand, has high elongation but low tensile strength and modulus. Thus it has little resistance to deforming forces other than elongation. As its extension is

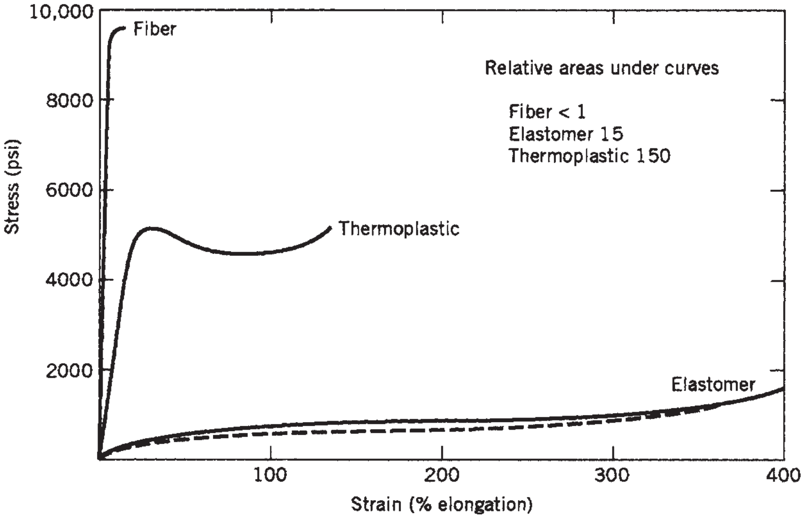


FIGURE 15.16 Stress–strain curves.

reversible, a return stress–strain curve can be obtained if the stress is reduced before the sample breaks. This curve is indicated by the dotted line. The area within this hysteresis loop is the work dissipated as heat during the cycle.

The thermoplastic shown has quite a high modulus and tensile strength and a fairly high elongation. The area under the curve is large; hence, this type of thermoplastic would be used if a wide variety of deforming forces were expected, whereas a fiber would have best resistance to simple tension. Elastomers are useful because they “bounce back” and can absorb energy by hysteresis.

15.6 CLASSES OF POLYMERS

Polymers are used in five main ways: as elastomers, plastics, fibers, surface coatings, and adhesives. Table 15.8 shows the combination of polymer properties required for the first three applications in terms of the four major properties.

Elastomers have a low modulus. Modulus is a measure of stiffness, and rubbers are not stiff. On the other hand, they need to be highly extensible, and elongations of 1000% are common. The crystallinity of an elastomer is low when the material is unstressed, but stretching leads to a higher degree of crystallization (Section 15.5.1). Molecular cohesion in elastomers must be low because otherwise the polymer chains will not easily slip over one another when the elastomer is stretched or slide back reversibly when the tension is released.

The second class of polymers is plastics. These are defined as polymers or resins that have been made into shapes, usually under pressure. Shaping may be done by processes such as molding, casting, extrusion, calendaring, laminating, foaming, blowing, and many others. Nonetheless, the term plastic has a specific meaning in this context and should not be used to refer to polymers in general. The moduli, as

TABLE 15.8 Polymer Properties

Properties	Elastomers	Plastics	Fibers
Modulus, (psi)	15–150	1500–200,000	150,000–1,500,000
kg cm^{-2}	1–10	100–14,000	10,000–100,000
Extensibility, upper limit (%)	100–1000	20–100	<10
Crystallization tendency	Low when unstressed	Moderate to high	Very high
Molecular cohesion (cal/monomer unit)	1000–2000	2000–5000	5000–10,000
Examples	Natural rubber, polychloroprene, polybutadiene	Polyethylene, polypropylene, polystyrene, poly(vinyl chloride), poly(vinyl acetate)	Silk, regenerated cellulose (rayon), nylon, polyester, acrylics, polypropylene

well as other properties of plastics vary widely according to their applications. For example, molding, calendering, or extrusion of a thin film or sheet requires a material with a low modulus so that the sheet is flexible. On the other hand manufacture of a bleach bottle demands a stiff polymer—the stiffer the better so long as it is not brittle–so that the walls can be made thinner and material saved.

The extensibility demanded in elastomers is not needed in plastics, although a degree of extensibility is important so that the work-to-break is high enough for the plastic to resist twisting and impact. Generally, the properties of plastics are intermediate between those of elastomers and fibers.

Fibers, if they are going to be knitted or woven into dimensionally stable garments, require unrelenting properties. They should have high modulus and low extensibility. The fibers must be strong so that a single thread will not "pull apart," and this requires a high modulus and molecular cohesion, properties closely related to high tensile strength and crystallinity.

It is more difficult to generalize about surface coatings and adhesives than about the other groups. A coating may require high extensibility and low modulus if it is to be applied to a soft rubber surface. On the other hand, a coating for a baked phenolic sheet may require low extensibility and high modulus. The property that both coatings and adhesives require is high adhesion, and the problem is to achieve this while maintaining a reasonable level of the diametrically opposed property of cohesion. In addition, a coating will require resistance to abrasion.

In general, coatings and adhesives tend to have low moduli, somewhere between those of elastomers and plastics. They must have some extensibility, particularly if the material is to be used on a dimensionally unstable substrate such as wood. It follows that coatings and adhesives have low crystallinity.

NOTES AND REFERENCES

The *Encyclopedia of Polymer Science and Engineering* and *The Encyclopedia of Chemical Technology* cited in Section 0.4.1 are major sources of information about polymers. P. T. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, although dated, has hardly been superseded for many of its discussions of basic polymer chemistry. A standard work, F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 2nd ed., John Wiley & Sons, Inc., New York, 1971 is also classical. Sound on polymer science and well referenced, it is nonetheless somewhat difficult to use.

Polymer research is summarized every few years in H. J. Canton, *Advances in Polymer Science*, Springer, Berlin, 1958 onward.

A user-friendly book is I. M. Campbell, *Introduction to Synthetic Polymers*, OUP, Oxford, UK, 1994.

Section 15.2 Functionality has been described by Flory, *op. cit*, p. 31 ff.

Section 15.3.3 Reactivity ratios of monomer pairs is described in detail in *Copolymerization*, G. E. Ham, Ed., *High Polymers Series No. 18*, John Wiley & Sons, Inc., New York, 1964.

Section 15.3.4 An excellent discussion of molecular weight determination is contained in Flory, *op. cit.*, p. 266 ff.

Section 15.3.5 A brief review of new catalysts and new processes, dealing mainly with the gas phase and polyethylene is D. Foxley, *Chem. Brit.*, April 20, 1998, p. 305.

Section 15.3.6 The May 1978 issue of *J. Phys. Chem.* is devoted entirely to articles on radical ions. The issue is in honor of Professor M. Szwarc who did the early work in this field. P. Plesch (private communication) has proved that the first step in cationic polymerization by aluminum chloride is the disproportionation:

$$2AlCl_3 \rightleftharpoons AlCl_2^+ + AlCl_4^-$$

Section 15.3.7 M. Swarc (see above) himself contributed a relevant book, *Living Polymers and Mechanisms of Anionic Polymerization*, Springer, Berlin, 1983.

Section 15.3.8 For a discussion of block copolymers see D. C. Allport and H. Janes, *Block Copolymers*, Wiley-Interscience, New York, 1973.

Section 15.3.10 A celebration of Ziegler–Natta catalyst science and technology is contained in a book entitled *Coordination Polymerization, A Memorial to Karl Ziegler*, J. C. Chien, Ed., Proceedings of the American Chemical Society Symposium, UCLA, Los Angeles, CA, April 1974, Academic, New York, 1975. Figure 15.8 is taken from F. W. Billmeyer, *op. cit.*, p. 322.

Section 15.3.12 The pioneering work on metallocenes was reported by H. Sinn, W. Kaminsky et al. *Angew. Chem.* **69**, 686 (1957). Because of their commercial significance, few of the modern developments have been published in the scientific literature, but there is an revolution in olefin polymerization, see *Chem. Ind.* 857 (1994). Books include G. M. Benedikt and B. L. Goodall, *Metallocene Catalyzed Polymers*, B. F. Goodrich, Brecksville, OH, 1998; G. M. Benedikt, *Metallocene Technology in Commercial Applications*, Noyes, Geneva, 2000; and a two-volume set, Metallocene-Based Polyolefins, J. Scheirs and W. Kaminsky, Eds., John Wiley & Sons, Inc., 2000, New York. The claims for high catalyst activity appeared in *Chem. Mkt. Rep.*, June 13, 1994, p. 1. Dow's plans were discussed in *Chem. Week*, Feb. 2, 1994, p. 10. and Jan. 5/12, 1994, pp. 27–31. The Exxon–Dow competition is reviewed in *Chem. Week* Sept. 15, 1993, p. 5. Hundreds of patents have been filed. Exxon's basic patents are European Patent Appl. 0,206,794 A1 (Dec. 30, 1986) and 0,128,045 A1 (Dec. 12, 1984); World Patents 8,702,991 A1 (May 21, 1987) and 9,200,333 A2 (January 9, 1992), and US Patent 5,026,798 (March 17, 1992). The most important constrained geometry catalyst patent is Dow's European Patent Appl. 0,416,815 A2 (March 13, 1991).

Section 15.3.11 Several companies, including Du Pont, Hercules, Phillips, Montecatini and Standard Oil of Indiana, filed patents almost simultaneously on polypropylene production. A bitter patent suit of almost 30 years duration resulted, and Phillips Petroleum Co. emerged the victor with a composition of matter patent on crystalline polypropylene. The decision was based on the fact that the inventors, P. Hogan and R. Banks, had tried a supported chromia–silica–alumina catalyst, on propylene in an attempt to prepare C_6 and C_8 oligomers in the gasoline range. They obtained mostly a liquid polymer with ~10% of a solid material. The solid turned out to be identical with Natta's polypropylene. In further work, P. Hogan and R. Banks decided that the chromia catalyst was not adequate for polypropylene production and turned to ethylene where results were far better and Phillips “Marlex” catalyst was born. Phillips patent applies only to the United States.

Section 15.4.2 Chlorofluorocarbons used to be the favorite foaming agent for polyurethanes but have been phased out. For other agents, see H. A. Wittcoff and B. G. Reuben, *Perspective*, Part 2, Section 2.7, cited in Section 0.4.2.

Section 15.4.4 Vögtle’s seminal paper appeared in E. Buleier, W. Wehner, and F. Vögtle, *Synthesis*, 155 (1978). Some early general references are listed at www.mmackay-dendrimer.htm, which also provides more information on viscosity. This apparently peaks at about the fifth generation. There is a more recent list at www.ipfdd.de/people/komber/structures.html. General background is provided at http://ky.ky.essortment.com/whatisdendrime_rsnz.htm. The state of dendrimers in 1999 was described in some detail in M. Freemantle, *Chem. Eng. News* **77**, **44,** Nov. 1, 1999, p. 27, which is the source of Figure 15.11 by V. Balzani. Details of the hyperbranched compound based on 1,3,5-benzenetricarboxylic acid come from www.nedo.go.jp/kiban/zairyo/eng/poly/poly005. html. Use of dendrimers in microelectrics will be found at www. almaden.ibm.com. Interest in hyperbranched polymers is summarized in *Chem. Eng. News*, Sept. 6, 1999, p. 37. Dendrimers are a topic of great current interest and a number of books made up of edited collections of articles have appeared. Examples are *Dendrimers, Assemblies and Nanocomposites*, R. Ashady and A. Guyot, Ed., Citus, London, 2002; *Dendrimers and other Dendritic Polymers*, J. M. J. Fréchet, D. A. Tomalia, Ed., Wiley, Chichester, 2001; *Dendrimers IV, Metal coordination, self assembly, catalysis*, F. Vögtle and C. A. Schilley, Ed., Springer, Berlin, 2001. G. R. Newcome, C. N. Moorfield, and F. Vögtle, *Dendrimers and Dendrons*, VCH, Weinheim, 2001 is a multiauthor book.

Section 15.5.3 The cohesive energy density δ^2 can be calculated from the latent heat of vaporization, δH_v cal mol^{-1}, or the surface tension, ρ dynes cm^{-1}, by the relationships:

$$\delta^2 = \frac{\Delta H_v - RT}{M/D} = \frac{14\rho}{(M/D)^{1/3}}$$

where R is the gas constant (1.987 cal mol^{-1}K^{-1}; 8.314 J mol^{-1}K^{-1}), T is the absolute temperature, M is the molecular weight, and D is the density in grams per cubic centimeter. The units of δ^2 are calories per cubic centimeter and those of δ are cal$^{1/2}$ cm$^{-3/2}$. The latter unit is called the hildebrand.

Section 15.5.4 A modern view is provided in *Characterization of Materials*, (2 Vols.) E. N. Kaufmann, Ed., Wiley, New York, 2003.

The following is a brief review of plastics fabrication techniques, adapted with permission from *The Chemical Economy*, cited in the general bibliography in Section 0.4.2.

Compression molding (Fig. 15.17) is practically the oldest method of fabricating plastics and is still widely used. The polymer is placed in one half (the “female” half) of a mold and the second or “male” half compresses it to a pressure of ~1 tonne per square inch (1.55×10^6 kg m^{-2}). The powder is simultaneously heated, which causes the resin to cross-link. Transfer molding is a cross between this and injection molding.

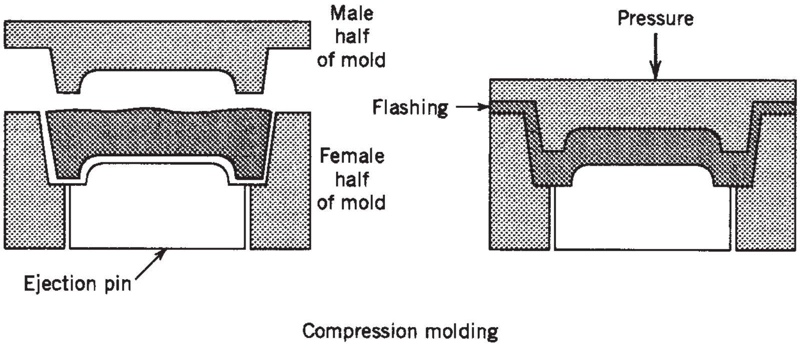


FIGURE 15.17 Compression molding.

Casting was also used before World war II. In the sheet casting of poly(methyl methacrylate), monomer is partly polymerized and the viscous liquid then poured into a cell made up of sheets of glass separated by a flexible gasket that allows the cell to contract as the casting shrinks.

Injection molding (Fig. 15.18). In injection molding, polymer is softened in a heated container and then forced under pressure into a cooled mold where it is allowed to harden. Pressure is released, the mold is opened, the molding is expelled, and the cycle is repeated. Injection molding is a versatile technique and can be used for bottle manufacture by a method identical with blow molding except that the initial "bubble" is injected rather than extruded.

Extrusion (Fig. 15.19) is a method of producing lengths of plastics materials of uniform cross-section. The extruder is similar to a domestic mincing machine with the added facility that it can be heated or cooled. The pellets enter the screw section via the hopper, are melted, and then pass through the breaker plate into the die. The

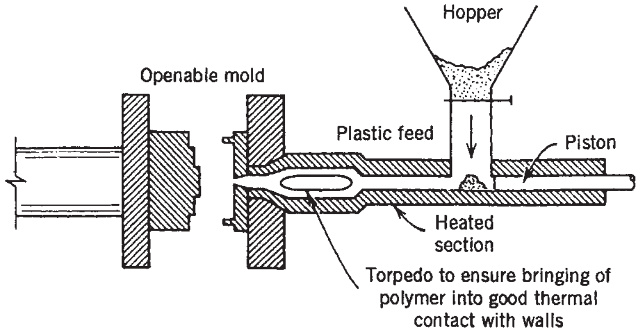


FIGURE 15.18 Diagrammatic representation of an injection molding machine.

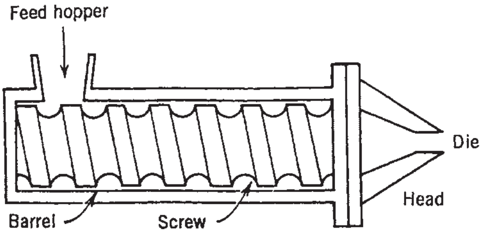


FIGURE 15.19 Extrusion.

molten plastic is forced out of the die with its cross-section determined by the shape of the die, but not identical with it because of stresses induced by the extrusion process. Extrusion can be used for coating electrical wiring by means of a cross-head die.

Blow molding Blow extrusion (Fig. 15.20), in which the initial lump of polymer is formed by an extrusion process, is the commonest form of blow molding. A short length of plastic tubing is extruded through a crossed die and the end is sealed by the closing of the mold. Compressed air is passed into the tube and the "bubble" blown out to fill the mold. Suitable control of this process can lead to the biaxial orientation of the polymer as in poly(ethylene terephthalate) soft drink bottles.

A variation of the process is used in the manufacture of thin film (Fig. 15.21). A tube of plastic is continuously extruded and expanded by being blown to a large volume and consequently a small wall thickness. The enormous bubble of plastic is cooled by air jets and taken up onto rollers. This material can either be slit down the side to give thin film or turned into plastic bags by sealing the bottom of the tube.

Vacuum forming (Fig. 15.22) is the opposite of blow molding A sheet of heat-softened plastic is placed over a mold and the air sucked out. The plastic is drawn down and conforms to the shape of the mold.

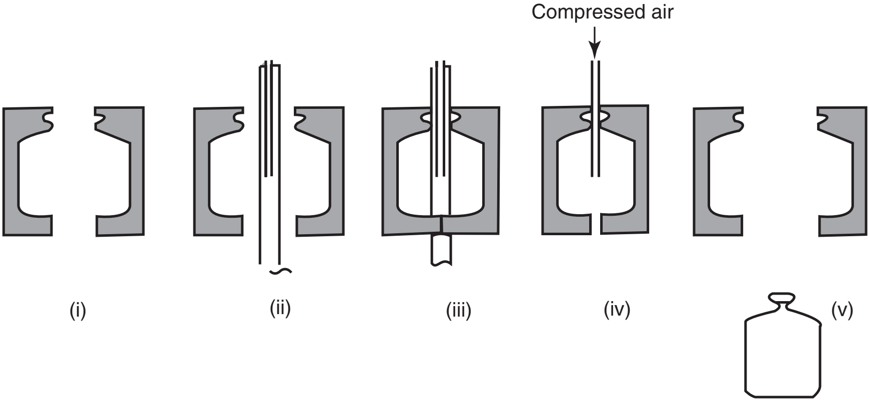


FIGURE 15.20 Blow extrusion.

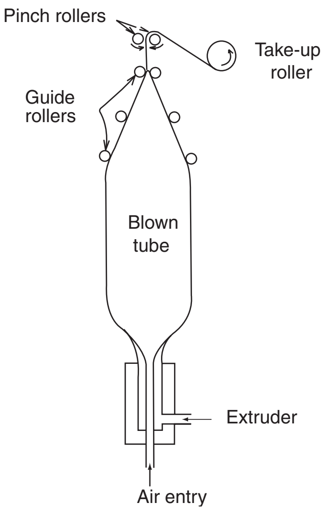


FIGURE 15.21 Production of film by extrusion and blowing.

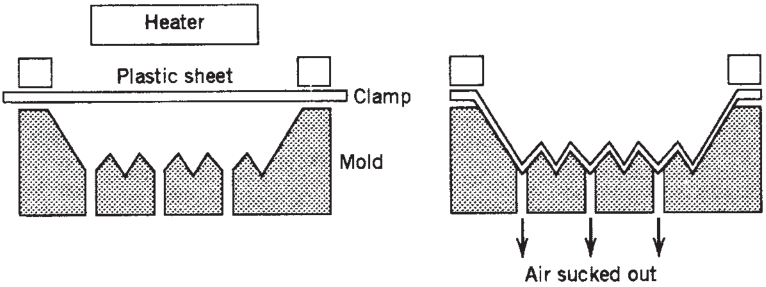


FIGURE 15.22 Vacuum forming.

Calendering makes use of a preheated polymer mix that is turned into a continuous sheet by passage between two or more heated rolls that squeeze it to the appropriate thickness. If fabric or paper is fed through the final rolls, the plastic can be pressed on it to give a plastic coated material. If the rolls are patterned, a "sculpted" appearance can be obtained.

Laminating The best known laminates are the Formica-type decorative laminates for household use. Brown paper is impregnated with an alcoholic solution of a resole and is then cut up and arranged in piles with a suitably printed melamine–formaldehyde impregnated decorative sheet on top. Also, a photograph of wood grain may be used with a melamine–formaldehyde topcoat. The whole is pressed at ~150–80°C and 3 tonnes/in.^{2} (4.65×10^6 kg m^{-2}) to give the finished laminate.

CHAPTER 16

INDUSTRIAL CATALYSIS

Many of the organic chemicals discussed in the previous chapters were already being made before World War II. They were made by fermentation or from coal by "traditional" organic chemistry in batch processes. The advent of cheap olefinic feedstocks derived from oil and natural gas led to a switch to "hot tube" industrial organic chemistry, that is, to continuous processes that produce hundreds of thousands of tonnes of product per year. The basis for this modern organic chemistry is frequently the "appropriate" catalyst, whose exact nature and formulation is often a closely guarded industrial secret.

In 1966, when catalyst theory was in its infancy, it was estimated that 70% of industrial processes involved catalysis. The percentage is now said to have reached 90%. Catalysis was said in 1999 to be used in the manufacture of more than \$3 trillion worth of goods and services. Annual royalties and fees from technology process licensing exceeded \$3.5 billion and the global merchant market for catalyst products approached \$8.5 billion. About 30% of the US gross national product is generated with the help of catalysis. This chapter is therefore devoted to a brief review of catalyst technology with emphasis on ways in which the concept of a catalyst has changed and on recent trends in the industry. First, we shall discuss the questions of catalyst choice, and second, some of the chemical engineering aspects of catalyst use. Third, comes the markets for catalysts and then a discussion of the different types of catalysts encountered in industry. Table 16.1 shows a summary of catalytic reactions.

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

TABLE 16.1 A Summary of Catalytic Reactions[a]

Class	Functions	Examples
Transition metals	Hydrogenation Dehydrogenation Hydrogenolysis (Oxidation)	Fe, Ni, Pd, Pt, Ag
Semiconductors and transition metal oxides	Oxidation Dehydrogenation Desulfurization (hydrogenation)	NiO, ZnO, MnO_2, Cr_2O_3, Bi_2O_3/MoO_3, WS_2, SnO_2, Fe_2O_3
Insulator oxides (main group oxides)	Dehydration (hydration)	$A1_2O_3$, SiO_2, MgO
Acids and acidic mixed oxides	Polymerization Isomerization Cracking Alkylation (hydrolysis) Esterification	H_3PO_4, H_2SO_4, BF_3, $SiO_2/A1_2O_3$, zeolites V_2O_5/Al_2O_3
Bases	Polymerization (esterification)	Na/NH_3
Transition metal complexes	Hydroformylation Polymerization Oxidation Metathesis	$[Co_2(CO)_8]$ $TiCl_4/Al(C_2H_5)_3$ $CuCl_2/PtCl_2$ WO_3, WCl_6
Dual function catalysis	Isomerization plus hydrogenation/dehydrogenation	Pt on SiO_2/Al_2O_3
Enzymes	Varied	Amylase, urease, proteinases
Reactions between immiscible reactants	Varied	Quaternary ammonium salts

[a] Data partly based on G. C. Bond, *Heterogeneous Catalysis: Principles and Applications*, Clarendon Press, Oxford, 1974 (see notes at end of this chapter). Less important functions are given in parentheses.

16.1 CATALYST CHOICE

Unlike feedstocks and raw materials, the overriding factor for industrial catalysts is not their cost. As long as catalysts can be reused, cost is not crucial. First, the outstanding feature of modern industrial catalysts is their selectivity, that is, the extent to which they make a reaction go in a desired direction. Second, there is the access they provide to unusual "nonequilibrium" products. Third, there is the conventional role of catalysts in increasing the rate of reaction. Fourth is the problem of recovering catalysts for reuse. In choosing a catalyst, there is also the question of homogeneous versus heterogeneous catalysis. We shall discuss these in turn.

16.1.1 Reaction Velocity and Selectivity

Catalysts are defined as materials that increase reaction velocity without themselves being consumed. That is only part of the story. The effect of a catalyst can be so large that a quantitative difference becomes qualitative. Thus platinum catalyzes the combination of hydrogen and oxygen. In the absence of a catalyst, the reactants can apparently remain for hundreds of years without reaction. It would appear that the platinum did not accelerate the reaction but rather that it brought it about. The same applies to many industrial catalysts. Silver "catalyzes" the oxygen–ethylene reaction to ethylene oxide, but yield of ethylene oxide in its absence is zero.

Selectivity is crucial. A material that does not react at a measurable rate in the absence of a catalyst may react to give quite different products in the presence of different catalysts and at different temperatures and pressures. Ethanol passed over copper can give either acetaldehyde or ethyl acetate depending on conditions. Passage over alumina gives ethylene or diethyl ether.

$$C_2H_5OH \xrightarrow{Cu} CH_3CHO + H_2$$

$$2C_2H_5OH \xrightarrow{Cu} CH_3COOC_2H_5 + 2H_2$$

$$C_2H_5OH \xrightarrow{Al_2O_3} CH_2{=}CH_2 + H_2O$$

$$2C_2H_5OH \xrightarrow{Al_2O_3} C_2H_5OC_2H_5 + H_2O$$

Thus catalysis often provides a reaction route that proceeds in parallel with other existing thermal or catalytic routes. Useful catalysts cause the desired reaction to be favored overwhelmingly. Increasing the selectivity of catalysts is an important activity of development chemists. A high selectivity not only brings the financial reward of increased yield, it also reduces the problems of byproduct sale or effluent disposal.

A catalyst often permits a reaction to take place at measurable speed under milder conditions than would otherwise be possible. That, in turn, may lead to a different equilibrium and a different major product. In the production of ethylene oxide (Section 3.7), no reaction would take place at 275°C in the absence of a catalyst. At a temperature at which a reaction *would* take place, only carbon dioxide and water would be formed. The silver catalyst enables the temperature to be kept sufficiently low for the ethylene oxide-forming reaction to proceed at a rate higher than the overall combustion reaction. It also means that the sequential oxidation of ethylene oxide proceeds slowly enough for the ethylene oxide to be isolated.

This is illustrated in a semiquantitative way in Figure 16.1. Ethylene and oxygen exist in a potential energy well, as shown, and there are other potential energy wells corresponding to ethylene oxide, acetaldehyde, peracetic acid, and carbon dioxide/water

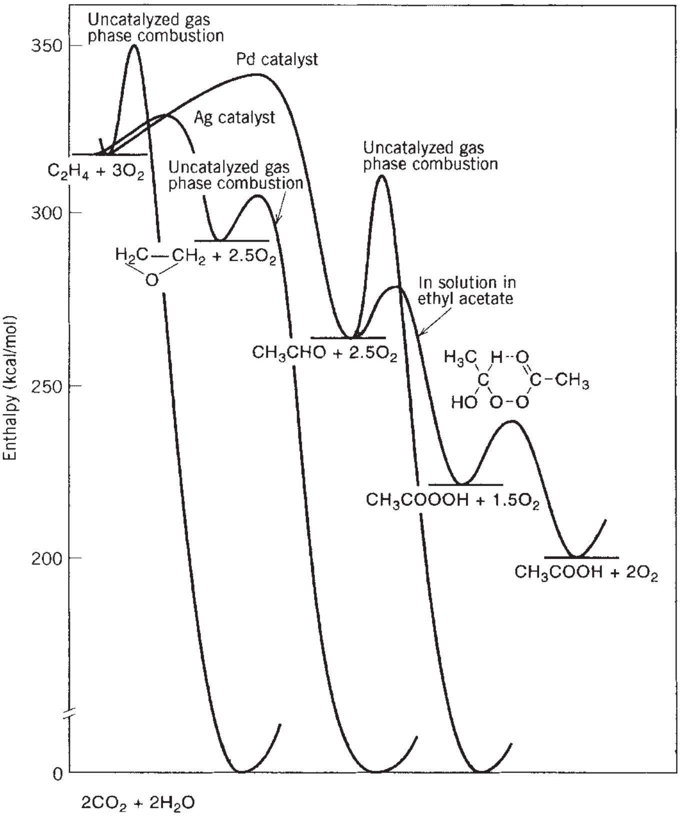


FIGURE 16.1 Potential energy diagram for the ethylene–oxygen system (based on enthalpy of $2H_2O + 2CO_2$ as zero).

as indicated. The maxima are the activation energies required for the various possible catalyzed and uncatalyzed reactions.

In the absence of a catalyst, ethylene and oxygen combust directly to carbon dioxide and water. In the presence of a silver catalyst, however, the initial activation barrier is reduced and the ethylene oxide minimum becomes accessible. In the presence of a palladium catalyst, a different potential energy surface becomes accessible with acetaldehyde and peracetic acid as local minima.

The commercial development of the ethylene oxide process has concentrated on these points. The silver catalyst consists of about 15% silver as a finely divided layer on a support that acts as a heat sink to prevent undue temperature rise of the catalyst by the reaction exotherm. Furthermore, an inhibitor—several ppm of dichloroethane—is often added to the system. Inhibitors are “anticatalysts.” This one decomposes to ethylene and chlorine. The chlorine adsorbs on the silver surface, influences the chemisorption of oxygen, and hence inhibits the combustion reactions.

Other measures to increase selectivity have included the promotion of the catalyst with 3.5×10^{-4} to 3×10^{-3} equivalents of potassium, rubidium, or caesium ions per kilogram of catalyst (measured as silver oxide). The effect is specific. Sodium and lithium have no effect and quantities of the active metals outside the above range do not seem to improve selectivity.

In Figure 16.1, the effect of the catalyst is always to reduce the activation enthalpy (energy) of a reaction. If the rate constant k of a reaction is represented by the Arrhenius equation $Ae^{-E/RT}$, where A is the preexponential factor, E the activation enthalpy (energy), R the gas constant, and T the absolute temperature, then the implication is that E is always reduced and A remains more or less unchanged. Indeed many textbooks state that catalysts always act in this way.

In fact, catalysts act to reduce the *free energy of activation*, so that A varies as well as E. In some examples, a catalyst raises E but also raises A by such a large amount that it still acts as a catalyst. For different catalysts of the same reaction, it often happens that a graph of log A against E gives a straight line. This phenomenon is called the compensation effect and variations in A of up to 10^{14} have been reported (see note at end of this chapter).

16.1.2 Recovery of Unchanged Catalyst

If catalyst cost is to be unimportant, catalysts must be cheap or have exceptionally high activity or be recoverable in high yield. Many catalysts, especially in homogeneous reactions, cannot be recovered unchanged at the end of a reaction.

When sulfuric acid catalyzes the esterification of ethanol with acetic acid, the reaction products contain materials such as ethyl hydrogen sulfate. The sulfuric acid has also been solvated by the byproduct water. This dilution reaction is highly exothermic. Because the catalyst alters the overall chemistry of the reaction, it alters the position of equilibrium and the free energy change, and fails to increase the backward and forward rates proportionately. The sulfuric acid is not present in its original form at the end of the reaction. Its recovery from the reaction products requires a further process involving expenditure of chemical energy and reversal of the hydration and sulfate-forming reactions. In practice, sulfuric acid is so cheap that, after use as an esterification catalyst, it would probably be discarded.

An example of a high activity catalyst is the fifth generation Ziegler–Natta catalyst (Section 4.1) for polypropylene, which produces 70,000 lb of product for only 1 lb of catalyst. Although the catalyst is expensive, its activity is so high that only a tiny quantity is required, and its recovery is not worthwhile. Metallocene catalysts are claimed to be even more active.

Expensive catalysts include the platinum group metals (platinum, palladium, and rhodium) used in automobile emissions control catalysts. They contribute about 75% of the cost of such catalysts. United States consumption of such metals in this end-use in 2002 was about 100 tonnes. At a typical price of \$15/g for precious metals, this amounts to about \$1.5 billion, and the recovery and recycling are worthwhile. In 2001, about 6 tonnes of platinum group metals were recovered from new and old scrap.

16.1.3 Catalyst Deactivation

Homogeneous catalysts are obviously more difficult to recover than heterogeneous catalysts which, in principle, can simply be removed by filtration. With heterogeneous catalysts, however, the difficulty is not so much in the "recovery" part of the definition but in the "unchanged" part. Three routes to deactivation of heterogeneous catalysts are recognized—sintering, poisoning, and fouling. Sintering covers changes in surface area and structure and is irreversible. Poisoning involves chemisorption on active sites of the catalyst and is more likely to be reversible. Fouling involves physical blockage of active sites and is usually reversible.

All these processes may result from chemical reactions. Practically all industrial solid catalysts must be removed from the reactor at intervals, varying from a few months to a year, for regeneration. In the catalytic cracking of hydrocarbon fractions to gasoline (Section 2.2.2), a second reactor is included in the plant for continuous regeneration of catalyst and it is only this that makes the process feasible.

In the manufacture of SNG by the Catalytic Rich Gas Process (Section 12.5), the catalyst is nickel on high surface area γ-alumina promoted with potassium. The alumina has a cubic close-packed structure. When not used as a catalyst, γ-alumina is stable up to 1100°C. In plant use, however, at a temperature as low as 400°C, it undergoes an irreversible phase change to a hexagonal close-packed structure, α-alumina or corundum. The collapse of the fine pore structure of γ-alumina and subsequent formation of corundum also leads to agglomeration of the nickel crystallites and loss of metal surface area. Hence, there is a drastic reduction in catalyst activity. The lifetime of the catalyst, which cannot be recovered unchanged, is governed by the rate of sintering of alumina and nickel.

A final example is the gas-phase coking of hydrocarbons at high temperatures. It is catalyzed by surfaces, especially those containing metal particles. Nickel is especially active. Electron micrographs show that the carbon deposits as spiral fibers growing from the surface and topped by a metal crystallite, which promotes further growth. The etching of the surface is thus an essential part of the catalytic process. As in the previous examples, the textbook requirement that a catalyst be recoverable "unchanged" at the end of a reaction is not strictly met.

16.1.4 Access to Nonequilibrium Products

Thermodynamicists stress the importance of equilibrium in chemical reactions. If hydrocarbons were to react to equilibrium, however, the products would be carbon and hydrogen. If sufficient oxygen were added, furthermore, the equilibrium products would be carbon dioxide and water. Most useful chemical reactions do not go fully to equilibrium. They are stopped at some local minimum in the free energy surface as in the case of ethylene oxide discussed in Section 16.1.1. Selective catalysts direct reacting systems toward these local minima.

Catalysts are said not to affect the position of equilibrium in chemical reactions but may do so in a number of ways. In the esterification reaction described in

Section 16.1.2, the amount of sulfuric acid added pushes the equilibrium to the right because of its effect on the overall free energy change accompanying the reaction.

A more modern example of a catalytic system where the catalyst appears to affect the position of equilibrium is the disproportionation of toluene (Section 8.1). The zeolite catalyst results in much greater than thermodynamic yields of *p*-xylene. The desired isomer, the *p*-xylene, is able to diffuse away from the catalytic site much more quickly than the undesired isomers. Thus, as *p*-xylene is removed, a fresh equilibrium is continually being established. This is described further in Section 16.9.

16.2 HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

Catalysts are designated homogeneous or heterogeneous depending on whether they function in a single phase or at a phase boundary. This distinction appears to have little theoretical significance. A homogeneous acid catalyst such as sulfuric acid acts in the same way as a heterogeneous acidic catalyst such as silica–alumina. In certain examples of the Friedel–Crafts reaction, it is uncertain whether catalysis is homogeneous or heterogeneous. In some industrial processes, there is the possibility of operating in either mode.

Homogeneous catalysts can be added easily to a reaction system but may be difficult to remove from the products. They are usually used in the liquid phase although some reactants may be introduced as gases or solids. There is only a handful of homogeneous gas-phase catalyzed reactions. One example is the air oxidation of sulfur dioxide to sulfur trioxide catalyzed by nitric oxide—the old lead chamber process for sulfuric acid. Another is the cracking of acetic acid to ketene at about 700°C, catalyzed by diethyl phosphate (Section 10.5.2.3).

For most but not all homogeneous catalysts, the rate increase is proportional to the amount of catalyst added. Some catalytic effects saturate, and a few appear in the rate equation with a power other than one. Homogeneous catalysts are readily reproducible and give high selectivities. For this reason, they are the preferred systems for academic study and have led to most of the insights we have into the mechanisms of catalytic reactions.

In heterogeneous catalysis, the mass of the catalyst is much less important than its surface area. Preparation and pretreatment of solid catalysts is an art and the activity of a catalyst depends on its previous history. Catalysts achieve high surface areas because of their microporosity. Areas of 1000 m^2/g are not uncommon. Diffusion of reactants to a surface and of products away from it may present problems, as may heat transfer into or out of catalyst particles. On the other hand, heterogeneous catalysts have the great advantage of being easily recoverable. They can be used in static or fluidized beds in continuous processes. They can be used in systems where thermodynamic constraints demand high temperatures and where solution methods would therefore be impossible. They are therefore more widely used in industry.

16.2.1 Reactors for Heterogeneous Catalysts

The mixing of homogeneous catalysts with reactants presents few problems. In polymerization reactions, there may be difficulties if the mixture becomes viscous, but in general stirring is adequate. It is sometimes possible to stir a heterogeneous catalyst into a liquid reaction mixture in the same way, but gas-phase reactions occurring on solid catalysts are usually carried out either in fixed or fluidized beds.

In fixed beds (Fig. 16.2*a*), the catalyst is compressed into pellets of approximately one centimeter diameter, and these are packed into long tubes, which are contained in a shell through which a heating or cooling medium can be circulated. The advantage of the system is its reliability. It works for varying flows of gases and for catalysts that are "sticky" or liable to agglomerate. There are three main drawbacks. First, the tubes are difficult to remove and repack when the catalyst needs to be regenerated. Second, there are problems with diffusion of reactants into and products out of the compressed pellets. Third, there are problems with heat transfer. Even if tubes as narrow as 3 cm in diameter are used in the reactor, it is still difficult to maintain a constant temperature. Active sites in the middle of catalyst pellets achieve much higher temperatures than the rest of the system. Thermal shock may even fragment the pellets leaving dust, which may block the tube. In endothermic reactions, local cooling may bring the reaction to a halt.

Fluidized beds (Fig. 16.2*b*) contain catalyst in small particles like grains of sand. The particles are suspended in a rapid flow of gas, which may be the reactant or an

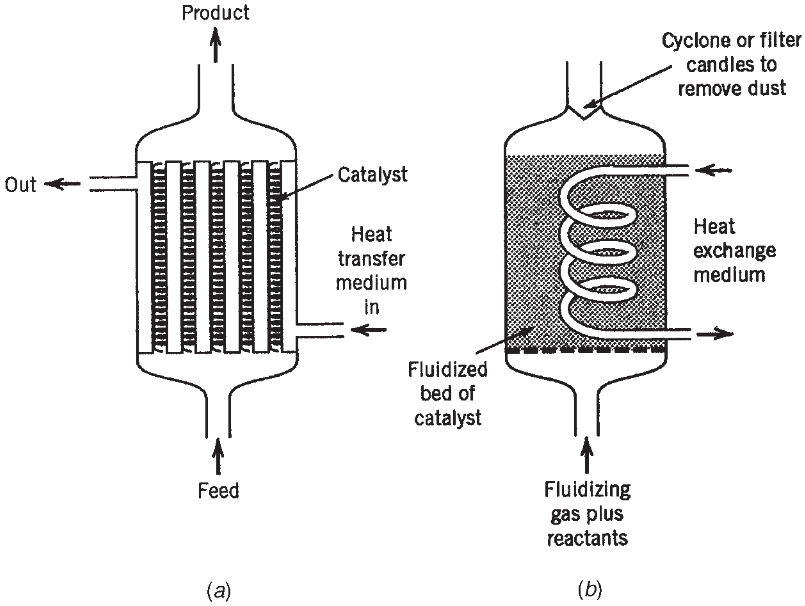


FIGURE 16.2 (*a*) Fixed-bed-reactor and (*b*) fluidized-bed reactor.

inert fluidizing gas. If the flow is accurately maintained, the bed behaves like a homogeneous fluid. It can be drawn off into other vessels for regeneration (Section 2.2.2). Heat can be added or removed by coils in the bed. Temperature equilibration is rapid. Problems of diffusion are much reduced because the catalyst particles are smaller. One drawback of the system is its intolerance to variations in gas flow. Fluidization of the bed may also be hindered by attrition, channelling, and slugging. Attrition means the wearing away of the catalyst particles as they rub against each other in the bed. A fine dust is continuously carried out of the bed and must be removed by cyclones at its exit. Channelling occurs when the gases manage to find a channel through the bed, perhaps near the wall, and travel through without adequate contact with the catalyst. Slugging is a similar phenomenon, where the catalyst particles, agglomerating into large lumps, do not fluidize.

Fluidized beds are the more advanced technology and are used whenever the nature of the catalyst and the reaction conditions permit it. They are especially valuable when accurate control of temperature is important as in highly exo- or endothermic reactions. The use of a fluid-bed catalyst for polyethylene production by the Unipol process (Section 3.1.3) is an example as is the use of a fluid bed for the production of acrylonitrile, which is highly exothermic (Section 4.4).

16.2.2 "Immobilization" of Homogeneous Catalysts

The ease of separating heterogeneous catalysts from reaction mixtures means that there is sometimes a need to turn homogeneous catalysts into heterogeneous ones. An early example is the proton-catalyzed hydration of ethylene (Section 3.9). This was originally carried out indirectly by passage of ethylene into sulfuric acid at 55–80°C and 10–35 bar, followed by hydrolysis of the ethyl hydrogen sulfate and regeneration of the sulfuric acid. In the newer process, ethylene is passed over phosphoric acid absorbed into celite—a porous diatomaceous earth that serves as a support. The lower effectiveness of phosphoric acid as a protonating agent means that more drastic conditions are required (300°C and 70 bar) but the phosphoric acid remains physically absorbed onto the porous interior of the celite. There is still pore space to allow access of the ethylene.

An example of the anchoring of a more sophisticated catalyst to a solid surface is the binding of the so-called Wilkinson complex (Section 16.7.2) to a polystyrene support. The polystyrene is first converted (functionalized) with a diphenylphosphino group to a polymer that may be represented as $[PS]{-}P(Ph)_2$, which then reacts with the Wilkinson complex, chlorotris(triphenylphosphine) rhodium:

$$[PS]{-}P(C_6H_5)_2 + RhCl[P(C_6H_5)_3]_3 \longrightarrow [PS]{-}P(C_6H_5)_2RhCl[P(C_6H_5)_3]_2 + P(C_6H_5)_3$$

The immobilized complex preserves the ability of the Wilkinson complex to hydrogenate olefins, although the reaction may be slower.

Another example is Chiyoda's process, "Acetica," for making acetic acid. In this process, the rhodium-based methanol carbonylation catalyst is anchored to a poly(vinyl pyridine) resin. This immobilization significantly simplifies catalyst recovery.

Organic polymers are not the only supports for the anchoring of catalysts. Inorganic materials are also useful. Silica is an example, and the catalyst combines with the hydroxyl groups on its surface.

Immobilization of manmade catalysts generally leads to deactivation, hence there are only a few useful examples of it. Highly active "natural" catalysts such as enzymes and complete living cells such as bacteria, on the other hand, can be attached to solid substrates without serious loss of catalytic activity. They can usefully be employed as heterogeneous catalysts. Immobilized enzymes and methods of immobilization will be discussed further in Section 16.8.

16.3 CATALYST MARKETS

The US market for catalysts in 2002 was \$10.2 billion, about 40% of the world market of approximately \$25 billion. The world merchant market for catalysts (i.e., excluding catalysts manufactured and consumed internally by industrial companies) was worth about \$10 billion and divides almost evenly between petroleum refining, petrochemicals, chemical processing, polymerization, and environmental applications (mainly automobile emissions) with a smaller contribution from fine chemicals and intermediates (see note at the end of this chapter). This is shown in Figure 16.3. The similar sales hide large differences in tonnage.

The total US market for catalysts for chemical processing in 1990 amounted to \$660 million by value and about 200 million lb by weight, an average of \$3.30/lb. (More recent figures for tonnage are not available.) Catalysts are expensive and are truly specialty chemicals. They are typically more expensive than the bulk pharmaceutical aspirin (~\$1/lb) and about the same price as vitamin C (~\$3–4/lb). Tonnages are also of the same order of magnitude as for pharmaceuticals.

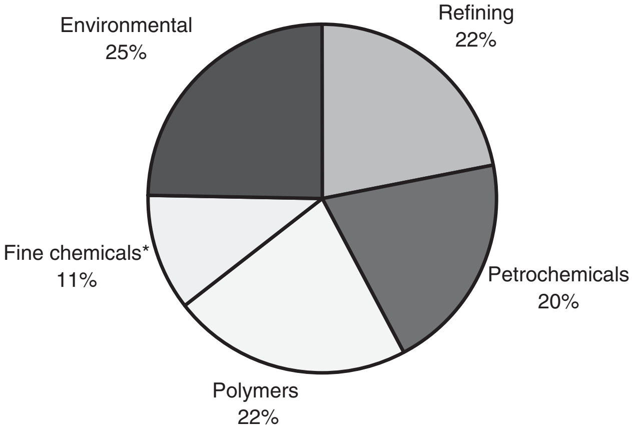


FIGURE 16.3 Global catalyst market 2001 (total = \$10,157 million). The asterisk represents a surrogate figure that provides the merchant market for four segments. It includes intermediates and "others."

Furthermore, of the approximately 650 billion lb of chemicals produced annually in the United States in the early 1990s (including inorganics), about 60% were produced with the aid of catalysts. Thus a pound of an average catalyst produced about 1500 lb of chemicals (allowing for the catalyst volume being somewhat out of date). The polypropylene example in Section 16.1.2, where 1 lb gives 70,000 lb, is exceptional for a catalyst although typical for olefin polymerization.

Petroleum refining catalysts on average are the cheapest and cost about one-half as much per pound as chemicals catalysts. They are dominated by the cheap acid catalysts used for alkylation, which account for 90% by weight but only about 32% by value in this sector. The new solid acid catalysts are more expensive. The high activity zeolite catalysts used for catalytic cracking are also more expensive and account for about one-tenth of the tonnage but about 40% of sales value. The other petroleum refining catalysts—for hydrotreating, hydrocracking, reforming, and isomerization—are of less significance.

Figure 16.4 shows the global market for polymerization catalysts. Unfortunately, there is a problem of definition. Materials that promote polymerization may be divided into true catalysts such as metal complexes, metal oxides, and anionic and cationic catalysts (Chapter 15) and initiators, which appear as end groups in the final polymer. Although the formal equations depicting the polymerization reactions are similar, compounds that appear in the final product differ fundamentally from those that are regenerated and can in principle be separated and reused. Nonetheless, this distinction is not always recognized in the commercial world, and the figure given above is inflated by the inclusion of free radical initiators. The most expensive polymerization catalysts are the single-site metallocene catalysts. Sales have grown from $1 million in 1994 to $25–30 million in 1998 and $ 100 million in 2000. Ziegler catalysts used for polypropylene and polyethylene, and the dibutyl tin and triethylenediamine (Fig. 16.4) (DABCO or diazabicyclooctane) for polyurethanes are also expensive.

The main group in the chemicals category is general organic synthesis. It includes a variety of catalysts for esterification, hydrolysis, alkylation (cumene and ethylbenzene dominate), and halogenation.

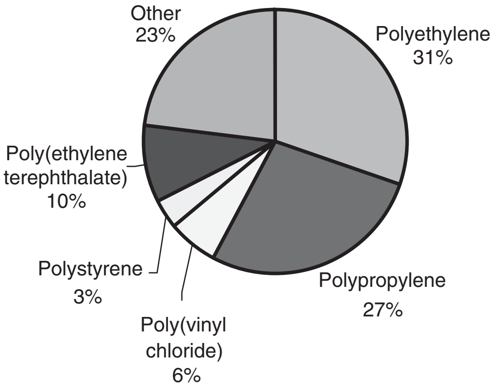


FIGURE 16.4 Global market for polymerization catalysts, 2000 (total = $2020.5 million).

Oxidation catalysts are a special class and about one-half of this market by value is the silver catalyst used to make ethylene oxide. In terms of tonnage, the relatively cheap catalysts for the oxychlorination of ethylene (Section 3.4) make up about a one-third by weight but only 5% by value. Another expensive oxidation catalyst is the manganese and cobalt salts in acetic acid plus bromine promoter for oxidation of *p*-toluic acid to terephthalic acid (Section 9.3.1). Palladium on charcoal is also used in this process to catalyze hydrogenolysis of byproduct 4-carboxybenzaldehyde to *p*-toluic acid (Section 9.3.1), Added together, these produce a process that is expensive in terms of catalyst. Further cost is added by the decomposition of the acetic acid, only part of which can be recovered for reuse.

The final category of chemical synthesis catalysts is the iron-based catalysts for ammonia, and chromium-based catalysts for methanol from synthesis gas. The cost is relatively low but the tonnage for ammonia alone is about one-fifth of total catalysts for chemicals.

Apart from the *p*-toluic acid catalyst mentioned above, the main hydrogenation catalysts are

1. Raney nickel for margarine and related processes.
2. Nickel and to a lesser extent palladium or platinum on lithium oxide for hydrogenation of benzene to cyclohexane.
3. Silver gauze for dehydrogenation or oxidative dehydrogenation of methanol to formaldehyde.
4. Cobalt and rhodium catalysts for the oxo process.

The main dehydrogenation process is the conversion of ethylbenzene to styrene.

The fine chemicals and intermediates category embraces the catalysts used by the pharmaceuticals, agrochemicals, and flavors and fragrances industries. It is fragmented, if only because of the number of chemicals produced, and depends to a greater extent than the heavy chemicals industry on the catalysts that would be found in an academic chemistry laboratory.

The catalysts for automobile emission control are based on precious metals. Platinum, palladium, and rhodium are the main ones. These are almost an order of magnitude more expensive than the chemicals catalysts, and the tonnage is correspondingly smaller. Total US consumption of platinum group metals in 2002 was a mere 146 tonnes, down from 214 tonnes in 2001 and 246 tonnes in 2000. Fifty-six percent of that went into automobile emission control, 19% into jewellery, and 19% into industry. The industrial demand includes dental alloys, glass for computer screens, chemical catalysts, biometal applications, and computer hard disks, where a layer of platinum increases storage capacity. Demand is volatile and the figures over a five-year period are shown in Figure 16.5. The precipitous drop in palladium consumption is at least partly due to to its replacement by platinum in dental alloys and automobile emission catalysts.

Thus the automobile market is dominated by precious metals, but the petroleum and chemicals markets are dominated in terms of tonnage by simple acidic or metal oxide catalysts. Nonetheless, there is a range of relatively modern high-technology

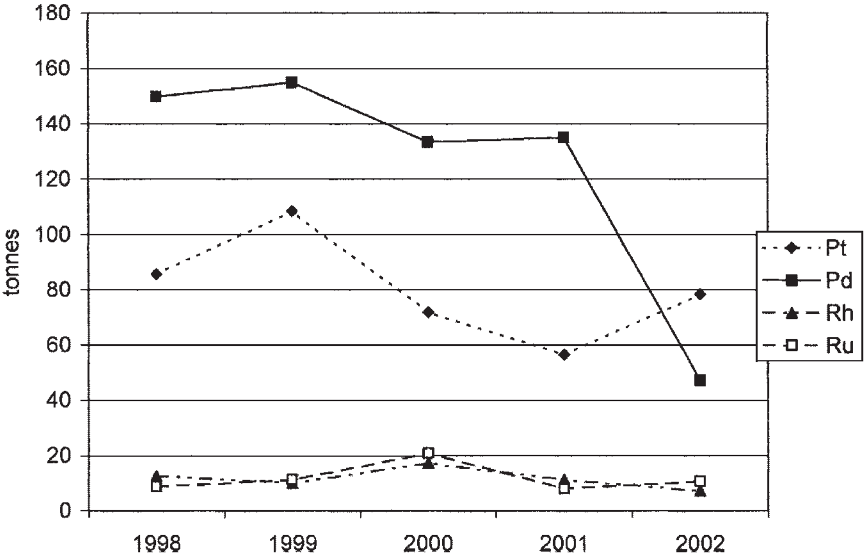


FIGURE 16.5 United States demand for platinum group metals, 1998–2002.

catalysts, which repay their higher prices. They are often sold together with "know-how" and are steadily improved. Examples are the zeolites, and the catalysts for ethylene oxide production and Ziegler polymerization.

Environmental applications are seen as the growth market for catalysts, while petroleum refining catalysts are expected to be static. Figure 16.3 shows environmental catalysts as 25% of the global market, but the figure for the United States, where there is extensive environmental legislation, is as high as 30%. Growth is also expected in the polymerization area.

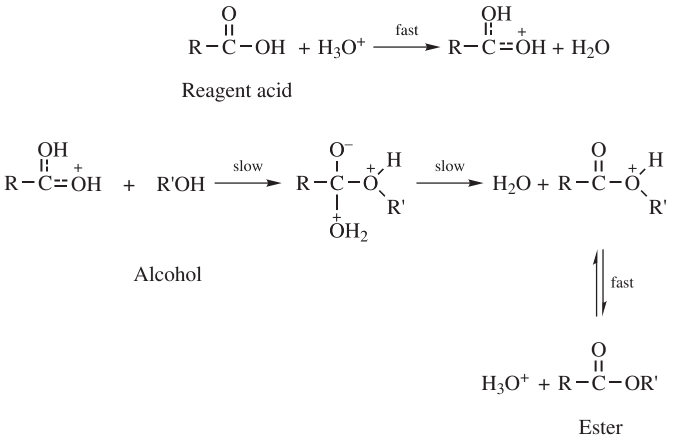
16.4 CATALYSIS BY ACIDS AND BASES

Acid catalysis is the most widely used form of catalysis in the chemical and refining industries. Alkylation was described in Section 2.2.5 and is brought about by cheap acidic catalysts. Sulfuric acid was used in the past but hydrogen fluoride has replaced it in most modern refineries. The mechanism is a typical acid catalysis in which the catalyst donates a proton to the reactant to give an ion, in this case a carbocation, that reacts as shown below for the alkylation of isobutane by butene:

$$(CH_3)_2C{=}CH_2 + HF \longrightarrow (CH_3)_2C{-}CH_3^+ + F^-$$

$$(CH_3)_2C^+{-}CH_3 + (CH_3)_2CHCH_3 \longrightarrow (CH_3)_3C{-}CH_2{-}CH(CH_3)_2 + H^+$$

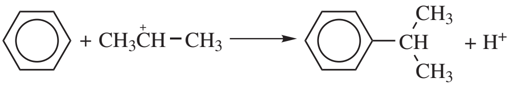
Sulfuric acid is also the usual catalyst in esterification reactions, which proceed by a similar mechanism:



Brønsted and Lewis acids also act as catalysts by proton donation. $HCl/AlCl_3$ catalyzes the Friedel–Crafts reaction between benzene and propylene (Section 4.9) by the following mechanism, which has been confirmed by isotopic labeling.

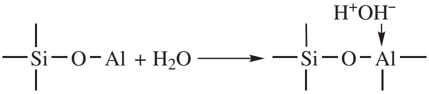
$$AlCl_3 + HCl \rightleftharpoons H^+[AlCl_4]^-$$

$$CH_3CH{=}CH_2 + H^+ \rightleftharpoons CH_3\overset{+}{C}H-CH_3$$



Catalytic cracking (Section 2.2.2) resembles alkylation and provides another example of acid catalysis. It differs in that a solid surface provides the acidity, and it acts either by willingness to accept an electron pair from another species (Lewis acid) or to donate a proton (Brønsted acid). The original catalytic cracking catalyst was silica–alumina, developed by Houdry in the 1930s. The modern catalyst is the rare earth form of a zeolite structure and it largely suppresses the reactions leading to the excessively volatile C_3—C_4 products.

Zeolites are aluminosilicates and are the basis for shape-selective catalysis (Section 16.9). Their structure is dominated by the fourfold coordination of silicon, each atom being bonded to four tetrahedrally arranged oxygen atoms. Substitution of a silicon atom in such a structure by aluminum, with its valency of 3, leaves a vacant tetrahedral position in the lattice at which a pair of electrons can readily be accepted to complete the valency octet. Thus the species can function as a Lewis acid. Alternatively, interaction with water can lead to a Brønsted acid site with an available proton:



The cracking of a larger to a smaller alkane on such an acid site may be represented as in Figure 16.6.

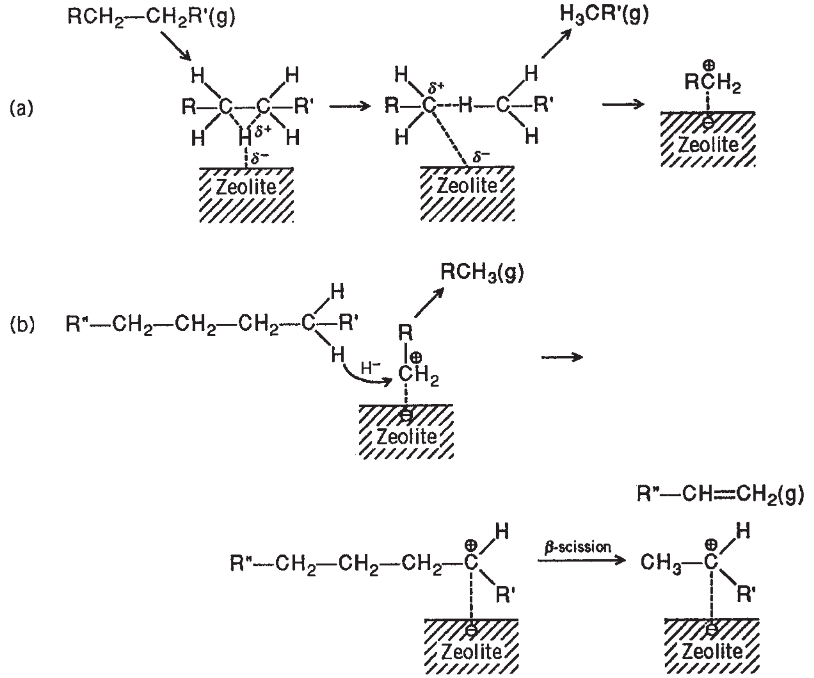


FIGURE 16.6 Scheme postulated for the mechanism of alkane cracking on acidic zeolite catalysts. (*a*) Protolytic route to formation of chemisorbed carbenium ion *via* cracking of larger alkane (RCH_2—CH_2R'). (*b*) Route for replacement of carbenium ion *via* hydride transfer from a gas phase alkane (R''—CH_2—CH_2—CH_2—CH_2—R'), showing the β-scission process leading to the release of an alkene (R''—$CH{=}CH_2$) to the gas phase. After a scheme given by A. Corma, J. Planelles, J. Sáuchez–Marîn, and F. Tomás *J. Catal.* **93**, 30 (1985). Reproduced with permission from *Catalysis at Surfaces*, I. M. Campbell, Chapman and Hall, 1988.

The zeolite-catalyzed alkylation of benzene with ethylene and propylene to give ethylbenzene and cumene, respectively, is a specific example of the trend toward solid acid catalysts in the chemical industry. A further example is UOP's Detal process for making linear alkylbenzene (LAB). In this process, monoolefins, both internal and α-olefins, are reacted with benzene over a solid acid catalyst believed to be a fluorided silica–alumina.

The production of bisphenol A by the reaction of acetone and two equivalents of phenol was historically carried out using mineral acids such as HCl. Modern plants have now switched to solid catalysts composed of cationic ion exchange resins. In all of these cases, the use of solid catalysts simplifies the plant layout and obviates the need to handle and dispose of the noxious liquid acid catalysts.

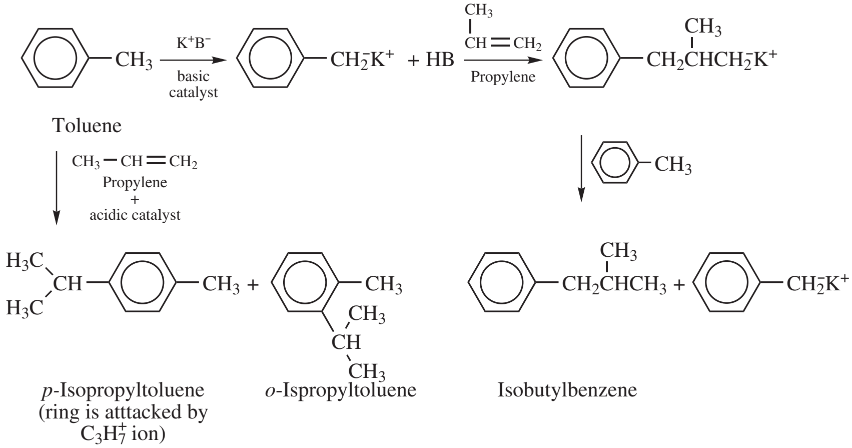
Catalysts for catalytic cracking provide the most valuable market in the field of petroleum refining. They have to be tailored to meet changing demands for the balance and specification of products. In the past, gasoline was required to meet only a few specifications; now it must meet strict composition standards. In the past, catalytic cracking produced 30–35% of the gasoline pool. Now, it is seen as a source of feedstocks for other applications such as increased yields of C_4 and C_5 olefins for the production of octane-building oxygenates and alkylates, as well as propylene for the chemical industry.

Basic catalysis is rarer in industry than acidic catalysis. Examples include one-shot phenol–formaldehyde resins (see note at the end of this chapter) and isocyanate formation. The opening of an epoxide ring frequently depends on a basic catalyst. An example is the reaction of ethylene oxide with acrylic acid to give hydroxyethyl acrylate, a trifunctional monomer used in baking enamels. The catalyst is a tertiary amine or quaternary ammonium salt.

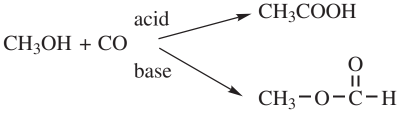
$$CH_2{=}CHCOOH + \underset{\diagdown\,O\,\diagup}{H_2C{-}CH_2} \longrightarrow CH_2{=}COOCH_2CH_2CH_2OH$$

Acrylic acid Hydroxyethyl acrylate

Whether a catalyst is acidic or basic can alter the reaction products. Alkylation of toluene with propylene in the presence of a Friedel–Crafts (acidic) catalyst leads to ring alkylation to give *o*- and *p*-isopropyltoluene. A potassium catalyst, however, promotes alkylation of the methyl group to give isobutylbenzene, an intermediate for the manufacture of the nonsteroidal anti-inflammatory agent, ibuprofen.



Similarly, methanol and carbon monoxide give acetic acid in the presence of an acid catalyst and methyl formate in the presence of a base.



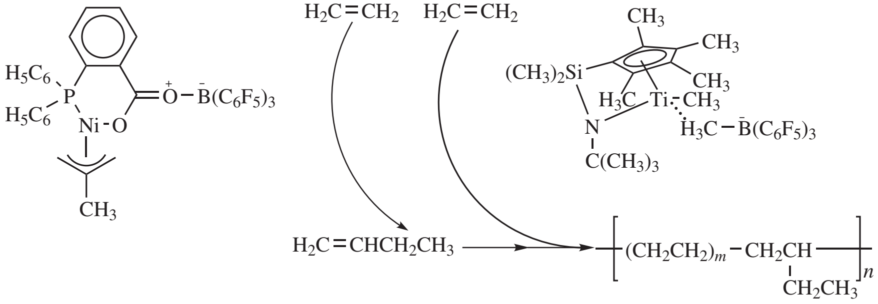
16.5 DUAL FUNCTION CATALYSIS

Catalytic reforming (platforming, Section 2.2.3) is brought about by a dual function catalyst, a mixture of two catalysts each of which performs differently. Reforming catalysts are based on a mixtures of an acidic isomerization catalyst ($SiO_2/A1_2O_3$) with a hydrogenation–dehydrogenation catalyst (Pt). The modern form is a platinum–rhenium alloy supported on alumina with sufficient sulfur added to poison partially the metal surface. The combined action of rhenium and sulfur inhibits coking.

Typical feedstocks are cyclohexane and methylcyclopentane. A dehydrogenation catalyst can convert cyclohexane to cyclohexene and then to benzene, and an acidic catalyst can convert methylcyclopentene to cyclohexene. Only a dual function catalyst can convert methylcyclopentane to benzene. For this transformation, the two types of catalytic sites are required with transfer of an olefinic intermediate between the sites. The same effect could not in many cases be achieved by successive beds of the two catalysts. In a reaction of the type, $A \rightleftharpoons B \rightarrow C$, in which the equilibrium of the first reaction lies to the left, two beds of single function catalyst would not bring about reaction because not much of B would be formed in the first bed. On a dual function catalyst, however, the small quantity of B is removed as soon as it is formed. More A consequently changes to B, and the reaction to give C is accomplished. The distances between the different catalytic sites govern the effectiveness of a dual function catalyst. *n*-Heptane will reform over a mixture of catalysts of particle size 1.0–10 μ but not 100–1000 μ.

Hydrotreating catalysts are cobalt–molybdenum or nickel–molybdenum on alumina or possibly silica. These are typical hydrogenation–dehydrogenation catalysts based on transition metals. Hydrocracking catalysts are palladium or nickel tungsten on zeolites. Increasingly, strict regulations on sulfur content of refinery products mean that there is pressure on catalyst producers to upgrade their products. There was the possibility of a move from transition metals to the more expensive but more efficient noble metal catalysts, but this seems to have been abandoned.

A recent example of dual function catalysis is provided by a process, not yet commercialized, that produces polyethylene copolymers directly from ethylene. The catalyst system consists of a nickel–borane adduct based on tris(pentafluorophenyl)boron, which catalyzes the dimerization of ethylene to 1-butene, and a commercial organotitanium catalyst for polyethylene modified to include borane functionality that copolymerizes the ethylene with the 1-butene. The extent of branching in the product depends on the nickel/titanium ratio. The advantage of such a process is that it provides a linear low-density polyethylene (Section 3.1.4) without the added cost of an α-olefin component such as 1-hexene.



16.6 CATALYSIS BY METALS, SEMICONDUCTORS, AND INSULATORS

The majority of heterogeneous catalysts are metals and metal oxides. Pure metals are rarely used in industrial processes, except for silver for ethylene oxide, and noble metals for hydrogenation/dehydrogenation and hydrogenolysis.

Metals and metal oxides may alternatively be classified as *p*- and *n*-type semiconductors and insulators. At the surfaces of these materials, reactants can adsorb. Physical adsorption is weak ($\Delta H \approx -40$ kJ mol^{-1}) and does not lead to catalytic activity. Chemisorption (dissociative adsorption) on the other hand is strong ($\Delta H \approx -400$ kJ mol^{-1}) and the adsorbents themselves dissociate and form chemical bonds with the surface.

In the Haber process, for example, the reactants both adsorb and dissociate on iron. Hydrogen dissociates freely even at liquid air temperatures, but nitrogen does not do so until about 450°C, and this is the rate-determining step. Once the nitrogen molecules have dissociated (with adsorbed atoms written $\mathrm{Cat{\equiv}N}$, where Cat is the catalyst) the atoms can react readily with neighboring hydrogen atoms to give $\mathrm{Cat{=}NH}$, $\mathrm{Cat{—}NH_2}$, and finally $\mathrm{Cat\cdots NH_3}$ from which the NH_3 is easily desorbed.

Table 16.2 lists the heats of adsorption of nitrogen on various surfaces. On glass and aluminum only physical adsorption occurs, and these materials do not catalyze ammonia production. Iron, tungsten, and tantalum all give dissociative adsorption, but the preferred catalyst is iron because it has the smallest heat of adsorption, and therefore the products are most easily desorbed.

The theory of catalysis by way of chemisorption provides a reasonable explanation for catalysis by metals. The mode of action of "pure" metal oxides and non-stoichiometric metal oxides is more complicated, and an explanation had to await a quantum mechanical theory of solids and the application of this to heterogeneous catalysts. Together with the crystal and molecular orbital ligand field theories, these now provide substantial theoretical underpinning for the catalytic effects of semiconductive metal oxides.

The large majority of catalytically active metals belong to the transition series. Consequently, it appears that catalytic activity is related to the state of the *d* bands, corresponding to the assembly of *d* orbitals at the catalyst surface. The crystal surface of a semiconductor may be thought of as having a supply of electrons and a supply

TABLE 16.2 Heats of Adsorption of Nitrogen on Various Surfaces

Surface	ΔH (kJ mol^{-1})
Glass	~ −7
Aluminum	~ −42
Iron	~ −293
Tungsten	~ −397
Tantalum	~ −585

of "holes" where electrons can locate themselves. These either donate electrons to adsorbed molecules or draw them out. Thus they participate in reactions as free valences, so that the addition of a heterogeneous catalyst to a reactant system is in some ways like the addition of free radicals. In general, oxidation reactions are catalyzed by *p*-type semiconductors that have surplus "holes," whereas hydrogenations are brought about by *n*-type semiconductors that have excess electrons. This fits in with a definition of oxidations as reactions in which electrons are lost and reductions as reactions in which they are gained. Insulators are effective for dehydration.

Another way of looking at this is to think of catalysts as weakening chemical bonds either by feeding electrons into antibonding orbitals on adsorbed molecules or by withdrawing them from bonding orbitals.

The theory of heterogeneous catalysis by semiconductors is complicated and is still developing. Fundamental knowledge about the mechanism of heterogeneous catalysis may make it possible one day to tailor-make a catalyst that functions as efficiently and selectively as the semiconductor devices used in modern electronics. It may also be possible to minimize problems of catalyst poisoning either by modification of catalyst structure or by the admixture of antidotes to the feedstock or intermittently to the catalyst.

16.6.1 Catalysts for Automobile Emission Control

The most widespread application of metal catalysts is in automobile emission control. The exhaust gases from an internal combustion engine running on unleaded gasoline contain nitrogen, water, oxygen, and carbon dioxide, all of which are harmless, if one discounts the possible contribution of carbon dioxide to the greenhouse effect. They also contain unburned and cracked hydrocarbons, carbon monoxide, and oxides of nitrogen NO and NO_2 (known together as NO_x.) These are the major pollutants.

A catalytic converter must oxidize the hydrocarbon and the carbon monoxide while reducing the NO_x to nitrogen. It must perform at a low temperature, because unburned hydrocarbons are worst during start-up, but it must also operate as high as 600–700°C. Contact times are likely to be between 100 and 400 milliseconds, so efficient catalysis is essential. To ensure adequate contact between gases and catalyst, the catalyst is supported on a monolith with narrow channels.

The demands on the catalyst are so severe that the base metals proved inadequate and noble metals on alumina supports must be used. At one point, it was thought that a two-stage conversion would be necessary. First, the engine would run with excess fuel to permit easy reduction of NO_x in an oxygen-poor environment. Air would then be added to the exhaust gases, and the hydrogen and carbon monoxide would be oxidized in an oxygen-rich environment. The addition of rhodium to the platinum catalyst made this unnecessary. If market conditions favor it, then palladium could replace platinum, although the reverse is happening in the early 2000s. If the engine is controlled to operate at the stoichiometric air:fuel ratio of 14.6:1, the oxidation and reduction reactions proceed simultaneously. Addition of palladium and cerium to the catalysts can also provide benefits.

Diesel engines, if properly maintained, are more efficient than gasoline engines in terms of both fuel economy and carbon dioxide emission. Emission catalysts, meanwhile, are restricted to platinum. The major problem is emission of sooty particulates, and catalysts are usually used near the exhaust filter to burn them off. Rhodia has recently suggested a fuel-borne catalyst to facilitate the burning off. If it is to be added to diesel fuel in a fixed proportion, it will need to be inexpensive, and there is a question as to whether it can be considered a true catalyst.

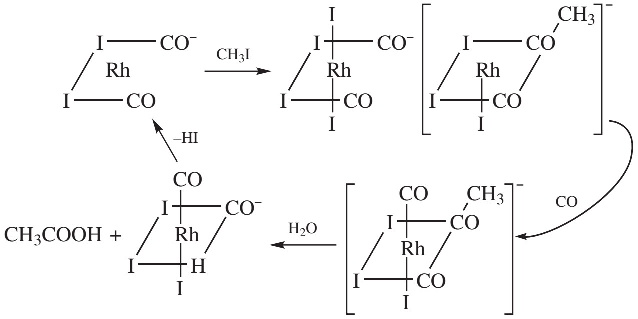
16.7 COORDINATION CATALYSIS

Coordination catalysis uses transition metals or their compounds bound to ligands. As noted in Section 16.6, transition metals have long been used as catalysts. Their *d* orbitals can activate organic molecules to undergo otherwise inaccessible reactions. The addition of ligands, moreover, produces a highly organized environment in the coordination sphere. Such an environment permits stereochemical control of reactions leading to the synthesis of pure optical isomers or *cis* or *trans* products.

Coordination catalysis has provided many of the dramatic synthetic advances since World War II. The first industrial example was the oxo reaction (Section 4.12) in which an α-olefin was treated with CO and H_2 at 150°C and 200 bar in the presence of a cobalt catalyst to give the linear and branched-chain aldehydes with one more carbon atom. The mechanism goes via the hydrocarbon soluble intermediate $Co_2(CO)_8$, dicobalt octacarbonyl, and is shown in Section 4.12.

Carbon monoxide insertion or alkyl transfer to carbon monoxide occurs widely in organometallic chemistry (Section 10.5.2.2). In the simple case, the usually less desirable branched-chain product predominates because of the greater stability of the secondary organometallic intermediate. The use of triphenylphosphine rhodium hydrocarbonyl with its bulky ligands permits milder conditions and a preponderance of linear product (Section 4.8).

The Wacker process (Section 3.5) proceeds by way of a coordination complex as does the carbonylation of methanol to acetic acid (Section 10.5.2.2), which is believed to involve a methyl iodide intermediate and a rhodium–iodine–carbon monoxide complex:



Similar intermediates are probably involved in the Halcon/Eastman route to acetic anhydride (Section 10.5.2.3).

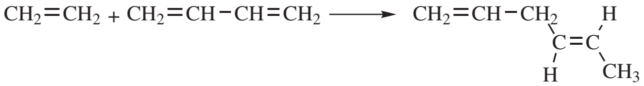
The Du Pont synthesis of adiponitrile from butadiene and hydrocyanic acid (Section 5.1.2) involves a coordination catalyst with a ligand to give anti-Markovnikov addition.

Coordination catalysis is usually performed homogeneously in solution but sometimes there is a choice. In the metathesis of olefins, for example (Section 2.2.9), WO_3 will act as a heterogeneous catalyst, whereas WO_3 plus $C_2H_5AlCl_2$ in ethanol will work in solution. Similarly, in the Wacker process for vinyl acetate (Section 3.6), the mechanism was worked out for the homogeneous liquid-phase reaction, but the system proved too corrosive, and the workable industrial process finally involved a gas phase reaction with a heterogeneous catalyst.

16.7.1 Catalysts for Stereoregular Compounds

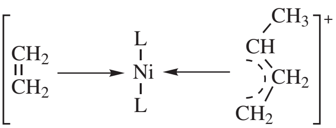
Coordination catalysis can lead to stereoregular and regioselective products. An example is Ziegler–Natta catalysis, which gives stereoregular polymers (Section 4.5). A further example is *trans*-1,4-hexadiene, which is used as the diene in ethylene–propylene–diene monomer elastomers (Section 5.1.3.6). *Trans*-1,4-hexadiene has been made from ethylene and butadiene by Du Pont since 1963 and has the distinction of being the first chemical to be made by a rhodium-catalyzed process. United States production approaches 10,000 tonnes/year.

The catalyst is a dilute solution of rhodium chloride in ethanolic hydrogen chloride, which gives $RhCl_3(H_2O)_n$. This rhodium compound is reduced to a rhodium(I) complex, which may be in equilibrium with a rhodium(III) hydride. Ethylene and butadiene are passed into the mixture. Butadiene reacts with the rhodium complex to give a η-crotyl complex, which, in turn, couples with ethylene to give *trans*-1,4-hexadiene:



$$CH_2{=}CH_2 + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}CH_2{-}CH{=}CH{-}CH_3$$

Ziegler catalysts based on nickel, cobalt, and iron salts also bring about the reaction. Cobalt and iron give the *cis* isomer while nickel gives the industrially important *trans* isomer. The butadiene–nickel–ligand–ethylene complex has the approximate structure:



in which the two hydrocarbons are bonded to the nickel atom, as ligands, through their double bonds.

A third example is the synthesis of β-formylcrotyl acetate, shown in Figure 16.7. β-Formylcrotyl acetate (**I**) is an important intermediate in the synthesis of vitamin A

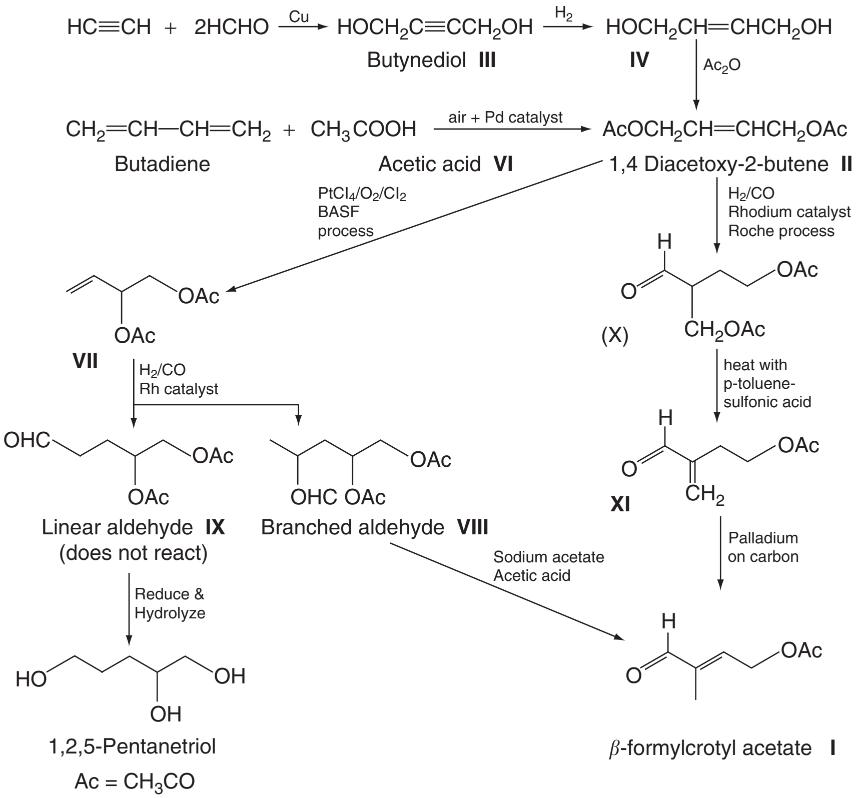


FIGURE 16.7 Syntheses of β-formylcrotyl acetate.

(see note at the end of this chapter). Its precursor is 1,4-diacetoxy-2-butene (**II**). The precursor is made as a *cis–trans* mixture from acetylene and formaldehyde via butynediol (**III**) and butenediol (**IV**) or, in a newer process, from butadiene (**V**) and acetic acid (**VI**). The latter process also gives 1,2-diacetoxy-3-butene (Section 10.3.1).

Two routes to β-formylcrotyl acetate have been developed. In the BASF process, the mixture of diacetoxybutenes is heated with platinum(IV) chloride in a stream of oxygen and chlorine. The lowest boiling isomer (**VII**) distils out in high yield and is hydroformylated with a rhodium catalyst. Usually, in such reactions, a ligand is added to give a linear aldehyde but, in this case, it is omitted and the desired branched product (**VIII**) predominates in the mixture of products (**VIII**) and (**IX**). Also, the rhodium, unlike cobalt, does not promote the migration of the double bond that would be required for the formation of a linear product.

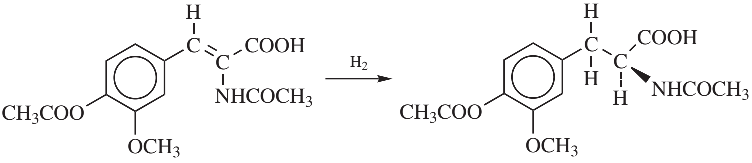
Treatment with sodium acetate in acetic acid selectively eliminates acetic acid from the branched product to give the desired β-formylcrotyl acetate. The linear aldehyde does not react and is separated, reduced and hydrolyzed to 1,2,5-pentanetriol, used as an intermediate in the manufacture of synthetic lubricants.

The Roche process uses rhodium in a different way. It starts with the isomer (**II**) in Figure 16.7, which is hydroformylated with a conventional catalyst RhH(CO)$[P(C_6H_5)_3]_3$ that has been pretreated with sodium borohydride. Because the original double bond was internal, the aldehyde that results is still branched but has the structure (**X**). Heating with *p*-toluenesulfonic acid selectively eliminates acetic acid to give (**XI**), and palladium on carbon isomerizes the double bond to β-formylcrotyl acetate.

The latest catalysts for stereoregular polymer synthesis are the metallocenes, and they are discussed in Section 15.3.12.

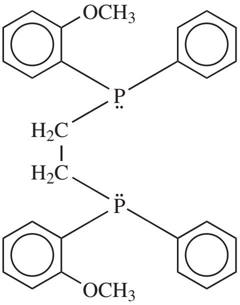
16.7.2 Asymmetric Synthesis

Monsanto's asymmetric synthesis of levodopa (see note at the end of this chapter) was a landmark not only in industrial chemistry but in organic chemistry generally. The key step was the hydrogenation of the olefin (**XII**) to a specific optical isomer of dihydroxyphenylalanine (**XIII**):



XII **XIII**

The hydrogenation was carried out in the presence of a soluble rhodium catalyst bearing a chelating biphosphine ligand, DIPAMP:



DIPAMP

XIV

The ligand is itself asymmetric and creates an unsymmetrical environment about the rhodium atom that leads to selective hydrogenation on the back face of the C=C bond.

Most of the early stereospecific syntheses involved hydrogenation. Different stereospecific catalysts turned out to be valuable in different hydrogenations. The

Wilkinson catalyst $RhCl[P(C_6H_5)_3]_3$ is selective for unhindered C=C double bonds and causes little isomerization in the substrate, that is, the organic reagent. The catalyst $[Ir(cod)(PCy_3)py]^+$ (cod = 1,5-cyclooctadiene, py = pyridine, and PCy_3 = tricyclohexylphosphine) is active for very hindered C=C groups and, if a functional group such as —OH is present in the olefin, the catalyst will bind to it and then add hydrogen to the double bond.

In addition to hydrogenation, a reaction of potential importance is stereoselective epoxidation, which adds an oxygen atom to one face of an olefinic double bond. The olefin is treated with *tert*-butyl hydroperoxide in the presence of a titanium complex of diethyl tartrate. The (+) and (−) tartrate isomers produce different optical isomers of the epoxide. For example, allyl alcohol reacts to give either (2*R*)- or (2*S*)-glycidol. Either isomer can be reacted with 1-naphthol to give an epoxide which, with isopropylamine, gives the active (2*S*) form of the anti-angina drug propranolol (see note at the end of this chapter). The naphthol is so large, it sterically prevents (*R*)-formation.

Chiral syntheses are increasingly important in the pharmaceutical and fine chemical industries. In May 1992, the FDA published a policy statement "strongly urging companies to evaluate racemates and enantiomers for new drugs" and urging that drugs be sold only in their enantiomerically effective form. This hard line has softened and the marketing of single enantiomers is not yet mandatory, but it is nonetheless encouraged. In 2000, 35% of drug sales were single isomers up from 7% in 1985. Chiral synthesis is and will be of much less importance in the bulk organic chemicals industry.

16.8 ENZYMES

Enzymes are the oldest industrial catalysts. In certain respects, they are also among the newest. Enzymes are biological catalysts, and many show high specificity. For example urease will only catalyze urea hydrolysis:

$$OC(NH_2)_2 + H_2O \xrightarrow{\text{urease}} CO_2 + 2NH_3$$

Some enzymes will attack certain chemical groups, wherever they occur (group specificity). For example, proteolytic enzymes will split the peptide linkage. Proteolytic enzymes will only attack peptides made up either from L-amino acids or from D-amino acids, and this is called stereochemical specificity.

Enzymes are proteins but may be associated with nonproteins (cofactors) essential to their activity. Cofactors may either be simple metal ions like Zn^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, or Cu^{2+}, or organic molecules. In the latter case, they are called coenzymes or prosthetic groups. Enzyme activity is usually related to a small region of the molecule referred to as the active center. At low concentrations of substrate, the rate of enzyme action is directly proportional to both enzyme and substrate concentration. If the concentration of substrate is raised, however, the rate ceases to increase and becomes independent of substrate concentration. Thus enzymes are only efficient in dilute solution. Furthermore, they operate only under a limited range of pH (rarely < 4) and temperatures (usually $<50°C$), and reactions become very slow as 0°C is approached. Nonetheless, molecule for molecule, enzymes are much more effective than nonbiological catalysts.

The mechanism of their action varies widely. The push–pull mechanism of acid–base catalysis is one route. The enzyme forms a complex with a molecule of reactant. The latter is bound to two active sites on the enzyme molecule and one of these "pushes" electrons while the other "pulls" them, to give a concerted action. Another mechanism is transition state compression to facilitate simultaneous bond-making and breaking. Hydrogen bonding stabilizes intermediates.

Enzymes are used in isolated applications such as the addition of proteolytic enzymes to detergents. Fermentation is, of course, based on enzymes (Section 14.5). Although that was an important route to chemicals between World Wars I and II, enzymes as opposed to fermentation have not recently found application in large tonnage chemical production except for high-fructose syrups (Section 14.1) and 6-aminopenicillanic acid. These and various lower tonnage enzyme processes are discussed in Section 14.5.1.

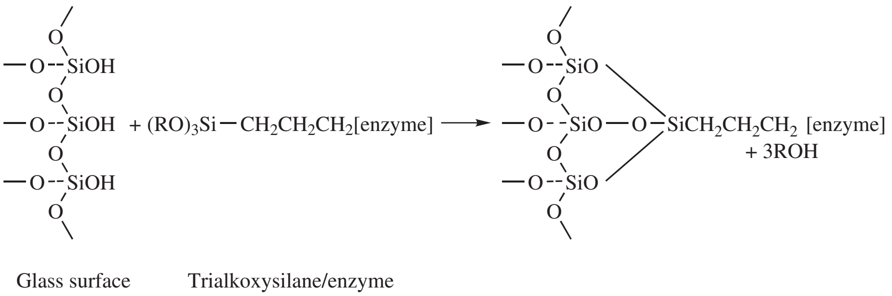
One problem of enzyme technology was solved when it was realized that enzymes retain their activity when attached to an insoluble matrix by a chemical linking agent. Such enzymes are described as immobilized. There is continuing interest in immobilized enzyme processes because, unlike fermentation processes, they do not use whole cells that require separation from reaction batches. They can be treated more like conventional heterogeneous catalysts and can work in continuous processes.

In all likelihood, the enzyme is not truly "fixed" and retains some ability to accommodate itself to the shape and conformation of the molecules whose chemical reactions it is catalyzing. Similarly, the substrate to which the enzyme attaches must be able to accommodate to the shape presented by the enzyme. The "immobilization" means that enzymes can be reused may times in continuous reactors. Enzymes are manufactured in bulk by conventional fermentation techniques. They are immobilized in various ways. For intracellular enzymes, either the cells are stabilized by entrapment in an aqueous gel or attached to the surface of spherical particles, or they are homogenized and cross-linked onto glass with glutaraldehyde, $OHCCH_2CH_2CH_2CHO$, to form an insoluble yet penetrable matrix.

Extracellular microbial enzymes are immobilized in the form of proteins purified to varying degrees. This usually involves the coupling of the free amino groups on lysine [$H_2N(CH_2)_4CH(NH_2)COOH$] residues within the enzyme onto a substrate, again with glutaraldehyde, to give an insoluble, active, stabilized enzyme.

There are more sophisticated, less widely used methods. Thus one may start with polystyrene lightly cross-linked with divinylbenzene to give a gel. Treatment with formaldehyde, hydrochloric acid, and zinc chloride gives a chloromethylated polystyrene, in which some of the benzene rings contain $—CH_2Cl$ groups and these will react with amino groups on the enzyme to bind it to the polymer.

Another method uses trialkoxysilanes as coupling agents. A range of agents is available and they couple with enzymes to give compounds of the type [enzyme] $CH_2CH_2CH_2$—$Si(OR)_3$. The three carbon bridge is sufficient to ensure that the active site of the enzyme is not obstructed on immobilization. The trialkoxysilicon group will bind to a glass surface to immobilize the enzyme:

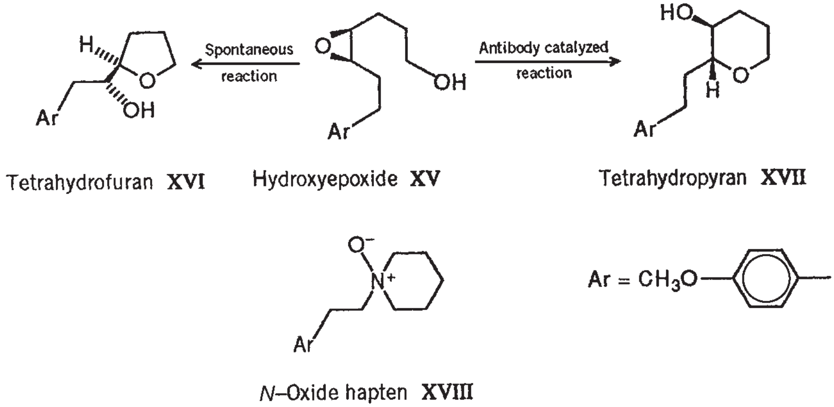


16.8.1 Catalytic Antibodies

Catalytic antibodies are an exciting area of catalyst development in the pharmaceutical industry. Antibodies are chemicals produced by the body as part of its defense against antigens, that is, infecting organisms (pathogens) or their toxic products. Cells may be stimulated by infection to produce these antibodies. A person infected with measles, for example, develops the measles antibody and does not get the disease a second time. Immunization with attenuated measles virus produces the same effect. An alternative method, known as passive immunization (e.g., for diphtheria) is to inject the antibodies (immunoglobulins) from one person into another. Once an antibody has been identified, it is also possible by genetic engineering techniques to develop cells that will yield larger quantities of it. The technique is an elegant way to produce enzymes to order. The interaction between an antigen and its antibody is chemical and specific. A known antigen can be used to identify an unknown antibody and vice versa. Antibodies can be isolated.

An example of the sort of reaction that can be carried out with the aid of catalytic antibodies is the selective catalysis of an unfavorable reaction pathway. In the normal way, the hydroxyepoxide (**XV**) (Fig. 16.8) cyclizes spontaneously to the substituted tetrahydrofuran (**XVI**). The aim of the researchers was to direct the reaction toward the disfavored tetrahydropyran (**XVII**). They first synthesized a hapten. A hapten is a small molecule that reacts with proteins, polypeptides or other carrier substances to give an antigen. In this case, an *N*-oxide hapten (**XVIII**) was synthesized, which resembled the transition state of the disfavored reaction pathway. It was injected into an animal and induced a range of antibodies against an antigen that had the structural features of the transition state. The researchers extracted and purified 26 antibodies and evaluated their catalytic properties. Two of them were regioselective for the formation of the desired product and one was highly stereoselective, so that the desired tetrahydropyran resulted.

Catalytic antibodies have recently been reported that catalyze peptide bond formation without the need for multiple protecting groups and without residual hydrolytic side reactions. Peptide synthesis is potentially an important branch of biotechnology.



Tetrahydrofuran **XVI** Hydroxyepoxide **XV** Tetrahydropyran **XVII**

N–Oxide hapten **XVIII**

FIGURE 16.8 Antibody-catalyzed reactions.

16.9 SHAPE-SELECTIVE CATALYSTS

Many naturally occurring clays and minerals are microporous and may be used as adsorbents (e.g., Fuller's earth as cat litter), drying agents and support for catalysts. Synthetic zeolites with uniform and structured porosities are available. These act as specific catalysts, which not only bring about selective chemical reactions but can even generate greater-than-equilibrium concentrations of products.

Zeolites are aluminosilicate solids with a three-dimensional polymeric framework. Their basic building block is a tetrahedral unit with a silicon or aluminum atom (the so-called T-atom) at the center and oxygen atoms at the corners (Fig. 16.9*a*). Each oxygen atom is bonded to a further T-atom, that is, it is shared with another tetrahedral unit. The T-atoms can unite via T—O—T linkages to give squares (Fig. 16.9*b*) or hexagons (Fig. 16.9*c*) of T-atoms. Combination of these square and hexagonal units gives the sodalite cage (Fig. 16.9*d*), a basic substructural unit. The sodalite cage has oxygen atoms with free bonds able to link to other sodalite cages.

If the sodalite cages unite via their hexagonal faces, an X- or Y-type zeolite is obtained (Fig. 16.9*e*). These have voids in the center, called supercages, with a diameter of 1.3 nm, and pores or apertures leading to them with a diameter of 0.74 nm. If the sodalite cages unite via their square faces, an A-type zeolite (Fig. 16.9*f*) is obtained with supercage diameter 1.1 nm and pore aperture 0.42 nm.

Thirty-six zeolite structures are recorded in the literature. The size of voids and apertures can nonetheless be fine-tuned to an even greater extent than this suggests by chemical and physical treatments. In a particularly significant development, Mobil included tetrapropylammonium ions instead of sodium ions in the parent solutions. Between 40 and 90% (typically 70%) of sodium ions were replaced in this way. The $(n\text{-}C_3H_7)_4N^+$ ions are much bigger than Na^+ ions and the resulting zeolite had a structure intermediate between those of the A- and X- or Y-type zeolites. It was called ZSM-5. Incorporation of tetramethylammonium ions as a template led to

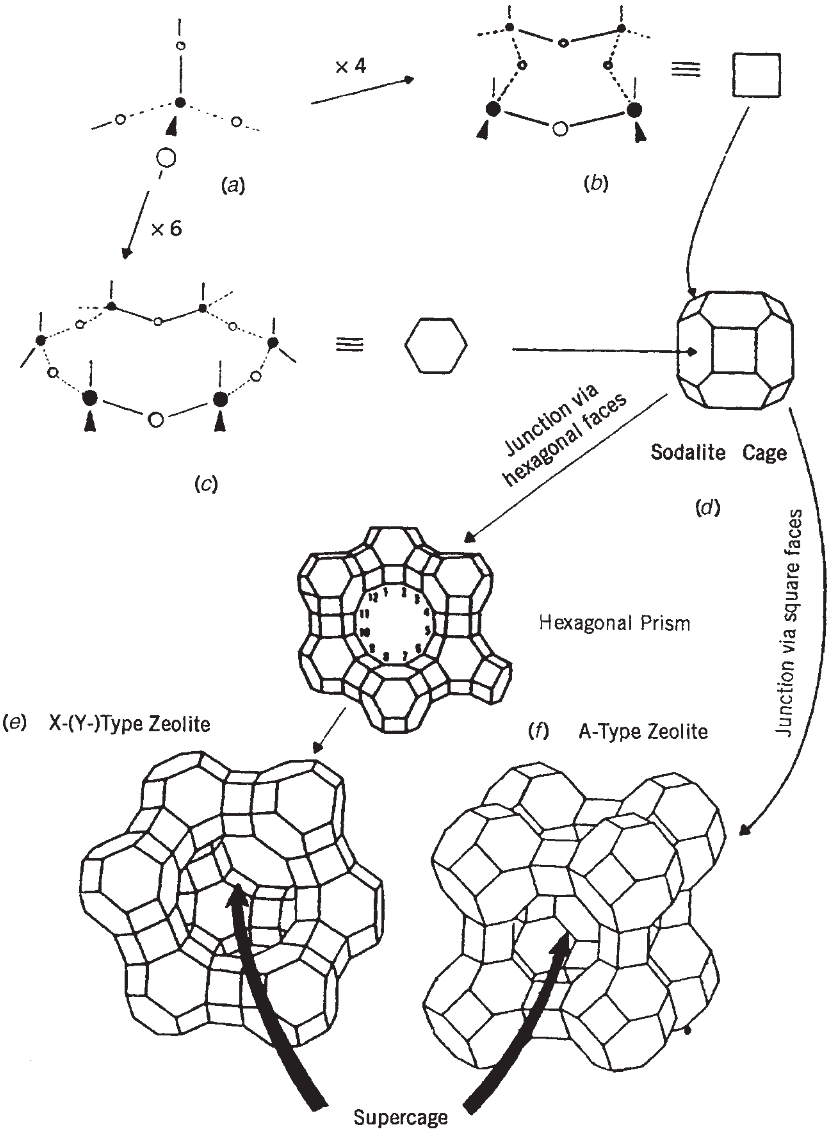


FIGURE 16.9 Basic structural units and the modes of their combination in the common zeolites. T atoms (Si or Al) are denoted as ● in the simple structures and lie at the intersections of lines in the complex structures. Oxygen atoms are shown in the simple structures when they are represented as ○: in the complex structures an oxygen atom lies at the midpoint of each line. Reproduced from *Biomass*, *Catalysts and Liquid Fuels*, I. M. Campbell (1983) Holt, Rinehart and Winston Ltd, Eastbourne, p. 116, with permission.

offretite, and tetrabutylammonium ions to ZSM-11. Mobil discovered ZSM-5 in 1968, but failed to recognize its activity for 5 years. They then found it would convert methanol by way of dimethyl ether to a gasoline containing aliphatic compounds and mixed aromatics up to durene (1,2,4,5-tetramethylbenzene). It also provided aromatics from paraffins, olefins, and oxygenated material and can thus be used to increase the octane number of gasoline. Fischer–Tropsch hydrocarbons (Section 12.2) have an octane number of about 60 and passage over ZSM-5 can raise this to 90. The major use for ZSM-5 is for xylene isomerization, discussed below. It catalyzes the disproportionation of toluene to benzene and *p*-xylene (Section 8.1) and is important in one process for the condensation of benzene and ethylene to ethylbenzene (Section 3.8) as well as the condensation of benzene and propylene to cumene (Section 4.5).

Zeolites are normally made from sodium silicate and aluminate. Hence, the finished structures contain sodium ions. If the zeolite is required for catalyst use, it is usual to replace the sodium by ammonium in an ion-exchange process, and then to heat the ammonium zeolite so that ammonia is given off and the zeolite is left containing strongly acid H^+ sites. Such zeolites have names preceded by an H, that is, ZSM-5 becomes HZSM-5.

Pores and voids make up about half the volume of zeolites but these “holes” are not accessible to all molecules. Small molecules can diffuse in and out with ease, but larger ones cannot. A-type zeolite admits *n*-alkanes but not branched-chain alkanes. Benzene is also rejected. There is thus a *molecular sieve* action. Sometimes, this provides a method of separation, such as straight-chain from branched-chain hydrocarbons. In other cases, molecules are excluded from catalytic sites because of their size. Molecules that do gain access to the voids, however, are subject to strong localized electrostatic fields. In most current industrial applications, this leads to acid catalysis.

The shape selectivity of a zeolite catalyst may apply to the reactants, the transition state, or the products. An example of reactant selectivity used to raise the octane number of gasoline is the cracking of straight-chain alkanes over A-type zeolites. Branched-chain materials are excluded from the acid sites. Over an amorphous silica–alumina, the branched-chain alkanes would be preferentially cracked or isomerized.

An example of product selectivity is the transalkylation of toluene over HZSM-5 modified with magnesium and phosphorus. The products are benzene and *p*-xylene (Section 8.1). Benzene diffuses very rapidly out of the pores. *p*-Xylene diffuses moderately fast, while the other two isomers diffuse at 0.1% of the rate of the *p*-isomer. Thus they have a high chance of isomerizing again before they escape. At operating temperatures, the thermodynamic distribution of xylenes is about 25% *ortho* and *para* and 50% *meta*; zeolites are claimed to give 88–95% *para*.

The most important example of transition-state selectivity is the absence of coking in such processes as the formation of gasoline from methanol over HZSM-5 in the Mobil process. Coking proceeds via polynuclear aromatic hydrocarbon intermediates, but the zeolite discriminates against molecules with more than 10 carbon atoms.

Hence, coking is avoided and the spread of molecular weights is narrow compared to products from the Fischer–Tropsch or similar processes.

The Mobil process still appears to be the cheapest route to gasoline-from-methanol but it was commercialized only in New Zealand. Rises and falls in crude oil prices revive or reduce interest in it. Toluene disproportionation, however, has been commercialized.

Related to work on zeolites is research on clay minerals and particularly smectite clays. These are aluminosilicates like zeolites and consist of layers, the separation of which can be varied and between which catalysts can lodge. They are known as intercalated catalysts. The collapse of the layered structure at temperatures above 200°C may be avoided by incorporation of "spacers" such as aluminum or zirconium hydroxides to give so-called pillared clays. Currently, the only commercial process based on smectite clays is the dimerization of oleic acid (Section 13.4).

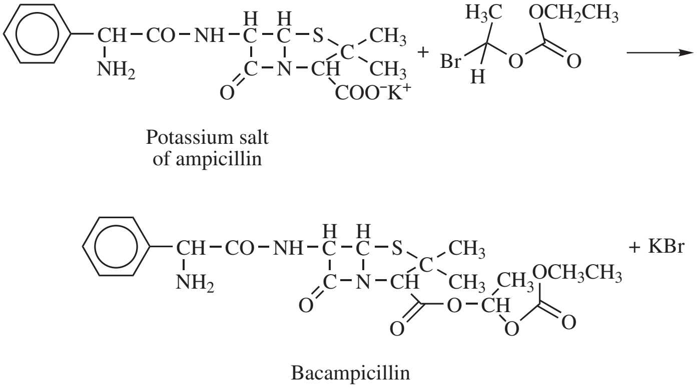
The number of commercialized processes involving synthetic zeolites is also small. Nonetheless, there is extensive research in progress on microporous aluminophosphates, showing that silica is no longer necessary in the formation of a molecular sieve. A British group has converted hexane to adipic acid at low temperature by means of an aluminophosphate molecular sieve with cobalt(III) ions located on the inner walls of cages inside the sieve. Yields at the time were only 30%. The same group converted cyclohexane to adipic acid by air oxidation using an aluminophosphate sieve containing iron(III) ions. Yields were again poor (33% for the hexane), but these processes are early examples of extra-large pore molecular sieves where catalytically active metal atoms are deposited in the pores to give "uniform" heterogeneous catalysts, in which active sites are distributed in a spatially uniform way throughout the bulk of the solid.

Another zeolite-catalyzed oxidation process is Solutia's nitrous oxide-based oxidation of benzene to phenol (Section 7.1). This reaction is reportedly catalyzed by ZSM-5 or ZSM-11 incorporating iron. Among other things, these oxidations confirm the possibility of zeolite and sieve-based industrial processes other than acid catalysis. Dendrimers offer related opportunities (Section 15.4.4). Shape selective catalysis is intriguing and holds great potential.

16.10 PHASE-TRANSFER AND FLUOROUS BIPHASE CATALYSIS

Phase-transfer catalysis is used for the preparation of polycarbonates (Section 7.1.2.2), estradiol carbamate and various fine chemicals. It is not likely to be involved in the manufacture of large tonnage heavy organic chemicals but is an unusual and elegant catalytic technique that is energy sparing and gives high yields at low-residence times under mild conditions. It is therefore typical of the methods that will be attractive in the future.

It finds application where reactants are immiscible. An example is the production of penicillin esters (see note at the end of this chapter) in which the free carboxyl group of the aminopenicillanic acid is esterified with a labile group that will hydrolyze in the gut. The desired reaction is



but the ampicillin salt is water soluble, whereas the acycloxymethyl bromide dissolves in organic solvents and would be hydrolyzed by water. Mild conditions are essential to avoid decomposition of the bromide and the lactam ring of the ampicillin. The acycloxymethyl bromide is therefore dissolved in an organic solvent such as dichloromethane or chloroform and brought into contact with an aqueous solution of the ampicillin salt at 25°C. A phase-transfer catalyst such as tetrabutylammonium chloride is added to the aqueous phase.

A simple interpretation of what occurs is that the tetrabutylammonium cation is lipophilic and migrates into the organic layer as an ion pair carrying with it the ampicillin anion, which is less hydrophilic than the other anions present. Esterification of the ampicillin anion then takes place in the organic layer, and the tetrabutylammonium ion pairs with the bromide ion that is generated. The latter is so hydrophilic that it carries the tetrabutylammonium cation back into the aqueous phase and the procedure is repeated until esterification is complete. Kinetic measurements indicate that the mechanism is more complicated and may involve inverse micelle formation and interfacial reactions.

An opportunity for phase-transfer catalysis to be used in a large-tonnage process was frustrated by environmental considerations. Ethylene dibromide is at present made by bromination of ethylene. The elemental bromine is obtained from bromide-containing brines from which it is displaced by chlorine and steam in an expensive energy-intensive process. Dead Sea Bromine, in Israel, developed a process by which ethylene dichloride was mixed with Dead Sea brines in the presence of a phase-transfer catalyst. Bromine is more lipophilic than chlorine, hence the bromide ions were carried to the organic layer to yield the dibromide. The main use for ethylene dibromide, however, was as a lead scavenger in leaded gasoline. Its market therefore declined and it was never worthwhile to commercialize the new process.

Fluorous biphase catalysis is a further technique involving phase separation. At low temperatures, many systems consisting of an organic and a fluorinated solvent such as toluene and perfluoro(methylcyclohexane) are immiscible but, on heating, the solvents coalesce to a single phase, allowing homogeneous reactions to take place. An example given in the literature and shown in Figure 16.10 shows the selective

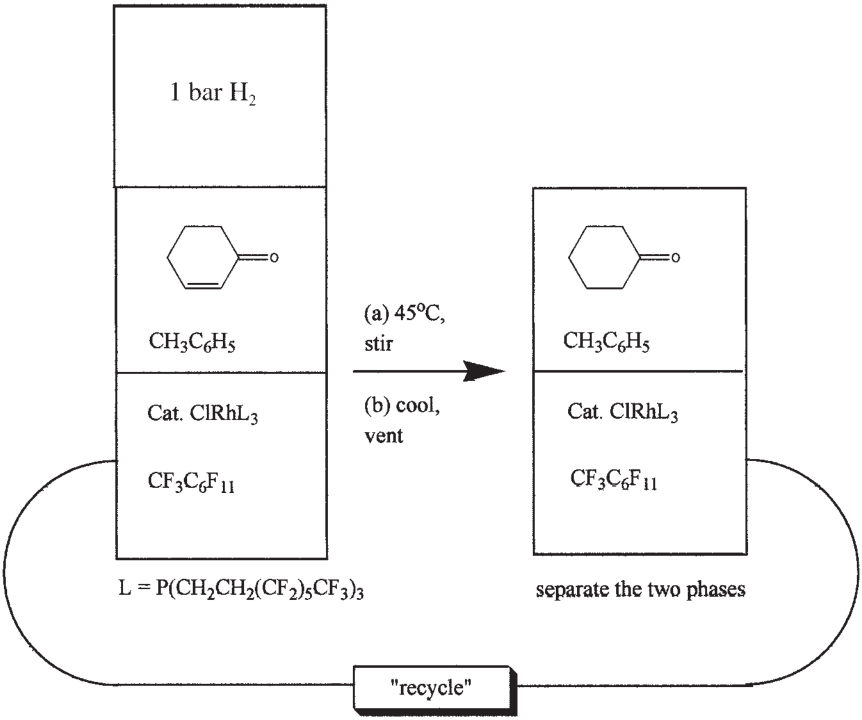


FIGURE 16.10 Fluorous rhodium-catalyzed alkene hydrogenation.

hydrogenation of the carbon–carbon double bond in cyclohexenone. Cyclohexenone in toluene is brought into contact with gaseous hydrogen and a solution of a rhodium catalyst in perfluoromethylcyclohexane. The phases do not mix and there is no reaction. On heating to 45°C, the organic layers become miscible and hydrogenation takes place. The system in cooled and vented. The catalyst-containing phase reappears and can be recycled (see note at the end of this chapter).

16.11 CATALYSTS OF THE FUTURE

Some of the objectives of catalyst research in the future are discussed in the following sections.

16.11.1 Catalyst Design

An objective is to advance catalyst theory to the point where catalysts can be designed. Remarkable progress has been made in the past few years in understanding catalyst action. The use of computer modeling, routine for many years in the development of new pharmaceuticals, is now being used in the design of catalysts. Computer techniques can aid catalyst design not only at the molecular and electronic level, but also in the modeling of transport phenomena. There is scope for a breakthrough.

16.11.2 Higher Selectivities

A further aim is to achieve higher selectivities in known reactions. This might involve improvement of existing catalysts or development of new ones. Most of the catalysts discussed above were primarily developed to give higher selectivities, and we may expect to see advances in, for example, catalysis by zeolites.

Ammoxidation of propylene to acrylonitrile (Section 4.8) shows what is possible. The earliest catalysts (in the laboratory) gave 6% yields. Bismuth phosphomolybdate raised this to 65% and a plant was built in 1959. An antimony–uranium oxide catalyst gave laboratory yields of 80% in 1966 (72.5% in the plant). In 1972, promoted bismuth–molybdenum oxides on silica raised plant yields to 77%. A fourth generation catalyst composed of an oxide complex of iron, selenium, and tellurium appears to give about 83% and a series of patents in the early 1980s claimed 87% for a related complex. In the 1990s, the newer catalysts have reduced byproduct acetonitrile production to the point that there is a shortage for the small volume uses that do exist. Asahi and BP developed more active catalysts with longer lives and these have produced further challenges. With high activity catalysts, less needs to be used. The surface area of the catalyst bed is thus reduced and heat removal becomes more difficult. Mitsubishi Chemical has designed a special fluidized-bed reactor that enhances the contact between the gaseous reactants and the catalyst.

There is still scope for improvement in the classic iron catalysts for the Haber process for ammonia. Yields in the mid-1990s were between 15 and 17% per pass. Kellogg and BP then reported a new catalyst with 10–20 times greater activity (Section 10.5.1). It was more tolerant to variations in the N_2/H_2 ratio. The saving in energy was estimated at $21\,\text{kJ mol}^{-1}$ and the saving in cost at $2–6/tonne of ammonia. Other workers have reported promoted catalysts containing Fe_3Mo_3N, Co_3Mo_3N, and Ni_2Mo_3N, but it is not clear which of these has been commercialized. The Haber process is said to account for 1% of world energy consumption. Hence, there is a great incentive for improved catalysts, but there are formidable difficulties in finding them.

16.11.3 Catalysts with Greater Activity

An objective is to synthesize catalysts with greater activity (e.g., Ziegler catalysts as in Section 16.1.2). Greater activity improves economics. An important goal is the synthesis of homogeneous catalysts with high enough activity for conversion to heterogeneous catalysts that still retain activity. Enzymes may be immobilized without substantial loss of activity but, in general, only a highly active homogeneous catalyst can be successfully immobilized.

There has been considerable interest in the use of clusters of metal atoms bound to carbon monoxide as highly active catalysts. Many catalytically active metals such as palladium, rhodium, platinum, osmium, rhenium, and ruthenium form clusters. The $Rh_6(CO)_{16}$ complex is active in the methanol–carbon monoxide route to acetic acid, but appears to cleave during the reaction. In spite of much research, cluster catalysts have not yet been commercialized.

Clusters of metal atoms of a size where they are just beginning to develop the properties of a solid metal are also very active as are intermetallic compounds. Many of these are known, one component being a rare earth. Lanthanum pentanickel ($LaNi_5$), for example, absorbs large quantities of hydrogen reversibly and may be used in low-temperature hydrogenations. Currently, $Rh_6(CO)_{16}$ is used in acetic acid production. Sometimes the two metals may be bonded either directly or via a ligand. One metal activates a hydrogen atom and the other the molecule.

There is also interest in the catalytic properties of heteropolyacids. An example that has been commercialized is the production of *tert*-butanol from the isobutene in mixed butenes over the heteropolyacid $H_3PMo_{12}O_{40}$.

16.11.4 Pollution Problems

Catalysts are needed to solve pollution problems. The breakthrough in this area was the development of the platinum–palladium–rhodium catalysts that oxidize unburned hydrocarbons and carbon monoxide in the catalytic converter of automobiles. All the same, a cheaper catalyst is a desirable aim, as is a catalyst that would promote decomposition of nitrogen oxides to molecular nitrogen and oxygen in the presence of water and carbon dioxide. Other aims are catalysts to desulfurize flue gases and to remove organochlorine compounds from water. The latter might involve hydrogen or hydrogen donors such as hydroaromatics, and a catalyst, based perhaps on iron, cobalt, or ruthenium. There is a host of other environmental problems that could be helped by novel catalysts.

16.11.5 Catalysts for New Reactions

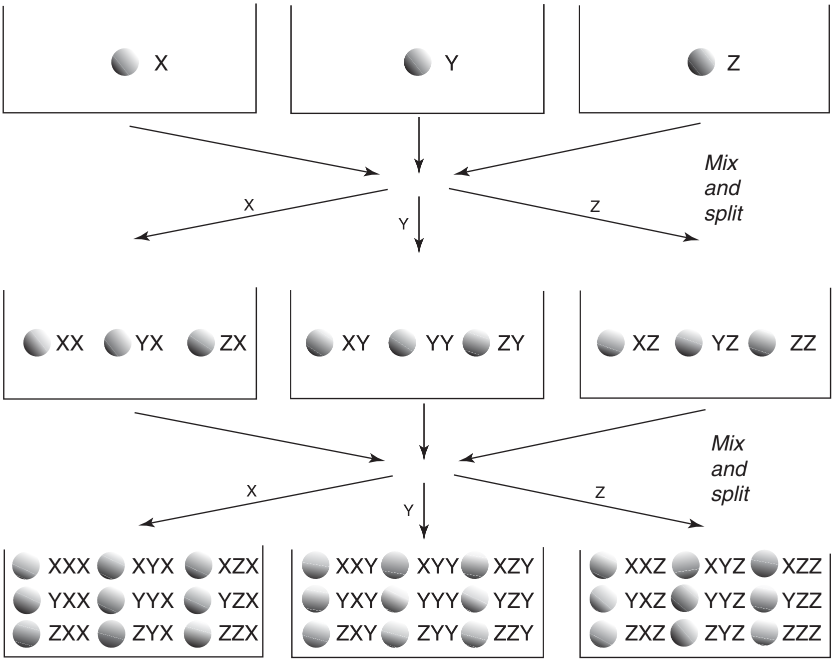
Catalysts are needed for new reactions. A major research aim today is the functionalization of methane, ethane, propane, and butane to replace more expensive olefins as petrochemical precursors. Selective catalysts for low-temperature liquid-phase oxidation of methane to methanol and for oxidative coupling of methanol to ethylene would be especially valuable (Section 11.1). Among the few successes so far in the functionalization of alkanes is the conversion of *n*-butane to maleic anhydride (Section 5.4). Processes for conversion of propane to acrylonitrile and ethane to vinyl chloride are slated for commercialization in the mid- to-late 2000s (Section 11.2.1). A laboratory process, typical of many, has also been reported for direct conversion of methane to acetic acid in aqueous solution at 100°C. The oxidants are carbon monoxide and oxygen and the catalyst rhodium trichloride plus a source of iodide ions or 5% palladium on carbon.

16.11.6 Catalysts that Mimic Natural Catalysts

Catalysts are needed that mimic natural catalysts. Nature manages to produces complex organic molecules in a single stereochemical form under mild conditions. The synthesis of stereoregular and optically active compounds is already possible in some cases (Sections 16.7.1 and 16.7.2). Some natural enzymes may be isolated, immobilized, and used as catalysts to give “natural” products. Most remarkable of all is recombinant DNA engineering or gene splicing, which makes possible the synthesis of proteins and peptides.

16.11.7 Catalyst Discovery via High Throughput Experimentation

Combinatorial chemistry was first developed to speed the synthesis and discovery of pharmaceutically active compounds, but these methods have since been adapted for wider applications, in particular catalyst development. The term combinatorial chemistry covers a variety of synthetic methods, but the basic concept is simple. Techniques are used that quickly generate a vast collection of compounds that might be therapeutically or catalytically active or whatever is sought. Figure 16.11 shows the generation of a library of 27 compounds in just three steps, starting with the reagents X, Y, and Z bound to polymer beads. Treatment of these entities with further reagents X, Y, and Z generates nine compounds and, if these are mixed and split again, 27 compounds have been generated after a relatively small number of operations. The compounds can then be displaced from the beads and screened. The deconvolution technique to identify the



Note: Mix and split synthesis: using three reagents bound to resin beads, a library of 27 products can be generated in just three steps

Source: Tapolczay DJ, Kabyleck: RJ, Payne LJ, Hall B. "Extracting order from chaos" Chem. Ind. 1998; 772-775

FIGURE 16.11 Combinatorial chemistry.

active compound is similar but in reverse (see note at the end of this chapter). Combinatorial chemistry provides libraries of novel compounds at a rate perhaps a thousand times greater than if they are synthesized by conventional laboratory chemistry.

In order to take advantage of combinatorial chemisry, however, techniques for rapid screening, analyzing, data manipulation, and interpretation must also be developed. The broad term used to cover this activity is high throughput experimentation or HTE.

The first independent company established to exploit combinatorial chemistry and HTE for developing commercially useful catalysts was Symyx Technologies, CA, founded in 1994. Symyx, screens more than one million new materials per year with applications ranging from X-ray storage phosphors to polymers for DNA and carries out research on new catalysts for the manufacture of chemicals and plastics. In April 2003, Dow Chemical and Symyx jointly claimed to have discovered by HTE a new class of single-site polyolefin catalysts composed of amide–ether-based hafnium complexes. Other HTE companies have since been established for developing new catalytic materials including Avantium in Holland, HTE AG in Germany, and Torial in the United States.

NOTES AND REFERENCES

An excellent general account of industrial catalysis is given in the new fourth edition of J. I. Kroschwitz and M. Howe-Grant, Eds. *Kirk–Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., New York, 1993, Vol. 5, pp. 320–460, and the chemical engineering aspect is summarized in R. H. Perry, D. W. Green, and J. O. Maloney, *The Chemical Engineer's Handbook*, 7th ed., McGraw-Hill, New York, 1997.

The Royal Society of Chemistry, London, produces a specialist periodical report, J. J. Spivey, Ed. *Catalysis: A Review of Chemical Literature*. By 2003, the series had reached Vol. 16.

There are two authoritative continuing multivolume series: W. G. Frankenburg, D. D. Eley, *et al.*, Eds., *Advances in Catalysis*, Academic Press, New York 1948— and J. R. Anderson, and M. Boudart, *Catalysis—Science and Technology* (7 vols.), Springer-Verlag, Berlin, 1981. What may become a series is *Catalysts for fine chemical synthesis*, S. M. Roberts, I. V. Kozhevnikov, and E. Derouane, Eds., John Wiley & Sons, Inc., Chichester. Two volumes—hydrolysis, oxidation and reduction, and catalysis by polyoxometalates—had appeared by the end of 2002. The second edition of B. Cornils, W. A. Herrman and R. Shlögl, *Catalysis from A to Z: a concise encyclopedia*, John Wiley & Sons, Inc., New York, appeared in 2003.

Classic books on heterogeneous catalysis include G. C. Bond, *Catalysis by Metals*, Academic Press, New York, 1962; J. M. Thomas and W. J. Thomas, *Heterogeneous Catalysis*, Academic Press, London, 1967; and C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, Cambridge, MIT, MA, 1970. Table 5.1 is largely drawn from G. C. Bond, *Heterogeneous Catalysis: Principles and Applications*, Clarendon Press, Oxford, 1974. More recent are B. C. Gates, *Catalytic Chemistry*, John Wiley & Sons, Inc., New York, 1992, and an exceptionally useful paperback, I. M. Campbell, *Catalysis at Surfaces*, Chapman & Hall, London, 1988.

Homogeneous catalysis is tackled in the review series R. Ugo, Ed., *Aspects of Homogeneous Catalysis*, Kluwer, Dordrecht, Holland, 1970—Both types of catalysis are covered in B. Delmon and G. Jannes, Eds., *Catalysis: Heterogeneous and Homogeneous*, Elsevier, 1975.

M. V. Twigg, catalysis doyen of ICI Agricultural Divison many years ago, has produced a second edition of his *Catalyst Handbook*, Wolfe, London, 1989. Other publications with a practical slant include a chapter: J. Pennington, "Catalysts and Catalysis," in *Introduction to Industrial Chemistry*, 2nd ed., C. A. Heaton, Ed., Glasgow, 1991; a book: R. Pearce and W. R. Patterson, Eds., *Catalysis and Chemical Processes*, Leonard Hill, London, 1981 (we liked this one particularly) and a 3-volume *magnum opus*: B. E. Leach, *Applied Industrial Catalysis*, Academic Press, New York, 1984.

Plenum Press, New York, is publishing a series under the general titile *Fundamental and Applied Catalysis*. The first—J. T. Richardson, *Principles of Catalyst Development*, 1989, is a crisp and clear introduction to heterogeneous catalysis. Other volumes are V. P. Zhdanov, *Elementary Physicochemical Processes on Solid Surfaces*, 1991; J. R. Jennings, *Catalytic Ammonia Synthesis: Fundamentals and Practice*, 1991; K. Famaru, *Dynamic Processes on Solid Surfaces*, 1993, and J. Vedrine, *Catalyst Characterization*, 1994. J. R. Jennings has also produced a volume in the *Critical Reviews of Applied Chemistry Series* entitled *Selected Developments in Catalysis*, Elsevier, Barking, Essex, 1991.

Section 16 The size of catalyst markets was derived from *Catalysts* published with *Chem. Week*, September 1999. Earlier estimates appeared in the Pimental report, *Opportunities in Chemistry*, NAS/NRC/02-86, National Academy Press, Washington, DC, 1985.

P. N. Rylander, H. Greenfield, and R. L. Augustine, *Catalysis of Organic Reactions*, Dekker, New York, 1993 is primarily an academic text but two of the authors have been in industry, and it provides an up-to-date survey of the issues of concern in catalyst research.

Section 16.1 For a not too technical introduction to the subject, see V. Haensel (the discoverer of catalytic reforming) and R. L. Burwell, Jr., "Catalysis," *Sci. Am.,* **225**(6), 46 (1971).

Section 16.1.1 Figure 16.1 is based mainly on standard thermodynamic data together with activation energies from G. J. Minkoff and C. F. H. Tipper, *Chemistry of Combustion Reactions*, Butterworth, London, 1962; C. Bamford and C. F. H. Tipper, *Comprehensive Chemical Kinetics*, Vol. 5, Elsevier, Amsterdam, The Netherlands, 1972; and K. Weissermel and H. J. Arpe, *Industrial Organic Chemistry*, Verlag Chemie, Weinheim, 1978. The last of these claims that the peracetic acid → acetic acid reaction goes via an α-hydroxyethyl peracetate transition state formed from peracetic acid and acetaldehyde. The peracetic acid and transition state enthalpies were deduced by the methods in S. W. Benson, *Thermochemical Kinetics*, 2nd ed., John Wiley & Sons, Inc., New York, 1976.

The spread of A values in the compensation effect is reported by F. S. Feates, P. S. Harris, and B. G. Reuben, *J. Chem. Soc. Faraday Trans.* **70**, 2011 (1974).

Section 16.1.2 The irreversible degradation of CRG catalysts is documented in A. Williams, G. A. Butler, and J. Hammonds, *J. Cat.*, **24**, 352 (1974); W. H. Gitzen, *Alumina as a Ceramic Material p 35. Special Publication #4*, American Ceramic Soc. Columbus. OH (1970); and G. Yamaguchi and H. Yanagida, *Bull. Chem. Soc. Jpn.*, **36**, 1155 (1963).

Section 16.1.3 See J. B. Butt, and E. E. Petersen, *Activation, deactivation and poisoning of catalysts*, Academic Press, San Diego, CA, 1988.

Section 16.3 This section is based on "Catalysts" published with *Chem. Week*, September 1999 and "Chemical Week Associates Custom Publication," July 24, 2002. The Catalyst Group www.catalystgrp.com/catalystsandchemicals.html omits the fine chemicals category and allocates 23–24% of markets to petroleum refining, chemicals, and polymers and 30% to environment.

Section 16.4 The classic book on acid–base catalysis is R. P. Bell, *The Proton in Chemistry*, Cornell University Press, Ithaca, NY, 1959. The neglected area of basic catalysis was covered in H. Pines and W. M. Stalick, *Base Catalyzed Reactions of Hydrocarbons and Related Compounds*, John Wiley & Sons, Inc., New York, 1977.

Section 16.5 Physical techniques for investigation of the properties of adsorbed layers are summarized by J. T. Yates, *Chem. Eng. News*, August 26, 1974, p. 9.

Section 16.6 Catalysis by chemisorption is relatively well understood and is discussed by R. P. H. Gasser, *An Introduction to Chemisorption and Catalysis by Metals*, OUP, Oxford, UK, 1985. It is possible that catalysis at surfaces can be understood nonmathematically on the basis of organometallic chemistry. Readers unhappy with the quantum theory of solids should try J. M. Basset, Ed., *Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis*, Dordrecht, Kluwer, Holland, 1988. The mechanism for the carbonylation of methanol appeared in D. Forster, *J. Am. Chem. Soc.* **98**, 846 (1976).

A short and inexpensive book is R. A. Henderson, *The Mechanism of Reactions at Transition Sites*, OUP, Oxford, 1994.

Section 16.6.1 See *Catalysts and Automotive Pollution Control*, A. Crucq, Ed., Elsevier, Barking, 1991, especially M. Bowker et al., *ibid.* p. 409. Rhodia's plans are outlined in *Chem. Mkt. Rep.*, October 7, 2002, p. 6. Catalytic converters are described in K. C. Taylor, *CHEMTECH*, **20**, 551 (1990). See also R. M. Heck and R. J. Farrauto, *Catalytic Air Pollution Control: Commercial Technology*, 2nd ed., John Wiley & Sons, Inc., New York, 2002.

Section 16.7.1 The Du Pont hexadiene synthesis is described by C. A. Tolman, *J. Am. Chem. Soc.* **92**, 6777 (1977). See also "New Perspectives in Surface Chemistry and Catalysis," *Chem. Soc. Rev.* **6**, 373 (1977). The synthesis of vitamin A is described by H. A. Wittcoff and B. G. Reuben, *Industrial Organic Chemicals in Perspective*, *Part II: Technology, Formulation and Use*, John Wiley & Sons, Inc., New York, 1980, p. 373.

Section 16.7.2 For the synthesis of levodopa, see H. A. Wittcoff and B. G. Reuben, Part II, *op. cit.*, p. 268. There is a continuing series on asymmetric synthesis: J. D. Morrison, et al., Eds., *Asymmetric Synthesis*, John Wiley & Sons, Inc., New York. Three seminal articles appeared in the late 1980s by G. W. Parshall and W. A. Nugent. They were "Making Pharmaceuticals via Homogeneous Catalysis," *CHEMTECH* **18**, 184 (1987), "Functional Chemicals via Homogeneous Catalysis," *ibid.* p. 314; and

"Homogeneous Catalysis for Agrochemicals, Flavors and Fragrances," *ibid.* p. 376. The accumulated wisdom has appeared in book form G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, John Wiley & Sons, Inc., New York, 1992.

There are many other books on what is the fashionable topic of asymmetry. For the industrially oriented reader, we suggest R. A. Aitken and N. Kilenyi, *Asymmetric Synthesis*, Chapman & Hall, London, 1992; A. N. Collins, G. N. Sheldrake, and J. Crosby, *Chirality in Industry—the Commercial Manufacture and Applications of Optically Active Compounds*, John Wiley & Sons, Inc., Chichester, UK, 1992; R. A. Sheldon, *Chirotechnology: Industrial Synthesis of Optically Active Compounds*, Dekker, New York,1993 and R. Noyori, *Asymmetric Synthesis in Organic Catalysis*, Chichester, UK, John Wiley & Sons, Inc., 1994.

Use of the chiral auxiliary [$(C_2H_5)Fe(CO)(PPh_3)$] for asymmetric synthesis is discussed by S. G. Davies, *Aldrichimica Acta* **23**, 31 (1990). The original FDA views on chiral drugs are explained in J. Fox, *Chem. Ind.* 270 (1993).

Section 16.8 The broad topic of biocatalysis is covered in A. S. Bommarius and B. R. Riebel, *Biocatalysis: Fundamentals and Applications*, John Wiley & Sons, Inc., New York, 2003. A sound introduction to enzyme catalysis is provided by T. Palmer, *Understanding Enzymes*, Ellis Horwood, New York, 1991. The industrial angle is excellently covered in W. Aehle, *Enzymes in Industry: Production and Applications*, 2nd ed., John Wiley & Sons, Inc., New York, 2003. See also, J. E. Bailey and O. F. Ollis, *Biochemical Engineering Fundamentals*, 2nd ed., McGraw-Hill, New York, 1986 and A. Fersht, *Enzyme Structure and Mechanism*, 2nd ed., W. H. Freeman, San Francisco, 1988. Immobilization techniques are discussed in K. Musbach, Ed., *Methods in Enzymology*, Vol. 44, Academic Press, New York, 1976. Binding of enzymes to polystyrene is discussed in H. H. Szmant, *Industrial Utilization of Renewable Resources*, Technomic, Lancaster, PA, 1986, and by silanes in E. P. Plueddemann, *Silane Coupling Agents*, Plenum, New York, 1982.

The 6-aminopenicillanic acid synthesis is described in B. G. Reuben and H. A. Wittcoff, *Pharmaceutical Chemicals in Perspective*, John Wiley & Sons, Inc., New York, 1989, p. 132 and in E. J. Vandamme, Ed., *Biotechnology of Industrial Antibiotics*, Dekker, New York, 1984. Lysine synthesis is described in H. A. Wittcoff and B. G. Reuben, *Perspective* Part II, *op. cit.*

Section 16.8.1 We have drawn on two secondary sources: R. M. Baum, *Chem. Eng. News*, 33, (April 19, 1993) and G. M. Blackburn and P. Wentworth, *Chem. Ind.*, 338 (1994), together with J. K. Janda, C. G. Shevlin, and A. Lerner, *Science* **259**, 490 (1993). Peptide synthesis is reported by R. F. Hirschmann and A. B. Smith, *Science* **265**, 234 (1994) and reviewed in *Chem. Eng. News*, July 11, 1994.

Section 16.9 J. D. Idol, "Horizons in Catalysis," *Chem. Ind.*, 272 (1979), is an excellent general article on the development of molecular sieve catalysis.

Zeolites for Industry—a full issue of *Chem. Ind.*, April 2, 1984—has articles by J. Dwyer, A. Dyer, R. P. Townsend, L. V. C. Rees, and S. M. Csicsery, "An article on Shape Selective Catalysis in Zeolites" appears in *Chem. Br.* **21**, 473 (1985). The New Zealand methanol-to-gasoline process is described by C. J. Maiden, "Catalysis Research Bears Fruit," *CHEMTECH*, 32, January, 1988. A rare article on clays is E. Chynoweth, "Shaping Environmental Solutions with Clay-Based Catalysts," *Chem. Week*, June 26, 1991, p. 55. Extra-large pore molecular sieves are described in M. E. Davies, *Chem. Ind.*, 137 (1992), and "uniform" heterogeneous catalysts in J. M. Thomas, J. Chen, and A. George, *Chem. Br.* **28**, 991 (1992).

The idea of encapsulating metal complexes in zeolite to give biomimetic catalysts is discussed by P. C. H. Mitchell, *Chem. Ind.* 308 (1991). Computer-aided design of zeolites is the theme of *Modelling of Structure and Reactivity in Zeolites*, C. R. A. Catlow, Ed., Academic Press, London, 1992.

The *n*-hexane and cyclohexane conversions to adipic acid are reported in J. M. Thomas et al., *Angew. Chem. Int. Ed. Engl.* **39**, 2310 and 2313 (2000). See also *Chem. Eng. News*, July 3, 2000, p. 7.

Section 16.10 Phase-transfer catalysis is discussed exhaustively in the classic E. V. Dehmlov, and S. S. Dehmlov, *Phase Transfer Catalysis*, 3rd ed., VCH Verlag, Weinheim, 1993. Ch. M. Starks, another pioneer of the technique, has edited *Phase Transfer Catalysis*, No. 326 in the ACS Symposium series, ACS, Washington DC, 1987. Still useful is W. E. Keller, *Phase Transfer Reactions—Fluka Compendium*, 2 vols., G. Thieme Verlag, Stuttgart, 1986–1987. Industrial aspects are covered by B. G. Reuben and K. Sjøberg, *CHEMTECH* **11**, 315 (1981). The penicillin esters are discussed in B. G. Reuben and H. A. Wittcoff, *Pharmaceutical Chemicals in Perspective*, John Wiley & Sons, Inc., New York, 1989, p. 134. Fluorous biphase catalysis has not yet been commercialized but a number of examples and a bibliography are given at www.organik.uni-erlangen.de/gladysz/ research/fluor.html.

Section 16.11 The future is overt in *Perspectives in Catalysis: A Chemistry for the 21st Century Monograph*, J. M. Thomas and I. Zamaraev, Eds., Blackwell Scientific, Oxford, 1992.

A pioneering book is E. R. Becker and C. J. Pereira, *Computer-Aided Design of Catalysts*, Decker, New York, 1993. See also C. R. A. Catlow, note to Section 16.9.

Relevant patents on acrylonitrile production are US Patent 5,770,757 (June 23, 1998) to Standard Oil Co; US Patent 5,780,664 (July 14, 1998) to Asahi Kasei Kogyo; and US Patent 5,914,424 (June 22, 1997) to Mitsubishi Rayon Co.

Haber process catalysts are discussed at www.globaltechnoscan.com/21stMar-27thMar01/energy.htm and in *Chem. Commun.*, 1057 (2000).

Methane conversion is discussed by J. Haggin in several articles in *Chem. Eng. News*, January 22, 1990, pp. 20–26. A methane to acetic acid process with a peroxysulfate catalyst has been known for some time but a newer route uses simpler reagents. It is reported by M. Lin and A. Sen, *Nature* (*London*) **368**, 613 (1994) and in *Chem. Br.* **30**, 624 (1994).

Section 3.12 Excellent descriptions on the application of combinatorial chemistry and high throughput experimentation for catalyst discovery are J. Newsam, and F. Schuh, *Biotechnology and Bioengineering (Combinatorial Chemistry)*, Vol. 61, No. 4, 1998–1999; R. Crabtree, *CHEMTECH*, 21–26, April 1999, B. Jandeleit, D. Schaefer, T. Powers, H. Turner, and W. Weinberg, *Angew. Chem. Int. Ed.*, **38**, 2494 (1999). See also, D. J. Tapolczay, R. J. Kobylecki, L. J. Payne, and B. Hall, *ibid.* 772–775. The overview of combinatorial methods here describes only one of many procedures. Another useful secondary source is S. Borman, *Chem. Eng. News*, March 8, 1999, pp. 33–48.

CHAPTER 17

SUSTAINABILITY AND GREEN CHEMISTRY

In the 1950s and 1960s, the organic chemical and pharmaceutical industries grew at an astonishing pace, twice as fast as the chemical industry in general and four times as fast as the economy as a whole. The market was flooded with new and exciting polymers that provided synthetic fibers for clothes, plastics for all sorts of household goods, together with elastomers, paints, and adhesives. In the pharmaceutical field, there was a flood of new drugs that cured traditional infectious diseases and eased the cardiovascular and psychological problems of modern life. Standards of living rose so rapidly and novel processes succeeded one another so frequently that few paused to consider possible adverse consequences of such growth.

For the pharmaceutical industry, the party came to an end with the thalidomide tragedy in 1962, in which an inadequately tested but supposedly safe sleeping pill, designed to replace the dangerous barbiturates, turned out to cause birth defects when taken by pregnant women. New regulations for drug testing and safety were swiftly implemented, and the number of new chemical entities reaching the market each year more than halved.

The problems of the organic chemicals industry started perhaps 10 years later. The publication of Rachel Carson's *Silent Spring* in 1962 was a portent. Carson claimed that the synthetic chemicals being emitted into the environment, especially DDT, were spreading worldwide and accumulating in the body fat of species high up the food chain. Birds were being harmed, their eggshells weakened. In 1972, *The Limits to Growth* by D. H. Meadows *et al*. appeared. They claimed that population, standards

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

of living, pollution, and the consumption of nonrenewable natural resources were all linked in a fairly simple way, and all were increasing exponentially. The future could be modeled even on the relatively unsophisticated computers of the time, and the conclusion was that any limited problem one could solve was part of a larger problem one could not solve. Doom was just around the corner. Thirty years later, the predictions have all been falsified, but the book was immensely influential in bringing to world notice the genuine problems of pollution and resource depletion. This was a classic example of the truth that prediction *per se* is not important; what is important is what action the prediction motivates. The book's message was emphasized by the Yom Kippur Arab–Israel war in 1973, which highlighted the fact that about two-thirds of world long-term oil reserves are concentrated in the Middle East in countries not noted for political stability, democratic traditions, nor concern for human rights.

Since then, issues of sustainability in general have been of central concern to policy makers in the developed world, and green chemistry has become important to the chemical industry. Sustainability covers problems such as the depletion of nonrenewable natural resources and the control of pollution. Green chemistry is the use of chemical techniques to reduce or eliminate feedstocks, products, byproducts, solvents, and reagents that are hazardous to human health and the environment. We shall mention only a few of the issues of sustainability here, especially those affecting the chemical industry (Sections 17.1–17.2.5) and we shall then give examples of the evolution of green chemistry and the impact it is having on the chemical industry (Sections 17.3–17.3.11). This agenda is limited, and we are not attempting to tackle the broader environmental problems.

Apart from the energy issue (see below), depletion of resources is no longer seen as an immediate problem. The gloomier forecasters of the 1970s saw the world running out of numerous nonrenewable natural resources within 30 years. None of these forecasts have been vindicated. Mercury reserves were supposed to be depleted within ten years, but consumption fell dramatically, as it was seen to be a dangerous pollutant anyway. Mercury cells for making chlorine and sodium hydroxide were replaced by membrane cells, mercury arc rectifiers were replaced by more effective solid-state devices, and even mercury in thermometers was replaced by alcohol or by thermoelectric materials. One of the few remaining uses for mercury is for the illegal extraction of gold from the Amazon basin, where it is discharged into the world's largest fresh water source, but the quantity of water in the Amazon is so huge that the mercury has not yet attained toxic levels and the process, while illegal, is not easy to police.

Tin was another metal said to be facing rapid depletion. Instead, new can-making technology displaced its major use in food cans, and demand dropped to the point at which tin mines in southwest England, operated since the days of the Romans, have had to be decomissioned.

Reserves/production ratios of other nonrenewables have, if anything, increased over the past 30 years. Hydrometallurgical techniques, for example, have made accessible large deposits of copper in spoil heaps around the world, left over by less efficient methods of extraction. Exploration has discovered fresh reserves. The industrialists' claim that "If you have thirty years reserves under your belt, you don't bother to look for more" seems to have at least an element of truth about it.

17.1 ENERGY SOURCES

The area of ongoing concern, however, is that of energy. The world as a whole, and the chemical industry in particular, relies on supplies of fossil fuels to support its lifestyle. In 2000, the world consumed 8752.4 million tonnes oil equivalent (MTOE). The United States was the most profligate consumer. With 4.6% of the world population, it consumed 2278.6 MTOE—26% of the total. The European Union, with 5.8% of the population, consumed 15.4% of the energy, and Japan with 2.1% consumed 5.8%. Thus, Americans annually consume 8.0 tonnes oil equivalent per capita, West Europeans 3.8 tonnes, and Japanese 4.0 tonnes against a world average of 1.4 tonnes.

The pattern of primary energy sources varies from region to region. In Southeast Asia, coal accounts for about 40%, whereas in the United States it is about 23% and, in Europe, where the coal is more deeply buried and difficult to mine, about 19%. China and India get most of their energy from coal. Hydroelectricity provides 6.3% of world energy and 2.5% of United States energy and is generally small except in countries well endowed with mountains and water. In Scandinavia, it accounts for 40% of the total primary energy consumption, and in Central and South America, Canada, Switzerland, and Austria it accounts for close to 27% in each region. Nuclear energy has 13.8% of the energy supply in Europe as a whole and 8.5% in the United States, but little elsewhere. Overwhelmingly, in developed countries, the main sources of energy are oil and natural gas.

Where are these huge quantities of energy to come from in the future? Two-thirds of long-term oil reserves are in the Middle East, another 5% in Libya and Nigeria, and 6.4% in the former Soviet Union. North America including Mexico still has 6.1% of reserves and Venezuela 7.3%, but that is a long way from pan American self-sufficiency. The whole of Europe has a miserly 1.9%, which reflects itself in many ways including foreign policy. Gas reserves are slightly less biased to the Middle East, which has only 35%. The former Soviet Union has 37.8% and North America 4.9%.

How fast will these reserves be depleted? Coal will last for hundreds of years—250 years in the United States—but is dangerous to mine and polluting to burn. The US Government in 2002 was still regarding it as a worthwhile energy reserve. Nuclear energy is boundless but carries its own unique dangers. Hydroelectricity is renewable but not available on the scale that the world requires. And oil and natural gas? Here is the difficulty. In spite of their lavish exploitation, reserves are larger than they were 30 years ago, when Meadows *et al.* predicted their rapid depletion. The reserves/production ratio dropped from about 35 to 28 years in the 1970s, hence the prophecies of doom, but rose to a peak of 43 years in 1992, partly because of a reassessment of Saudi reserves, and has since dropped back to 40 years. Natural gas coasted along at 50 years in the 1970s, rose to 58 years for most of the 1980s as a result of discoveries in the Soviet Union, peaked at 67 years in 1992, and has since dropped back to 61 years.

Everyone is agreed that fossil fuel reserves are finite, but there is no way of knowing how finite. It is getting more difficult every year to locate additional reserves, but the world is getting better at it. The reserves would last dramatically longer if energy conservation was a priority, and non-Americans are baffled as to why US citizens need to use twice as much fuel as anyone else, even people in other developed countries. Conservation would also decrease carbon dioxide pollution and impact on global warming, but the question of how finite is finite would still exist. Unconventional methods of generating energy have made slow progress.

Before discussion of alternative methods, however, mention should be made of enhanced oil recovery. A time may come in the life of an oilfield when the natural pressure of the reservoir has dropped to the point at which it is no longer sufficiently large to force the oil out of the pores of the rock into the bottom of the well. At this point, as much as 80% of the oil may remain in the ground. It can be displaced by enhanced oil recovery—the injection of fluids—to force out the remaining oil. Water is widely used, sometimes mixed with a water-soluble polymer to increase its viscosity or reduce its mobility. Steam may be used to reduce the viscosity of heavy crudes. Hydrocarbon gases may be injected or even carbon dioxide, this last also being a way of reducing carbon dioxide in the atmosphere. It is unclear how much oil remains in oil wells. Enhanced recovery in 2000 was approximately 3% of total oil production. In the mid-1970s, BP was talking about having raised typical extraction rates to 40%. One estimate from the early 1990s was that global petroleum reserves were about four times proven reserves but not all this petroleum can be recovered economically. Indeed, the very fact of its remaining in place indicates the expense of bringing it to the surface.

17.1.1 Wind Power

Wind power is a renewable source of energy on which substantial research has been done. Global total wind capacity by 2001 was 23,000 MW, about 0.2% of world energy consumption, and about one-thirtieth of hydroelectricity's 6.3%. Germany, Denmark, Spain, and the United States are the largest wind power nations. In the United Kingdom, a windier region than mainland Europe, there are 70 wind farms with more than 800 turbines, and wind power contributes 0.38% of total energy. Wind energy, unfortunately, is intermittent and unpredictable. The best locations for wind farms are in remote areas, which leads to losses when the electricity is transferred to users. Typical turbines are 50–60 m tall with three 30 m blades, but future ones may be double that size. They make a visual impact on remote areas and are therefore a target for some groups of environmentalists, and planning permission in developed countries is frequently withheld. The future of wind power may rest with offshore turbines, which are feasible but cost about a third more. The British Government gave permission in 2002 for 18 small-scale trial wind farms around the coast, intended to produce 1400 MW by 2010. It is nonetheless hard to see wind power ever contributing more than 1–2% of energy demand.

17.1.2 Wave Power

Wave power is still at the development stage. Only one fully operational wave-energy power plant exists, based on the Isle of Islay in northwest Scotland. The design is based on an oscillating wave column and a so-called Wells turbine. The oscillating wave column consists of a container, broad at the bottom with a hole in it. The bottom of the container sits 2.5 m below sea level, and it has a narrow top above water level leading to the turbine. As the wave passes, water streams through the hole and compresses or rarefies the air above it. The Wells turbine has the unique property that it turns in the same direction regardless of which way air flows over the turbine blades, hence it is driven systematically by the rise and fall of the water level.

There are other ideas, including installing turbines in tidal races such as the bottleneck between an island and the mainland, but the setting up of a wave power plant is expensive and wave power is a long way from widespread application.

17.1.3 Solar Power

In a sunny climate, solar energy provides about 800 watts per square meter, which is the intensity of radiation received if one sits 10 cm from a 100 watt electric light bulb. Solar energy equivalent to the total world fossil fuel energy reserves falls on the earth in less than 14 days and the annual world's energy requirement within 26 minutes. The problem is to concentrate the energy.

Roof-mounted water heaters, deriving energy from the sun, are standard in Israel and widely used elsewhere. They account for 3.5% of energy requirements in Israel and 2% in Jordan. Simple pumping and reflector systems provide hot water in sunny climates pretty much all the year round, although an electrical heater is usually added to provide backup. Solar furnaces, in which mirrors concentrate sunlight onto a furnace, have been built in Sicily (Eulios) and California (SEGS 1 + 11). They have an efficiency of 10% but a high capital cost. Solar ponds, pioneered in Israel, produce a temperature difference of 60–70°C, which can be used to drive generators, but are hampered by high capital cost and low thermodynamic efficiency.

17.1.3.1 Photovoltaic Cells Generation of cheap electricity from solar energy via photovoltaic cells is not an option in the medium term, but there are several demonstration plants. A typical photovoltaic cell consists of layers of crystalline silicon alternately doped with boron and phosphorus to make them *n*- and *p*-type semiconductors. When light falls on the cell, the atoms in the *p*-type layer become excited and emit an electron, which passes to the *n*-layer. Excess electrons in the *n*-layer pass to the *p*-layer and the holes in the *p*-layer transfer to the *n*-layer. This creates surpluses of electrons and holes at the semiconductor junctions. A metallic grid on top of the photovoltaic cell collects the electrons and transfers them to the electron deficient junction via an electrical circuit. An array of photovoltaic cells is covered with glass to protect it from the weather and the glass has an antireflective coating to prevent light from being reflected away from the cells.

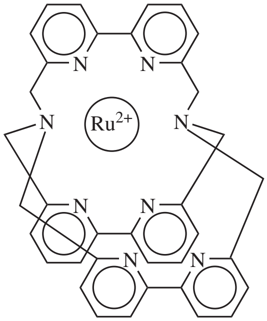
Photovoltaic cells produce electricity at efficiencies between 10 and 20%, but widespread use is inhibited by the high cost of the very pure silicon, gallium arsenide, or gallium antimonide required. Photovoltaic cells are unlikely to enter general use, but in remote areas they are an option. In September 2001, 870 solar generators were installed in 150 isolated Philippine villages to power homes, schools and health clinics, and to purify and distribute water. A plant at Kibbutz Samar north of

Elath, Israel, is expected to provide energy at 20 ¢/kWh compared with coal-fired power stations at 8 ¢/kWh. United States installations are projected to have ridiculously low costs but it is uncertain how these were compiled. The capacity being installed at Samar is 400 kilowatts peak and is part of a Friends of the Earth collaborative project to build similar facilities for Jordanian and Egyptian villages. Its fate is still uncertain because of political problems.

Another type of solar cell is being manufactured on a pilot scale in Australia. It consists of a molecule-thick layer of an organometallic dye on a porous matrix of titanium dioxide. Sunlight strikes the dye that coats the inner-surface of the matrix and excites electrons. These pass rapidly through the matrix, the spaces of which are filled by an electrolyte that supplies electrons to replace the ones lost by the dye. The electrons lost by the electrolyte are supplied by a second electrode, and a load between the two electrodes completes the circuit. At present, the cells are only 5% efficient, much worse than photovoltaic cells. On the other hand, they are cheaper to make and involve fewer toxic materials in their production.

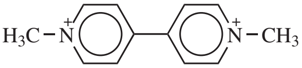
17.1.3.2 Artificial Photosynthesis Nature uses solar energy to convert carbon dioxide and water to carbohydrates by means of the catalyst chlorophyll. Sugar cane is said to be the most efficient photosynthesizer but only achieves an efficiency of about 1%. A research aim is the development of a photosynthetic catalyst with a higher efficiency than chlorophyll. The feedstock would have to be carbon dioxide or water or both. Water requires only 238 kJ mol^{-1} to split it into hydrogen and oxygen; carbon dioxide requires 283 kJ mol^{-1} to give carbon monoxide and oxygen. Carbon dioxide and water will give methanol at a cost of 703 kJ mol^{-1}. These energies correspond to wavelengths of light of 502, 422, and 170 nm, respectively. The first falls acceptably in the green region of the spectrum, the second is in the blue, but a high proportion of visible light will be useless, and the third is in the vacuum ultraviolet and could not be brought about by solar energy in a single step. Much research has focused on mimicking chlorphyll and trying to produce multistep reaction carbon dioxide absorbing systems, many of which are based on porphyrins, but no breakthroughs are in sight. The use of dendrimers (Section 15.4.4) to absorb and convert several quanta is an attractive but remote possibility. Thus the work that seems to offer the best prospects—and even these are long in the future—has concentrated on splitting of water.

No reproducible cyclic system for artificial photosynthesis by a single quantum of light has yet been found, but the system shown in Figure 17.1*a* will work in principle. Ruthenium-trisbipyridine, Ru(bpy)_3(**I**) (called the sensitizer) absorbs visible light and is promoted to an excited state. The excited state transfers its energy to methylviologen (called the quencher) and is oxidized to the trivalent state. This interacts with water and ruthenium(IV) oxide to generate oxygen and regenerate the bivalent compound. Meanwhile, the methylviologen (MV)(**II**), better known as the herbicide paraquat, is reduced to the monovalent state. In contact with a platinum–titanium dioxide catalyst, it splits water to hydrogen and a hydroxyl ion and reverts to the bivalent state. The titanium dioxide serves as a support for the platinum, thus stabilizing it in a suspension. The MV^{2+}/Pt electron transfer can then occur on the surface.



Ruthenium trisbipyridine

I



Methylviologen
(Paraquat)

II

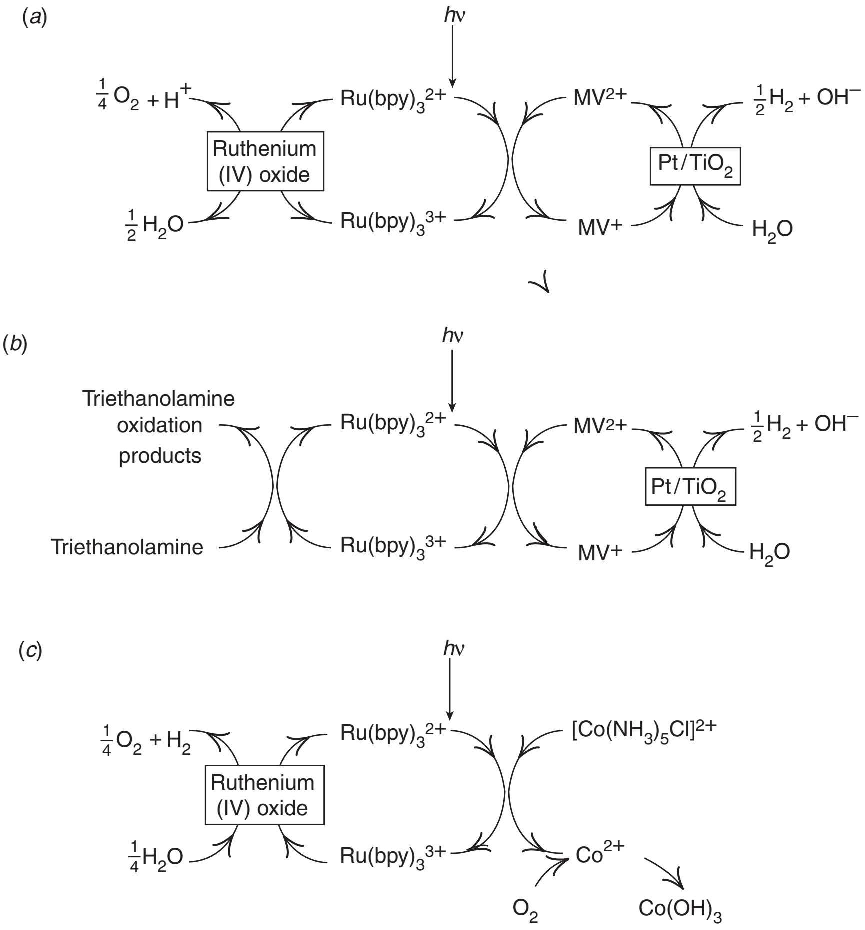


FIGURE 17.1 Photoinduced production of hydrogen and oxygen from water.

This system is not reproducible in a very clear way. In particular, the oxygen-carrying step requires high purity and selectivity for the requisite catalytic step. Research has focused on improvements in the separate halves of this system, with sacrificial compounds to transfer energy to or from the ruthenium-trisbipyridine. Figure 17.1*b* shows a system for the generation of hydrogen, with triethanolamine being sacrificially oxidized. Figure 17.1*c* shows the generation of oxygen with a cobalt complex in place of the methylviologen quencher accepting energy from the ruthenium trisbipyridine. This half-cycle is the more difficult and requires rigorous exclusion of atmospheric oxygen.

Systems of this kind are capable of wide variation with changes in sensitizer, quencher, and catalysts. There is great interest in light-harvesting polymers in which the sensitizer and quencher exist in a single molecule and their interaction occurs by energy transfer along a series of covalent bonds (see note at the end of this chapter).

A second approach is to use a so-called Z-scheme system. In a conventional photocatalytic water splitting, only one quantum of light is absorbed per molecule of water decomposed. The Z-scheme truly mimics natural photosynthesis in that there is two-step photoexcitation with a redox mediator between the stages. The Photoreaction Control Research Center of the National Institute of Australian Advanced Industrial Science and Technology (AIST) has recently reported such a system that splits water into hydrogen and oxygen by visible light. It uses two types of oxide semiconductor powder—chromium-doped, platinum-carried strontium titanate ($SrTiO_3$) (the PSII system), and platinum-carried tungstic oxide (WO_3) (the PSI system). The powders were irradiated in a solution of sodium iodide. The PSII system produced oxygen from water while simultaneously reducing iodate to iodide and the PSI system produced hydrogen while oxidizing iodide to iodate. This is the first time that simultaneous hydrogen and oxygen production has been demonstrated. The drawback is that the quantum efficiency at 420.7 nm was only about 0.1%.

The difficulties with these artificial photosynthetic systems are that the absorbed energy can be degraded in a number of ways, only one of which leads to the desired products. Efficiencies of 2.8% have been achieved, and it is thought that 10% is an achievable target with the present technology. The advantage of these systems is that they are largely homogeneous. Capital costs would be relatively low. The product hydrogen is a useful, nonpolluting source of energy and can be transported over distances more cheaply and efficiently than electricity.

Artificial photosynthesis is still a long way from commercialization but is attractive in the sense that it avoids extremes of temperature and rather resembles the mild conditions that characterize natural processes. On the other hand, the efficiencies of current photosynthetic processes are simply not good enough.

17.1.4 Methane Hydrate

Because of water's hydrogen bonding, ice has an open structure and there is space within it for methane molecules to be trapped. The combination, which is not chemically bonded, is a clathrate and is known as methane hydrate. Figure 17.2 shows the structure. Although it looks like ice, it is a poor conductor of heat and feels like expanded polystyrene. When ignited, it burns, leaving a water residue.

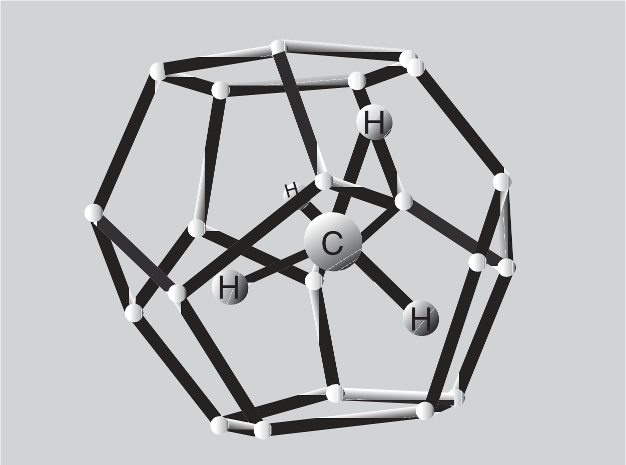


FIGURE 17.2 Methane hydrate structure showing carbon (center) and hydrogen (attached to the center) trapped in an ice lattice. (*Source*: USGS)

Until the 1970s, methane hydrate was merely a nuisance that plugged natural gas transmission lines when the weather was cold. In the 1960s, it was realized that it occurred naturally and, since then, it has been found to be ubiquitous. The United States Geological survey now estimates that methane hydrate may contain more organic carbon—perhaps twice as much—than all the world's reserves of coal, oil, and non-hydrate natural gas combined. The reservoir is in constant flux, absorbing and releasing methane in response to ongoing natural changes in the environment. The US Methane Hydrate Research and Development Act of 2000 launched a program to investigate this unsuspected source of methane locked up in polar permafrost and the deep oceans (because the hydrate is stable above 0°C at high pressures).

The downside is first that there is no obvious way to mine the methane inexpensively, and second that methane is a greenhouse gas, ten times as potent as carbon dioxide. Global warming of the permafrost as a result of current carbon dioxide emissions could melt some of the permafrost and release quantities of methane from the hydrate that could precipitate runaway global warming. The implications of this vast, dynamic and previously unnoticed methane reservoir on long-term climate stability, sea floor stability, and long-term fuel reserves are only just being recognized.

17.1.5 The Hydrogen Economy

The media are full of predictions that the energy source in the future world will be hydrogen. Hydrogen, it is said, is nonpolluting and it combusts to give nonpolluting water. The source material (water again) is ubiquitous. There are several obvious objections to the proposal, some of which may be overcome and some of which are fundamental.

Hydrogen is not an energy source, it is an energy carrier. The basic problem is how to obtain it. Although about 40 million tonnes of hydrogen is produced annually by the oil and chemical industries, most of it is captive production used in ammonia and methanol production and refinery processes. To obtain it from water requires as much energy as can be recovered when it is burned to water, so electrolytic hydrogen is only worthwhile if cheap electricity is available. This concept is not wholly absurd. Technology Convergence, a Canadian company, has launched a "green" methanol process in which only 60–100 kg of carbon dioxide per tonne methanol is produced compared with 300–700 kg in conventional plants. The process employs water electrolysis and partial oxidation. It offers the hope of methanol and hydrogen production in small portable plants but depends on cheap hydroelectricity.

Apart from electrolysis, the cheapest route to hydrogen (but from a nonrenewable source) is by steam reforming or partial oxidation of methane (Sections 10.4.1, 10.4.5). Each molecule of methane gives eventually four molecules of hydrogen and one molecule of carbon dioxide with $\Delta H^\circ_{298} = -65\,\text{kJ mol}^{-1}$. The four hydrogens combust to give $967\,\text{kJ mol}^{-1}$. Methane combustion direct gives $\Delta H^\circ_{298} = -802\,\text{kJ mol}^{-1}$, so that 17% of the combustion energy is lost in the conversion, and the amount of carbon dioxide produced is the same. On the other hand, it is produced in a concentrated form and could conceivably be "buried" in the deep ocean or elsewhere. Other possible hydrogen sources are methanol, ethanol, Fischer–Tropsch hydrocarbons and low-sulfur gasoline. Methane is attractive for static use but requires a high reforming temperature. Methanol is the most attractive for automotive use. It is easier to contain than methane and can more easily be reformed. Meanwhile, the reforming process generates carbon dioxide, and the hydrogen economy combats global warming only insofar as fuel cells are more efficient than traditional power stations or internal combustion engines, thus producing less CO_2.

17.1.5.1 Fuel Cells The drawback of generating electricity by burning fuel and using the heat to raise steam and power a turbine is that the efficiency is limited by the second law of thermodynamics. The best thermal efficiency that can be achieved is about 33%. The use of combined heat and power systems (CHP) can nudge this into the upper 30s. Power station generated electricity is thus inevitably expensive.

A fuel cell is a device that generates electricity directly from chemical energy. Fuel cell research has been in progress for several decades and shows signs of coming to fruition. A typical fuel cell generates about 1.1 volts at zero load dropping to about 0.8 volts on moderate loads, and then dropping rapidly at current offtakes greater than $1.1\,\text{amp cm}^{-2}$. Because the voltage output is low, fuel cells have to be produced in stacks, and each unit requires separate supplies of fuel.

The attraction of the fuel cell lies in its circumventing the second law of thermodynamics. The Carnot efficiency of a heat engine operating between an upper temperature T_1 and a sink temperature T_2 is $(T_1-T_2)/T_1$. The maximum fuel cell efficiency based on the combination of hydrogen and oxygen is the ratio of the Gibbs free energy change (ΔG°) to the enthalpy (ΔH°) change accompanying the reaction. These are shown in Figure 17.3 for $T_2 = 298\,\text{K}$. At high temperatures, the efficiency of a heat engine is higher than that of a fuel cell but, because of the need for rotary or reciprocating motion

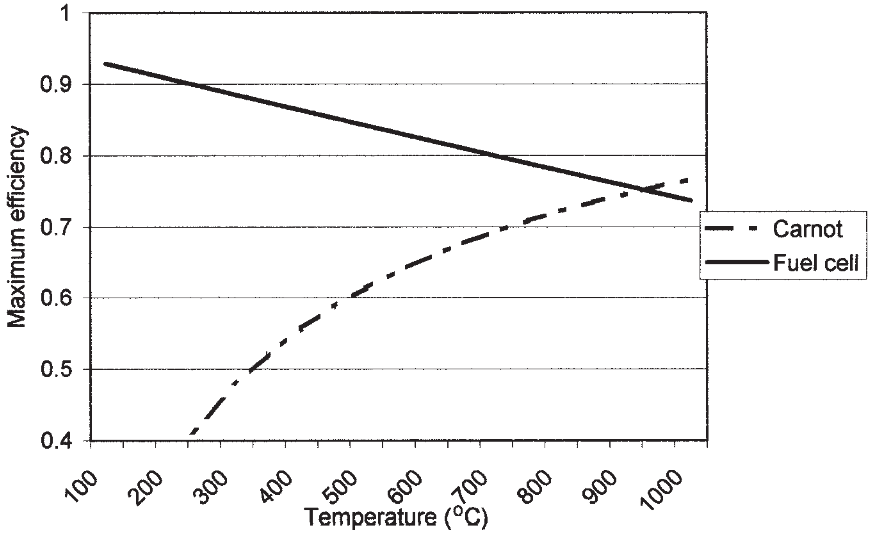


FIGURE 17.3 Carnot and fuel cell maximum efficiencies.

in a heat engine, there are associated operating costs that do not apply to fuel cells. Meanwhile, a high-temperature fuel cell operating in a CHP system can achieve fuel cell efficiencies of nearly 70% and total energy efficiencies of 90%.

Some of the types of fuel cell are listed in Table 17.1 together with the abbreviations used to represent them, their operating temperatures, electrolyte, electrocatalyst, fuel, and probable mode of application. They fall into two groups characterized by low- and high-operating temperatures. The low-temperature cells require pure or almost pure hydrogen and are regarded as suitable for transport applications, while the high-temperature systems are more suitable for stationary generation especially in CHP systems. The low-temperature AFC system was used in the Gemini, Apollo, and space shuttle programs. PEMFCs are regarded as the most suitable for transport applications, having a high-power density and therefore occupying relatively little space. They are also attractive as battery replacements in, for example, laptop computers, where they would operate longer than traditional batteries, cost less, and be refueled in minutes rather than hours. The structure of the PEMFC is an example of the assembly of fuel cells. It consists of platinum-based catalysts supported on carbon current collectors separated by a membrane that will conduct protons. Hydrogen flows over one electrode, air over the other. The reactions are almost the simplest possible:

$$\text{Anode} \quad H_2 \longrightarrow 2H^+ + 2e^-$$

$$\text{Cathode} \quad 2H^+ + \tfrac{1}{2}O_2 + 2e^- \longrightarrow H_2O$$

An electrolyte is required to transport the protons from the negative to the positive interface. It must have minimum resistance to proton conductivity, be an effective

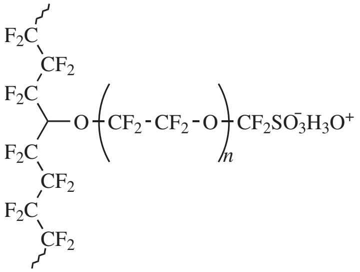
TABLE 17.1 Types of Fuel Cell

Type	Abbreviation	Operating temperature (°C)	Electrolyte and electrocatalyst (incorporated in anode and cathode)	Electrocatalysts (incorporated in anode and cathode to promote electrode reactions)	Fuel	Uses and comments
Alkali	AFC	60–250	At 250°C: 85% w/w KOH Below 120°C: 35–40% w/w retained in porous matrix (asbestos)	Nickel and noble metals	Restricted to pure H_2 and O_2. Poisoned by the CO formed when hydrocarbon or alcohol feeds are reformed. CO_2 in air reacts with KOH	Space vehicles. Possible transport applications
Polymer electrolyte–proton exchange membrane	PEMFC	80–120	Proton conducting polymer, e.g., Nafion	Pt or Pt/Ru (more tolerant to traces of CO)	H_2 or hydrogen-rich reformate from methanol or gasoline	Transport; battery "replacement"
Phosphoric acid	PAFC	150–220	100% phosphoric acid in silicon carbide matrix	Pt	Steam-reformed natural gas	Medium CHP. Preferred design at present for stationary power generation
Molten carbonate	MCFC	600–700	Alkali carbonates in a ceramic $LiAlO_2$ matrix	Ni and NiO	H_2-rich gases such as methane. Fuel contaminants less important	Stationary power generation; Large CHP
Solid oxide	SOFC	600–1000	A dense ceramic usually yttria stabilized zirconia (YSZ)	Cathode: a perovskite material such as Sr-doped lanthanum manganite, often mixed with YSZ. Anode: cermet of nickel and YSZ	H_2-rich gases such as methane. Fuel contaminants less important	Stationary power generation; all sizes of CHP. Auxiliary power units for vehicles

Source: www.benwiens.com/energy3.html, *The Scientist*, 28, November 11, 2002, N. Brandon, *Encyclopedia of Energy*, in press and N. Brandon and David Hart, *An Introduction to fuel cell technology and economics*, Imperial College, London, Occasional paper 1.

barrier to electronic short circuit, have low permeability to hydrogen and oxygen and be chemically stable to hydrogen and air even in the presence of the catalyst. In addition, the membrane needs to be compact, because fuel cells produce an output of less than a volt.

The preferred material for PEMFCs at present is a Nafion polymer, similar to the type used in membrane cells for chloralkali production:



This is an ion exchange resin. If kept moist, protons can pass from one sulfonic acid site to another through nanometer-scale ionic channels.

PAFCs were the most successful fuel cells between 1997 and 2002, when 220 commercial power plants were delivered. Typical applications lie in hospitals, army facilities, and leisure centers, where there is a suitable heat and power requirement. In the longer term, PEMFC plants are liable to prove cheaper, and SOFC or MCFC plants may provide more useful heat output and run on hydrocarbon fuels.

The MCFCs and SOFCs can operate on a range of fuels, hydrocarbons being reformed *in situ* on the electrodes, although some designers prefer a separate catalyst bed. They are effective in CHP installations and can operate efficiently on a smaller scale than traditional power stations.

The storage and extreme flammability of hydrogen present problems, especially for the low temperature cells. As hydrogen boils at only 20 K, liquefaction is an extreme option. Very high pressure reinforced plastic filament wound storage tanks have been proposed. Storage in the form of metal hydrides or in carbon nanotubes or other specialized molecular structures are topics of research, but they usually require pressure swings and/or heating to release the stored hydrogen. An alternative is to use a liquid fuel either instead of hydrogen or that can be reformed to hydrogen in an ancillary unit. Methanol is the preferred candidate. The snag is that methanol oxidation at the negative electrode passes through carbon monoxide, which poisons the activity of the platinum catalysts. A further problem is that fuel cells do not respond well to sudden increases in load and they need to be accompanied, in automobiles, by batteries or supercapacitors to provide surges of power during acceleration.

In spite of all these difficulties, automobile manufacturers have built Fuel Cell Electric Vehicle prototypes in which hydrogen is either carried as a compressed gas or adsorbed on a special alloy or produced *in situ* by the reforming of methane, methanol or gasoline. Daimler-Chrysler, Toyota, Honda and BMW all have prototypes. Buses are a particular target in that they can all refuel at the same point and thus do not need a hydrogen distribution infrastructure. Daimler-Chrysler uniquely has demonstrated a go-cart based on direct methanol conversion.

When hydrocarbons are reformed, it is claimed that they give far less hydrocarbon pollution than when they are burned directly in an internal combustion engine. Figures of 15–20% are quoted for the efficiency of internal combustion engines for converting gasoline to energy. A variety of figures is quoted for fuel cells ranging from 35% for small fuel cells rising to 45% for the largest, if one starts from methane. Oxides of sulfur are low because low sulfur fuels such as methanol or desulfurized natural gas are used. NO_x emissions are low because even the high-temperature fuel cells do not operate in the region where the N_2/O_2 reaction occurs. Other sources say that a fuel cell power plant will produce 20–30% less CO_2 than a conventional plant, that a reformed-gasoline powered vehicle will produce little or no reduction in greenhouse gas emissions, but that methanol will cut them by 25% and natural gas by 40%. Hydrogen from wind or solar power emits no greenhouse gases.

The US government launched a “major automotive fuel cell development program” in 2002, and the associated announcements quoted 40–65% efficiency, with a figure of 90% for CHP, but those figures start from hydrogen not methane. The widespread use Fuel Cell Electric Vehicles, however, is not envisaged for another 10–15 years. Regrettably, all fuel cells are still substantially more expensive than fossil fuel options. Large scale production could reduce this, but there is still a crucial problem, glossed over by the media, of economic hydrogen supply.

17.2 POLLUTION

Sustainability also involves issues of pollution. Are the byproducts of modern living accumulating at a rate that presents a danger to future generations? Pollutants fall broadly into two categories—those affecting the global ecosystem, such as the ozone layer and the global climate, and those affecting individuals, such as carcinogenic chemicals in the environment. The latter may be subdivided into air pollution, water pollution, and pollution by solids.

Many of the pollution problems are basic to living—people burn fuel to keep warm and hence produce particulates and sulfur dioxide; they excrete waste materials. As populations increase, the self-renewing aspects of natural ecosystems fail, and pollution may threaten health and comfort or even destabilize the environment as, for example, by deforestation. There are also numerous localized pollution problems connected with the chemical and allied industries. Even to know which chemicals are being produced presents a problem. Of the order of 100,000 chemicals are manufactured (Section 1.3.7). Producers are expected to provide the government with premanufacturing notice before going ahead and should submit process flow data, but the task of assessing the chemicals and their byproducts in any detail is an insuperable task. Meanwhile, the Environmental Protection Agency monitors the release of toxic materials including persistent bioaccumulative toxic chemicals (PBTs). In 2000, 7.1 billion lb of chemicals were released to air, land, and water and 12.1 million lb of PBTs, as shown in Table 7.2. Most of these came from the primary

TABLE 17.2 Total Emissions of Chemicals and Persistent Bioaccumulative Toxic Chemicals (PBTs) (United States, 2000)

NAICS	Industry	All Chemicals (million lb)	PBTs (million lb)	All Chemicals (%)	PBTs (%)
10	Metal mining	3357	3.15	47.3	26.0
491/493	Electric utilities	1152	n.a.	16.2	n.a.
28	Chemicals	648	1.30	9.1	10.7
33	Primary metals	607	3.25	8.6	26.9
4953/7389	Hazardous waste/solvent recovery	285	2.48	4.0	20.5
	Total	7100	12.1		

n.a. = not available

metal and metal mining industries (NAICS 10 and 33). The chemical industry comes third in the table of all emissions and fourth in the table of PBTs, being responsible for about 10% of emissions in each case. The majority of PBTs emitted were polycyclic aromatics, with mercury and mercury compounds second (Fig. 17.4). This is surprising in view of the widespread replacement of mercury chloralkali cells by membrane cells. Figure 17.5 shows the scale of emissions and the way in which they are disposed of. About 48% of the manufacturing industry emissions were to the air, 13.4% to land, 11.1% to surface water, and 9.1% was disposed of by underground injection. The chemical industry releases have been declining steadily through the 1980s and 1990s, and they are rarely harmful. Meanwhile, they are of the same order of magnitude as production of phthalic anhydride or *o*-xylene, and there is no way they can be ignored.

17.2.1 The Ozone Layer

The surface of the earth is protected from ultraviolet radiation from the sun with a wavelength below about 360 nm by the ozone layer in the atmosphere about

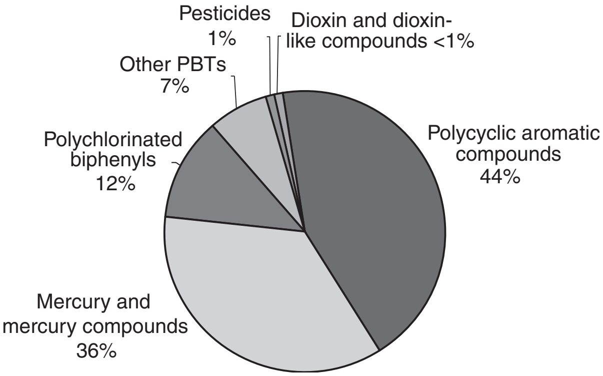


FIGURE 17.4 Releases of persistent bioaccumulative toxic chemicals by class of compound (USA, 2000). (*Source:* Environmental Protection Agency.)

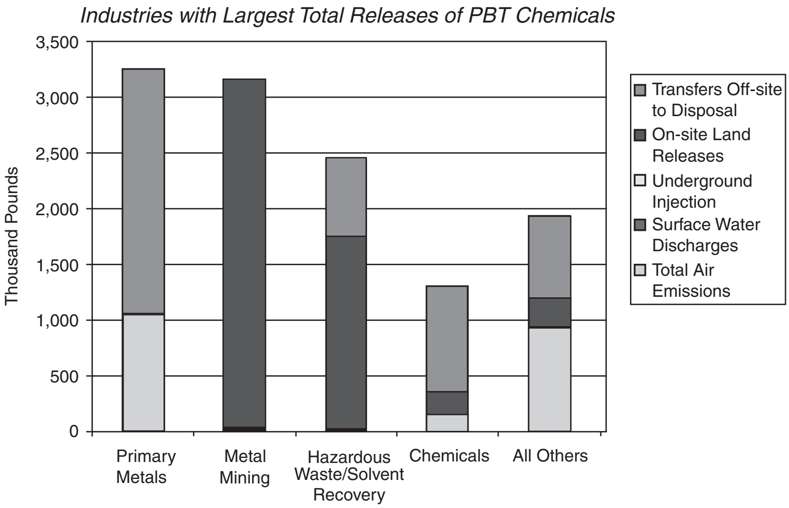


FIGURE 17.5 Releases of PBT chemicals by industry and disposal method (USA, 2000). *Source*: Environmental Protection Agency.

20–40 km above the ground. It is maintained by a photochemical equilibrium between ozone and oxygen (M is any third body that carries away some of the heat of reaction):

$$O_2 + h\nu \xrightarrow{<242.4\text{ nm}} O + O$$

$$O + O_2 + M \longrightarrow O_3 + M$$

$$O_3 + h\nu \xrightarrow{<350\text{ nm}} O_2 + O$$

$$O + O_3 \longrightarrow 2O_2$$

$$O + O + M \longrightarrow O_2 + M$$

A reduction in ozone levels allows more UV light to reach the earth, which leads to an increase in skin cancer, especially among sunbathers. It also leads to cataracts, DNA changes in marine species and degradation of plastics.

The ozone layer is being destroyed primarily by halogen atoms generated by photolysis of fluorocarbons used as aerosol propellants, refrigerator working liquids, blowing agents for foams, cleaning fluids, and solvents for the electronics industry. Fluorocarbons having no hydrogen atoms are termed CFCs and those with hydrogen atoms are termed HCFCs. The two predominant CFCs were CCl_3F, trichloromonofluoromethane, and CCl_2F_2, dichlorodifluoromethane (known as CFC-11 and CFC-12; see Table 10.1 and Section 10.2.3). They photolyze in UV light of less than 230 nm in the stratosphere to give chlorine atoms, which then participate in the cycle shown in Figure 17.6. It is estimated that one chlorine atom can degrade over 100,000 ozone molecules before it is removed from the atmosphere by the processes:

$$OH + ClO \longrightarrow HCl + O_2$$

$$HO_2 + Cl \longrightarrow HCl + O_2$$

Hydrogen chloride may then be removed from the stratosphere by water, in which it is soluble. It is said that methane and other hydrogen-containing species including HCFCs can also convert chlorine atoms to HCl.

The potency of halogenated compounds varies and depends on the relative stability of compounds such as $ClONO_2$, collectively called reservoirs, which hold chlorine in an inactive form but can be photolyzed by UV light. The reservoir compound hydrogen fluoride is so stable that fluorocarbons have no effect on ozone. On the other hand, the bromine compounds HBr and $BrONO_2$ are said to be 10–100 times more effective ozone depleters than the chlorine equivalents.

In the lower stratosphere and troposphere, oxides of nitrogen and hydroxyl radicals can also catalyze ozone degradation, but they are also able to tie up chlorine in relatively stable reservoir compounds, where they get rained out of the atmosphere.

The upshot of this was that the large-scale production of CFC-11 and CFC-12 was halted in the United States in October 1978. All CFCs and some HCFCs were designated class I ozone depleters and were rapidly phased out. The remaining HCFCs, designated class II ozone depleters, were less damaging. They were and are permitted for transitional periods. Hydrofluorocarbons (HFCs), containing no chlorine, appear to be industry's replacement for refrigerators. The HFCs pose no direct threat to the ozone layer and are energy-efficient refrigerants. Environmental groups argue, however, that HFCs are powerful global warming gases and damage the environment in other ways. Electronic component fabricators have replaced CFCs for cleaning with various oxygenates such as acetone and isopropanol, allied to flammability precautions. They also use microfiber polyester cloth.

The hole in the Antarctic ozone layer was smaller in 2002 than in 2000 or 2001 and levels of CFCs are slowly declining. The World Meteorological Organization and the United Nations Environment Program jointly announced that the Montreal

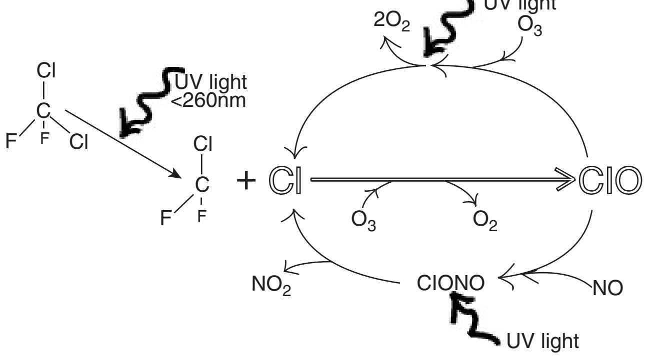


FIGURE 17.6 Destruction of ozone by halogen atoms.

Protocol of 1997 was working, but the weather patterns in the stratosphere in 2002 were unusual and too much significance should not be attached to the reduction in the size of the hole.

The above mechanisms are much simplified. There is still ignorance about many of the mechanisms governing the ozone layer and arguments concerning the policies to be followed (see note at end of this chapter). An example of the dilemmas that are encountered is provided by methyl bromide. About 70% of methyl bromide is used as a soil fumigant. In warm regions, where termite infestation is a problem, it is used to fumigate housing and is also used on fruit and flowers, and on durable commodities such as timber. World production was 61,436 tonnes in 1998 down from a peak of about 66,000 tonnes.

Methyl bromide has a lifetime in the atmosphere of 1.5–2 years, and it takes 2–5 years to reach the stratosphere, so that very little arrives there. But what does arrive is very damaging. Methyl bromide was listed as a class I ozone depleter in the 1990 US Clean Air Act. The Montreal Protocol meeting agreed that industrial nations would cut production and use by 25% starting from 1999 in relation to the quantity they produced in 1991, by 50% from the year 2001, by 70% from 2003, and total phase-out would follow by 2005.

This was all very well, but for developing nations a threat to food production was a serious matter. Banning fluorocarbon propellants in hair sprays was one thing; banning soil fumigants was another. The Montreal Treaty partners agreed to delay the compliance of developing countries with the Protocol. Methyl bromide production and use would be frozen in 2002 at average 1995–1998 consumption levels. In 2005, production and use would be reduced by 20% and by 2015 would cease, apart from various exemptions. The exemptions are complicated and appear to suggest permitted production and use at 10–15% of 1991 levels, but the accompanying statement mentions “critical or emergency situations where no reasonable substitute exists either from a technical or economic point of view” or where “the nonavailability of methyl bromide would cause significant harm in the relevant market . . . .” The precise meaning that will be attached to this clause depends on how easy it is to find effective and inexpensive substitutes, and it is not inconceivable that the whole initiative in developing countries could collapse with supplies of methyl bromide coming from countries not signatories to the Montreal Protocol. Replacements for methyl bromide are not easy to come by. 1,3-Dichloroprene, Dazomet, chloropicrin, and metham sodium have been proposed but each has its drawbacks. Methyl iodide is an attractive option in that it can be used with the same equipment as the bromide, and it photodegrades rapidly, hence is not ozone-depleting, but it is prohibitively expensive.

Worse, the contribution of the chemical industry to methyl bromide pollution is not clear. It has been suggested that some 42,000 tonnes/year of the methyl bromide used for soil fumigation is consumed by soil bacteria and presumably converted to harmless bromides. Furthermore, marine organisms (macroalgae) produce tens of thousands of tonnes/year of organobromines, and there are claims that 85% of atmospheric methyl bromide is of natural origin. Other workers provide figures as low as 70%, but combination of any of these figures with the Greenpeace figure of 3%

(itself an upper limit) for the contribution of methyl bromide to ozone depletion, still leaves less than 1% attributable to soil fumigation. Is this worth the disruption of agriculture?

Meanwhile, some countries have signed the Montreal Treaty unwillingly (China and India) and others have done so conditionally depending on financial recompense (Brazil). There is a Chinese venture into bromine production. This may be part of an industrialization program, but it could also be a preemptive measure should external bromine sources dry up. After all, the United States and Israel (the world's two major bromine producers) and 161 other countries have signed the Treaty. In 2003, the United States made a formal request to the ozone secretariat of the United Nations to allow methyl bromide after 2005 at a level of 39% of what it was in 1991.

17.2.2 Global Warming

A second problem arising in the ecosystem is the threat of global warming. As noted above, the earth is protected from UV radiation from the sun below 360 nm by the ozone layer. Longer wavelength radiation, including visible light, is transmitted through the atmosphere and degraded into heat, which is reradiated as infrared (IR) radiation. Some of this radiation is reabsorbed as heat by gases in the atmosphere, and this keeps the surface of the earth at a tolerable temperature, about 33°C higher than it would otherwise be. Arrhenius coined the term "greenhouse effect" for this phenomenon in 1896, believing mistakenly that the carbon dioxide in the atmosphere acted like the glass in a greenhouse, but the term has remained in use.

Oxygen, nitrogen, and argon are transparent to IR radiation and ozone absorbs only slightly and at a high altitude. The principal absorbers are water and carbon dioxide. Water has two broad bands in the IR around 3800 and 1600 cm^{-1} (2630 and 6250 nm). It is the most important absorber, and its absence is the reason why deserts with dry atmospheres are cold at night. Carbon dioxide has narrow absorption bands at 700 and 2400 cm^{-1} (14,300 and 4,170 nm) and is responsible for less warming. It has been estimated that water contributes about 33°C to the temperature at the surface of the earth while carbon dioxide contributed about 0.5°C, which might rise to another 1 or 2°C depending on its concentration. Other greenhouse gases include methane, sulfur hexafluoride, nitrous oxide, CFCs, and HCFCs. Nitrous oxide is formed naturally in thunderstorms, but there are also manmade contributions. Methane is a potential problem and has strong absorption bands around 3010 and 1300 cm^{-1} (3320 and 7700 nm). The effect of additional greenhouse gases depends on whether they absorb in the spectral gaps between water and carbon dioxide. This is far from the whole story, however. Water vapor forms clouds, which reflect radiation from the sun and keep the earth cooler during the day. They also reflect heat from the earth and keep it warmer at night. There are equilibria in which carbon dioxide is locked up in oceans, sediments, vegetation (as organic carbon), and carbonates. The situation is complex.

Atmospheric levels of carbon dioxide in the nineteenth century in the free air of the North Atlantic region before large-scale industrialization were about 280 ppm by volume. They have since risen to 370 ppm and are predicted, under various assumptions, to rise to 540–970 ppm by 2100. Methane levels have risen since 1750 by 151% and nitrous oxide levels by 17%. The reflection of these figures on world climate is not straightforward. World temperatures increased from about 1850 onward and reached a peak in the mid-1930s. They then declined until the mid-1970s, at which time respectable academics were publishing articles on global cooling. The reasons, apparently, were increased dust hazes over deserts and bluish-green hazes over forests, probably due to terpenes. These were reflecting incident radiation, and hence lowering temperatures. There are also soot, sulfate aerosols and soot-sulfate aerosols. Some of these have a warming, some a cooling effect, but the effect of soot in promoting warming is believed to be greater than that of methane. The rise in temperatures during the twentieth century has been 0.6 ± 0.2°C. The 1990s appear to have been the hottest decade, 1998 the hottest year and 2001 the second hottest year since instrumental records began. Data from tree rings, corals and ice cores suggest, at a lower level of confidence, that the twentieth century was the warmest century in the Northern hemisphere for the past 1000 years. In the Alps, between 230 and 650 m altitude, average snow depths have decreased by 50% from the long-term trend. The Eiger and Fee glaciers in Switzerland have retreated several miles from Kleine Scheidegg and Saas Fee, respectively. The ice fields on top of Mount Kilimanjaro have shrunk by 80%. The projected increase in temperatures between 1990 and 2100 indicate a sea level rise of between 0.3 and 0.5 m. The predicted average temperature rise between 1990 and 2100 is estimated between 1.4 and 5.8°C.

The correlation between climatic change and carbon dioxide concentrations is tenuous, but there now seems to be a better understanding of the complexity of the interactions and feedback loops, many unfortunately positive. The consequences of increase in temperatures could well be nonlinear and might lead to major climatic instabilities. On the other hand, a nuclear war—the great concern of the cold war years—would throw dust into the upper atmosphere and could lead to a nuclear winter. Maybe this will become a concern again with the proliferation of nuclear weapons. The earth's climatic changes are driven by macro events, and it is still uncertain what brought on the Ice Ages.

The effect of human intervention on climate depends on future economic and environmental activity and technical developments. The feeling in the 1980s was that the consequences of getting it wrong were so serious that greenhouse gas levels should at least be stabilized. In 1992 the United Nations agreed on a Framework Convention on Climatic change, which came into force in 1994. In 1997, the Kyoto Protocol committed industrial countries to achieve quantified targets for decreasing the emission of greenhouse gases. Germany, for example, has already banned lignite. The United States agreed to reduce overall emissions of greenhouse gases to 5% below 1990 levels by 2008–2012, but has since withdrawn from this commitment. There are various plans to tie up carbon dioxide in depleted oil reservoirs and unminable coal beds or to sequester it in the ocean or to use it in enhanced oil recovery.

There is a consensus that the recent hot decade was a result of long-term climatic change associated with greenhouse gases. The things that combating global warming require us to do, such as conserving energy, are mostly good things that we should be doing anyway, even if it later turns out to be for the wrong reason. Meanwhile, the future of the Kyoto Protocol is in doubt. Rich countries are reluctant to restrain their profligate lifestyles. Poor countries feel that it is hypocritical that rich countries, who have brought about the problems, should now be asking them to abandon their short-term development plans in favor of relatively diffuse long-term objectives. One-half of Africa's electricity, for example, is generated from South African coal, so that criticism of its contribution to pollution and global warming is muted. China is already exempt from the Kyoto provisions.

17.2.3 Trace Chemicals

A central worry of the environmentalists is the presence of trace chemicals in the environment that are known to be or, on the precautionary principle, might possibly be detrimental to health. Some of these have already been banned as a result of their concerns. Lead has been removed from gasoline and benzene levels have been minimized. Mercury pesticides have been banned in paint; DDT use has been heavily restricted. There is a continuing review in developed countries of the danger from manmade chemicals. A selection of topics is discussed below.

17.2.3.1 Pesticides Pesticides have been a prime target for environmentalists, mainly because such materials may appear in our food and may thereby lead to cancer. While the causes of cancer are difficult to identify specifically, Richard Doll, who first demonstrated the link between smoking and lung cancer, estimated in 1981 that 35% of cancers were diet induced. Meanwhile, we all have to go on eating, and society should be cautious that materials dangerous to health are excluded from diet. Pesticides are divided into four groups—chlorinated hydrocarbons, organophosphates, carbamates, and chlorophenoxy acids. Chlorinated hydrocarbons are the most persistent, with a lifetime in the environment of several years. They are absorbed by creatures a long way down the food chain and, by the time they reach our dinner plates, they have already become concentrated with respect to their level in the environment generally.

The mosquito eradication program on Long Island, New York, showed levels of DDT in sea water of 3 ppm, in the fat of plankton of 0.04 ppm, in the fat of minnows 0.5 ppm, in the fat of needlefish 2 ppm and in the fat of cormorants and osprey 25 ppm. People contained similar levels to birds of prey. While the adverse effects of DDT on birds have been amply documented, there are still doubts as to whether it actually thins eggshells. It is worrying to reflect on the persistence of DDT in human tissue, but reassuring to record that no demonstrable ill effects of organochlorine insecticides on humans have been detected in spite of levels of up to 600 ppm being found in workers in a DDT factory. Meanwhile, the use of chlorinated hydrocarbons was forbidden or discouraged to the extent that, by 1985, usage in developed countries had been restricted to about 5% of its peak value.

Organophosphorus pesticides biodegrade in a matter of months. Parathion is the most persistent of the widely used materials with a typical half-life of 120 days. It has probably been responsible for more deaths than any other pesticide. It has high mammalian toxicity and is absorbed through the skin, inhaled, or swallowed during spraying operations. Exposure to organophosphorus insecticides is dangerous, but the fact that they are less persistent means that, despite their constant monitoring as part of public health, they are only peripherally part of the sustainability debate. Their use is restricted both to protect agricultural workers and to prevent even small pesticide residues persisting on food products. The same applies to other pesticides.

17.2.3.2 Nonpesticide Lipophiles Many pollutants owe their toxic effects to their accumulation in the body. They are lipophilic and biochemically rather inert. The body is capable of dealing with some lipophiles. Benzene and toluene are both lipophilic, but benzene has no functional group that can be attacked by an enzyme. Toluene, on the other hand, is enzymatically oxidized to benzoic acid, which subsequently couples with either glucuronic acid or glycine to give hippuric or benzoylglucuronic acid, both of which are readily excreted. Thus benzene is listed as a carcinogen while toluene is nontoxic.

The classic group of lipophiles, banned as long ago as 1976 (the Toxic Substances Control Act), were the polychlorinated biphenyls. They were used in industry mainly as electrical insulators in transformers and capacitors. A domestic application was in the capacitors in fluorescent light ballasts. Polychlorinated biphenyls take several decades to degrade and are still produced inadvertently in small quantities in plants where organochlorines are made (Fig. 17.4). Like the chlorinated hydrocarbon pesticides, they accumulate in fatty tissue and are damaging to the animals high up the food chain, that is to humans.

The majority of organochlorine lipophiles have been phased out. Various organobromine compounds are still in widespread use. A range of polybrominated compounds—polybrominated diphenyl ethers (PBDEs) polybrominated biphenyls (PBBs) and tetrabromobisphenol A—are used to prevent or deter fires in electronic devices (mainly television sets), furniture, and textiles. PBDEs have been found in the body fat of many wildlife species, including sperm whales in the Atlantic Ocean and in mothers' milk in Sweden. The European parliament voted in 2001 to ban the pentabromo-, octabromo-, and decabromodiphenyl ethers in spite of the European Commission's advice that there was evidence only against the pentabromo compound. The legislation was passed in 2003.

Even the evidence raises a series of questions. Toxicological studies indicated that large doses of the flame retardants given to neonatal mice hindered their intellectual development, but there have been few reports of ill effects on humans, even those working in television dismantling plant, who had 70 times the usual levels of brominated compounds in their fat. There are questions as to the transport of the compounds. They are involatile and insoluble. Whales do not watch television, nor are discarded sets dumped at sea. There are suggestions that the brominated compounds may originate naturally from marine organisms, but that is unsubstantiated too.

A third set of lipophiles is the plasticizers for PVC, of which dioctyl phthalate is easily the most widely used. In addition to softening plastics, it is used in cosmetics and as a replacement for polychlorinated biphenyls as a dielectric fluid in capacitors. Like the brominated fire retardants, it is insoluble and involatile but, like other lipophiles, it accumulates in fatty tissue. About 500,000 lb year^{-1} enter the environment in hosepipes, rubbers, and plastics. It adheres to soil but is rapidly degraded in water. In the short term, high exposure causes mild gastrointestinal disturbances, nausea, and vertigo. In the longer term, it is said to damage the liver, testes, and respiratory function and "may reasonably be anticipated to be a carcinogen." The campaign to ban dioctyl phthalate has been in progress since the 1950s, showing persistence of a different kind from that of chemicals. In 1974, the Safe Drinking Water Act limited permitted concentrations in drinking water to 6 ppb and it was subsequently withdrawn from use in babies' pacifiers. It has now largely been phased out from children's toys. In 2002, the European Commission proposed a ban on phthalates in cosmetics on the grounds that they might cause genital abnormalities.

17.2.4 Air Pollution

Air pollution has been tackled more vigorously by legislators than almost any other form of pollution. Laws to limit smoke from coal burning were passed in England in 1273. Queen Elizabeth I stayed away from London in 1578 because of the "noysomme smells of coal smoke" and in 1661, John Dryden, the diarist, addressed a pamphlet to King Charles II describing the evil from smoke as 'epidemicall' and a danger to health. Meanwhile, the chemical nature of air pollution in the developed world changed entirely in the middle of the twentieth century, although it has remained unchanged in much of the third world.

17.2.4.1 Sulfur Dioxide and Particulates Air pollution is mainly the result of combustion processes. Cigarette smoke, where a person directly inhales the combustion products, is the most dangerous air pollutant known. Other traditional combustion processes produce particulates (smoke), sulfur dioxide, and minute amounts of polycyclic hydrocarbons. Some of these polycyclics are known to be carcinogenic, but we know of no solid evidence linking their presence in the air to cancer. Under humid conditions, the sulfur dioxide may react further to give sulfuric and sulfurous acids and sulfates. They also interact with the particulates to give the sulfate aerosols that made up the traditional London fogs. These irritate the lung and exacerbate existing respiratory conditions. About 4000 people died as a direct result of the great fog of London in 1952, which precipitated the Clean Air Act of 1956. Sulfur dioxide (plus nitrogen oxides) also leads to acid rain, which attacks vegetation and destroys fish life in lakes.

Legislation in many developed countries limited the use of solid fuels and the emission of smoke, and this has reduced air pollution of that kind. Countries with cheap and/or indigenous coal reserves retrofitted flue gas desulfurization units to their coal-fired power stations. Typically, these involved scrubbing the combustion products with a slurry of limestone, lime, or dolomite. The end product is a high-quality calcium sulfate. The process is much more complicated than it sounds because of the need to keep the exit gases flowing up a chimney and to get the sulfate, which can be used in plasterboard, rather than the sulfite. In Japan, there was a problem because the supplies of high-quality sulfate threatened to put out of business the traditional calcium sulfate producers, who obtained it as a byproduct of the manufacture of phosphate fertilizer from phosphate rock and sulfuric acid. The

Japanese government's ingenious response was to double the thickness of plasterboard required in new buildings.

Flue gas desulfurization was emphasized in the United States in the 1990s, but the administration in the early 2000s seems less concerned. Its importance in Europe has been much diminished by the availability since the 1970s of natural gas from the North Sea and, since the 1980s, the former Soviet Union. Natural gas is a clean and easily handled fuel, and the size of the Russian reserves has muted criticism that it is a mistake to use an attractive material for chemical and domestic use for such a mundane purpose as electricity generation.

Sulfur dioxide and smoke pollution remain problems, but ones that are being tackled. In the United States, the overwhelming majority of sulfur dioxide pollution comes from coal and oil burning and metal smelting. Between 1986 and 1994, average emissions (measured at 473 sites) decreased by 5% and concentrations by 20%. Between 1994 and 1995, as a result of the Acid Rain Program, emissions dropped by 13% and concentrations by 17%. In Western Europe, coal burning is less prevalent than in the United States, and effort is being put into desulfurizing gasoline and diesel fuels. In 2002, the European parliament decreed that by 2005 "zero sulfur" fuels ($<$10 ppm sulfur) be widely available and that by 2009 they be standard. By 2005, the legal limit will be 50 ppm. While the Europeans set fuel quality standards for specific categories of vehicles and plants, the United States imposes "refinery average" limits on sulfur, set at 30 ppm by 2005 with an 80 ppm cap. By 2006, Diesel will have a 2006 ppm sulfur cap. These improvements come not only at an economic cost but also have an environmental price. The production of entirely "zero sulfur" fuels in Europe will increase refinery carbon dioxide emission because of the additional energy required by 5%, equivalent to about 4.6 million tonnes/year of carbon dioxide, to make its contribution to global warming.

Sulfur dioxide pollution remains serious in the developing world, and also in eastern Europe, where cheap and readily available soft coal or lignite are traditional fuels. In low-technology grates, coal combustion is better described as destructive distillation and is only slightly better than burning camel dung in a tent. The health consequences are not trivial. In the United States in 1995, 9% of deaths were attributed to respiratory disease arising from combustion-related air pollution. In China, where coal is extensively used as a domestic fuel, the proportion was 21.8%.

It is ironic that sulfur dioxide, while a health threatening pollutant and precursor of acid rain, also mitigates the greenhouse effect. Sulfate aerosols formed from it reflect sunlight back into space, and their removal increases global warming. It was suggested that sulfur dioxide also protected the ozone layer because it absorbs in a similar region, but other theories suggested it would destroy ozone, and it now seems that the two effects cancel out.

17.2.4.2 Automobile Exhaust Emissions The problems of pollution from coal burning were superseded by those from gasoline burning. In the United States, 77% of carbon monoxide emissions arise from transportation as do 49% of nitrogen oxides, 40% of volatile organic compounds, and 32% of carbon dioxide. Los Angeles smog replaced London fog in the public perception. They differed diametrically in that smog was associated with warm and dry rather than cold and damp weather, and it had oxidizing rather than reducing properties. Smog was formed in many cities, but it was particularly bad in Los Angeles because the pollution was confined by meteorological inversions above the city. The damaging materials in smog are oxides of nitrogen (lachrymatory and causing pulmonary edema at higher concentrations), ozone, and peroxyacetyl nitrate (PAN) (vegetation killers; ozone causes lung damage). Figure 17.7 shows the concentrations of the main pollutants during a typical Los Angeles day. Early in the morning, background levels of hydrocarbons, nitrogen oxides, and ozone are low. Automobile activity starts at 6 a.m., and nitric oxide and unburned or cracked hydrocarbons increase. Nitrogen dioxide reaches a peak in mid-morning but subsequently decreases in favor of ozone, which reaches a peak mid-afternoon. There is also a build up of aldehydes, nitro compounds, and other partially oxidized species, together with aerosols containing nitric and sulfuric acids and related materials.

Smog formation starts with the production of nitric oxide in automobile engines (Fig. 17.8). This, in itself, is an unlikely process. The reaction $N_2 + O_2 \rightarrow 2NO$ has $\Delta H^\circ_{298} = 207\,\text{kJ mol}^{-1}$ and $\Delta S^\circ_{298} = 24.8\,\text{J deg}^{-1}\,\text{mol}^{-1}$, so it is thermodynamically slightly unfavorable with a very high activation energy, but nitric oxide is actually formed in small quantities at the high temperatures in an internal combustion engine. If emitted in the exhaust gases, it is oxidized by atmospheric oxygen to the brown gas nitrogen dioxide (NO_2). This is a slow termolecular process. Nitrogen dioxide absorbs strongly between 300 and 400 nm, wavelengths abundant in sunshine. The products are nitric oxide and oxygen atoms, and the latter go on to generate ozone that can react with nitric oxide to regenerate nitrogen dioxide and oxygen. The oxygen atoms can also react with water to give hydroxyl radicals, which can interact

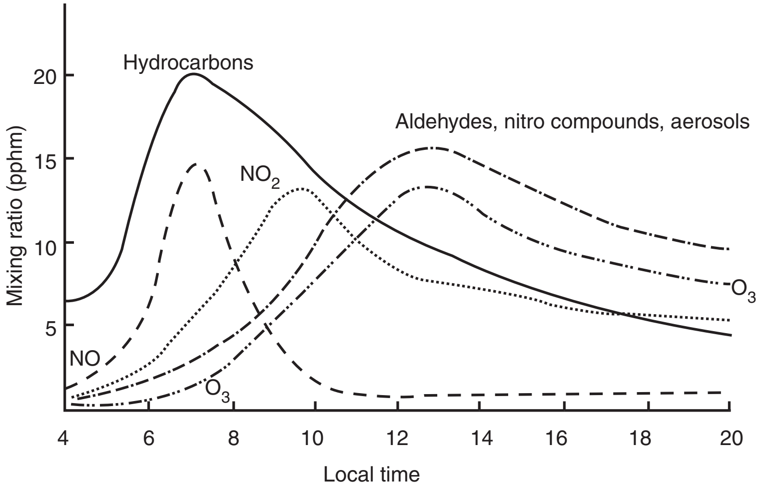


FIGURE 17.7 The typical mixing ratio profiles as functions of time of day in the photochemical smog cycle.

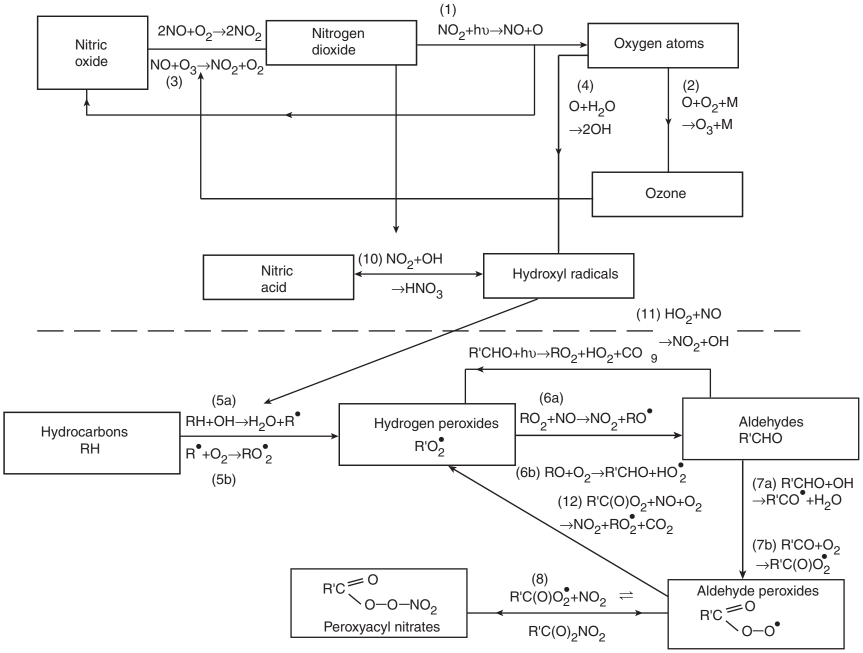


FIGURE 17.8 Los Angeles smog cycle.

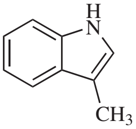
with nitrogen dioxide to give nitric acid. There is thus a complete cycle involving nitrogen- and oxygen-containing molecules, shown in the upper section of Figure 17.8. It would lead to a steady but low concentration of ozone and much lower concentrations of nitrogen dioxide than are actually found.

It is the presence of hydrocarbons and aldehydes that make the difference. They are attacked by hydroxyl radicals to give hydrocarbon radicals, which in turn give hydrocarbon peroxides and then aldehydes. The aldehydes give aldehyde peroxides and then peroxyacyl nitrates (e.g., PAN). Any volatile organic compounds discharged into the atmosphere from other sources usually also interact with hydroxyl radicals and lose a hydrogen atom to give a free radical. The reaction scheme in Figure 17.8 is much simplified and ignores sulfate and nitrate aerosols and many gaseous chemical species. A state-of-the-art model has 88 chemical species and 178 reactions (see note at the end of this chapter).

The smog problem has been tackled in the United States by legislation requiring catalytic converters to be fitted to automobiles to oxidize hydrocarbons and carbon monoxide while reducing nitrogen oxides (Section 16.6.1). In 1979, the Department of the Environment set an upper limit for ozone of 0.12 ppm. average over a one hour period, and in 1997 this was reduced to 0.08 ppm average over an eight hour period, the reduction to be achieved by 2004. There were also fresh limits on the emission of particulates of less than 2.5 μ from heavy-duty diesel truck and similar vehicles and on emissions of volatile organic compounds. The surface coating industry switched in part to water-based or solvent-free formulations. In other areas, of which Singapore is perhaps the most widely publicized, the pollution problem continues.

17.2.5 Water Treatment

Domestic sewage is a very dilute liquid. Strong sewage (urban sewage undiluted by rainwater) contains only about 500 ppm of impurities. Untreated, however, it leads to odor, spread of water-borne diseases such as cholera, pollution of watercourses, and the death of aquatic life. Sewage is a powerful reducing agent, and its decay involves the reduction of sulfate ions by organic material in the sewage to give hydrogen sulfide and mercaptans. The breakup of proteins and other nitrogenous matter in the sewage leads to amines, which mix with unpleasant nitrogenous compounds already present in the sewage (such as skatole, which gives the smell to feces) to accentuate the odor from the sulfur compounds.



Skatole

The methods of treating waste water have been standard for much of the past century, even though the traditions of dumping wastes in the sea or a river have been hard to overcome. Waste water is carried through sewers to a treatment plant, where it is screened to remove large solid objects. It is then sent to a settling tank where a sludge deposits, possibly with the help of flocculating agents, leaving a supernatant “clear effluent.” If land is reasonably cheap, the clear effluent is sprinkled via a rotating arm over a trickling filter—a bed filled with pieces of broken rock 5–10 cm in diameter, which have become covered with biological growth—and the organic compounds are oxidized aerobically to carbon dioxide, water, and nitrites/nitrates. The activated sludge method uses a tank with a spinning cone on top. This throws the clear effluent out in a spray and aerates it thoroughly. The liquid in the tank is inoculated with microorganisms similar to those in the trickling filter, and a similar oxidation process occurs. The activated sludge method occupies less space, hence is more suitable where land prices are high. On the other hand, it requires more maintenance. It has high electricity costs, whereas the rotating arm in the trickling filter is driven by the effluent being pumped out of the holes in its side.

The sludge from the settling tank is generally treated by anaerobic oxidation, in which it is maintained in a closed tank and putrefies to methane and carbon dioxide. The digested sludge has no odor and dries easily but has no value as a fertilizer. The methane, however, can be used to make the sewage plant independent of outside sources of energy.

An early problem with synthetic detergents is that they were based on branched-chain dodecene and nonene (Section 4.6). They were not degraded by the microbiological treatment and passed into waterways to cause foaming at waterfalls and weirs. The substitution of straight-chain materials reduced the problem, and biodegradability is now a key requirement for detergents.

A second problem arose with sodium tripolyphosphate, a so-called builder, added to detergent formulations to sequester polyvalent metal ions in hard water. The polyphosphate also passed unchanged into rivers and lakes. Phosphates are plant nutrients and, in their presence, blue-green algae may grow at an explosive rate and cover large areas of surface. The algae underneath each fresh growth rot and extract oxygen from the water. Fish die and the ecological balance is upset. The phenomenon is called eutrophication. Various solutions to the problem were implemented. Some zero-phosphate detergents were marketed; levels of phosphate in others were reduced; alternative builders were employed. Tertiary treatment of sewage was also practiced. One method is to add aluminum sulfate as a coagulant and then calcium chloride:

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{2-}$$

$$Al(OH)_3 + PO_4^{3-} + 3H^+ + 4NaOH \longrightarrow NaAlO_2 + Na_3PO_4 + 5H_2O$$

$$Na_3PO_4 + 3CaCl_2 \longrightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$$

The calcium phosphate is then filtered off. An alternative precipitant is iron sulfate, prepared by reaction of scrap iron with sulfuric acid. Iron phosphate is precipitated. Both these methods help to break colloids in the sewage and aid precipitation of sludge at the sedimentation stage.

17.2.6 Solid Wastes

Disposal of solid wastes is another area where there is a threat to the environment. Industry, especially the chemical and metallurgical industries, produces gaseous, liquid and solid wastes that may be toxic or hazardous or both. The range of these is so wide, however, that there is no general method of disposal and the reader is referred to specialist publications. Municipal solid wastes present more general problems. Both are regulated in the United States by the Office of Solid Waste under the Resource Conservation and Recovery Act, although a few wastes such as animal, medical, and radioactive wastes, are controlled by other federal agencies.

Municipal solid wastes (trash or garbage) have grown in the United States from 88.1 m tons (2.7 lb/person/day) in 1960 to 231.9 m tons (4.5 lb/person/day) in 2000. Their nature has changed since earlier in the century. In the days of open fires, much of the garbage would be burned, and the food wastes possibly composted. Packaging materials were few and plastics nonexistent. Domestic waste consisted largely of clinker and ashes, which could be compacted to a stable structure. In some regions, controlled dumping of these solids produced usable land (see note at the end of this chapter). Modern wastes have a totally different composition, shown in Figure 17.9. The dominant material is paper—not only newspapers but advertisements, promotional material, and packaging. Food wastes are about one-ninth of the total. This

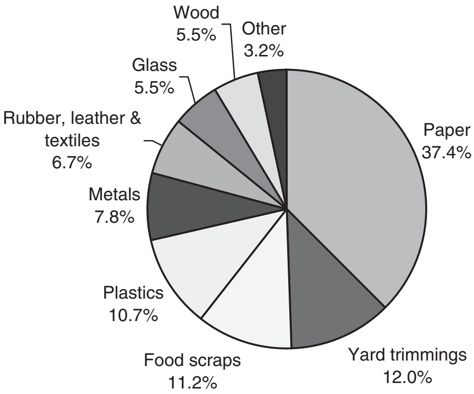


FIGURE 17.9 Municipal solid waste (US, 2000, before recycling, total: 232 million tons).

figure compares with over 40% in most Mediterranean countries, reflecting that American foods come ready washed and often ready prepared. The level of plastics reflects shopping habits and the ubiquitous plastic bags and food packaging, even though each bag weighs only 5–10 g. The "other" category includes materials such as paint, cleaners, used lubricating oils, pesticides, and batteries that could present toxic hazards.

The core economic problem at the heart of waste disposal is that the cheapest way to get rid of waste is to dump it. This method is given the dignified title of landfill. The main cost is shipping the waste to the landfill site. The drawbacks are numerous. Solid waste is generated principally in cites, and transport costs mean that one needs to purchase a landfill site on the edge of a city, not too far out. Inevitably the city then expands past the site, and there is immediately a problem with amenity, land values, visual pollution, and so on. There is also the problem that rain trickling through the waste can contaminate groundwater and the central problem that, even in thinly populated countries, one runs out of holes in the ground where waste can be dumped. Dumping at sea is forbidden under various international agreements. Whatever the economic analysis, political pressures in developed countries mean that municipal waste cannot merely be dumped. What are the options? The Environmental Protection Agency offers the following hierarchy.

17.2.6.1 Waste Prevention Like saving energy, waste prevention is an attractive option if only one can persuade people to cooperate. Two-sided copying of paper, backyard composting, reduction in packaging and charging for plastic bags at supermarkets are all possibilities. Those with an economic spur have the greatest chance of success.

17.2.6.2 Recycling Recycling including composting diverted 64 million tons (28%) of materials away from landfill in 1999, up from 34 million tons in 1990. Table 17.3 indicates that automobile batteries achieved a 96.9% recycle rate, paper

TABLE 17.3 Recycling Rates of Selected Materials (United States, 2000)

	%
Automobile batteries	96.4
Steel cans	57.2
Yard trimmings (grass cuttings) composted	56.9
Aluminum beer and soft drink cans	54.6
Paper and paperboard	45.4
Plastic soft drink containers	34.9
Glass containers	26.3
Tires	26.1

Source: US Environmental Protection Agency web page on municipal solid waste (see note at the end of this chapter).

41.9%, and yard trimmings (grass cuttings), through composting, 45.3%. Recycling requires a degree of householder-led segregation of garbage, but householders seem prepared to carry out a limited degree of sorting. It has been suggested in the United Kingdom, which has the worst recycling record in Western Europe, that people might be charged by weight for the disposal of unsorted garbage. Once the waste has been collected, ferrous metals can be separated by magnetic methods and light materials (paper and plastics) can be separated from heavier ones (glass and other metals) by air classification. All this comes at a cost, and the cost in countries where labor is expensive and recycling is more likely to be adopted is much higher than in developing counties where labor is cheap and, indeed, where the very poor frequently sort through garbage heaps voluntarily in the hope of finding something of value. There is also an environmental cost attached to recycling, in the sense that recycling of paper results in organochlorine compounds in water supplies (Section 17.3.7).

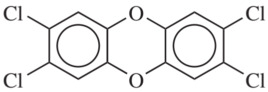
Europe is a more crowded continent than North America, and the European Union is increasing the range of materials that cannot be dumped. Refrigerators have already been declared hazardous waste and legislation on other electrical waste was scheduled for March 2003. Local authorities will have to separate electronic items (television sets, video recorders, personal computers, children's toys, etc.) from other rubbish, take out any hazardous chemicals and arrange for the dismantling and or disposal of the remainder. Companies and members of the public will have the option of returning their old goods to retailers when they buy new ones.

17.2.6.3 Combustion–Incineration Burning municipal solid waste can reduce the waste by 90% in volume and 75% in weight. The heat output can be used to generate electricity and, as metals must first be separated, their sale contributes to the economics. Sixteen percent of United States municipal solid waste was disposed of in this way in 2000.

The disadvantages are that incineration has high capital and operating costs. Because of the variability of input, there are numerous solids handling problems together with high-maintenance requirements and lack of reliability of equipment. Inefficient plant operations causes emission of odor, smoke, and pollutants. Generation of waste water from residue quenching can lead to air and water pollution and disposal of the residue, much reduced in volume though it is, produces other problems.

Combustion inevitably leads to emission of carbon dioxide. Air pollutants emitted from incinerators are mainly smoke, odors, fly ash, sulfur and nitrogen oxides, and hydrogen chloride. Some of these can be removed by scrubbing the exit gases, others by filters. Regulations call for waste to be exposed to a temperature of at least 980°C for at least 1 second. If combustion is inadequate, flue gases may contain black smoke, partially combusted organics and carbon monoxide. Greenpeace rejects incineration as a method of waste disposal and has claimed that incomplete combustion of chlorinated organics produces airborne dioxins, furans, polycyclic aromatic hydrocarbons, hydrogen chloride, and heavy metals.

Dioxin itself has the structure



It is produced as a byproduct in the manufacture of chlorinated phenols and phenoxy herbicides, chlorine bleaching of paper pulp, and combustion of chlorine-containing wastes. It is said to be one of the most poisonous substances known, and animal tests certainly support that conclusion. Congenital malformations in laboratory animals subjected to dioxin were reported as early as 1969. The effect on humans is less well documented, but one would expect the material to be a carcinogen. Industrial workers exposed to it have developed chloroacne, porphyrinuria, and porphyria cutanea tarda. The Seveso accident in 1976, in which 2 kg were discharged to the atmosphere, resulted in an unexpectedly low incidence of health damage. Dioxin's notoriety is based primarily on its occurrence as a contaminant in the manufacture of Agent Orange, a defoliant used in the Vietnam war in the 1960s. It has been implicated in some of the symptoms described by veterans exposed to it. Some 78,000 people have reported complaints since 1979, and in 1991 the United States Congress recognized 10 illnesses as being linked to Agent Orange, but by 2002 only 4000 compensation claims had been agreed. The Vietnamese themselves also report an increased incidence of birth defects. As is always the case in such situations, direct causal links are difficult to prove.

The mention of dioxins and related compounds such as bromodioxins immediately raises fears. The amounts of dioxins emitted by incinerators are hotly disputed by environmentalists on the one hand and incinerator manufacturers on the other, but plans to construct incinerators anywhere are certain to meet with opposition from the inhabitants and this, allied to the need for the incinerator to be near a town, both for ease of garbage collection and electricity transmission, make it surprising that even one-sixth of United States garbage is disposed of in this way.

Worries about incineration have even led to attacks on cremation, long accepted as the most environmentally acceptable way of disposing of the dead. It now appears that cremation consumes substantial amounts of natural gas and increases the burden of carbon dioxide and nitrogen oxides in the atmosphere. Because of dental fillings, it also produces mercury pollution. In Britain, emissions of mercury from most sources have been reduced sharply and in 1999 cremation was responsible for 1.34 out of 8.53 tonnes of atmosphere mercury pollution. It is now estimated that 10% of the mercury in North Sea fish comes from cremations.

17.2.6.4 Sanitary Landfill Given the effort expended on the problem, it is disappointing that 57% of municipal solid wastes in the United States is still disposed of by landfill. The number of sites has decreased from 8000 in 1988 to 2300 in 1999, but the capacity has remained more or less constant. New landfills are much larger than old ones. They are also organized according to stricter standards. Federal landfill standards are listed in Table 17.4. Landfill still relies on large holes in the ground, but these have to be lined to prevent contamination of groundwater and generally regulated in other ways.

Because biodegradable organic matter is present, landfill sites exude gas. The principal gases are nitrogen, oxygen, carbon dioxide, and methane, but ammonia, carbon monoxide, hydrogen, hydrogen sulfide, and volatile organic compounds are also present in small amounts. The last of these probably arise from household cleaners, hair sprays, and paints. The gases cannot be left to diffuse into the atmosphere. Methane in particular is a powerful greenhouse gas. Ammonia and hydrogen sulfide have an unpleasant odor. Methane–oxygen mixtures are liable to explode. Landfill sites are normally capped and mined for their combustible gases, which are sometimes burned to provide electricity.

A landfill site has a life cycle for gas emissions (Fig. 17.10) In stage I, nitrogen and oxygen are displaced from the landfill as aerobic decomposition starts. In stage II, aerobic decomposition is dominant and produces carbon dioxide. The oxygen is consumed by stage III and methane production rises as anaerobic digestion takes over. By stage IV, the site has settled down to a steady production of methane, which

TABLE 17.4 Federal Landfill Standards

Location restrictions ensure that landfills are built in suitable geological areas away from faults, wetlands, flood plains, or other restricted areas.

Liners are geomembrane or plastic sheets reinforced with two feet of clay on the bottom and sides of landfills.

Operating practices such as compacting and covering waste frequently with several inches of soil help reduce odor; control litter, insects, and rodents; and protect public health.

Groundwater monitoring requires testing groundwater wells to determine whether waste materials have escaped from the landfill.

Closure and postclosure care include covering landfills and providing long-term care of closed landfills.

Corrective action controls and cleans up landfill releases and achieves groundwater protection standards.

Financial assurance provides funding for environmental protection during and after landfill closure (i.e., closure and postclosure care).

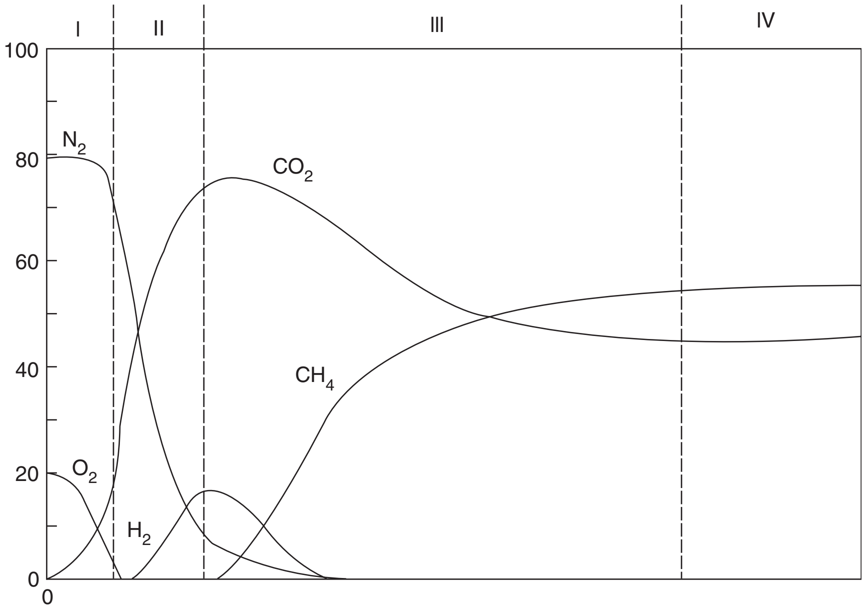


FIGURE 17.10 Percentage composition of gases from landfill.

may be maintained for several years. That is not to say that everything biodegrades. Ten year old hotdogs and newspapers have been brought up intact.

The availability of potential landfill sites is decreasing rapidly even in such huge countries as the United States, and the problem is more acute in crowded areas such as northeast Europe. To encourage other forms of waste disposal, there are landfill taxes throughout the European Union (e.g., \$70/tonne in the Netherlands, \$53/tonne in Denmark, and \$20/tonne in Britain), and these are soon to be raised. An increase in incineration facilities, however, is probably not politically practicable, nor necessarily desirable. Recycling and reduction of waste are the only clear solutions and they are more easily recommended than achieved. The adoption of biodegradable plastics would be a contribution to the problem and would at least avoid the unsightliness of plastic bags being blown about the landscape but, if landfilled, the fact that they decomposed would be of little help. Indeed, there is evidence that plastic bags help stabilize landfill sites and prevent garbage avalanches.

17.2.7 Petrochemical Industry Wastes

The petrochemical industry operates on a huge scale and produces waste organics and catalyst residues together with large quantities of water contaminated with small amounts of hydrocarbons, phenol, and their derivatives. These would appear not to be sensitive to sewage plant microorganisms and might kill them, thus bringing the sewage works to a halt. It has proved possible, however, to develop strains of microorganism that can cope. Petrochemical plants thus have highly aerated “bug pits” in which petrochemical-eating “bugs” digest the effluents.

Heavy metals are not normally found in organic chemical plants except as part of a catalyst system. The most toxic metals are cadmium, lead, mercury, beryllium and arsenic; several others are harmful. If they do occur, every trace of them must be removed and the methods employed are

1. Precipitation if an insoluble derivative is accessible and does not give colloids.
2. Cation exchange techniques, which are suitable for lead, copper, zinc, mercury, chromium, nickel, and arsenic.
3. Solvent extraction. Nickel ions may be extracted with dinonylnaphthalenesulfonic acid; zinc and cadmium with di-2-ethylhexylphosphoric acid and copper with fatty chelating agents.

Harmful dissolved salts are removed by ion exchange or electrodialysis. Activated carbon and activated silica will adsorb small quantities of toxic organic compounds. Powerful oxidation will render harmless such materials as amines or aldehydes. Chlorination is suitably powerful but leads to the danger of organochlorine compounds that have then to be separated. Electrochemical methods are often used to remove suspensions of oils or paints in a type of froth flotation. Electrolytic hydrogen carries suspended oils upwards for removal by skimming.

Organic chemical wastes usually occur as gases, liquid streams, or sludges and do not present the handling difficulties of municipal solid wastes. Gases are flared at the stack if combustible; if not they may be scrubbed out or treated with the liquids. Liquids and sludges are usually treated thermally at a high temperature (400–850°C) with or without oxygen. Sophisticated furnaces are required to avoid formation of dioxins and other toxic combustion products. Liquid injection incinerators work for gases and liquids; rotary kilns and fluidized-bed incinerators will handle gases, liquids, solids, and sludges. Combustion heat is recovered by raising steam. Pyrolysis technology, in contrast, uses high temperatures in a low-oxygen environment to break down waste products into less complex materials. One advantage associated with this technology is that inorganic constituents are not volatilized; instead, they form an insoluble residue.

Particularly dangerous wastes may be handled in a plasma incineration system where the waste is introduced into an electric arc at above 3000°C, where molecules are completely atomized or ionized and, on cooling, recombine to give small, simple, nontoxic molecules.

17.2.8 Other Environmental Problems

A discussion of the numerous sources and types of pollution in addition to the above are beyond the scope of this book. For example, endocrine disruptors—the mimicking of the female hormone in males—have been widely publicized. Numerous chemicals have been implicated including bisphenol A and nonylphenol ethoxylate. Indeed a book has been written on the subject with a foreword by a former US vice president. Although it is possible that endocrine disruption exists in lower species, it has not been proved in humans. This is not to say that other suspected problems are trivial.

What it does mean is that the utmost in scientific sophistication and integrity must be applied to their analysis.

17.3 GREEN CHEMISTRY

Green chemistry, as defined at the beginning of this chapter, has moral overtones but is also predicated on a belief that neglecting environmental considerations will not only make people's lives worse but will, in the end, damage the chemical industry itself. The use of sustainable technologies benefits industrialists just as much as customers in the long term. One can do well by doing good.

Green chemistry is a subset of industrial organic chemistry, the theme of this book. Just as industrial chemistry focuses on the chemical reactions that are characterized by simple, cheap reagents operating on intermediates obtained in a small number of steps from cheap and readily available feedstocks, so green chemistry focuses on the environmental implications of industrial chemical processes. The twelve commandments of green chemistry are displayed in Table 17.5. These represent an ideal—few chemical processes could comply with every one of the commandments—but they provide a standpoint from which technologies can be viewed. We emphasize that the emergence of green chemistry as a discipline in the early 1990s does not imply that chemists before that date were indifferent to environmental considerations. After all, the replacement of the Leblanc process by the Solvay process and the use of byproduct hydrogen chloride to make bleaching powder in the nineteenth century were both steps toward a cleaner environment. Baekeland's invention of phenolic resins obviated the need to kill elephants for ivory for billiard balls. The improvement of processes in general increases yields, which improves profitability, and it also decreases byproducts and emissions. Replacement of traditional catalysts by others that are less toxic, more specific, and more easily separated from product are an important source of "greening." The improvement in propylene polymerization (Section 4.5.1) is an excellent example as are the production of bisphenol A with a solid catalyst rather than hydrochloric acid (Section 7.1.2) and the production of cumene with a solid catalyst rather than aluminum chloride or phosphoric acid (Section 4.9).

Meanwhile, worries about the environment, the poor public image of the chemical industry, and more stringent government legislation caused concerned chemists in the 1990s to draw together under the "green chemistry" banner. Certain topics, for example, avoidance of phosgene, use of dimethyl carbonate (Sections 7.1.2.2, 7.3.1 and note at the end of this chapter), elimination of organic solvents, and reactions in supercritical carbon dioxide and ionic liquids, are particularly associated with the movement, as are biphasic systems and solvent-free systems that use the surfaces or interiors of clays, zeolites, silica, and alumina.

Most of the modern "green" processes fall into the area of fine chemicals rather than bulk organic chemicals. Nonetheless, they have had an impact on bulk chemical processing and this may increase. Examples of the "greening" of chemistry are given in the following sections.

TABLE 17.5 The Twelve Commandments of Green Chemistry

Prevention

It is better to prevent waste than to treat or clean-up waste after it has been created.

Atom economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

Less hazardous chemicals syntheses

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

Design safer chemicals

Chemical products should be designed to effect their desired function while minimizing their toxicity.

Safer solvents and auxiliaries

The use of the auxiliary substances (solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

Design for energy efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

Use renewable feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

Reduced derivatives

Unnecessary derivitization—use of blocking groups, protection/deprotection, and temperature modification of physical/chemical processes—should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Design *for* degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

Real-time analysis *for* pollution prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring, and control prior to the formation of hazardous substances.

Inherently safer chemistry for accident prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Source: P. T. Anastas and J. C. Warner, *Green chemistry: theory and practice*, Oxford: New York, UK, 1998.

17.3.1 The Decline in Acetylene Chemistry

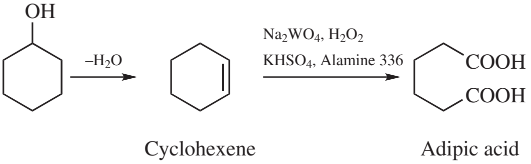
Before World War II, acetylene was the basic feedstock for many aliphatic organic chemicals, especially monomers. Production of acetylene via carbide (Section 12.6) produced about 28 tonnes of a slurry of calcium hydroxide in water for every tonne of acetylene (Section 10.3). The process was polluting and energy intensive. The replacement of acetylene by ethylene as a feedstock made possible the modern chemical industry—it is inconceivable that its growth could have occurred with such a polluting first step.

17.3.2 Nylon

The production of nylon 6 by the classical process (Section 7.2.2) produces 4.4 lb of ammonium sulfate for every pound of product. Processes are available (Section 7.2.2) that decrease or eliminate ammonium sulfate production. The Enichem ammoximation process being developed in the early 2000s with Sumitomo seems especially favorable as do two processes under development by DSM and BASF (Section 5.1.2).

The Flixborough disaster in 1974 led to a modification of the nylon 6 process in the United Kingdom in which phenol was substituted for benzene-based cyclohexane. A leak had occurred in the cyclohexane line, leading to an unconfined vapor cloud explosion that caused 28 deaths. Although the explosion was attributed to various design failures, the replacement plant started with the safer phenol (Section 7.1.3).

There are also some ecological problems associated with nylon 6,6 (Section 7.2.1). Adipic acid synthesis, like the traditional nylon 6 process, starts with benzene, which is toxic. Mild oxidation of benzene gives a cyclohexanol–cyclohexanone mixture. A more severe oxidation with nitric acid oxidizes this mixture to adipic acid. This is the only large scale industrial oxidation requiring this polluting reagent. BASF has developed a more benign process starting with butadiene (Section 5.1.3.4). Other processes have been proposed but not commercialized. One of these goes via cyclohexene and the phase-transfer catalyst, Alamine 336 [tri-(C_8–C_{10})alkylamine]:



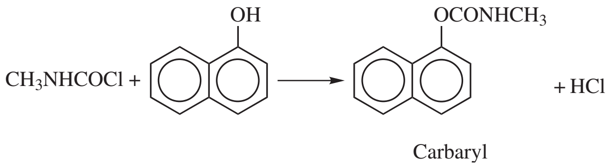
The reaction can be run in water. The Alamine serves to transfer the oxidizing system to the organic phase or, at least, to the interfacial layer, where reaction can take place (Section 16.10). The drawbacks are first that the reaction requires expensive hydrogen peroxide, and second that the phenol starting material is more expensive than benzene. However, a Japanese process (Section 7.1.3) hydrogenates benzene to cyclohexene in good yield. A cheaper process for hydrogen peroxide would make this process more favorable.

17.3.3 Replacement of Phosgene

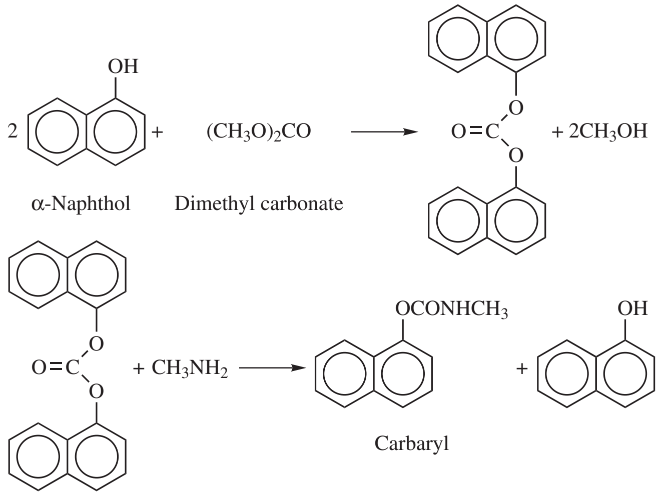
A central aim of green chemists is the development of reaction routes that do not involve the use of phosgene. A non-phosgene route to polycarbonate resins is described in Section 7.1.2.2 and non-phosgene routes to diphenylmethane diisocyanate (MDI) and to isophorone diisocyanate are described in Section 7.3.1. By the early 2000s, only isophorone diisocyanate was manufactured without phosgene. The process used here is not applicable to aromatic isocyanates and has not been applied to other aliphatic isocyanates.

The use of phosgene was also associated with but not directly implicated in the Bhopal disaster, the worst in the history of the chemical industry. As indicated in Section 10.5.2.5, phosgene was reacted with methylamine to give methyl isocyanate, which was stored and later reacted with α-naphthol to give the pesticide carbaryl. The disaster could have partly been averted by the maintenance of a much smaller inventory of methyl isocyanate, the agent that poisoned so many people. Makhteshim, in Israel, avoided the use of methyl isocyanate, but not the use of phosgene by the reaction sequence:

$$CH_3NH_2 + COCl_2 \longrightarrow CH_3NHCOCl + HCl$$



The pesticide could probably be made via dimethyl carbonate by the reactions:



17.3.4 Monomethylation by Dimethyl Carbonate

Apart from its role in replacing phosgene (see above), dimethyl carbonate is a "green" methylating agent and, in some reactions, it can replace dimethyl sulfate, methyl chloride, or sodium hydride. Two examples that have been commercialized are in the syntheses of the nonsteroidal anti-inflammatory drugs, ketoprofen, and naproxen. In both cases, insertion of a methyl group alpha to a carboxyl is required. The crucial stages are shown in Figure 17.11. Dimethyl carbonate is a methylating agent only at high temperatures and boils at 90°C, so reactions much be carried out

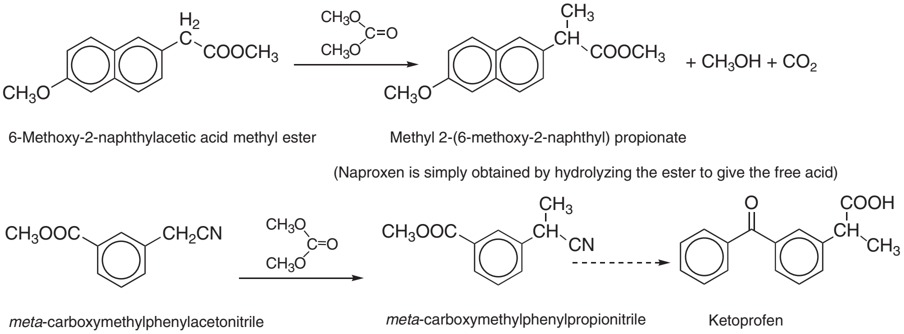


FIGURE 17.11 Methylation by dimethyl carbonate.

in an autoclave. Because it is harmless, it can be used in large excess and can serve as a solvent at the same time as a methylating agent.

17.3.5 Liquid and Supercritical Carbon Dioxide and Water

Carbon dioxide has a triple point, the conditions under which solid, liquid, and vapor can exist together in equilibrium, of −56.6°C and 5.2 bar. When cooled at atmospheric pressure, it condenses directly to a solid—dry ice. When compressed at room temperature it liquefies and is often supplied commercially in cylinders as a liquid exerting a pressure of 56.5 bar. When compressed above its critical point (31.1°C) it gives a supercritical fluid. The potential use of liquid carbon dioxide as a replacement for tetrachloroethylene (perchloroethylene) in dry cleaning was mentioned in Section 3.11.7. Liquid carbon dioxide is also used instead of hexane to extract caffeine to give decaffeinated coffee, and to obtain vegetable oils and perfumery oils from their substrates. The advantage in the first two cases is that there is no contamination issue and in the third that there is less decomposition and the resulting perfumes have cleaner "notes."

Reactions normally carried out in chlorofluorocarbon solvents have been found to proceed in liquid or supercritical carbon dioxide. DuPont announced in 2000 a plant to make polytetrafluoroethylene and its copolymers by such a process using fluorinated initiators. Thomas Swan, in England, opened a plant in 2002 to hydrogenate isophorone to trimethylcyclohexanone. Figure 17.12 shows various other reactions demonstrated to take place satisfactorily in supercritical carbon dioxide, some of which might find application in industrial processes. Liquid carbon dioxide is also a replacement for chlorofluorocarbons and other organic solvents in cleaning integrated circuits and other microelectronics components.

An advantage of liquid or supercritical carbon dioxide is that a large degree of control over product selectivity and yield is possible by adjusting the temperature and pressure of the reactor. Supercritical fluids also allow easy recovery of the product and separation of the catalyst. There are several drawbacks. First, the achievement of high pressures is expensive and offends one of the "green" commandments. Second,

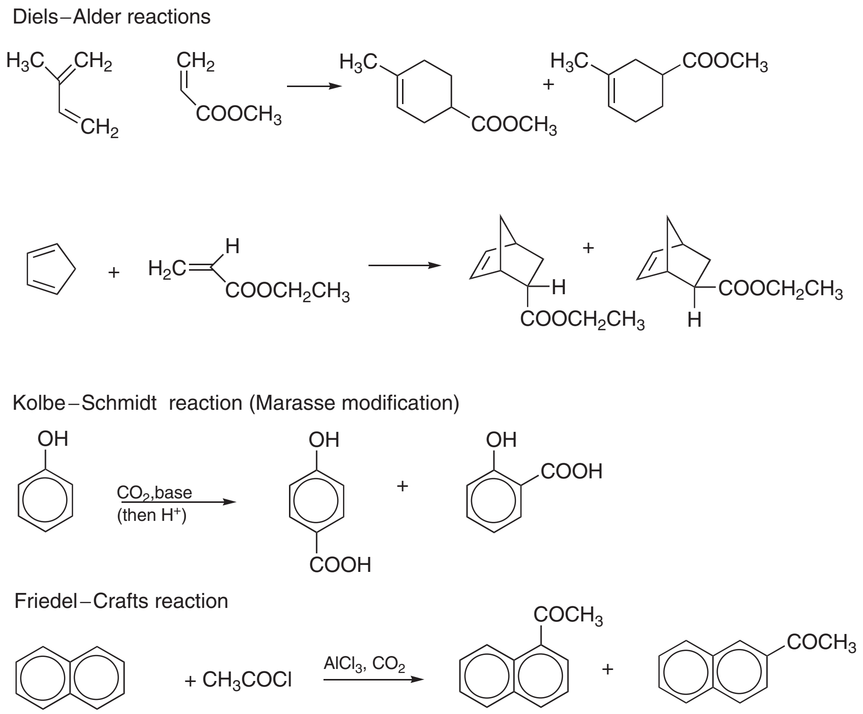
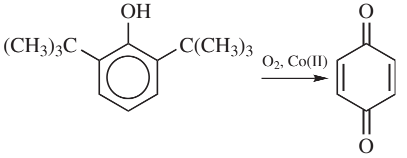


FIGURE 17.12 Some reactions occurring satisfactorily in supercritical carbon dioxide.

pure supercritical carbon dioxide frequently leads to low reaction rates and inadequate catalyst solubilities. The latter problem has led to the idea of a "CO_2-expanded" solvent, that is, a mixture of an organic solvent with the carbon dioxide. For example, 2,6-di-*tert*-butylphenol in acetonitrile may be oxidized to 1,4-benzoquinone in acetonitrile/supercritical CO_2 in a 1:1 ratio with a cobalt (II) catalyst.



Carbon dioxide increases the solubility of oxygen by nearly two orders of magnitude compared with pure acetonitrile, while the acetonitrile aids catalyst solubility and allows a rapid catalyst turnover rate. The system will operate at 60–90 bar compared with the 200 bar required for pure supercritical carbon dioxide, and the catalyst can be recovered simply by increasing the carbon dioxide pressure until the catalyst precipitates. Although the technique is ingenious, the question arises as to whether it could be applied to commercially more important systems.

17.3.6 Ionic Liquids

Ionic liquids are salts of nitrogen- or phosphorus-containing organic cations coupled with inorganic anions. Because of the asymmetry of the cations and size differences between them and the anions, they do not pack readily into a crystal, and consequently are liquids at room temperature. Typical ionic liquids are shown in Figure 17.13.

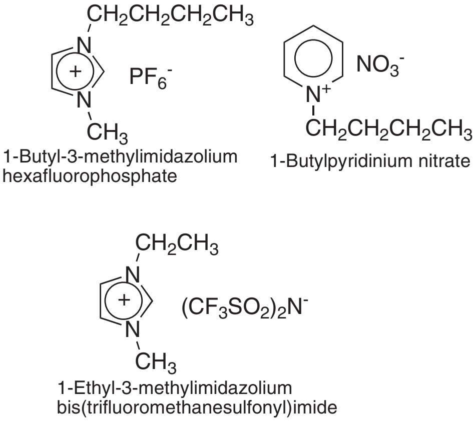
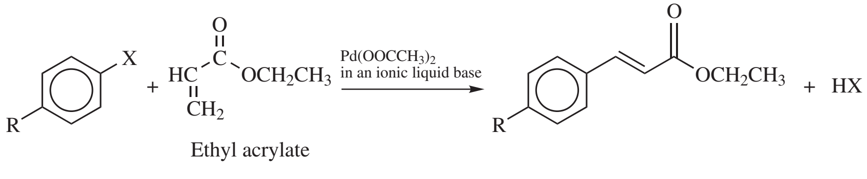


FIGURE 17.13 Ionic liquids.

The cations and anions can be varied to give different degrees of lipophilicity, and hence different solvating properties. They are usually air and water stable. They consist mainly of discrete dissociated ions or as strongly structured liquids, with the electric conductivity of salts. They have practically zero vapor pressures, which means that in terms of emissions they are ideal replacements for volatile organic solvents. The downside is that they themselves cannot be purified by distillation. There is also a possible problem in that ionic liquids are usually lipophilic and, as noted above, lipophiles accumulate in body fat and are not regarded as environmentally friendly. The reaction products in ionic liquids can either be distilled off or extracted with water or alkanes. There appear to be no immediate industrial applications but BP is said in 2001 to be on the point of using ionic-liquid Friedel–Crafts alkylation technology to upgrade an existing process. The technology apparently applies to the Heck reaction:



R = H or OCH_3; X = Br or I

17.3.7 Photocatalysts

There has been a feeling for many decades that there should be some way of using light instead of heat to activate molecules and bring about selective reactions—a sort of industrial flash photolysis. The Toray process to caprolactam, however, is one of the very few to be commercialized (Section 7.2.2). One of the difficulties is to get the light energy very far into the reacting system before it is absorbed and degraded to heat by chemical absorbers and turbidity.

There is, however, research interest in the use of UV light in water purification. One of the problems with paper recycling and water purification generally is that it involves chlorination. This has the desired effect of bleaching the pulp in the former case and killing bacteria in the latter, but it also results in the appearance of tiny quantities of organochlorine impurities in the waste water, and these add to organochlorine compounds from agrochemicals. Waste water contains tiny quantities of chlorophenols, dioxins, and polychlorobenzenes. Such chlorinated compounds are anathema because, although present in minuscule quantities, they are lipophilic and accumulate in body fat.

A possible solution is to irradiate the water with UV light over a titanium dioxide photocatalyst, perhaps loaded with platinum. Water is transparent to UV light. The photoreaction on the titanium dioxide yields hydroxyl ions, which displace the chlorine atoms on the aromatic rings. The mechanism by which the aromatic rings are fragmented is unclear, but it is known that the catalyst system yields hydrogen and oxygen from water but with very low quantum efficiency. The end products are certainly carbon dioxide, water and hydrogen chloride which, at the level at which it is formed, is harmless.

Water purification illustrates some of the dilemmas facing the green chemist. It is essentially an end-of-pipe process, which is against the general principles. One way of reducing the organochlorine compounds would be to reduce paper recycling, but recycling is a cardinal principle of greenness. A cheap route to hydrogen peroxide would provide a worthwhile series of alternative technologies, but such a route has not yet been forthcoming.

17.3.8 Paired Electrosynthesis

In the late 1990s, BASF developed a two-for-one electrochemical process to produce two complex chemicals [phthalide and *tert*-butylbenzaldehyde (TBA)] both of them intermediates in BASF crop protection products. The reaction sequences are shown in Figure 17.14. BASFs original process for manufacture of TBA involved alkylation of toluene with isobutene to give *p*-methyl-*tert*-butylbenzene, and this was oxidized in an electrochemical reactor to give TBA dimethylacetal, the precursor of TBA, at the anode and hydrogen at the cathode. The hydrogen was impure and had to be burned. On hydrolysis, the acetal loses methanol to give TBA.

When phthalide was required as an intermediate, BASF realized that the electrochemical reactor could be set up to give phthalide simultaneously from the dimethyl phthalate at the anode. Phthalide is an intermediate for the new, "green" strobin

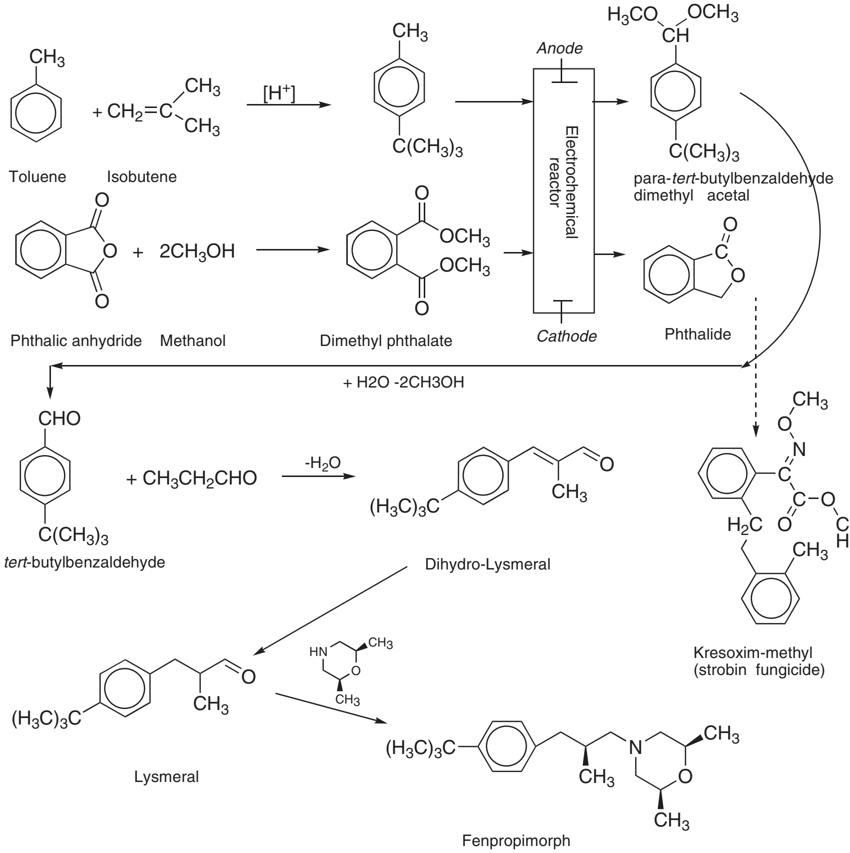


FIGURE 17.14 Paired electrosynthesis of phthalide and *tert*-butylbenzaldehyde.

fungicide, kresoxim-methyl. The TBA was reacted with propionaldehyde in an aldol condensation to give dihydro-Lysmeral. Regioselective hydrogenation of the double bond in the dihydro-Lysmeral gave Lysmeral, an aroma chemical with a lily-of-the valley fragrance. Reductive amination of Lysmeral with 2,6-dimethylmorpholine gives the agrochemical fenpropiomorph. The plant has a modular construction so that, if demand for phthalide is insufficient, TBA can be produced alone as it used to be.

17.3.9 Sertraline Synthesis

Sertraline is a pharmaceutical used to treat depression. Although not an industrial chemical in the narrow sense, it is made on a tonnage scale and is an example of an alternative synthetic pathway in which the three steps in the original process were reduced to one (Fig. 17.15). In the original synthesis, 3,4-dichlorobenzoyl chloride and benzene were converted to a benzophenone by a Friedel–Crafts catalyst. This was originally aluminum chloride and it is not disclosed if it has been replaced by a zeolite. A side chain

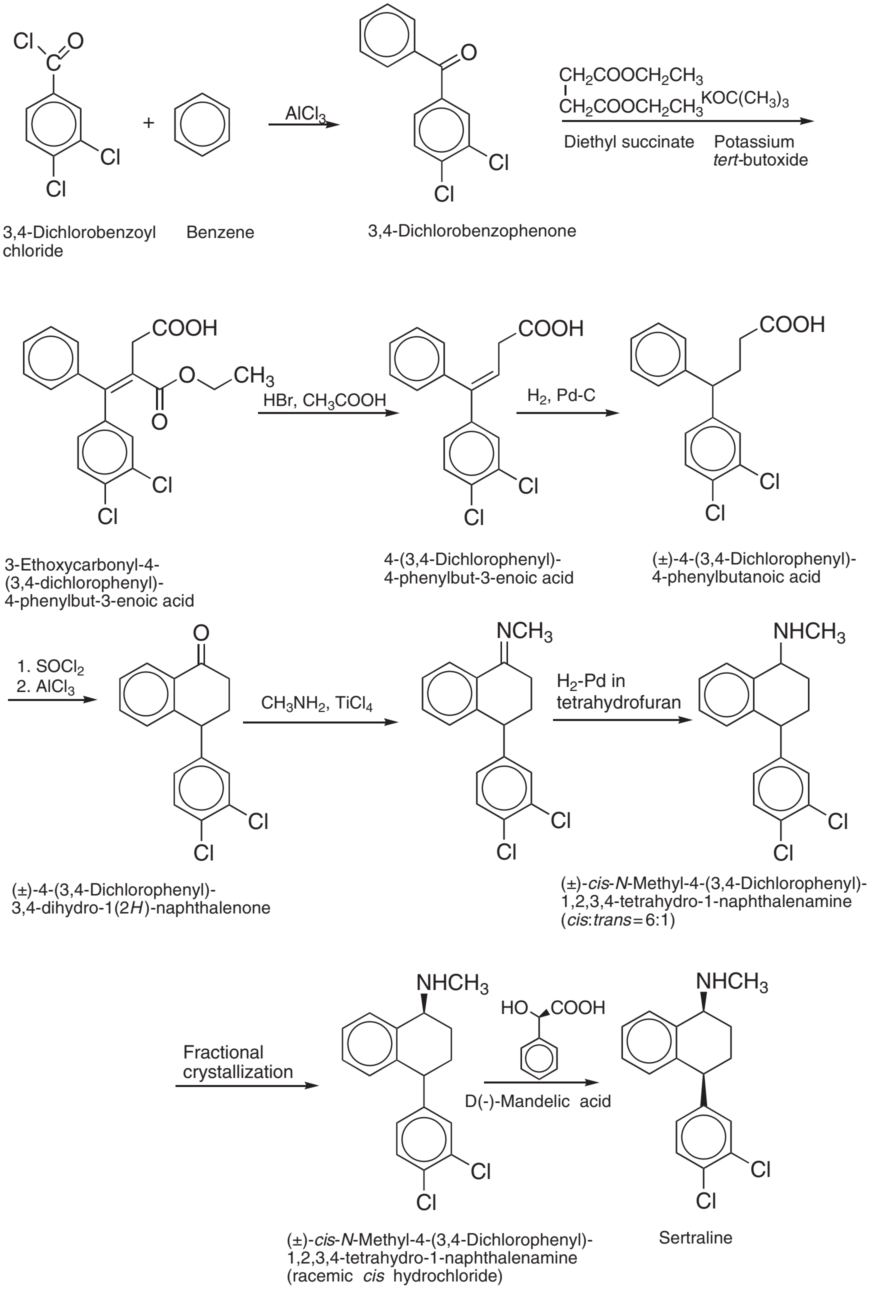


FIGURE 17.15 Synthesis of sertraline.

was built onto the ketone group and cyclized, again in a Friedel–Crafts reaction, to give (±)-4-(3,4-dichlorophenyl)-3,4-dihydro-1(2*H*)-naphthalenone. Three stages, later converted to one, followed. The carbonyl group of the naphthalenone was converted to an imine with methylamine in tetrahydrofuran (THF) or toluene. Titanium tetrachloride was used as a dehydrating agent to drive the equilibrium towards the imine. The imine was isolated and hydrogenated with hydrogen and a palladium–carbon catalyst in THF to form isomers (*cis*:*trans* = 6:1). Fractional crystallization isolated the racemic cis hydrochloride. This was finally resolved with D-mandelic acid in ethanol to give the desired (*S,S*)-*cis* isomer. The sertraline mandelate was then converted to the hydrochloride in ethyl acetate.

In the new process, the three stages starting with the naphthalenone are carried out in ethanol without isolating the intermediates. Only the environmentally benign ethanol is used as solvent throughout, and the unreacted methylamine is recovered by distillation. Titanium tetrachloride is no longer required to drive the first step since the imine is poorly soluble in ethanol and precipitates.

Palladium on calcium carbonate provides better selectivity than palladium–carbon giving a *cis*:*trans* isomer ratio of 18:1. Overall yield has been nearly doubled to 37% and raw material usages for methylamine, (±)-4-(3,4-dichlorophenyl)-3,4-dihydro-1(2*H*)-naphthalenone and D-mandelic acid have been cut by 60, 45, and 20%, respectively. Solvent requirements have been reduced from 60,000 to 6,000 gallons/tonne of sertraline, 440 tonnes/year of titanium dioxide–methylamine hydrochloride acid waste, 150 tonnes of 35% hydrochloric acid waste, and 100 tonnes of 50% sodium hydroxide waste have been eliminated. It is to be hoped that many more examples like this will accumulate in the next decade.

17.3.10 Catalytic Dehydrogenation of Diethanolamine

The environmentally friendly nonselective herbicide, Round-Up, is the monoisopropylamine salt of glyphosate [*N*-(phosphonomethyl)glycine; $HOOCCH_2NHCH_2OP(OH)_2$]. The key intermediate in the synthesis is disodium iminodiacetate, which was made by the traditional Strecker process from ammonia, formaldehyde, hydrogen cyanide, and hydrochloric acid, but the process produced one tonne of cyanide and formaldehyde-containing waste for every seven tonnes of product. The new route starts with diethanolamine (Section 3.11.6.4), which is oxidatively dehydrogenated over a copper-containing catalyst.

$$HOC_2H_4NHC_2H_4OH \xrightarrow{\text{Cu catalyst} + O_2,\ -2H_2} HOOCCH_2NHCH_2COOH$$

The reaction is endothermic, avoiding the possibility of a runaway reaction and negligible quantities of effluent are produced.

17.3.11 Genetic Manipulation

Biotechnology has been a buzzword among chemists for at least two decades as a way of using renewable raw materials and producing biodegradable products. Over that period, with the aid of recombinant DNA technology, it has led to of the development of the order of 50 pharmaceuticals, but tonnage products have been lacking. There is an economic problem in harvesting natural products rather than pumping them out of the ground, and there is a waste disposal problem in getting rid of the huge amounts of biomass that accompany the biotechnological product. The production of fermentation ethanol was discussed in Sections 2.3.3 and 3.9 (and the accompanying note), and Chapter 14. Immobilized enzyme production of high-fructose corn syrup is discussed in Section 14.2 and that of acrylamide in Section 4.14.3. Use of engineered enzymes is a route to 1,3-propanediol (Section 4.14.4).

17.3.12 Polyhydroxyalkanoates

The original semisynthetic polymers (the cellulosics) were based on renewable raw materials but the wholly manmade materials have been based on petroleum and natural gas. A new range of polymers (the polyhydroxyalkanoates) are more tractable than the cellulosics but are still based on renewable raw materials (Sections 14.1 and 14.5.2).

ICI developed a route to a biodegradable polyester copolymer of γ-hydroxybutyric and γ-hydroxyvaleric acids, by fermentation of glucose with *Alcaligenes eutrophus.*

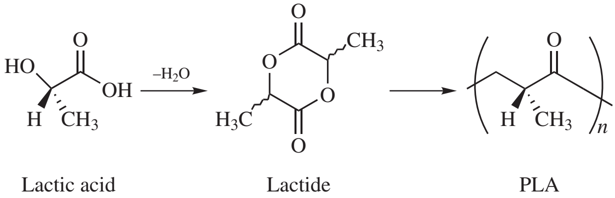
$HOCH_2CH_2CH_2COOH$	$HOCH_2CH_2CH_2CH_2COOH$
γ-Hydroxybutyric acid	γ-Hydroxyvaleric acid

The polymer, called Biopol, is stereoregular and has a molecular weight of 100,000–400,000. After separation from microbial cells and purification, it can be formed by conventional polymer processing techniques. The stereospecificity and high molecular weight, which give it strength, are unique for step growth polymerization which, when performed conventionally, gives molecular weights as low as 10,000. The polymer, *polyhydroxybutyrate*, is still expensive but its biodegradability makes it attractive and it is finding markets in the blow molding of bottles and other packages, particularly for "green" cosmetics. It appears to have been sold by ICI to Monsanto, who sold it to Metabolix, who have developed recombinant organisms that are much more efficient than the wild strains used by Monsanto. Metabolix is also developing crop plants such as tobacco or rape seed that could grow Biopol and other polyhydroxyalkanoates directly.

Proposed uses for Biopol include medical applications such as sutures, staples, ocular inserts, cardiovascular grafts, bone screws, and related surgical items. Because the polymer is biodegradable, postsurgical removal is not required. Also, because of its biodegradability, the polymer might be useful in controlled release of drugs, applicators for feminine hygiene products, for the encapsulation of pheromones, and for agricultural film in which fertilizers and insecticides are imbedded. A decreased price would make it a candidate for general purpose biodegradable film.

A related polyalkanoate is polylactate (polylactic acid, PLA), a polyester from lactic acid. Cargill Dow opened a 140,000 tonne/year plant in 2002, based on an engineered organism, and aims at a global capacity of 500,000 tonnes/year by 2006. The important difference is that lactic acid needs to be polymerized to give polylactate whereas Biopol is produced ready-polymerized by the organism.

Dextrose from corn is first fermented to lactic acid by a route similar to that in Section 14.1. The lactic acid is purified and condensed to make low molecular weight polylactic acid ($M_n \sim 5000$). This is then depolymerized in the melt with a tin octanoate catalyst to give a mixture of lactide stereoisomers. Traces of water formed in the condensation polymerization need to be removed because they limit molecular weight, and operation in the melt makes this easier than in solvents. The purification steps allow manipulation of the stereoisomers; the L-lactide is the primary product but the physical properties of the polymer can be varied by controlling the amount of D-lactide. The final product has a molecular weight of 60,000–150,000 and residual lactic acid and lactide are removed under vacuum.



Avoidance of a solvent and the use of vacuum distillation give a product claimed to be competitive with petrochemicals. Polylactate is biodegradable. It looks like polystyrene and has the stiffness and tensile strength of poly(ethylene terephthalate). Polylactate films are grease resistant and have good barrier properties, which suits them for food packaging. Like cellophane, they stay folded when twisted, making them suitable for candy wrappers, and the first commercial use has been as packing film for golf balls in Japan. Polylactate is said to bridge the gap between synthetic and natural fibers in clothing and carpeting and also to have wide applications in agriculture and gardening.

17.4 VALEDICTION

The above examples of green chemistry have no common theme. They comprise a series of attitudes rather than a coherent body of knowledge. One could not, for example, plan a degree course in green chemistry without having a prior requirement for a degree in chemistry. Nor are "green" routes to chemicals going to be adopted if they are economically inferior to less green routes. On the other hand, governments influenced by the green movement might well apply financial pressure to companies using less green processes, but are unlikely to do so unless alternative green routes exist. The preference for environmentally friendly routes could also influence companies in their choice of lines of research. "It is early days yet," the green chemist might say, "and if we keep in mind the commandments in Table 17.5, then the chemical industry of the future will be far more sustainable than in the past."

The issue of sustainability is more political and less tractable. It is easy to be cynical and to say that the whole "green" thing is a way of raising research money, and that the environmental movement is a middle class conspiracy to prevent developing countries and the poor in advanced countries from ever getting richer. It is equally easy to suggest that the movement is an alliance of noble idealists sacrificing themselves to halt the rape of the planet by a gang of profit-seeking capitalists (and Communists too—visitors to eastern Europe after the dissolution of the Soviet Union were appalled at the neglect of the environment). There are serious issues of sustainability and greenness not only within the narrow ambit of the chemical industry but on a global scale. As noted above, these are the subject of a huge literature and are beyond the scope of this book. We note merely that they have a political content, and that the things that get banned are not necessarily the things that damage the environment the most; they are often the politically easiest targets. That said, it is remarkable that governments are prepared, indeed eager, to legislate on environmental issues. Efforts to save the planet may be in vain, either because people in rich countries are unwilling to change their lifestyles or those in poor countries to reduce their birth rates, but the fact that so many people, including chemists, are concerned must offer hope for the future. There are still enormous gaps in scientific understanding of the interactions between the numerous variables affecting the global environment. Whatever earth's limitations are, it is to be hoped that mankind will not discover them by transcending them.

In conclusion, it is salutary to reflect on the different effects that sustainability and regulation have had on the organic and pharmaceutical industries, both of which, after all, are based on organic chemistry. The organic chemicals industry in developed countries faces the problems of maturity. In the 1990s, as noted in Chapter 1, in terms of sales growth in constant dollars, the European and Japanese industries grew not at all and the United States managed a miserly 1.1%/year. The industry faces the problem that its business is challenged by developing countries as the technology diffuses, and the compliance with environmental legislation in developed countries becomes increasingly expensive.

In the pharmaceutical industry, on the other hand, companies need to innovate to survive. They have to comply with FDA regulations and they have fewer worries about sources of raw materials. Few countries have the scientific resources to compete, and it is getting more difficult all the time. In the past generation, the only countries in the big league for pharmaceutical innovation were the United States, the United Kingdom, France, Germany, and Switzerland, with Japan and Sweden hoping to gain promotion. In the 1990s, everyone fell back relative to the United States, and more and more European companies are moving part or all of their research effort there. While the technology of the organic chemicals industry is diffusing ever further, the technology for modern pharmaceutical production seems to be getting less and less widespread. The irony of these opposite challenges will not be lost on the chief executives of the various multinational corporations that manufacture organic chemicals or pharmaceuticals or both.

NOTES AND REFERENCES

Section 17 The cited seminal books were R. Carson, *Silent Spring*, Houghton Mifflin, Boston, 1962 and D. H. Meadows et al., *The Limits to Growth*, Potomac Associates for the Club of Rome, Washington, DC, 1972.

Section 17.1 Most of the statistics in this section come from the *BP Statistical Review of World Energy*, 2002. It is published annually and copies are available for readers in the Americas from J. P. Morgan Chase Bank, PO Box 43013, Providence, RI 02940-3013. Everyone else should write to BP Distribution Services, 23 Hinton Road, Bournemouth, Dorset BH1 2EF, UK. It is also available at www.bp.com. BP's claim to raised extraction rates was in British Petroleum Company, *Our Industry Petroleum,* 5th ed., London, 1977, still one of the better books on the technical side of the oil industry. The early 1990s reserves estimate was in M. Tanaka *et al.*, *Energy conversion and management* **33**, 587 (1992).

Section 17.1.3.1 Details of the Middle Eastern initiatives in photovoltaic electricity will be found at www.solarbuzz.com/distributed generation. Costs of photovoltaic electricity in the United States appear much lower than in the Middle East and can be found at www.ncsc.ncsu.edu/fact/10body.htm. The Australian initiative is at www.ehpnet1.niehs.nih.gov/docs/2002/110-1/forum.html.

Section 17.1.3.2 A large group at Saarbrucken under H. Dürr works on artificial photosynthesis. See, for example, H. Dürr, S. Bossmann, R. Schwarz, M. Kropf, R. Hayo, and N. J. Tutto, *J. Photochem. Photobiol. A: Chem.* **80**, 341 (1994); H. Dürr, S. Bossmann, G. Heppe, R. Schwarz, U. Thierry, and H.-P. Trierweiler, *Proc. Indian Acad. Sci. (Chem. Sci.)* **105**, 435 (1993), and V. Schild, D. Van Loyau, H. Dürr et al., *J. Phys. Chem.* **A106**, 9149 (2002). Work on the production of molecules with sensitizer and quencher in the same molecule is reported in M. A. Fox, W. E. Jones, Jr., and D. M. Watkins, *Chem. Eng. News*, 38 (March 15, 1993), which also provides a detailed reading list. The two-step photoexcitation work is described by K. Sayama, K. Mukasa, R. Abe, Y. Abe, and H. Arakawa, *J. Photochem. Photobiol. A: Chem.* **148**, 71 (2002). A summary of research in this area is provided by J. R. Durrant, *Chem. Ind.* October 19, 1998, p. 838.

Section 17.1.4 Methane hydrate is featured in "Fire and Ice: the problems and promise of gas hydrates," *GTI Journal*, Summer 2002, 8–13. Figure 17.2 comes from an excellent background article on methane hydrate compiled by USGS, which can be found at http://www.net1.doe.gov/scng/hydrate/about-hydrates/about_hydrates.htm.

Section 17.1.5 We are grateful to Mr. Ronald Cascone of Nexant/Chemsystems for his assessment of the hydrogen economy. A vigorous attack on the idea is to be found at www.evworld.com/databases.

The point that hydrogen is not an energy source but an energy carrier seems to be overlooked in much of the less scientific literature. The energy roadmap unveiled in www.msnbc.com/news/834442.asp?vts=111320021210 and the associated sites assume cheerfully that hydrogen need only be obtained briefly from nonrenewable sources and after that wind or water power or something will come along.

The "Green" methanol process is described in *Eur. Chem. News*, **1–7**, 27 (October 2001).

Section 17.1.5.1 Much of this discussion came from N. Brandon, in *Encyclopedia of Energy*, Ed. C. J. Cleveland, Elsevier, Amsterdam, 2004, and N. Brandon and D. Hart, *An Introduction to fuel cell technology and economics*, Imperial College, London, Occasional paper #1.We have also drawn on J. Owen, *Chem. Ind.*, 572 (September 17, 2001), which also covers batteries and supercapacitators, the Department of Energy web site, www.eren.doe.gov/ hydrogen/infra, and Claire Curran, "Fuel cells—alternative energy?", *Chem. Ind.*, 767 (December 3, 2001). A recent book, E. Katz, A. Shipway and I. Willner, *Handbook of Fuel Cells*, Wiley, Chichester, 2003, discusses ethanol-based fuel cells and claims that ethanol as a fuel delivers 34% more energy than it takes to produce it (but cf. Section 14.5.5). See also R. Winder, *Chem. Ind.* September 1, 2003, p. 15.

DaimlerChrysler, Mercedes, Toyota, Ford, and Jeep have all built prototype fuel cell driven automobiles. See www.autoalliance.org/fuel_cells.htm. The direct methanol go-cart is illustrated in *Hydrocarbon Processing*, 15 (March 2002).

Section 17.2 The Toxic Release Inventory is published by the US Environmental Protection Agency, Office of Evironmental Information, Washington, DC 20460, www.epa.gov/tri/tridata.

Section 17.2.1 The basic chemistry of ozone depletion is to be found at www.nas.nasa.gov/about/education/ozone/chemistry, from which we have taken Figure 17.6. Conversion of methyl bromide to harmless bromides is reported in *Chem. Ind.*, 857 (November 6, 1995). The claims that much atmospheric methyl bromide is of natural origin appear in I. E. Galbally, J. D. Sekhon, and C. J. Marsden, *Clean Air* **25**, 100 (August 1991), and B. Selinger, ANUTECH, Environment Australia, HCB Waste: Background and Issues Paper, July 1995. There is a simplified discussion of the greenhouse gas issue in B. Selinger, *Chemistry in the Marketplace*, 5th ed. Harcourt Brace, Sydney, 1998. The request to allow methyl bromide use after 2005 was reported in *Chem. Eng. News*, February 17, 2003.

Section 17.2.2 Past and predicted levels of greenhouse gases are taken from *Intergovernmental Panel on Climate Change, Climate Change 2001: The Scientific Basis*, Contribution of Working Group 1 to the Third Assessment Report of the IPCC, Cambridge: CUP. *Ibid.* 2000, *Emission scenarios*. IPCC Special Report, Cambridge: CUP. Some of the participants at the Emission Scenarios workshop have questioned the scientific and statistical basis of the scenarios. We have drawn on an excellent report "Climate Change Science" from the Australian Academy of Technological Sciences and Engineering, 2002, www.atse.org.au.

Plans to sequester carbon dioxide in geological formations are discussed by B. Hileman, *Chem. Eng. News*, May 27, 2002, pp. 37–41.

Section 17.2.3.1 Richard Doll gave his estimate of the causes of cancer in R. Doll and R. Peto, *J. Natl. Cancer Inst.* **66**, 1191 (1981). He claimed 80% of cancers were environmentally produced: 30% were attributable to smoking, 3% to alcohol, and 1% to sexual behaviour. A more modern estimate would probably reduce the cancer rate, because fewer people smoke, and raise the obesity rate. We have taken DDT levels from B. Selinger, *op. cit.* p.174 and C. A. Edwards, *Persistent pesticides in the environment*, 2nd ed., CRC Press, Cleveland, OH, 1973.

There is a debate on brominated fire retardants between the industry associations and the environmentalists on the web. We have drawn on R. Renner, "PBDE Polybrominated diphenyl ether: what fate for brominated fire retardants?", *Environmental Science and Technology* May 1, 2000, American Chemical Society and *Chem. Brit.*, February 2003, p. 14.

Section 17.2.4 John Evelyn's pamphlet, *Fumifugium*, 1661, was reprinted by the UK National Society for Clean Air, 1961. Evelyn suggested that factories using coal should be moved further down the Thames Valley and a green belt of trees put around the center of the city "to rid London of the columns and clouds of smoke which are belched forth from the sooty throates of (those shops) rendering (the city) in a few moments like the picture of Troy sacked by the Greeks or the approaches of Mount Hecla." A more detailed discussion of the events surrounding the UK Clean Air Act will be found in B. G. Reuben and M. L. Burstall, *The Chemical Economy*, Longman, London, 1973.

Section 17.2.4.1 A summary of flue gas desulfurization processes is given by D. Strauss, "Formation and Control of Air Pollutants," in *Environmental Chemistry*, J. O'M. Bockris, Ed., Plenum, New York, 1977, pp. 179–212.

The proposed US regulations on low sulfur fuels are attractively explained in the China Forum of www.fossil.energy.gov. For an economic analysis of the cost of low sulfur fuels, see www.epa.gov/otaq/regs and *Chem. Brit.* **38**, 13 (2002).

Reports on changes in sulfur dioxide levels and their effect on global warming and the ozone layer will be found at www.volcanoes.usgs.gov/About/What/Monitor/remoteSensing/TOMSRSensing.html, www.epa.gov/air/aqtrnd95/so2.html, www.meteor.iastate.edu/gcp/studentpapers/1996/atmoschem/huff.html, and www.enn.com/news/enn-stories/1999/07/071999/sulfur_4414.asp

Section 17.2.4.2 Figure 17.7 is taken from I. M. Campbell, *Energy and the Atmosphere*, John Wiley & Sons, Inc., London, 1977. The smog model given in B. G. Reuben and M. L. Burstall, *The Chemical Economy*, Longman, London, 1973, p. 487 now seems embarrassingly dated. The change has come about because the development of atomic titration techniques has enabled the rate constants of hydroxyl radical reactions to be determined, and they dominate the modern mechanism. The authoritative book, J. H. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution*, John Wiley & Sons, Inc., Chichester, 1986, is now somewhat dated, but there is apparently a new edition, J. H. Seinfeld and S. N. Pandis, *From Air Pollution to Climate Change*, John Wiley & Sons, Inc., Chichester, 1998. The topic of smog is treated comprehensively on the web. See D. Daescu, A generalized reaction mechanism for photochemical smog, www.ima.umn.edu/~daescu/proj.html, M. Azzi, M. Cope, and P. F. Neso, Photochemical smog modeling using the generalized reaction scheme model, www.dar.csiro.au/publications/manins_2002axx.pdf, P. Viaene, W. Debruyn, F. de Leeuw, and C. Mensink, Evaluation of a compact chemical mechanism for photochemical smog modeling, http://artico.lma.fi.upm.es/gloream/ paper10/,and Photochemical Smog, http://jan.ucc.nau.edu/~doetqp-p/courses/ env440/env440_2/lectures/lec40/lec40.htm. The last of these is particularly good on the large number of nitrogen compounds formed.

Section 17.2.6 Figure 17.9 is taken from the US Environmental Protection Agency web site on municipal solid waste, www.epa.gov/epaoswer/non-hw/muncpl/facts. There are associated web pages dealing with waste disposal.

One of us (BGR) attended a school in Bradford, Yorkshire, England, built in 1939 on a controlled landfill site and watched football at a stadium constructed on a similar site.

The situation in Mediterranean countries including Israel is reviewed by M. R. Shadras, *Solid Waste Disposal in Eastern European Countries*, Ph.D. Thesis, South Bank University, London, 1992. The argument that land prices will be so high near a city as to make landfill uneconomic is not viable. The presence of a dump will reduce land values around it but, even at standard land prices, purchase of a landfill site, except perhaps right in a town center, is still the most economic option, although it would be forbidden by zoning and related regulations. The issue is discussed in detail in Shadras, *op. cit.*, and D. C. Wilson, *Waste Management: Planning, Evaluation, Technology*, OUP, Oxford, 1981.

The landfill gas life cycle (Fig. 17.10) comes from P. N. Cheremisinoff and A. C. Moresi, *Energy from Solid Wastes*, Dekker, New York, 1976. This section is based on R. M. E. Diamant, "The chemistry of sewage putrefaction," in *Environmental Chemistry*, J. O'M. Bockris, Ed., Plenum, New York, 1977.

Section 17.2.6.3 British emissions of mercury are published by the National Atmospheric Emissions Inventory, www.aeat.co.uk/netcen/airqual/index.html. Data given here were reported in the UK parliamentary transcript, *Hansard*, October 8, 2001.

Section 17.2.7 We have drawn on J. B. Phillips, M. A. Hindawi, A. Phillips, and R. V. Bailey, "Thermal Solutions to Petrochemical Waste" www.pollutionengineering.com/archives/2000/pol0801.00/pol0800multi.htm together with M. B. Borup, and E. J. Middlebrooks, *Pollution Control for the Petrochemicals Industry*, Lewis; Chelsea, MI, 1987 and D. J. Burton, and K. Ravishankar, *Treatment of Hazardous Petrochemical and Petroleum Wastes: Current, New and Emerging Technologies*, Noyes; Park Ridge, NJ, 1989.

Section 17.3 The launch of green chemistry as a discrete discipline has led to the appearance of a number of books that, one has to admit, bear rather depressing similarities. We have the impression that more books were published on this topic than on any other branch of chemistry during the 1990s. We have tried to get an overview of current areas of interest from *Green Chemistry*, P. T. Anastas and T. C. Williamson, Eds., ACS Symposium Series No. 626, Washington, DC, 1996; *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*, P. T. Anastas and T. C. Williamson, Eds., OUP, Oxford, 1998; *Green Chemical Syntheses and Processes*, P. T. Anastas, L. G. Heine, and T. C. Williamson, Eds., ACS Symposium Series No. 767, Washington, DC, 2000, *Green Chemistry: Challenging Perspectives*, P. Tundo and P. T. Anastas, Eds., OUP, Oxford, 2000, and J. H. Clark and D. J. McQuarrie, *Handbook of Green Chemistry and Technology*, Blackwell, Oxford, 2002. The pollution problem from polymers is different from that with chemicals and is discussed in A. Azapagic, A. Emsley, and I. Hamerton, *Polymers, the Environment and Sustainable Development*, John Wiley & Sons, Inc., Chichester, 2003.

The UK Royal Society of Chemistry has responded to the trend by starting a new journal *Green Chemistry* and there is also an encyclopedia of "green" chemicals that may be used to replace other less beneficent materials. They are classified, for example, as not-CFCs. The encyclopedia is M. & I. Ash, *Handbook of Green Chemicals, Synapse Information and Resources*, Endicott, New York, 1998. Two helpful overview articles are S. K. Ritter, *Chem. Eng. News* July 16, 2001, pp. 27–34, Green Chemistry gets Greener, *ibid.*, May 20, 2002, pp. 38–42. Routes to dimethyl carbonate in the mid-1990s are reviewed by F. Rivetti, U. Romano, and D. Delledonne, ACS Symposium Series No. 626, *op. cit.*, pp. 70–80.

Section 17.3.2 The Flixborough disaster is described in H. A. Wittcoff and B. G. Reuben, *Industrial Organic Chemicals in Perspective, Part 1*, John Wiley & Sons, Inc., New York, 1980, pp. 257–258. The cyclohexene based route to adipic acid is described in *J. Chem. Educ.* **77**, 1627 (2000).

A non-phosgene route to polycarbonates is described in K. Komiya et al., in ACS Symposium Series No. 626, *op. cit.*, pp. 20–33. W. D. McGhee *et al.* describe the generation of organic diisocyanates from amines, carbon dioxide, and electrophilic dehydrating agents such as *o*-sulfobenzoic anhydride in ACS Symposium Series No. 626, *op. cit.* pp. 49–58.

Section 17.3.5 The isophorone hydrogenation is described in *Chem. Eng. News* 19, November 25, 2002. Figure 17.12 is based on J. W. Tester *et al.*, Supercritical fluids as solvent replacements in chemical synthesis, ACS Symposium Series No. 767, *op. cit.* pp. 270–291.

Section 17.3.6 There is already a book on ionic liquids in industry, even though there are not yet commercial applications. It is R. D. Rogers and K. R. Seddon, *Ionic Liquids: Industrial Applications to Green Chemistry*, ACS Symposium Series No. 818, Washington, DC, 2002, also published by OUP, Oxford, 2002.

Section 17.3.7 The oxidation of di-*tert*-butylphenol is described in *J. Am. Chem. Soc.* **124**, 2513 (2002) and S. K. Ritter, *Chem. Eng. News*, May 30, 2002, p. 39.

K. A. Axelsson and L. J. Dunne, *J. Photochem.* **44**, 205 (2001) describe the photocatalytic destruction of dichlorobenzenes.

Section 17.3.8 H. Pütter and H. Hannenbaum were given a BASF innovation award in 1999 for this process. Details are given on various pages within www.basf.de.

Section 17.3.9 The conventional sertraline synthesis is taken from A. Kleemann, J. Engel, B. Kutscher, and D. Reichert, *Pharmaceutical substances, syntheses, patents and applications*, 4th ed, Thieme, Stuttgart, 2001. The "green" sertraline story is told in *Chem. Eng. News* April 22, 2002, p. 30 and *Chem. Eng. News* July 1, 2002, p. 29.

Section 17.3.10 The catalytic dehydrogenation of diethanolamine won the United States Environmental Protection Agency's 1996 Alternative Synthetic Pathways Award for Monsanto. Details are at www.epa.gov/greenchemistry/aspa96.html.

Section 17.3.12 The polylactate and Biopol stories come from S. K. Ritter, *Chem. Eng. News*, July 1, 2002, pp. 267–70 and C. Boswell, *Chem. Mkt. Rep.* August 20–27, 2001.

There is a constant battle between "green" and "anti-green" campaigners, and there are signs that the period of ascendancy of the "greens" on the European Commission is being threatened. Their high water mark seems to have been a 2001 White Paper demanding that the chemicals in use before 1981 should be brought within the regulatory framework. This would have involved 30,000 substances (including phthalates) and would have cost ~$2 billion. A new Competitiveness Council, set up in June 2002, pays lip service to sustainable development but also notes that "the deteriorating economic and industrial situation in the European Union makes it urgent to pay attention to European competitiveness and jobs" and even speaks of "biotech applications in healthcare, agriculture and foodstuffs," which is a euphemism for genetically modified crops. C. Mortished, *London Times*, November 27, 2002, p. 30, wonders if the European Commission is finally wriggling free of the green grip but comments sourly that "it may be too late to save Europe's rusting chemicals industry, which is closing down not because of Brussels (the seat of the European Commission) edict but by virtue of market forces . . . which have left chemicals firms in a constant state of restructuring, selling or shutting down plant . . . ."

APPENDIX 1

A NOTE ON COST CALCULATIONS

The accounting side of the chemical industry is perhaps even more complicated than the chemical side. A large chemical company will by law prepare an annual set of accounts (shareholder accounts) on a basis agreed between the company's accountants and its auditors, and as defined by legislation, regulation, and best practice. It will also produce a second set of accounts (tax accounts), used to calculate taxes, on a basis laid down by the Inland Revenue Service and legislation. A third set of accounts (management accounts), produced at monthly or weekly intervals, will be for the management, who will use it as a base for its decisions. From the point of view of this book, we are concerned with the items that are taken into account to estimate the cost of manufacture of a particular chemical.

The traditional method of costing a product was to include everything that contributed to its cost, which was called total costing. The items are shown on the left-hand side of Figure A.1. The right-hand side shows the revenue obtained from a sale of the main chemical (ethylene is the example) and possible coproducts (e.g., propylene, butadiene, and butenes).

The total cost is made up of variable costs plus fixed costs. Variable costs are more or less directly proportional to output; fixed costs are independent of output. Raw materials are generally the main variable cost, but one should also add catalyst, which needs regeneration and renewal, and additional chemicals used perhaps in the separation processes. Variable costs also include utilities—water, electricity, gas from outside sources—and bought-in services. The latter would be negligible in the

---

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

case of an ethylene cracker but would be larger in cases where more activities were out-sourced.

Fixed costs are those more or less independent of output and are made up of overheads, depreciation, interest on loans and labor (if that is company policy, otherwise they would be variable costs—see below). Overheads are costs that cannot be attached to any specific cost center, and are distributed between the various cost centers in a company on a predetermined basis. Overhead costs include head office costs, security personnel, research and development costs, plant maintenance, property taxes, insurance, lease rentals, sales programs, and certain other administrative expenses. (In the United Kingdom, the basis of rates is the ratable value of the property not of the land. It is a property tax not a land tax.)

None of these overhead costs are part of the direct production cost of the chemical being considered, but under total costing such costs have to be recovered for the company to be profitable. Fixed costs are further subdivided under two headings. Direct fixed costs are made up of operating costs from labor, maintenance, and direct overhead charges. Allocated fixed costs include general plant overhead, insurance, and property taxes. These costs are mostly site-related. If an environmental levy were charged, it would come under this heading.

Depreciation is an annual noncash accounting cost to recover the capital cost of the investment. In the nineteenth century, this money was put in a separate account called a sinking fund and could be used to rebuild a plant when it wore out. Today, there is no separate depreciation reserve—instead, the annual depreciation charge reduces the company's profits to reflect the ageing of the plant. The rate at which assets are depreciated is at the discretion of the company's accountants and auditors and will usually differ from the rules laid down by the Internal Revenue Service, who will base taxation on legislation and the tax accounts. If the company has borrowed money to finance its plant, interest on loans will be a fixed cost. This is called the finance cost and is included within the shareholder accounts and the tax accounts. If the company had used surplus funds to finance the plant, the management accounts may include an opportunity cost of capital, but only if it were the policy of the company. Opportunity cost is defined as the rate of return that could have been earned had the surplus funds been otherwise invested.

In-between the fixed and variable costs in Figure A.1, we have inserted the cost of labor. There has been much debate as to whether labor should count as a fixed or variable cost. In the nineteenth century, the foreman at a chemical plant could open the gates at 6 a.m. and sign on the exact amount of casual labor that he needed for the day. Labor was thus related to the output required and was truly a variable cost. In the chemical industry today, workers are generally highly trained and cannot be recruited or dismissed on a daily basis. Furthermore, a plant operating at 50% capacity requires exactly the same number of operatives as when it works at 100% capacity. Hence, a modern trend in the chemical industry is to treat labor as a fixed cost that is independent of output. To avoid ambiguity, the term cash cost includes raw materials, utilities, bought-in services, labor, and overheads, that is, a combination of fixed and variable costs.

The revenue received from the sale of the chemicals minus the total cost and other noncash charges is the pretax profit, some of which is owed to the Internal Revenue

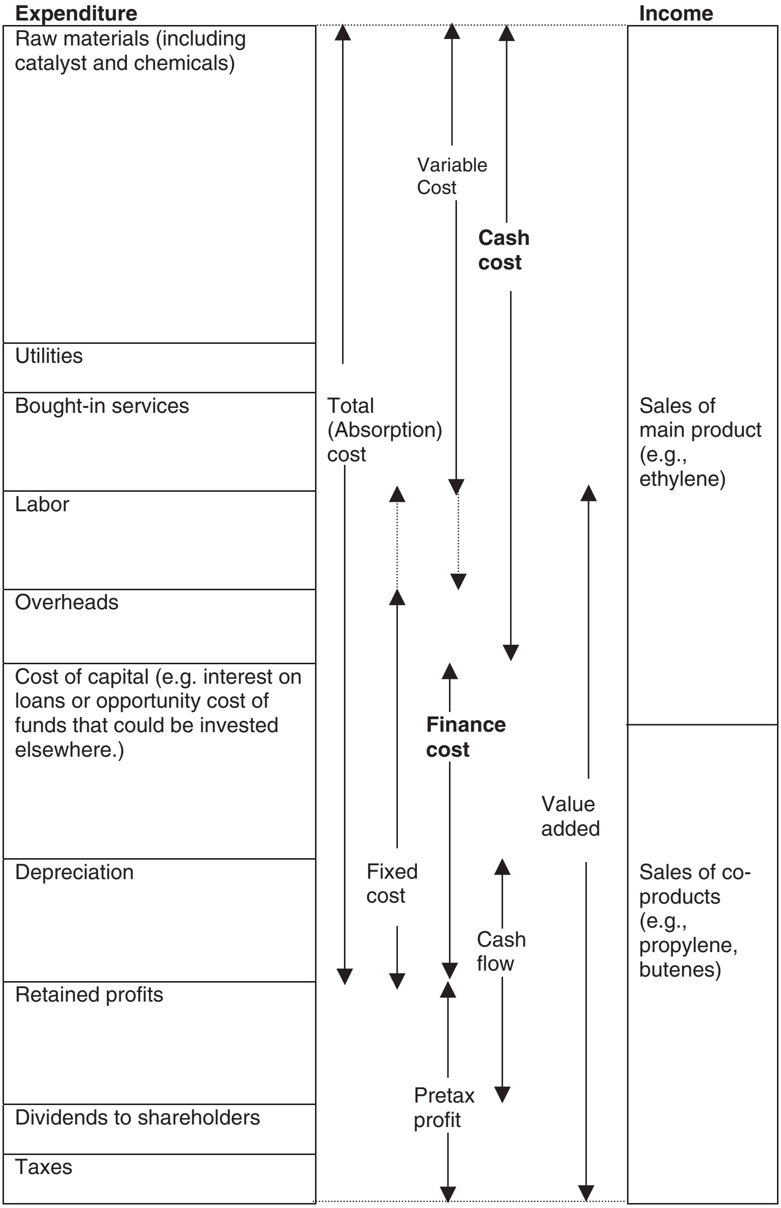


FIGURE A.1 Terms used in cost calculations. The size of the blocks attached to each item are arbitrary and do not correspond to any real costing.

Service as taxes. Some is distributed to the shareholders and some is retained to finance the company's expansion.

The cash flow has traditionally been defined as the combination of profits and depreciation. More definitively, it may be described as the surplus of cash received over cash paid from operations plus the net cash received from activities including financing (i.e., cash received from taking on loans and the issue of new shares) and investing (such as the acquisition of fixed assets or of a company). Value added is the amount added to the inputs by the company's efforts, hence it is the sales revenue minus raw materials, utilities and bought-in services.

Under total costing, the total costs must be recovered by the revenue. However, the use of total costing as a basis for decision making and pricing decisions has been criticized in that, for example, allocation of overheads is arbitrary, and past investments are "sunk" costs. For example, once the plant is built, there is no way one can recover the cost of building it, and as such should be ignored for decision making purposes. In addition, allocation of overheads is a zero sum game, that is, the net profit will be the same however they are allocated within a company's profit and loss account. The "sunk cost" approach is satisfactory if business improves each year. If it does not, depreciation accounting is the better part of valor.

In respect to pricing decisions, the loading of research costs for future products onto current products can be misleading. For example, many pharmaceutical companies claim that it costs them more to manufacture acetaminophen than it costs a generics company, because the research costs for the development of future products need to be included, even though these research costs are not part of the production cost of acetaminophen.

Hence, short-term management decisions tend to be based on cash costs. This is crucial. Suppose prices are dropping. If revenue drops below the *total cost*, in the short term the optimal decision may be to continue production as long as revenue is in excess of the variable costs. Technically, one is making a loss, but one would make a larger loss if one ceased production, because any excess of revenue over the variable costs contributes to fixed costs, which have to be paid anyway. If the price drops below the variable cost, then it is sensible to cease production. In the long term, if the price falls below total cost, the optimal decision would be to cease production.

In the long run, all costs become variable costs. Employees can retire or be made redundant. Plant wears out and does not need to be replaced. The total cost of the reinvestment option then needs to be considered. Once the money has been spent, however, the finance costs again become sunk costs and decisions are taken on the basis of variable and fixed costs.

APPENDIX 2

UNITS AND CONVERSION FACTORS

Weight

thousand lb	tonnes (metric tons or thousand kg)	long tons	short tons
1	0.4536	0.4464	0.5000
2.2046	1	0.9842	1.1023
2.2400	1.0160	1	1.1200
2.0000	0.9072	0.8929	1

Volume

liters (10^{-3} m^3)	cubic feet	US gallons	Imperial gallons
1	0.03532	0.2642	0.2200
28.32	1	7.481	6.229
3.785	0.1337	1	0.8327
4.546	0.1605	1.201	1

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

Pressure

atmospheres	bar	torr (mm Hg)	psi	kg cm^{-2}
1	1.01325	760	14.696	1.033
0.9869	1	750.06	14.504	1.020
0.001316	0.001333	1	0.01934	0.00136
0.06805	0.06895	51.715	1	0.0703
0.968	0.980	735.3	14.225	1

(1 bar = 10^5 Pascal or Nm^{-2})

Temperature

Expressed as °C (= degrees centigrade or degrees celsius)
Degrees Fahrenheit (°F) = 1.8(°C) + 32
(°C) = 0.556(°F − 32)
kelvin (K) = (°C) + 273.15
0 K = −273.15°C = −459.7°F

Heat

kJ	kcal	Btu (10^{-5} therms)
1	0.239	0.948
4.184	1	3.968
1.054	0.252	1

One tonne of oil is equivalent to
3.97×10^7 Btu
0.01 teracalories
0.042 terajoules

1.5 tonnes of coal (typical calorific value)
3 tonnes of lignite (typical calorific value)

0.805 tonnes of LNG
1111 m^3 of natural gas
39,200 cubic feet of natural gas

12,000 kWh of electricity

One ft^3 of natural gas = 1000 Btu
One m^3 of natural gas = 9000 kcal = 37,600 kJ
One kWh = 3412 Btu = 860 kcal

Noble Metals

Noble metals—gold, silver, platinum, palladium, rhodium, etc.—are traded in ounces. These are not the familiar avoirdupois ounces (= 28.35 g) but troy or apothecary ounces (= 31.15 g). One ounce troy = 1.097 ounces avoirdupois. 1 lb troy = 12 oz troy; 1 lb avoirdupois = 14.58 oz troy. 1000 oz troy = 31.15 kg = 0.03115 tonnes.

APPENDIX 3

SPECIAL UNITS IN THE CHEMICAL INDUSTRY

PETROLEUM AND REFINERY PRODUCTS

Crude oil and some refinery products are traded in barrels (bbl) of 42 US gallons (gal) (= 35 Imperial gal). As the gallon is a unit of volume, the weight of a barrel depends on the density of the product. Approximate conversion factors follow:

1000 lb = 3.32 bbl crude oil, 3.83 bbl gasoline, 3.54 bbl kerosene,
3.40 bbl gas oil, and 3.04 bbl fuel oil.
1 tonne = 7.33 bbl crude oil, 8.45 bbl gasoline, 7.80 bbl kerosene,
7.50 bbl gas oil, and 6.70 bbl fuel oil.

Liquefied petroleum gases are sold by the US gallons or by the tonne. One tonne contains 521 gallons of propane, 453 gallons of *n*-butane or 469 gallons of isobutane. LPG can be mainly propane, mainly butane, or a “mixed” cargo, in which case intermediate conversion factors based on composition must be applied.

GASES

Natural gas is measured in standard cubic feet (scf) at 1 atmosphere (atm) and 60°F or in cubic meters (m^3) at 1 atm and 0°C. $1\ m^3 = 37.33$ scf; $1\ \text{scf} = 0.0268\ m^3$.

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff,
Bryan G. Reuben, and Jeffrey S. Plotkin
ISBN 0-471-44385-9

Thermal units (heat liberated when a volume of gas is burned) are sometimes used. Calorific values depend on the composition of the gas but are usually 900–1000 Btu scf^{-1}. Accordingly 1 therm = 10^5 Btu = 100–110 scf.

Other gases are also measured in scf and m^3. If the molecular weight of a gas is M, then 10^6 scf of the gas weigh 2.635 M thousand lb. For example, 10^6 scf of hydrogen weigh 5.312 thousand lb and of oxygen 84.32 thousand lb. Similarly, 1000 m^3 of a gas weigh 0.0446 M tonnes. 1000 m^3 of hydrogen weigh 0.0900 tonnes and of oxygen 1.427 tonnes.

COAL TAR PRODUCTS

Coal tar and materials traditionally derived from it such as benzene, toluene, and xylenes are sometimes measured in thousands of US gallons. One thousand US gallons of benzene at 20°C weigh 7320 lb, of toluene 7210 lb, of *o*-xylene 7300 lb, of *m*-xylene 7161 lb, and of *p*-xylene 7134 lb.

ETHANOL

Ethanol is measured in mixed volume and concentration units. One Imperial gallon (1.201 US gal) of 100% ethanol contains the same amount of ethanol as 1.75 proof gal, and concentration is measured in degrees proof. The specific gravity of ethanol is 0.79, hence 1 proof gal contains 4.5 lb (2.04 kg) ethanol. It is also the alcoholic equivalent of a US liquid gal at 15°C containing 50% ethanol by volume. The metric units are hectoliters (= 100 liters), and concentration is expressed in degrees Gay-Lussac. Ninety-five degrees Gay-Lussac represents 95% by volume at 15°C. One hectoliter = 22 Imperial gal = 26.4 US gal. One hectoliter of 100% ethanol weighs 174 lb (79 kg). The US liquid gallon (as above) is identical with the Queen Anne wine gallon. A US tax gallon for spirits of 100 proof or over is equivalent to the proof gallon; for spirits of less than 100 proof, to the wine gallon.

INDEX

Industrial Organic Chemicals, Second Edition, by Harold A. Wittcoff, Bryan G. Reuben, and Jeffery S. Plotkin
ISBN 0-471-44385-9