Survey of Industrial Chemistry

Third Edition

Philip J. Chenier
University of Wisconsin–Eau Claire
Eau Claire, Wisconsin

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Preface

This book arose from the need for a basic text dealing with industrial chemistry for use in a one-semester, three-credit senior level course taught at the University of Wisconsin–Eau Claire. The course was added as a requirement for our B.S. degree in Chemistry with Business Emphasis and is strongly recommended as an elective in our other chemistry majors, including our American Chemical Society–accredited program. There are some good extensive texts and valuable reference works dealing with applied chemistry. What was needed for our course, and what I believe will be useful for similar courses at the graduate or advanced undergraduate level, is a basic text of introductory material, sufficient to cover all important areas of the chemical industry, yet limited in scope so that completion of the book in 40 to 45 hours of lecture may be a reasonable goal.

The book is also an excellent resource and reference for persons working in the chemical and related industries. It has sections on all important technology used by these industries and therefore is a one-step source for answers to most questions on practical applied chemistry. Young scientists and engineers just entering the workforce will in particular find it useful as a readily available handbook to prepare them for a type of chemistry quite different from what they have seen in their traditional coursework, whether graduate or undergraduate. Chemists and chemical engineers at every level of education and experience will have at their disposal a valuable resource.

Industrial chemistry means different things to different people. Most will agree that the phrase includes the practical applied chemistry that bridges the gap between basic research and development and at least two other disciplines, chemical engineering and chemical marketing. The present text attempts to lessen the lack of knowledge that most graduates have in both of these areas. Some attempt is made to instill in chemists an appreciation for both the manufacturing and the economic problems facing the chemical industry on a day-to-day basis, as well as to introduce them to the chemistry used by our industry every day. Although some space is devoted to economics and engineering, this is largely a chemistry book, and chemical reactions and processes, even mechanisms of reactions, are given full coverage.

In developing such a book the toughest job is always deciding what to include. I have tried to cover a little of everything, since the text is meant to be a survey of important sectors of industrial chemistry. The manufacture and uses of the top 100 basic chemicals are covered in detail. The chemistry of all important industrial polymers is included and their applications are discussed. Finally, certain selected specific technologies, the most important of the many areas that chemical manufacturing covers, are given one chapter each. If one measures treatment in terms of the value of shipments, the book covers more than 90% of the chemical industry, as well as providing information on other industries separate from chemical manufacturing that also contain interesting chemistry and employ many chemists, such as the paper, petroleum and coal products industry, and the plastics and rubber products industry.

Perhaps the most challenging part of teaching this course and of writing a good text is to keep the important economic data current. In some cases this is done easily; in others it is difficult. Rather than having to revise this material yearly or even monthly with changing economic times, I have had recourse to some references to periodic updates that students can consult for the latest data. An example of these series is "Chemical Profiles" in *Chemical Marketing Reporter.* Government figures are a particular challenge, since official numbers for shipments are not available in *Annual Survey of Manufactures* until three years later. But even those numbers give students a general feel for the economic trends of the industry. It is virtually impossible for a text to remain economically accurate and complete for more than a year or two, and the present text is no exception. In presenting this material in class I update these data periodically. The graphs and charts are easily updated for a course. The course material is also supplemented with over 200 color slides of various chemical plants, manufacturing sites, and research labs I have visited.

To attempt to thank everyone who has helped me expand my knowledge of this subject would be an impossible task, but certain organizations deserve a special mention. A University of Wisconsin System Undergraduate Teaching Improvement Grant allowed me to plan the course initially during one summer. University of Wisconsin–Eau Claire Faculty Development

Grants enabled me to visit chemical plants throughout the United States to get firsthand experience in manufacturing. They also funded some release time for one semester in which I wrote a portion of an earlier version of this book. A number of companies let me visit their facilities, talk with their personnel, and obtain pictures for use in the course. Their names are given in the figure captions. I also thank the Department of Chemistry at UW–Eau Claire for allowing me to develop and teach the course, and to the students who have given me valuable feedback on the course and book. In particular, I wish to thank the following students who have done research for me in connection with the preparation of materials used in the book: Danette Artibee, Lisa Bauer, Christine Benter, Leslie Bresina, Andrea Halberg, Kristin Halverson, Dawn Schroeder, Rich Vehlow, and Jennifer White. Thanks also to Michael Carney, Melvin Gleiter, Ben Etzkorn, and Paul Houslet who helped with information and proofing. Finally, I wish to thank one individual, Dr. Harold Wittcoff, who first got me interested in teaching industrial chemistry when I audited his graduate course during a sabbatical at the University of Minnesota.

Philip J. Chenier
January 2002

About the Author

Philip J. Chenier is Emeritus Professor of Chemistry at the University of Wisconsin-Eau Claire, which he joined in 1970. He has worked for General Mills Chemicals and 3M Company. Dr. Chenier received his B.A. from St. Mary's College, Winona, Minnesota, and his Ph.D. from Loyola University, Chicago, Illinois. He has done post-doctoral work at the University of Minnesota. He has published extensively in research and scholarly journals, and earlier versions of his book on industrial chemistry have been used by various schools since 1986. He has developed and taught an industrial chemistry course for the past twenty years.

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Chapter 1

Introduction to the Chemical Industry: An Overview

1. THE NATIONAL ECONOMY

Before beginning a detailed discussion of the chemical industry, we should have a basic appreciation for the main sectors of a developed economy so that we may understand the role that this industry plays in the overall picture. Table 1.1 gives the major divisions of the U.S. economy along with their official designations or Standard Industrial Classifications (SIC) by the U.S. Bureau of Census. A similar classification system is used in Western Europe, Japan, and other complex societies. These sectors are separate but interdependent. For example, manufacturing draws on mining to buy iron ore for steel manufacture. The manufacturing sector also converts steel to machinery to sell back to mining for its operations.

The third column gives an estimate of the size of these various sectors in terms of value added in billions of dollars. The value added is simply the difference between the output (goods and services) and the input (labor, land, and capital) of the industry. The total value added, $8,759.9 billion in 1998, is the gross domestic product (GDP) for the entire economy. This is the latest year that official government figures are available at the time of this writing.

Although the numbers change each year, percentages of each sector do not change very much. Note that manufacturing is one of the largest sectors in terms of value added and amounts to about 16% or almost one sixth of the GDP. The chemical industry is a part of this manufacturing sector.

Table 1.1 U.S. Gross Domestic Product by Industry

Industry	SIC	Value Added ($ billion)
Agriculture, forestry, and fishing	01-09	125.2
Mining	10-14	105.9
Construction	15-17	373.2
Manufacturing	20-39	1,432.8
Transportation and public utilities	40-49	759.1
Wholesale and retail trade	50-59	1,395.7
Finance, insurance, and real estate	60-67	1,674.2
Services	70-97	1,841.3
Government	98	1,100.1
Gross Domestic Product (GDP)		8,759.9

Source: Statistical Abstract of the United States

2. DEFINITION AND DIVISIONS OF THE CHEMICAL INDUSTRY

2.1 Chemical Process Industries

Just what exactly do we mean when we refer to "the chemical industry"? This is a general term that may mean different things to different people. In the manufacturing sector the U.S. switched from the SIC classification to the North American Industry Classification System (NAICS) in 1997. A very broad interpretation of the phrase "the chemical industry" might, according to the NAICS classifications, refer to the *chemical process industries* that include the following areas: Paper Manufacturing (NAICS 322), Petroleum and Coal Products Manufacturing (324), Chemical Manufacturing (325), Plastics and Rubber Products Manufacturing (326), and Nonmetallic Mineral Product Manufacturing (327). These are some of the manufacturing sectors dealing heavily in chemicals and chemical products, as listed in Table 1.2. However, this broader interpretation for the chemical industry is not commonly used.

Table 1.2 U.S. Chemical Manufacturing vs. Other Manufacturing Industries

NAICS	Industry	Value Added ($ billion)	Shipments ($ billion)
311	Food	175.4	431.8
312	Beverage and Tobacco Products	62.7	103.0
313	Textile Mills	24.0	57.6
314	Textile Products	13.4	31.5
315	Apparel	32.1	65.5
316	Leather and Allied Products	4.8	10.3
321	Wood Products	34.7	92.1
322	Paper	72.9	156.3
323	Printing and Related Support Activities	61.0	101.3
324	Petroleum and Coal Products	30.7	137.1
325	Chemical	236.1	424.2
326	Plastic and Rubber Products	85.5	164.0
327	Nonmetallic Mineral Products	52.9	92.9
331	Primary Metal	69.0	166.3
332	Fabricated Metal Products	139.4	253.3
333	Machinery	141.0	280.9
334	Computer and Electronic Products	255.3	440.3
335	Electrical, Appliances, and Components	59.4	116.8
336	Transportation	245.1	612.1
337	Furniture and Related Products	38.1	70.4
339	Miscellaneous	65.5	107.0
31-33	**Manufacturing**	**1,899.2**	**3,914.8**

Source: Annual Survey of Manufactures

2.2 Chemical Manufacturing

Most people, when referring to the chemical industry, really have in mind one specific division of manufacturing which is classified as Chemical Manufacturing (NAICS 325). Note that it is the fourth largest division of manufacturing in terms of manufacturers' shipments, which is the usual dollar amount quoted in the manufacturing sector to estimate division size. Shipment figures are easier to calculate than value added. The relationship between shipments and value added is given by the following expression:

value added = (shipments + services rendered) – (cost of materials, supplies, containers, fuel, purchased electricity, and contract work)

Table 1.3 Divisions of U.S. Chemical Manufacturing

NAICS	Industry	Shipments ($ billion)	%
3251	Basic Chemicals	110.0	25.9
3252	Resin, Synthetic Rubber, Fibers, Filaments	63.3	14.9
3253	Pesticide, Fertilizer, Other Agricultural Chemicals	24.3	5.7
3254	Pharmaceuticals and Medicine	103.0	24.2
3255	Paints, Coatings, and Adhesives	27.2	6.4
3256	Soap, Cleaning Compounds, Toilet Preparations	58.5	13.8
3259	Other Chemical Products	37.8	9.0
325	**Chemical Manufacturing**	**424.2**	**100.0**

Source: Annual Survey of Manufactures

In 1998 Chemical Manufacturing had shipments totalling $424.2 billion, or about 11% of all manufacturing. Unless specified otherwise, when we use the term *chemical industry* we mean this division.

What does Chemical Manufacturing include? This is summarized in Table 1.3 in terms of shipments. Note that Basic Chemicals is the largest division in percentage for shipments, and Pharmaceuticals and Medicine is a close second. We will cover the interesting chemistry and characteristics of each of these sectors in this book.

2.3 Complexity in the Chemical Industry

The chemical industry is actually a set of related industries with many diverse functions and products. Certain raw materials are used to prepare key chemicals, monomers, and intermediates that may be sold independently or used directly in additional steps to give various polymers and end chemicals. These in turn can be formulated and fabricated into chemical products, which can sometimes be modified into finished products. There is a flow of materials and products from raw sources to finished formulations. Although the division is approximate, about 60% of the chemical industry manufactures industrial products that are further modified, whereas 40% of their products are sold directly to the consumer. Chemistry may not be a household word, but it should be. Actually, the older name for the Chemical Manufacturing sector is Chemicals and Allied Products, still used sometimes and a term that adequately describes the breadth of the industry.

Further proof of complexity in the chemical industry is apparent in other statistics. There are over 12,000 manufacturing plants in operation in the

Table 1.4 U.S. Shipments

Year	All Manufacturing ($ billion)	Chemical Manufacturing ($ billion)
2000	4,514.3	438.8
1999	4,259.5	413.3
1998	4,052.2	391.8
1997	3,929.4	389.2
1996	3,735.4	372.8
1995	3,566.9	358.5
1994	3,433.8	333.3
1993	3,127.6	314.9
1992	3,004.7	305.4
1991	2,878.2	298.5
1990	2,912.2	292.8

Source: Chemical and Engineering News, "Facts and Figures for the Chemical Industry"

U.S. Over 55,000 chemicals are commercially produced, but only 10% of these account for over 99.9% of production and are made in excess of 1 million lb/yr in the U.S. The top chemical companies have a small percentage of sales compared to other industries like automobiles, airplanes, tires, and glass, where 80-99% of sales are taken by the top eight companies or less. Diversity of products in companies has increased in the last few years. Before 1940 chemical companies sold nothing but chemicals. Although some are primarily chemical, others have diversified so that it is possible to have chemicals account for a smaller percentage of the company's sales. Corporations such as the petroleum companies have chemical sales with a very low percentage of total sales.

3. SIZE AND CURRENT ECONOMICS OF THE CHEMICAL INDUSTRY

How big is the chemical industry? This is a difficult question to answer. What should be the best determining factor? One good measure of size is dollar value of shipments reported. Table 1.4 shows that this industry had shipments of $438.8 billion in the year 2000 compared to all manufacturing at $4,514.3 billion.

Despite periodic slowdowns in the economy the chemical industry continues to grow. From 1970-1980 it grew 13% per year (called an *average annual change*) whereas all manufacturing grew 11% per year. In 1980-1990 chemicals had an average annual change of 5% while manufacturing increased 4%. From 1990-2000 chemicals went up 4.1% per year and manufacturing 4.5%. It is unusual for shipments of chemicals to go down in a particular year, though it does happen in bad economic times.

To whom does the chemical industry sell all of its chemicals? It is its own best customer. It is estimated that over 50% of industrial chemicals are sold within the Chemicals and Allied Products sector. To give a simple example, chlorine might be sold to another company to make vinyl chloride, which in turn is sold to someone else to make poly(vinyl chloride) plastic, which can be made by another company into a finished plastic product. Some chemicals are exported; others are sold to the government for defense and to other industries, especially agriculture, petroleum refining, and paper products.

4. LOCATION OF THE CHEMICAL INDUSTRY

Table 1.5 shows a state-by-state breakdown of shipments in chemicals

Table 1.5 Top 10 Chemical-Producing States

Rank	% of Industry Total
Texas	11.0%
New Jersey	10.6
Illinois	6.2
Ohio	6.2
California	5.6
Louisiana	5.5
New York	5.4
Pennsylvania	4.7
Tennessee	4.1
Total of 10 States	**62.7**
U.S. Chemical Industry Total	**100.0**

Source: Chemical and Engineering News

for the top ten states. The West South Central (Texas and Louisiana), Atlantic (New Jersey and New York), and East North Central regions (Illinois, Ohio, Pennsylvania, Tennessee, and Indiana), along with California, account for the largest share of chemical manufacturing. These ten states have 63% or nearly two thirds of the industry. Research and Development (R & D) technical employment is centered more in the Middle Atlantic and East North Central regions.

5. EMPLOYMENT IN THE CHEMICAL INDUSTRY

If you are a chemist you have almost a 2:1 chance of eventually working in the chemical industry. About 58% of chemists are employed by private industry, 25% are in academics, 9% work for the government, and 8% are in other miscellaneous areas. Within this workforce 46% work in R & D, 17% are in management, 12% in teaching, 7% in production and quality control, 4% in marketing, sales, purchasing, and technical service, and 14% are in other fields. These other fields encompass many different jobs, including process development, personnel, public relations, patent literature, library service, and scientific writing. Many chemists start in R & D because it is most like academic chemistry. They progress into managerial positions where greater financial rewards are usually present. Many chemistry majors with some business background may start in marketing and sales. They may also enter management at a later point. It is interesting to note that of chemists age 35 and above, over 50% are in managerial capacities of one type or another.

Table 1.6 shows the average number of chemical and chemical engineering degrees granted at the B.S., M.S., and Ph.D. levels in the last few years. There are more chemists than chemical engineers each year. A

Table 1.6 Chemical Degrees

	Chemistry			Chemical Engineering		
Year	**B.S.**	**M.S.**	**Ph.D.**	**B.S.**	**M.S.**	**Ph.D.**
1995	9,722	2,099	2,273	5,901	1,085	571
1996	10,415	2,254	2,287	6,319	1,176	670
1997	10,644	2,240	2,259	6,564	1,131	650

Source: National Center for Education Statistics and *Chemical and Engineering News*, "Employment Outlook 2000"

Table 1.7 Total Employment

Industry	1990 (millions)	2000 (millions)
All Manufacturing	19.076	18.437
Chemicals and Allied Products	1.086	1.027
Petroleum and Coal Products	0.157	0.131
Rubber and Miscellaneous Plastics Products	0.888	1.005

Source: Department of Labor and *Chemical and Engineering News*, "Facts and Figures for the Chemical Industry"

fairly high percentage of chemists go on for their Ph.D.s; a lower number of engineers obtain their doctorate. Numbers of chemists and chemical engineers are up in the 1990s.

The breakdown by academic areas of chemistry in which chemists are employed is as follows: analytical, 21%; organic, 14%; polymer, 11%; environmental, 9%; physical, 7%; biochemical, 7%; medicinal and pharmaceutical, 7%; general, 6%; material science, 5%; inorganic, 5%; and other, 8%.

Table 1.7 shows the total employment of all workers, technical and nontechnical, by the chemical industry as well as by all manufacturing. Note that about 18.4 million workers are in all manufacturing, about 1.0 million in Chemicals and Allied Products. Employment in the chemical industry is relatively constant. This is to be contrasted to other major industries—construction and automobiles, for example—where employment can be down during a recession. Overall the chemical industry is in good shape. It is believed that about 160,000 chemists and 120,000 chemical engineers are employed in the U.S. The American Chemical Society alone has over 160,000 members currently. Unemployment of chemists is low, and in March 2001 it was 1.5%. It is always much lower than the nationwide unemployment.

6. SALARIES OF CHEMISTS

Table 1.8 compares Ph.D. chemists' salaries with other professions. In general, chemists have good salaries as compared to other scientists such as biologists and sociologists. They are usually not paid as high as engineers or physicists. Table 1.9 shows the average salary of chemists working in all areas, industrial and academic, at the B.S., M.S., and Ph.D. levels. Note that

Table 1.8 Salaries of Ph.D. Scientists and Engineers ($ thousands)

Physics/astronomy	$73.0
Chemical engineers	72.1
All engineers	72.0
Chemistry	70.0
Computer/math	65.0
Physical sciences	65.0
Earth sciences	62.0
All scientists	60.0
Agriculture/food sciences	60.0
Environmental life sciences	59.0
Life-related sciences	57.5
Biological sciences	55.0
Social sciences	55.0

Source: Chemical and Engineering News, "Employment Outlook," National Science Foundation, and Science and Engineering Indicators 2000. Based on median full-time salaries as of 1997.

Table 1.9 Chemists' Median Salaries

Degree	Salary ($ thousands)	Average Annual Increase 2000-2001	Average Annual Increase 1991-2001
B.S.	$55.0	3.6%	3.2%
M.S.	65.0	4.8	3.2
Ph.D.	82.2	4.1	3.5
All chemists	73.0	4.3	3.4
Consumer Price Index		2.9	2.7

Source: Chemical and Engineering News, "Salary Survey," based on 2001 data.

Ph.D. salaries are of course substantially higher than M.S., which in turn are higher than B.S. Both in 2001 and over the last decade salary increases were larger than inflation.

Table 1.10 summarizes in detail the salary ranges at degree levels and years of experience for chemists. Students will particularly note that the

Table 1.10 Chemists' Salaries vs. Experience

Salary ($ thousands)	Years Since B.S. Degree 2-4	10-14	20-24	40 or more
All chemists	$42.0	$66.0	$80.0	$84.0
By degree				
B.S.	41.0	55.0	67.6	70.0
M.S.	46.5	60.0	72.0	65.0
Ph.D.	--	72.0	87.2	87.4
By employer				
Industry	42.5	72.0	87.2	88.7
Government	36.5	60.0	72.1	87.1
Academia	31.0	48.0	60.0	89.6

Source: *Chemical and Engineering News*, "Salary Survey," based on 2001 data.

Table 1.11 Academic Chemists' Salaries

	9-10 month contracts		11-12 month contracts	
Salary ($ thousands)	Non-Ph.D. school	Ph.D. school	Non-Ph.D. school	Ph.D. school
Full Prof.	$65.0	$90.0	$99.3	$115.0
Associate Prof.	49.0	59.0	73.0	70.0
Assistant Prof.	42.0	50.4	50.0	58.0

Source: *Chemical and Engineering News*, "Salary Survey," based on 2001 data.

median salary for a recent B.S. chemist is now $41.0 thousand. A recent Ph.D. chemist is making $62.9 thousand.

The truly dedicated academic chemist's salary is substantially lower than that of nonacademic chemists. In academia (Table 1.11) only full professors compare favorably with nonacademic chemists.

Finally, salaries for chemists vary with the work function of individuals (Table 1.12). At the B.S. level salaries are highest by far in management and marketing, lowest in basic research and production.

Table 1.12 Chemists' Salaries by Work Function

Salary ($ thousands)	B.S.	M.S.	Ph.D.
R & D management	$80.0	$97.0	$112.0
General management	72.5	85.0	110.0
Marketing & sales	68.0	78.0	95.4
Applied research	58.0	65.0	84.0
Production/qual. control	53.8	63.9	82.0
Basic research	49.5	64.3	89.5

Source: *Chemical and Engineering News*, "Salary Survey," based on 2001 data.

7. GENERAL CHARACTERISTICS OF THE CHEMICAL INDUSTRY

Now that we have some idea about the chemical industry let us focus on a few general characteristics of this important industry. Wittcoff and Reuben define nine important traits that summarize some interesting concepts with regard to the industry, which are listed in Table 1.13. A brief summary of their observations along with other discussion is given in each of the following nine sections.

7.1 Maturity

For many years the chemical industry had rapid growth continuing

Table 1.13 Characteristics of the Chemical Industry

1. Maturity and it consequences
2. Participation in international trade
3. Competition from the developing countries
4. Capital intensity and economies of scale
5. Criticality and pervasiveness
6. Freedom of market entry
7. Strong regulation
8. High research and development expenses
9. Dislocation

Source: Wittcoff and Reuben

Table 1.14 U.S. Trade Balance

$ billion	1990	2000
Total exports	$394.0	$780.4
Total imports	495.0	1,216.9
Trade balance	-101.0	-436.5
Chemical exports	39.0	82.5
Chemical imports	22.5	73.6
Chemical trade balance	16.5	8.9

Source: Department of Commerce and *Chemical and Engineering News*, "Facts and Figures for the Chemical Industry"

through the 1950s, '60s, and '70s. Things slowed in the 1980s. It can now be considered a mature industry though its growth rate of 4.1% per year in shipments through the 1990s is strong. Maturity occurs because of market saturation, wide diffusion of technology, and low barriers to entering the industry. As a result of maturity we get overcapacity, competition, and low prices.

7.2 International Trade

Although some chemicals are transported only with danger and difficulty, many can be transported more easily and cheaply by truck, ship, and pipeline. This ease of transportation creates a large international trade. The U.S. also has a good supply of natural gas, from which many organic chemicals are made. Exports to other countries are substantial. Table 1.14 shows the U.S. total trade balance as compared to that for chemicals. Oil imports are the chief culprit in the U.S. trade picture, giving an overall trade balance that is a deficit. Were it not for oil imports the U.S. would probably enjoy a trade surplus. But other than in agricultural commodities, nowhere is the U.S. export strength more obvious than in chemicals, giving a chemical trade surplus of $8.9 billion. The chemical industry has been setting records for its trade surplus for many years. Finally, it should be noted that many companies have a large percentage of foreign sales compared to their total sales, sometimes as much as one third, again facilitating large amounts of international trade.

7.3 Competition from Developing Countries

Natural gas has been discovered in many places in the world and many countries have petroleum. The chemical industry has a greater value added than is possible when gas or oil is used for energy. Newcomers are Saudi Arabia, Canada, Mexico, South American countries, former members of the USSR, and Asian countries. In Taiwan the chemical industry is 30% of manufacturing compared to 11% in the U.S. Saudi Arabia has 25% of the world's oil reserves and a good supply of gas. These countries at least enter the chemical business to provide for their own needs.

7.4 Capital Intensity and Economies of Scale

There is a basic rule that applies to production in the chemical industry: invest huge capital to make a big plant so that there is less overhead and the product can be produced more cheaply on this larger scale. This is the principle of economy of scale. A typical ethylene plant capacity rose from 70 million lb/yr in 1951 to 2 billion lb/yr in 1991. In 1950 vinyl chloride sold for 14¢/lb and was produced at a rate of 250 million lb/yr. In 1969 it sold for 5¢/lb (in spite of 20 years of inflation) because it was being made at the rate of 3.6 billion lb/yr. In 1950 sulfuric acid, the number one chemical in terms of U.S. production, sold for $20/ton. In 1980 the price was only $40/ton despite many double-digit inflation years in the 1970s. The reason is that the production went from 20 billion lb to 80 billion lb.

The chemical industry has a high investment of current capital for an industry. Other industries invest more but their equipment lasts longer without becoming out-of-date. This high capital investment means that the industry is not so labor intensive. Personpower productivity (sales per employee) is high. Employee salaries are a small percentage of the cost in the chemical industry as compared to other industries. As a result, labor relations are usually good and pay increases are substantial.

7.5 Criticality and Pervasiveness

Another general characteristic of the chemical industry is its importance in everyday life. It is both critical and pervasive. It is critical to the economy of a developed country. In the first half of this century a nation's industrial development was gauged by its production of sulfuric acid, the chemical with the largest amount of production. It has been called "the grandfather of economic indicators." Lately ethylene, the largest volume organic chemical, is used to judge this development. The chemical industry cannot be replaced by any other industry. If a country does not have one, it must rely on imports. It is critical to the prosperity of a country, as well as pervasive—it is reflected in so many goods and services necessary for modern life as we know it. Finally, many of the problems concerning pollution, energy, and raw materials have been detected and monitored by chemical methods, and chemistry will have an important part to play in their solutions.

7.6 Freedom of Market Entry

Any company interested in getting started in the chemical industry can do so through buying a so-called "turnkey" plant from a chemical engineering contracting company. The plant is guaranteed to work and all you need to do is turn the key. Many developing countries are doing this to initiate their own chemical industries. Sounds easy? It is if you have the money. Large amounts of capital are needed for not only the plant but supporting activities as well, such as research, marketing, and license fees for the technology. But the potential for easy access into standard chemical manufacturing processes is there.

7.7 Strong Regulation

The chemical industry is one of the most highly regulated industries. Many laws have been developed that affect its operation. Most of these are good laws that are aimed at protecting workers and the nation in health, safety, and environment. Some may have gone too far so as to be unnecessarily stringent without good reason, thus affecting technological innovation and the good benefits of the industry. These laws are summarized in Chapter 25 and the whole problem of pollution and how it affects us and the chemical industry is discussed in detail there.

7.8 High R & D Expenditures

The chemical industry is research intensive. It hires over 15% of all scientists and engineers in the U.S. The four industrial sectors spending the largest amounts on R & D are aircraft and missiles, 25%; electrical equipment, 17%; chemicals and allied products, 11%; and motor vehicles and related equipment, 11%. Of the total for chemicals about 10% of chemicals and allied products R & D is federally financed, compared to 76% of aircraft and missiles R & D and 44% of electrical and communications equipment R & D. Thus chemical R & D is heavily subsidized by industry.

The chemicals and allied products industry is an investor in *basic research*—the planned search for new knowledge without reference to specific commercial objectives. But in industry only 14% of R & D money goes into basic research. Much of basic research occurs in the universities. *Applied research* is the use of existing knowledge for the creation of new products or processes. *Development* is commercialization of research and improvements to present products or processes. Applied research gets 27% of R & D funds, development corners 59%.

Some chemical companies spend a very high percentage of sales on R & D expenditures. Almost all of these companies are pharmaceutical companies, that portion of the industry that is highly competitive technically and requires substantial basic research to remain competitive. These types of companies can spend large percentages of their sales on R & D: Pfizer, 17%; Bristol-Myers Squibb, 9%; Eli Lilly, 18%. Most general large U.S. chemical companies spend a smaller portion of their sales on R & D: Du Pont, 6%; Dow, 5%; Rohm and Haas, 4%; Eastman Chemical, 4%.

There are two approaches to R & D and to its funding. There can be *technology push,* where a manufacturer discovers a certain technology through basic research and then creates a market for it. Television, sulfonamides, and lasers are products of this approach, for there was no established market for any of these before they were discovered. The second approach to R & D is *demand pull,* which examines a specific market need and then does R & D to solve the technology required to meet this specific need. Hard water detergents, jets, and automobiles with low exhaust emissions are examples of products derived from this mission-oriented approach. Large companies must have both attitudes toward expenditures for R & D to succeed, although there is a trend in the last few years toward demand pull research with specific targets.

7.9 Dislocations

Dislocations are defined as events over which a company has no control but which markedly affect that company's business. The chemical industry sometimes is difficult to predict. A close watch on changing markets is necessary to be successful, but sometimes changes cannot be controlled or predicted. For many years Ethyl Corporation made tetraethyllead for gasoline. When unleaded gasoline became necessary this caused real problems for them. They had to get into other products. They became a large supplier of the analgesic ibuprofen because they found a route involving organometallic chemistry, in which they were knowledgeable. The shift to methyl *t*-butyl ether (MTBE) as an octane enhancer in gasoline helped ARCO. They had a process to make propylene oxide with a side product *t*-butyl alcohol, which they then made into MTBE for this expanding market. The chemical industry is dynamic.

8. TOP 50 CHEMICALS

As part of an introduction to the chemical industry it is appropriate that we become acquainted with important chemicals, polymers, and chemical companies. Up to 1996 *Chemical and Engineering News* published a yearly list of the top 50 chemicals. These were ranked in terms of billions of lb of chemical produced in the U.S. for a given year. The 1995 production of these chemicals is given in Table 1.15. They stopped publishing the list because now it is difficult to find accurate totals for all these chemicals. The government quit publishing *Synthetic Organic Chemicals* each year, from which many of these data were taken. Because of the diversity in the types of chemicals (inorganic, organic, gases) no other single source is published that accurately ranks these chemicals anymore. We have attempted to prepare an estimated 2002 production of these chemicals from the data that is available. For some chemicals whose production is no longer easily found, a 2% per year increase was assumed. This list furnishes us with what is still probably the best starting place to examine basic chemicals. These fifty chemicals are leaders in production. The exact production and the ranking may not be accurate, but the list still gives us a feel for how important a chemical really is. Chapter 13 treats a list of "Second 50 Chemicals" which also are important in industry. These 100 chemicals form the basis for hundreds, probably thousands, of additional chemicals and products manufactured. It is appropriate then that we start with these in any study of the chemical industry. The top 50 chemicals are discussed at length in Chapters 2-12.

Sulfuric acid is number 1 by far, with a volume of over 90 billion lb produced yearly in the U.S. It is way ahead of number 2, nitrogen, which is produced at more than 75 billion lb annually. The highest volume organic chemical is ethylene, the basic petrochemical used to synthesize so many other important organic chemicals. It is the leader of the basic seven organics—ethylene, propylene, the C_4 mixture, benzene, toluene, xylene, and methane—from which all other important organic chemicals are derived. Methane does not itself appear in the list because it is not synthesized by a chemical process. However, it is the major constituent in natural gas and is used to make many other chemicals.

There are 19 inorganics making up the list, with a total volume of 492 billion lb in 2002. There are 31 organics with a substantially smaller production total of 346 billion lb. But the organics have much higher prices, so their overall commercial value is higher in dollar amount than would be thought otherwise. The total of 837 billion lb of chemicals represented by the top 50 is probably one half the weight of all chemicals and polymers produced yearly. Although there are thousands of chemicals commercially

Table 1.15 Top 50 Chemicals

1995 Rank	Chemical	Billion of lb 1995	Billion of lb 2002
1	Sulfuric acid	95.36	90.77
2	Nitrogen	68.04	77.57
3	Oxygen	53.48	60.97
4	Ethylene	46.97	58.01
5	Lime	41.23	46.09
6	Ammonia	35.60	34.43
7	Phosphoric acid	26.19	26.82
8	Sodium hydroxide	26.19	25.17
9	Propylene	25.69	30.27
10	Chlorine	25.09	27.51
11	Sodium carbonate	22.28	23.39
12	Methyl *tert*-butyl ether	17.62	21.00
13	Ethylene dichloride	17.26	23.75
14	Nitric acid	17.24	18.30
15	Ammonium nitrate	15.99	17.15
16	Benzene	15.97	18.36
17	Urea	15.59	18.53
18	Vinyl chloride	14.98	17.46
19	Ethylbenzene	13.66	13.63
20	Styrene	11.39	12.37
21	Methanol	11.29	19.31
22	Carbon dioxide	10.89	12.41
23	Xylene	9.37	10.14
24	Formaldehyde	8.11	9.69
25	Terephthalic acid	7.95	9.06
26	Ethylene oxide	7.62	9.24
27	Hydrochloric acid	7.33	9.93
28	Toluene	6.73	7.63
29	*p*-Xylene	6.34	6.86
30	Cumene	5.63	7.25
31	Ammonium sulfate	5.24	5.97
32	Ethylene glycol	5.23	7.50
33	Acetic acid	4.68	6.71
34	Phenol	4.16	5.19
35	Propylene oxide	4.00	3.50

Table 1.15 Top 50 Chemicals (Cont'd)

1995 Rank	Chemical	Billion of lb 1995	Billion of lb 2002
36	Butadiene	3.68	4.45
37	Carbon black	3.32	3.95
38	Isobutylene	3.23	3.68
39	Potash	3.22	2.98
40	Acrylonitrile	3.21	3.56
41	Vinyl acetate	2.89	2.80
42	Titanium dioxide	2.77	3.22
43	Acetone	2.76	3.16
44	Butyraldehyde	2.68	3.06
45	Aluminum sulfate	2.41	2.22
46	Sodium silicate	2.25	2.80
47	Cyclohexane	2.13	2.97
48	Adipic acid	1.80	2.20
49	Nitrobenzene	1.65	1.88
50	Bisphenol A	1.62	2.30
	31 Total Organics	**285.89**	**345.52**
	19 Total Inorganics	**464.10**	**491.66**
	Grand Total	**749.99**	**837.18**

Source: Chemical and Engineering News, Chemical Marketing Reporter, and *Chemical Economics Handbook*

produced, much of the approximately 1.5 trillion lb is centered in these top 50.

9. TOP POLYMERS

Polymers are very important chemicals derived from the top 50, and they play important roles in our everyday lives, giving us products made of plastics, fibers, elastomers, paints, coatings, adhesives, and many other materials. Representative top-selling commercial polymers are given in Table 1.16. These materials and products will be discussed in detail in Chapters 14-19.

Table 1.16 Top Polymer Production

Polymer	2000 Billion lb	Annual Change 1999-00	Annual Change 1990-00
Plastics			
Polyethylene			
Low density	7.617	-1.1%	0.5%
Linear low density	7.953	-1.9	7.4
High density	13.915	0.4	5.3
Polypropylene	15.595	0.7	6.5
Styrene Polymers			
Polystyrene	6.433	-0.6	2.5
Styrene-acrylonitrile	0.128	4.1	-0.5
Acrylonitrile-butadiene-styrene & other	3.122	0.7	2.9
Polyamide	1.275	-5.5	8.6
Polyvinyl chloride & copolymers	14.442	-3.2	4.7
Epoxy	0.706	7.5	3.5
Total	**71.186**	**-0.8%**	**4.6%**
Synthetic Fibers			
Acrylic	0.339	7.3	-3.9
Nylon	2.607	-2.6	-0.2
Olefin	3.185	3.6	5.8
Polyester	3.869	1.1	1.9
Acetate & rayon	0.349	18.3	-3.6
Total	**10.349**	**1.6%**	**1.8%**
Synthetic Rubber			
Styrene-butadiene rubber	1.927	-4.0	1.0
Polybutadiene	1.334	2.9	3.4
Ethylene-propylene	0.763	2.1	5.2
Nitrile, solid	0.196	1.1	2.6
Polychloroprene	0.141	-3.0	-2.1
Other	1.067	1.3	2.4
Total	**5.429**	**-0.3%**	**2.3%**

Source: *Chemical and Engineering News*, "Facts and Figures for the Chemical Industry," American Plastics Council, Fiber Economics Bureau, and International Institute of Synthetic Rubber Producers

Table 1.17 Top U.S. Chemical Companies

Rank 2000	Company	Chemical Sales 2000 $ billion	Change From 1999	Chemical Sales as % of Total Sales	Industry Class
1	Du Pont	$28.406	2.6%	89.2%	Diversified
2	Dow Chemical	23.008	15.1	100.0	Basic chemicals
3	ExxonMobil	21.543	35.1	9.3	Petroleum
4	Huntsman Corp.	8.000	0.0	100.0	Basic chemicals
5	General Electric	7.776	12.0	6.0	Diversified
6	BASF	7.757	16.5	100.0	Basic chemicals
7	Chevron Phillips	7.633	30.3	100.0	Basic chemicals
8	Equistar	7.495	37.9	100.0	Basic chemicals
9	Union Carbide	6.526	11.2	100.0	Basic chemicals
10	PPG Industries	6.279	14.1	72.8	Diversified
11	Shell Oil	6.265	38.0	21.1	Petroleum
12	Rohm and Haas	6.004	21.7	87.3	Basic chemicals
13	Eastman Chem.	5.292	15.3	100.0	Basic chemicals
14	Air Products	5.238	12.6	95.8	Basic chemicals
15	BP	5.100	-28.2	7.3	Petroleum
16	Praxair	5.043	8.7	100.0	Basic chemicals
17	TotalFinaElf	4.800	166.7	100.0	Basic chemicals
18	Honeywell	4.055	1.2	16.2	Diversified
19	Lyondell	4.036	9.3	100.0	Basic chemicals
20	Nova Chemicals	3.916	39.5	100.0	Basic chemicals
21	Monsanto	3.885	8.3	70.7	Agrochemicals
22	Occidental Pet.	3.795	24.9	28.0	Petroleum
23	ICI Americas	3.314	-20.4	100.0	Specialty chem.
24	Akzo Nobel	3.313	-0.1	100.0	Basic chemicals
25	Solutia	3.185	12.5	100.0	Basic chemicals

Source: Chemical and Engineering News, “Top 75 Chemical Producers”

Table 1.18 Top World Chemical Companies

Rank 2000	Company	Chemical Sales 2000 $ billion	Change From 1999	Chemical Sales as % of Total Sales
1	BASF (Germany)	$30.791	13.9%	93.0%
2	Du Pont (U.S.)	28.406	2.6	89.2
3	Dow Chemical (U.S.)	23.008	23.7	100.0
4	ExxonMobil (U.S.)	21.503	35.1	9.2
5	Bayer (Germany)	19.295	10.5	67.6
6	TotalFinaElf (France)	19.203	20.7	18.2
7	Degussa (Germany)	15.584	21.3	83.5
8	Shell (U.K./Netherlands)	15.205	18.0	10.2
9	ICI (U.K.)	11.747	-8.3	100.0
10	BP (U.K.)	11.247	19.8	7.0
11	Akzo Novel (Netherlands)	9.364	-12.1	72.6
12	Sumitomo Chemical (Japan)	9.354	8.8	96.8
13	Mitsubishi Chemical (Japan)	8.977	6.0	55.4
14	Mitsui Chemicals (Japan)	8.720	6.3	100.0
15	Huntsman Corp. (U.S.)	8.000	0.0	100.0
16	General Electric (U.S.)	7.776	12.0	6.0
17	Chevron Phillips (U.S.)	7.633	30.3	100.0
18	Dainippon Ink & Chem. (Japan)	7.513	6.1	82.5
19	Equistar (U.S.)	7.495	37.9	100.0
20	DSM (Netherlands)	7.295	27.6	97.9
21	Henkel (Germany)	7.216	13.9	61.3
22	SABIC (Saudi Arabia)	7.120	39.1	100.0
23	Syngenta (Switzerland)	6.846	-2.2	100.0
24	Rhodia (France)	6.835	34.3	100.0
25	Sinopec (China)	6.792	-6.4	17.4

Source: Chemical and Engineering News, “Global Top 50”

You should be somewhat familiar with the general production totals. More plastics are made each year, about 72 billion lb, than fibers or elastomers. The largest volume plastic is polyethylene, with combined low-, linear low-, and high-density types amounting to 30 billion lb. Linear low-density polyethylene is the rising star. These three polyethylenes serve different applications because of their different properties. The largest fiber market is polyester at 3.9 billion lb, but polyolefin is a close second and has had a rapid rise in production. The largest synthetic elastomer is styrene-butadiene at 1.9 billion lb.

10. TOP U.S. CHEMICAL COMPANIES

Chemical and Engineering News annually publishes a list of the top 75 chemical producers based on the amount of chemical sales, not total sales for the entire company. Table 1.17 lists the top 25 companies. Notice that, although many companies have 100% chemical sales, others are diversified and some, especially the petroleum companies, have a very small percentage of chemical sales vs. total sales.

11. TOP WORLD CHEMICAL COMPANIES

Table 1.18 lists the highest 25 of the top 50 chemical companies in the world, also published by *Chemical and Engineering News* annually, ranked by chemical sales. The full list includes 15 countries. The U.S. dominates the list with a total of 17 companies. Other countries represented are the following: Japan, 6; Germany, 5; United Kingdom, 5; France, 4; Netherlands, 3; Switzerland, 3; and one each for Belgium, Canada, China, India, Italy, Norway, Taiwan, and Saudi Arabia.

Suggested Readings

Chemical and Engineering News, annual reports on various topics, especially “Fact and Figures for the Chemical Industry,” “Top 75 Chemical Producers,” “Global Top 50 Chemical Producers,” “American Chemical Society Salary Survey,” “Facts and Figures for Chemical R & D,” “Employment Outlook.”

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 1-14.

Wittcoff and Reuben, *Industrial Organic Chemicals*, pp. 13-45.

Chapter 2

Sulfuric Acid and Its Derivatives

1. INTRODUCTION TO INORGANIC CHEMICALS

It is appropriate that we begin our study of industrial chemicals with important inorganic compounds and then progress into organic chemicals and polymers. Many of these inorganic chemicals are used in processes to be described later for organics. Usually 19 of the top 50 chemicals are considered to be inorganic, although the exact figure is dependent on what you count. For instance, carbon dioxide, sodium carbonate, and carbon black are counted as inorganic even though they contain carbon, because their chemistry and uses resemble other inorganics more than organics.

Table 2.1 lists the top 19 inorganics made in the U.S. They are listed in the order to be discussed. We also include various other materials in our discussion. Some important minerals such as sulfur, phosphate, and sodium chloride will be covered because these natural products are important raw materials for inorganic chemical production. They are not strictly speaking chemicals because they are not made synthetically by a chemical reaction, although they are purified with some interesting chemistry taking place. Hydrogen will also be considered because it is used in the manufacture of ammonia and is co-produced with carbon dioxide in the steam-reforming of hydrocarbons. Finally, urea is covered with inorganic nitrogen compounds because it is made from two "inorganics," ammonia and carbon dioxide.

The order of treatment of these chemicals is difficult to decide. Should it be alphabetical, according to the amount produced, according to important uses, etc.? We have chosen here an order that is dependent on raw material, which is summarized in Fig. 2.1. The most important, largest volume, basic

Table 2.1 Top Inorganic Chemicals

Sulfuric Acid Derivatives	Limestone Derivatives
Sulfuric acid	Lime
Phosphoric acid	Sodium carbonate
Aluminum sulfate	Sodium silicate
Industrial Gases	**Sodium Chloride Derivatives**
Nitrogen	Sodium hydroxide
Oxygen	Chlorine
Carbon dioxide	Hydrochloric acid
Inorganic Nitrogen Compounds	**Miscellaneous**
Ammonia	Titanium dioxide
Nitric acid	Potash
Ammonium nitrate	Carbon black
Ammonium sulfate	

(sometimes called heavy) chemicals from each important raw material are discussed first, followed by some of the derivatives for this chemical which also appear in the top 50. Although the uses of each chemical will be summarized, much of this discussion will be deferred until later chapters on selected specific technologies. Minor derivatives will not be considered.

Referring to Fig. 2.1, we proceed from left to right by first discussing sulfur's conversion into sulfuric acid, followed by some of sulfuric acid's derivatives, for example, aluminum sulfate and phosphoric acid. At times it will be necessary to delay covering a derivative until the other important starting material is described. Thus ammonium sulfate is mentioned later, after both sulfuric acid and ammonia are discussed. Exceptions to the general rule of raw materials to basic chemicals to chemical derivatives will be made where appropriate. For instance, the four industrial gases will be covered together even though nitrogen and oxygen have different sources as compared to carbon dioxide and hydrogen. After considering the inorganic nitrogen chemicals derived from ammonia we will continue with chemicals derived from limestone, and finally those made from sodium chloride. Note that all these chemicals are eventually made from the original four basic "elements" of the Ionian Greeks dating from 500 B.C.: earth, air, fire, and water. Admittedly the "earth" element is now known to be quite complex.

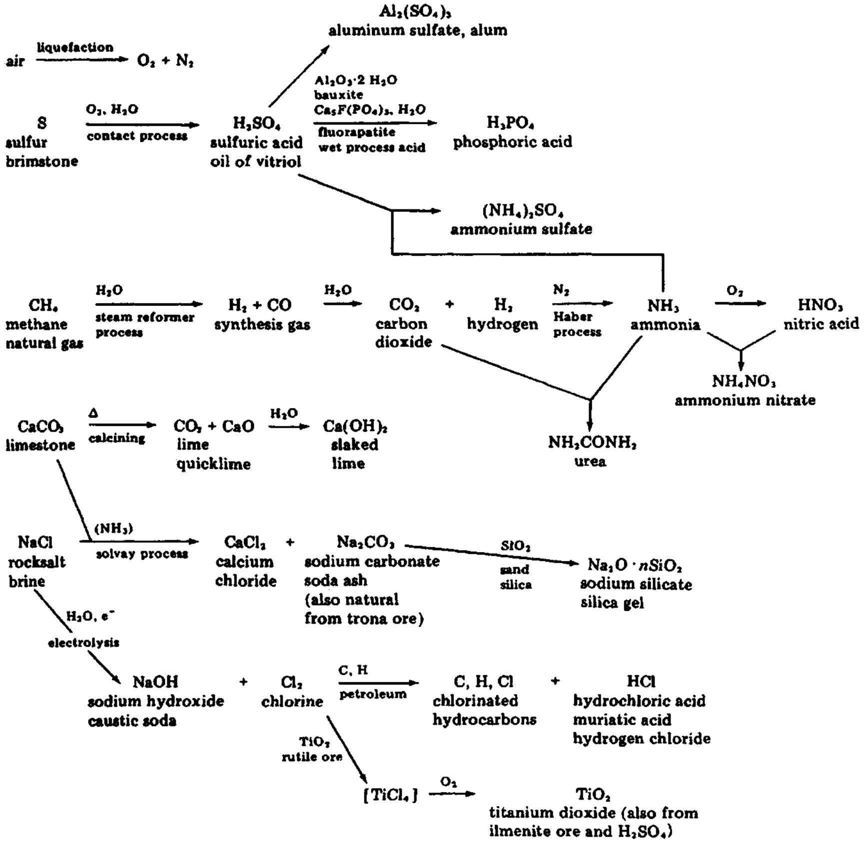


Figure 2.1 Manufacture of important inorganic chemicals. (*Source*: Reproduced with permission from the *Journal of Chemical Education*, Vol. 60, No. 5, 1983, pp. 411-413; copyright ©1983, Division of Chemical Education, Inc.)

Fig. 2.2 gives the U.S. production in billions of lb of one inorganic chemical from each of the main raw materials given in Fig. 2.1. This gives us some feel for the relative importance of these chemicals. Sulfuric acid, being the number one ranked chemical, has always had a large production compared to all other chemicals, even going back to the 1950s. Nitrogen has had a tremendous increase in production compared to most other chemicals, especially in the 1970s and ’80s. It is now ranked number two mainly because of its increased use in enhanced oil recovery. Sodium hydroxide and ammonia have shown slow steady increases through the years. Lime has decreased in the 1970s and ’80s with the suffering steel market, but has made a comeback in the ’90s.

The topics covered for each chemical will vary with their importance. The student should attempt to become familiar at least with the reaction used in the chemical’s manufacture and each chemical’s important uses. Details

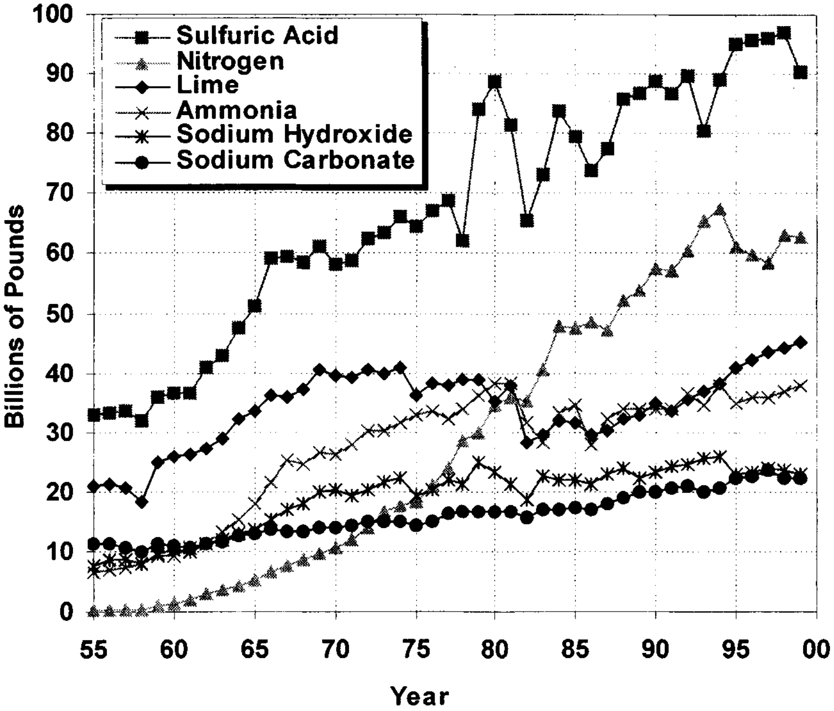


Figure 2.2 U.S. production of selected inorganic chemicals. (*Source*: Lowenheim and Moran and *Chemical and Engineering News*)

of the large-scale manufacturing process and economic trends for selected chemicals will also be summarized. History of manufacture, characteristics of raw materials, and environmental or toxicological problems will be mentioned occasionally.

Before we begin this systematic discussion of important chemicals and chemical products, note that, although the chemistry is most important, the discussions will include some engineering and marketing concepts. Many readers using this book are probably primarily chemists. It is a good idea to keep in mind that chemists, to be successful in industry, must be able to understand and relate to nonchemists. Chemists must work with engineers and marketing specialists who may have a limited or no background in chemistry. For communication to be possible, chemists must know and appreciate the questions and problems confronting these people in their jobs. In the following sections we have attempted to include enough of these concepts to provide the chemist with a working knowledge of these disciplines. One obvious example of an important difference between a chemical reaction in the laboratory and a large-scale industrial process is that many industrial reactions are run via continuous rather than batch processes. The batch technique resembles a laboratory scale, including loading the flask, doing the reaction, transferring the product, purifying the product, analyzing the product, and cleaning the equipment. Although many large-scale processes are also batch, with large stainless steel vessels and many safety features, there are disadvantages to the batch approach. In a continuous process the feed materials are continuously added to the reactor and the product is continuously withdrawn from the vessel. Advantages are eliminating "dead time" between batches, making product at higher rates, controlling the process more easily, and forming a more uniform product.

Keep in mind that many people from a variety of disciplines must be involved in making a process work and developing a successful product. The life cycle of most products includes basic research, applied research, development, scaleup, quality control, cost and profit evaluations, market research, market development, sales, and technical service to make a product grow and mature. Every person involved in this project must know something about the rest of the cycle, in addition to contributing a specific expertise to the cycle.

2. SULFURIC ACID (OIL OF VITRIOL)

$$H_2SO_4$$

2.1 Raw Material

We begin our discussion with what is by far the largest volume chemical produced in the United States: sulfuric acid. It is normally manufactured at about twice the amount of any other chemical and is a leading economic indicator of the strength of many industrialized nations. Since about 80% of all sulfuric acid is made by the contact process which involves oxidation of sulfur, we will examine this raw material in detail. The average per capita consumption of sulfur in the United States is a staggering 135 lb/yr.

Elemental sulfur (brimstone) can be obtained by mining with the Frasch method or by oxidation of hydrogen sulfide in the Claus process. Although the percentage of sulfur obtained by mining has decreased recently (76% in 1973, 54% in 1980, 26% in 1991, and 13% in 1999), the Frasch process is still important. Large deposits of sulfur along the Gulf Coast are released by heating the mineral with hot air and water under pressure (163 °C, 250 psi) to make the yellow sulfur molten (mp 119 °C) so that it is forced to the surface from a depth of 500-2500 ft. Alternatively, the Claus oxidation is performed on hydrogen sulfide obtained from "sour" natural gas wells or petroleum refineries. The hydrogen sulfide, being acidic, is readily separated from the gas or oil by extraction with potassium carbonate or ethanolamine, acidifying, and heating to release the gas.

$$K_2CO_3 + H_2S \longrightarrow H_2CO_3 + K_2S$$

$$HO{-}CH_2{-}CH_2{-}NH_2 + H_2S \longrightarrow HO{-}CH_2{-}CH_2{-}NH_3^+ + HS^-$$

The hydrogen sulfide is then oxidized with air at 1000°C over a bauxite or alumina catalyst. The reactions taking place are given below. The Claus process is increasing in popularity and accounted for 24% of sulfur in 1973, 46% in 1980, 74% in 1991, and 87% in 1999.

$$\begin{array}{rl} & H_2S + 3/2\,O_2 \longrightarrow SO_2 + H_2O \\ & SO_2 + 2H_2S \longrightarrow 3S + 2H_2O \\ \hline \text{overall:} & 3H_2S + 3/2\,O_2 \longrightarrow 3S + 3H_2O \\ \text{or:} & 2H_2S + O_2 \longrightarrow 2S + 2H_2O \end{array}$$

Approximately 90% of this sulfur is used to manufacture sulfuric acid. Sulfur is one of the few materials whose quantity is often expressed in "long tons" (2240 lb) which are different from short tons (2000 lb) or metric tons (2204.6 lb). There is no advantage to this unit. It has simply been used for this product for years and has resisted change without good reason.

2.2 Manufacture

Sulfuric acid has been known for centuries. It was first mentioned in the tenth century; its preparation was first described in the fifteenth century by burning sulfur with potassium nitrate. In 1746 Roebuck in England introduced the "lead chamber process," the name being derived from the type of lead enclosure where the acid was condensed. This process involves oxidation of sulfur to sulfur dioxide by oxygen, further oxidation of sulfur dioxide to sulfur trioxide with nitrogen dioxide, and, finally, hydrolysis of sulfur trioxide. The chemistry is more complex than that shown because a mixture of nitrogen oxides is used (from oxidation of ammonia). Modifications of the process by Gay-Lussac in 1827 and Glover in 1859 to include towers to recover excess nitrogen oxides and to increase the final acid concentration from 65% ("chamber acid") to 78% ("tower acid") made it very economical for many years, until the "contact process" displaced it in the 1940s. There have been no new lead chamber plants built since 1956.

$$\begin{aligned}
&S + O_2 \longrightarrow SO_2\\
&NO + 1/2O_2 \longrightarrow NO_2\\
&SO_2 + NO_2 \longrightarrow SO_3 + NO\\
&SO_3 + H_2O \longrightarrow H_2SO_4\\
\hline
\text{overall:}\quad &S + 3/2O_2 + H_2O \longrightarrow H_2SO_4
\end{aligned}$$

The contact process was invented by Phillips in England in 1831 but was not used commercially until many years later. Today 99% of all sulfuric acid is manufactured by this method. It was developed mainly because of the demand for stronger acid. All new contact plants use interpass absorption, also known as double absorption or double catalysis. This process will be described in detail in Fig. 2.3.

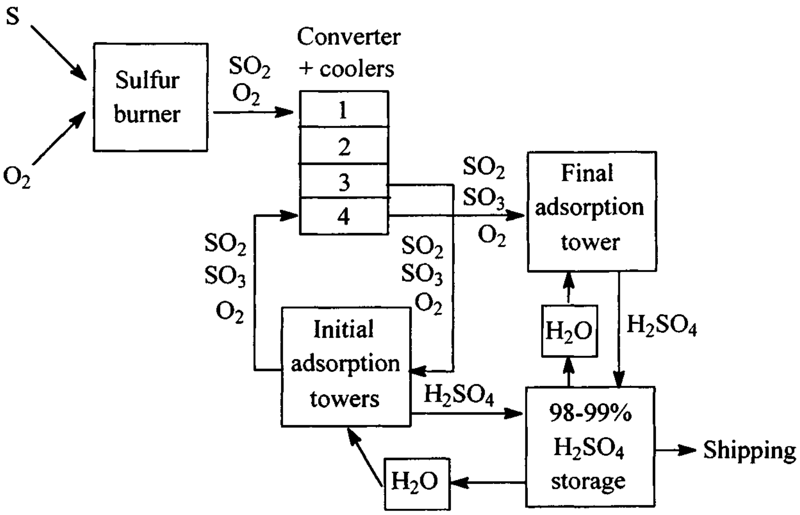


Figure 2.3 Contact process for sulfuric acid manufacture.

2.2.1 Reactions

$$S + O_2 \longrightarrow SO_2$$

$$SO_2 + 1/2O_2 \rightleftharpoons SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

---

overall: $S + 3/2O_2 + H_2O \longrightarrow H_2SO_4$

2.2.2 Description

Sulfur and oxygen are burned to SO_2, (Fig. 2.4, about 10% SO_2 by volume) at 1000°C and then cooled to 420°C. The SO_2 and O_2 enter the converter, which contains four different chambers of V_2O_5 catalyst. About 60-65% SO_2 is converted to SO_3 in the first layer with a 2-4 sec contact time. It is an exothermic reaction so the gas leaves at 600°C. It is cooled to 400°C with a heat exchanger (Fig. 2.5) and enters the second layer of catalyst.

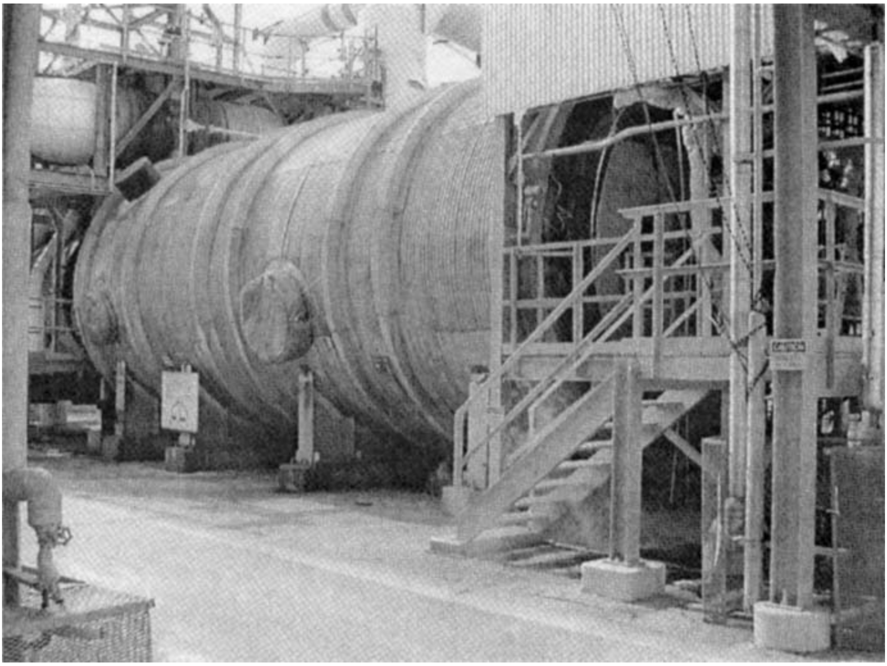


Figure 2.4 A sulfur burner where sulfur and oxygen are burned at high temperatures to make sulfur dioxide. (Courtesy of Du Pont, LaPorte, TX)

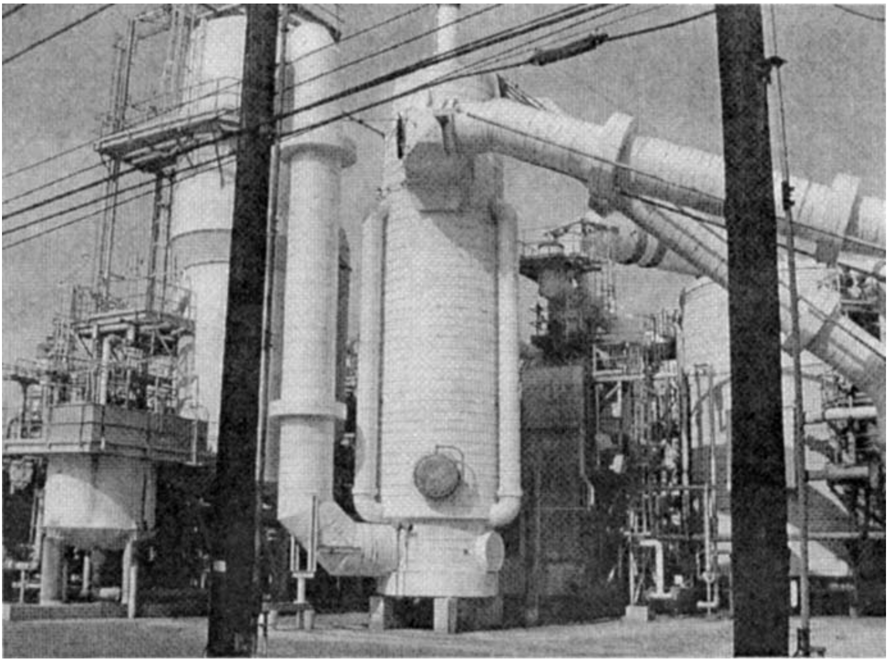


Figure 2.5 Cold heat exchangers in the sulfuric acid plant are linked to the converter, where sulfur dioxide and oxygen form sulfur trioxide, to maintain proper temperatures of the catalyst in this exothermic reaction. (Courtesy of Du Pont, LaPorte, TX)

After the third layer about 95-96% of the SO_2 is converted into SO_3, near the limit of conversion unless SO_3 is removed. The mixture is fed to the initial absorption tower, where SO_3 is hydrated to H_2SO_4 with a 0.5-1% rise in acid strength in the tower. The mixture is then reheated to 420 °C and enters the fourth layer of catalyst, which gives overall a 99.7% conversion of SO_2 to SO_3. It is cooled and then fed to the final absorption tower (Fig. 2.6) and hydrated to H_2SO_4. The final H_2SO_4 concentration is 98-99% (1-2% H_2O). A small amount of this is recycled by adding some water and recirculating into the towers to pick up more SO_3, but most of it goes to product storage.

The V_2O_5 catalyst has been the catalyst of choice since the 1920s. It is absorbed on an inert silicate support. It is not subject to poisoning and has about a 20-year lifetime.

As we will see, many industrial processes are successes because the right catalyst was found. Around 70% of all industrial chemical conversions involve a catalyst. Sometimes the catalysis is not understood. In this case it is known that the V_2O_5 catalysis is promoted by the presence of small

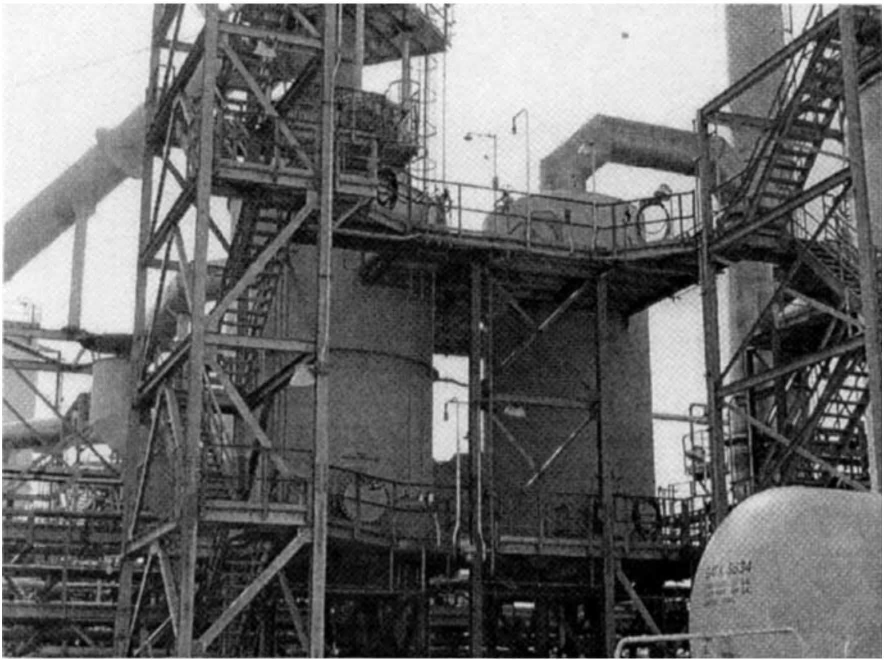


Figure 2.6 Adsorption towers convert sulfur trioxide and water into sulfuric acid. (Courtesy of Du Pont, LaPorte, TX)

amounts of alkali metal sulfates, usually Na_2SO_4, which react in the presence of SO_3 to give $S_2O_7^=$ in an initial step. This is the source of the oxide ion, $O^=$, which then reduces V^{+5} to V^{+4}. In turn the V^{+4} is reoxidized to V^{+5} by oxygen.

initiation $SO_4^= + SO_3 \longrightarrow S_2O_7^=$ (containing $O^=$)

(1) $2V^{+5} + O^= + SO_2 \longrightarrow SO_3 + 2V^{+4}$

(2) $2V^{+4} + 1/2O_2 \longrightarrow 2V^{+5} + O^=$

overall, (1) + (2) $SO_2 + 1/2O_2 \longrightarrow SO_3$

This exothermic process enables heat recovery in many places: after the sulfur burner, after the converter pass, and after the absorption towers. The waste heat can be used to generate steam for heating. A plant operating at 10% SO_2 feed and at a conversion rate of 99.7% SO_2 to SO_3 has a stack gas of 350 ppm of SO_2. The equilibrium conversion (theoretical best) is 100 ppm of SO_2. Regulations require that no more than 4 lb of SO_2 come out of the stack for each ton of H_2SO_4 made. This is not an appreciable source of acid rain, primarily caused by electrical generating plants burning coal containing sulfur. In fact, the total sulfur emitted from coal-burning power station stacks is more than the total sulfur feed used in sulfuric acid plants. Nevertheless, efforts are continuing to reduce sulfur emissions from acid plants. A low-temperature process is being studied which would make lower SO_2 emission possible.

Although sulfur is the common starting raw material, other sources of SO_2 can be used, including iron, copper, lead, nickel, and zinc sulfides. Hydrogen sulfide, a by-product of natural gas, can be burned to SO_2. Some countries use gypsum, $CaSO_4$, which is cheap and plentiful but needs high temperatures to be converted to SO_2, O_2 and H_2O and the SO_2 recycled to make more H_2SO_4. About 5% of all H_2SO_4 is recycled.

2.3 Properties

Anhydrous, 100% sulfuric acid is a colorless, odorless, heavy, oily liquid, bp 338 °C, where it decomposes by losing SO_3 to give 98.3% H_2SO_4. It is soluble in all ratios with water. This dissolution in water is very exothermic. It is corrosive to the skin and is a strong oxidizing and dehydrating agent. Common concentrations and names are battery acid, 33.5% H_2SO_4; chamber or fertilizer acid, 62.18%; tower or Glover acid, 77.67%; and reagent, 98%.

Oleum is also manufactured. This is excess SO_3 dissolved in H_2SO_4. For example, 20% oleum is 20% SO_3 in 80% H_2SO_4 (no H_2O). If water were added to 20% oleum so that the SO_3 and H_2O made H_2SO_4, then 104.5 lb of H_2SO_4 could be made from 100 lb of 20% oleum. This is sometimes called "104.5% H_2SO_4." Other common oleum concentrations are 40% oleum (109% H_2SO_4) and 65% oleum (114.5% H_2SO_4).

Sulfuric acid comes in different grades: technical, which is colored and contains impurities but which can be used to make fertilizer, steel, and bulk chemicals; certified pure (CP); and U.S. Pharmacopeia (USP). The last two are used to make batteries, rayon, dyes, and drugs. Rubber or lead-lined containers can be used for dilute acid; iron, steel, or glass can be used for concentrated acid. Shipments require a white DOT label.

2.4 Economics

Fig. 2.7 gives the production of sulfur and sulfuric acid from the 1950s to the present. Note the similarities in the curves for both, since one is made primarily from the other. With some exceptions the general pattern is a slow

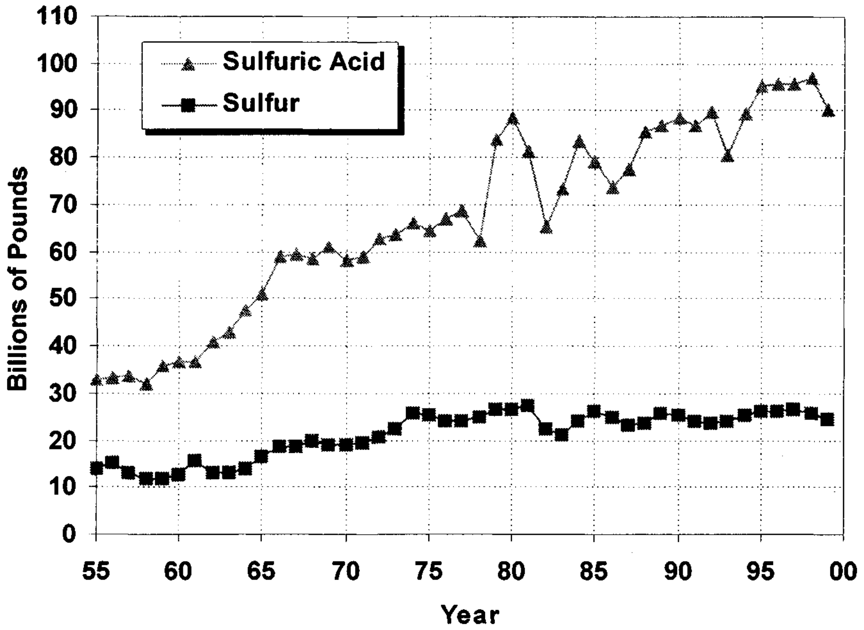


Figure 2.7 U.S. production of sulfur and sulfuric acid. (*Source*: Lowenheim and Moran, *Chemical and Engineering News*, *Chemical Economics Handbook*)

steady increase. Note the slump in the early 1980s, indicative of the chemical industry's and all of manufacturing's general slowdown in those years. Sulfur and sulfuric acid had decreased production in 1986-87, '92-93, and '99. The difference in the ratio of sulfur to sulfuric acid through the years is a reflection on other uses of sulfur (agricultural chemicals, petroleum refining, etc.) or other sources of raw material for sulfuric acid (metal pyrites, recycling of used sulfuric acid, etc.). Future projections for growth are only 1%/yr because of the depressed fertilizer market.

Fig. 2.8 gives the average price trends for these two chemicals. Notice the sharp rise in the 1970s for both chemicals. We will see this phenomenon for many chemicals, especially in 1974-1975, when the Arab oil embargo occurred. Throughout the 1970s many years of double-digit inflation, in part caused by the oil embargo, produced a steep rise in prices of many chemical products, more so for organic chemicals derived from oil, but even spilling over to inorganics because of increasing energy costs in production. The decreases of the price of sulfur in the 1990s is not easily explained, but may in part be due to other sources of raw material for making sulfuric acid, including more recycling of acid.

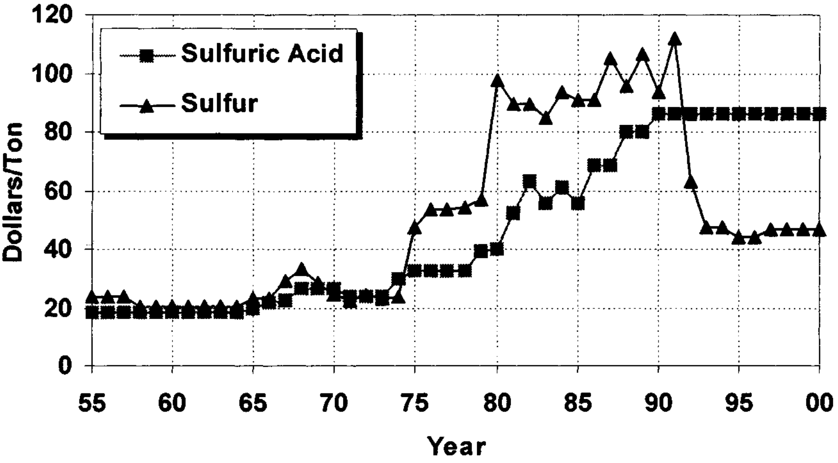


Figure 2.8 U.S. prices of sulfur and sulfuric acid. (*Source*: Lowenheim and Moran and *Chemical Marketing Reporter*)

The commercial value of a chemical is another method of measuring the importance of a chemical. It is estimated by multiplying the price by the amount produced, giving an indication of the total money value of the chemical manufactured in the U.S. each year. The more important chemicals and polymers have well over \$1 billion/yr commercial value. For example, for 1999 the average price of sulfuric acid was \$86/ton or 4.3¢/lb and the amount produced was 90.2 billion lb or 45.1 million tons. Some chemicals are also routinely quoted as ¢/lb. To convert \$/ton to ¢/lb we multiply by 0.05:

$$\frac{\$86 \text{ dollars}}{\text{ton}} \times \frac{1 \text{ ton}}{2000 \text{ lb}} \times \frac{100 \text{ cents}}{\$ \text{ dollars}} = \frac{4.3 \text{ cents}}{\text{lb}}$$

To convert from million tons to billion lb we multiply by 2:

$$45.1 \text{ million tons} \times \frac{2000 \text{ lb}}{\text{ton}} \times \frac{1 \text{ billion}}{1000 \text{ million}} = 90.2 \text{ billion lb}$$

Either of these units can be used to calculate a commercial value of \$3.9 billion for sulfuric acid:

$$\frac{\$86}{\text{ton}} \times 45.1 \text{ million tons} = \$3879 \text{ million} = \$3.9 \text{ billion}$$

$$\frac{\$0.043}{\text{lb}} \times 90.2 \text{ billion lb} = \$3.9 \text{ billion}$$

A good indicator of the economic strength of a chemical is its high percentage of capacity being used. If production is 70-90% of capacity, it usually means that the product is in appropriate demand. Table 2.2 shows the total nameplate capacity of sulfuric acid plants in the U.S. for selected years and production as a percent of capacity. Nameplate capacity means what the plant could routinely produce, though at times some plants can actually make more than this amount if necessary. Most sulfuric acid plants manufacture between 200-2400 tons/day. There are about 70 plants in the U.S. making sulfuric acid.

Table 2.3 shows the uses of sulfuric acid. The largest use by far is in the manufacture of phosphate fertilizers, as we will see in the next section. It is the fastest growing use as well, being only 36% of sulfuric acid in 1957, 58% in 1975, 69% in 1991, and slowing to 70% in 2000.

Table 2.2 U.S. Sulfuric Acid Capacity

Year	Capacity, billion lb	Production as % of Capacity
1981	104	79
1985	95	82
1990	92	96
2000	96	94

Source: Chemical Profiles

Table 2.3 Uses of Sulfuric Acid

Fertilizer	70%
Mining	9
Petroleum alkylation	6
Inorganic chemicals, pigments	5
Pulp and paper	3
Miscellaneous	7

Source: Chemical Profiles

3. PHOSPHORIC ACID (ORTHOPHOSPHORIC ACID)

H_3PO_4

3.1 Manufacture

By far the most important derivative of sulfuric acid is phosphoric acid. It has been unknowingly used as fertilizer for hundreds of years. The wet process method of manufacture was important until 1920, when furnace acid began increasing in popularity. The wet process, however, has made a comeback because of plant design improvements; 60% of phosphoric acid was made by this method in 1954, 88% in 1974, and over 90% currently. The furnace process is used only to make concentrated acid (75-85%) and pure product. It is very expensive because of the 2000°C temperature required. In the furnace process phosphate rock is heated with sand and coke to give elemental phosphorus, which is then oxidized and hydrated to phosphoric acid. A simplified chemical reaction is:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 10CO + 6CaSiO_3$$

$$P_4 + 5O_2 + 6H_2O \longrightarrow 4H_3PO_4$$

Since almost all phosphoric acid is now made by the wet process, we will discuss this more fully.

3.1.1 Reaction

$$Ca_3(PO_4)_2 + 3H_2SO_4 \longrightarrow 2H_3PO_4 + 3CaSO_4$$

$$\text{or} \quad CaF_2 \cdot Ca_3(PO_4)_2 + 10H_2SO_4 + 20H_2O \longrightarrow 10(CaSO_4 \cdot 2H_2O) + 2HF + 6H_3PO_4$$

$$\text{or} \quad Ca_5F(PO_4)_3 + 5H_2SO_4 + 10H_2O \longrightarrow 5(CaSO_4 \cdot 2H_2O) + HF + 3H_3PO_4$$

These three equations represent the wet process method in varying degrees of simplicity and depend on the phosphate source used. There is usually a high percentage of fluorine in the phosphate, in which case the mineral is called fluorapatite. It is mined in Florida, Texas, North Carolina, Idaho, and Montana. The United States has 30% of known phosphate reserves.

3.1.2 Description

Fig. 2.9 outlines the wet process. The phosphate rock is ground and mixed with dilute H_3PO_4 in a mill. It is transferred to a reactor and H_2SO_4 is added. The reactors are heated to 75-80°C for 4-8 hr. Air-cooling carries the HF and SiF_4 side products to an adsorber, which transforms them into H_2SiF_6. Filtration of the solid $CaSO_4 \bullet 2H_2O$ (gypsum) gives a dilute H_3PO_4 solution (28-35% P_2O_5 content). Evaporation of water to 54% P_2O_5 content is optional. The H_2SiF_6 is formed in the process by the following reactions. SiO_2 is present in most phosphate rock.

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

$$2HF + SiF_4 \longrightarrow H_2SiF_6$$

$$3SiF_4 + 2H_2O \longrightarrow 2H_2SiF_6 + SiO_2$$

There are two useful side products. The H_2SiF_6 is shipped as a 20-25 % aqueous solution for fluoridation of drinking water. Fluorosilicate salts find use in ceramics, pesticides, wood preservatives, and concrete hardeners. Uranium, which occurs in many phosphate rocks in the range of 0.005-0.03% of U_3O_8, can be extracted from the dilute phosphoric acid after the filtration step, but this is not a primary source of the radioactive substance. The extraction plants are expensive and can only be justified when uranium prices are high.

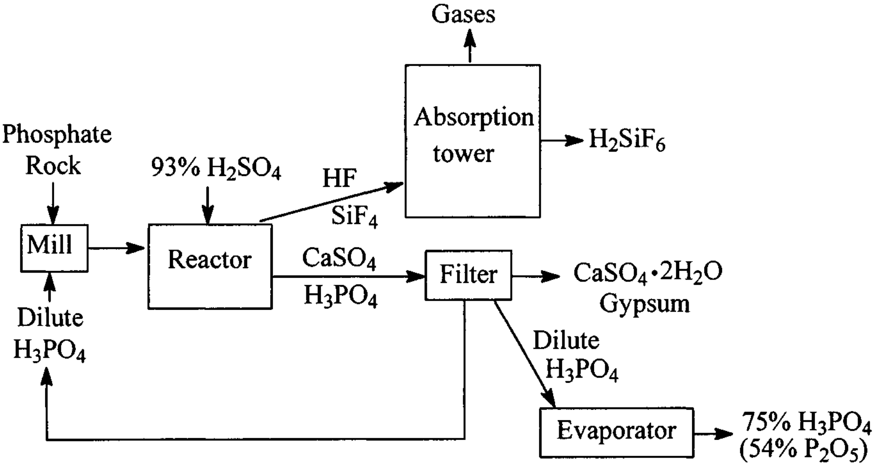


Figure 2.9 Wet process for phosphoric acid.

Table 2.4 Uses of Phosphoric Acid

Phosphate fertilizers	88%
Animal feed	6
Miscellaneous	6

Source: Chemical Profiles

3.2 Properties

One hundred percent H_3PO_4 is a colorless solid, mp 42°C. The usual laboratory concentration is 85% H_3PO_4, since a crystalline hydrate separates at 88% concentration. Table 2.4 shows the percentages for phosphoric acid use, almost all of which goes to the fertilizer industry.

4. ALUMINUM SULFATE (FILTER ALUM, ALUM, OR PAPERMAKER'S ALUM)

$$Al_2(SO_4)_3 \cdot 18H_2O$$

This lower-ranking chemical, which has nowhere near the production volume of sulfuric and phosphoric acids, is consistently in the top 50 and is very important to some industries. Aluminum sulfate is manufactured from aluminum oxide (alumina, bauxite). The crude ore can be used. A mixture with sulfuric acid is heated at 105-110°C for 15-20 hr. Filtration of the water solution is followed by evaporation of the water to give the product, which is processed into a white powder.

$$Al_2O_3 \cdot 2H_2O + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 5H_2O$$

Alum has two prime uses. About two thirds of it is bought by the pulp and paper industry for coagulating and coating pulp fibers into a hard paper surface by reacting with small amounts of sodium carboxylates (soap) present. Aluminum salts of carboxylic acids are very gelatinous.

$$6RCO_2^-Na^+ + Al_2(SO_4)_3 \longrightarrow 2(RCO_2^-)_3Al^{+3} + 3Na_2SO_4$$

One third of it is used in water purification, where it serves as a coagulant, pH conditioner, and phosphate and bacteria remover. It reacts with alkali to give an aluminum hydroxide floc, which drags down impurities in the water. For this reason it also helps the taste of water.

$$Al_2(SO_4)_3 + 6NaOH \longrightarrow 2Al(OH)_3 + 3Na_2SO_4$$

Suggested Readings

Austin, *Shreve's Chemical Process Industries*, pp. 320-345.
Chemical Profiles in *Chemical Marketing Reporter*, 9-7-92 and 1-10-00.
Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 347-366, 458-479.
Lowenheim and Moran, *Faith, Keyes, and Clark's Industrial Chemicals*, pp. 628-639, 786-795.
Thompson, *Industrial Inorganic Chemicals: Production and Uses*, pp. 93-121.
White, *Introduction to Industrial Chemistry*, pp. 10-17, 22-25.

Chapter 3

Industrial Gases

Three inorganic gases, nitrogen, oxygen, and carbon dioxide, appear in the top 50 chemicals. A fourth gas, hydrogen, would also be included if it were not for the large amounts of captive use of hydrogen to manufacture ammonia, which makes it difficult to estimate hydrogen production. It is convenient to discuss all four at this time in our study of inorganic chemicals. Two of them, nitrogen and hydrogen, are used to produce ammonia, which in turn has important derivatives that will be discussed in the next chapter. Not all four major gases are manufactured by the same method. Nitrogen and oxygen, obtained by the liquefaction of air, will be discusses first. Next, carbon dioxide and hydrogen, made by the process of steam-reforming of hydrocarbons, will be considered.

1. NITROGEN

1.1 Manufacture

The large-scale availability of nitrogen, oxygen, and argon from liquefaction of air began about 1939-40. A 90% recovery is now feasible for these three major components in air. Nitrogen makes up 78% of all air, oxygen 21%, and argon 0.9%. Two major processes are used, differing only in the way in which the expansion of air occurs. The Linde-Frankl cycle is based on the classic Joule-Thompson effect of a gas, which means that there is a tremendous cooling effect of a gas when it is rapidly expanded, even though no external work is done on the system. Alternatively, the Claude process employs an expansion engine doing useful work on the gas. The

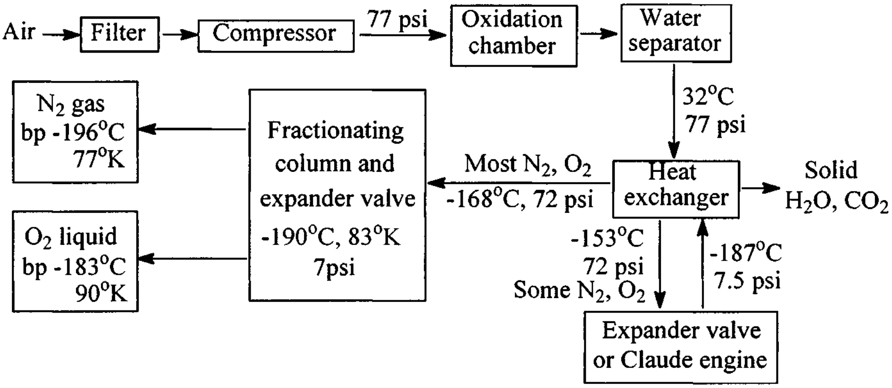


Figure 3.1 Liquefaction of air.

temperature is reduced because of the removal of energy. This process is more efficient than relying on the Joule-Thompson effect.

Fig. 3.1 outlines the liquefaction of air. Air is filtered to remove particulates and then compressed to 77 psi. An oxidation chamber converts traces of hydrocarbons into carbon dioxide and water. The air is then passed through a water separator, which gets some of the water out. A heat exchanger cools the sample down to very low temperatures, causing solid water and carbon dioxide to be separated from the main components.

Most of the nitrogen-oxygen mixture, now at -168°C and 72 psi, enters the bottom of a fractionating column. An expansion valve at this point causes further cooling. The more volatile nitrogen rises to the top of the column as a gas since nitrogen (bp = -196°C, 77°K) has a lower boiling point than oxygen (bp = -183°C, 90°K), and the column at 83°K is able to separate the two. The oxygen stays at the bottom of the column as a liquid because it is less volatile.

A small amount of nitrogen-oxygen mixture after being recooled in the heat exchanger is shunted to the main expander valve (operated by the Joule-Thompson effect or by a Claude engine). This extremely cold gas is recycled into the heat exchanger to keep the system cold. Some argon remains in the oxygen fraction and this mixture can be sold as 90-95% oxygen. If purer oxygen is required, a more elaborate fractionating column with a greater number of plates gives an oxygen-argon separation. Oxygen can be obtained in 99.5% purity in this fashion.

Argon can be obtained from a middle fraction between nitrogen and oxygen and redistilled. A small amount of hydrogen can be added to react with any remaining oxygen to give oxygen-free argon. Not only argon, but other rare gases, neon, krypton, and xenon, can also be obtained in

Table 3.1 Merchant Uses of Nitrogen

Chemicals	33%
Oil & gas extraction	14
Electronics	13
Primary metals	11
Petroleum refining	10
Food industry	5
Glass	2
Rubber & plastics	1
Miscellaneous	11

Source: Chemical Economics Handbook

separations. Helium is *not* obtained from liquefaction of air. It occurs in much greater concentrations (2%) in natural gas wells and is isolated in the petroleum refinery.

1.2 Uses

By far the largest use of nitrogen is in ammonia synthesis. However, this use is not included here because it is "captive," that is, the same company immediately reuses the gas internally to make another product, in this case ammonia. This nitrogen is not isolated, sold, or inventoried. Only "merchant" use is included in Table 3.1. Chemicals manufactured with nitrogen include many reactions where nitrogen is the inert blanketing atmosphere to prevent reaction with oxygen and minimize the possibility of fire and explosion for reactions sensitive to oxygen. Oil and gas extraction is a fast-growing use of nitrogen. This application is called advanced oil recovery (AOR) or enhanced oil recovery (EOR), where nitrogen maintains pressure in oil fields so that a vacuum is not formed underground when natural gas and oil are pumped out. It competes with carbon dioxide in this application. In the electronic industry nitrogen is an important blanketing and purge gas in the manufacture of semiconductors and integrated circuits. It is used in liquid form for cryogenic (low temperature) testing. In primary metals manufacture it is an inert atmosphere for making steel, blanketing the powdered coal and other fuel for the furnace. Petroleum refining makes use of it for its inert atmosphere and the food industry uses liquid nitrogen for freezing.

Table 3.2 Merchant Uses of Oxygen

Primary metals production	49%
Chemicals & gasification	25
Clay, glass, & concrete products	6
Petroleum refineries	6
Welding & cutting	6
Health sciences	4
Pulp & paper	2
Water treatment	1
Miscellaneous	1

Source: Chemical Economics Handbook

2. OXYGEN

The manufacture of oxygen is described along with that of nitrogen. Both are formed from the liquefaction of air. Oxygen gas is colorless, odorless, and tasteless, but it is slightly blue in the liquid state. Up to 99.995% purity is available commercially. It is commonly used from seamless steel cylinders under 2,000 psi pressure. A 1.5 cu ft cylinder holds 15 lb of oxygen, equivalent to 244 cu ft at standard temperature and pressure.

Table 3.2 gives the uses of oxygen. The steel industry and other primary metals production prefers to use pure oxygen rather than air in processing iron. The oxygen reacts with elemental carbon to form carbon monoxide, which is processed with iron oxide so that carbon is incorporated into the iron metal, making it much lower melting and more pliable. This material is called fusible pig iron. Common pig irons contain 4.3% carbon and melt at 1130°C, whereas pure iron has a melting point of 1539°C. The following equations summarize some of this chemistry.

$$2C + O_2 \longrightarrow 2CO$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

$$2CO \longrightarrow C(\text{in Fe}) + CO_2$$

Oxygen also removes sulfur, phosphorus, silicon, and other impurities in the iron. Steel is a mixture of several physical forms of iron and iron carbides. Properties are controlled by the amount of carbon and other elements present, such as manganese, cobalt, and nickel. Since the steel industry uses approximately half of all oxygen, the production of oxygen is very dependent on this one use.

Gasification involves partial oxidation of hydrocarbons to produce synthesis gas, a mixture of carbon monoxide and hydrogen. This will be discussed under the section on hydrogen manufacture. Chemicals made from oxygen include ethylene and propylene oxide, titanium dioxide, acetylene, vinyl chloride, and vinyl acetate. These are discussed in later sections of this book. Welding and cutting with an oxygen-acetylene torch is common in industry. The health sciences use oxygen to ease patients' breathing. Pulp and paper bleaching and sewage treatment and aeration are other examples of oxygen's broad importance to many industries that affect our everyday lives.

3. HYDROGEN

3.1 Manufacture

Hydrogen does not actually appear in the top 50. One reason is that most of it is captive and immediately reused to make ammonia, hydrogen chloride, and methanol—three other chemicals with high rankings. Since it is a feedstock for these chemicals it is even more important than these three and we will study its manufacture in detail. Hydrogen is our first example of a "petrochemical" even though it is not organic. Its primary manufacturing process is by steam-reforming of natural gas or hydrocarbons. Approximately 80% of the hydrogen used for ammonia manufacture comes from this process.

3.1.1 Reactions

A variety of low molecular weight hydrocarbons can be used as feedstock in the steam-reforming process. Equations are given for both methane (natural gas) and propane. The reaction occurs in two separate steps: reforming and shift conversion.

Methane

Reforming $CH_4 + H_2O \longrightarrow CO + 3H_2$

Shift conversion $CO + H_2O \longrightarrow CO_2 + H_2$

Propane

Reforming $C_3H_8 + 3H_2O \longrightarrow 3CO + 7H_2$

Shift conversion $3CO + 3H_2O \longrightarrow 3CO_2 + 3H_2$

The reforming step makes a hydrogen:carbon monoxide mixture that is one of the most important materials known in the chemical industry. It is called *synthesis gas* and is used to produce a variety of other chemicals. The old method of making synthesis gas was from coke, but this gave a lower percentage of hydrogen in the mixture, which was called water gas or blue gas.

$$C + H_2O \longrightarrow CO + H_2$$

Higher H_2:CO ratios are now needed, and thus the newer hydrocarbon feedstocks are used. Coal gives a 1:1 ratio of H_2:CO, oil a 2:1 ratio, gasoline 2.4:1, and methane 4:1.

Note that in the second step, the shift conversion process (also known as the carbon monoxide or water gas shift reaction), more hydrogen is formed along with the other product, carbon dioxide. A variety of methods is used to make carbon dioxide, but this process is the leading method.

3.1.2 Description

Fig. 3.2 diagrams the steam-reforming process. The hydrocarbon

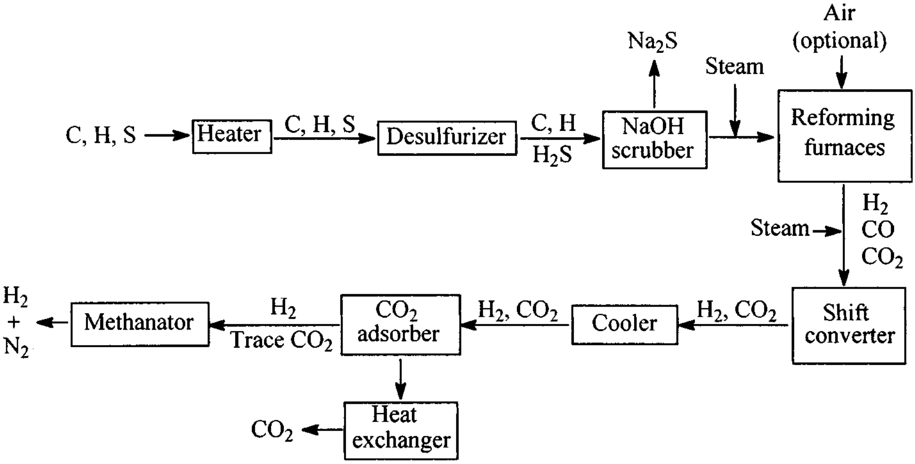


Figure 3.2 Steam-reforming of hydrocarbons.

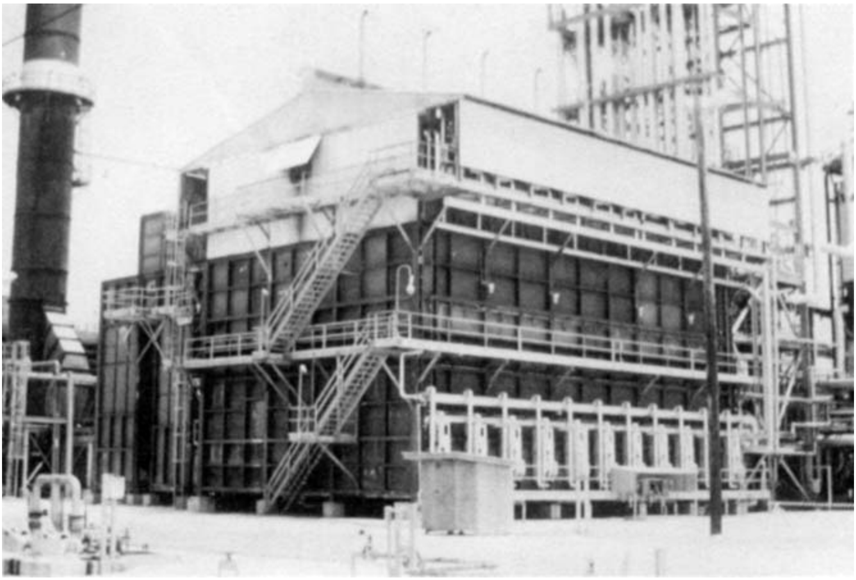


Figure 3.3 The primary reformer for methane conversion to carbon monoxide and hydrogen. (Courtesy of Solutia Inc., Luling, LA)

feedstock, usually contaminated with some organosulfur traces, is heated to 370°C before entering the desulfurizer, which contains a metallic oxide catalyst that converts the organosulfur compounds to hydrogen sulfide. Elemental sulfur can also be removed with activated carbon absorption. A caustic soda scrubber removes the hydrogen sulfide by salt formation in the basic aqueous solution.

$$H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O$$

Steam is added and the mixture is heated in the furnace at 760-980°C and 600 psi over a nickel catalyst. When larger hydrocarbons are the feedstock, potassium oxide is used along with nickel to avoid larger amounts of carbon formation. There are primary (Fig. 3.3) and secondary (Fig. 3.4) furnaces in some plants. Air can be added to the secondary reformers. Oxygen reacts with some of the hydrocarbon feedstock to keep the temperature high. The nitrogen of the air is utilized when it, along with the hydrogen formed, reacts in the ammonia synthesizer. More steam is added and the mixture enters the shift converter (Fig. 3.5), where iron or chromic oxide catalysts at 425°C further react the gas to hydrogen and carbon dioxide. Some shift converters have high and low temperature sections, the high temperature section

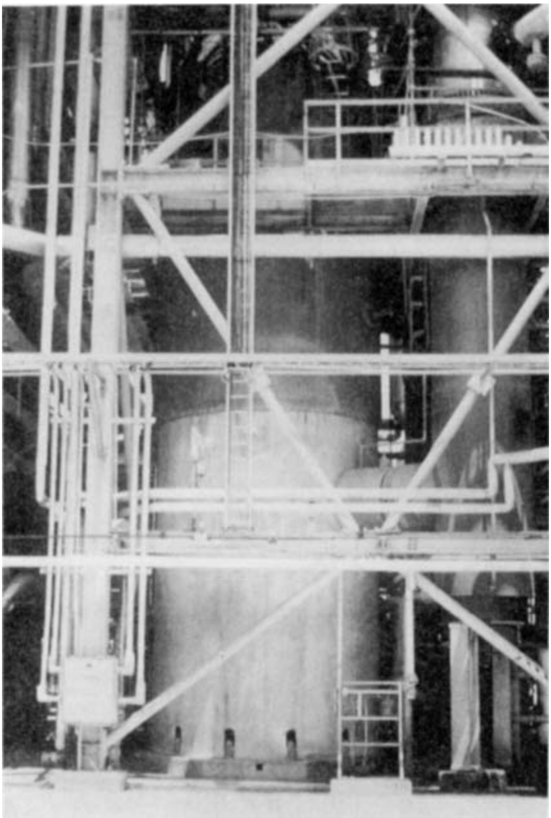


Figure 3.4 A secondary reformer converts the last of the methane. (Courtesy of Solutia Inc., Luling, LA)

converting most of the CO to CO_2 relatively fast, the low temperature section completing the process and taking advantage of a more favorable equilibrium toward CO_2 at the low temperatures in this exothermic reaction. Cooling to 38°C is followed by carbon dioxide absorption with monoethanolamine. The carbon dioxide is desorbed by heating the monoethanolamine and reversing this reaction. The carbon dioxide is an important by-product. Alternatively, hot carbonate solutions can replace the monoethanolamine.

$$HO{-}CH_2{-}CH_2{-}NH_2 + H_2O + CO_2 \rightleftharpoons HO{-}CH_2{-}CH_2{-}NH_3^+ + HCO_3^-$$

A methanator converts the last traces of carbon dioxide to methane, a less interfering contaminant in hydrogen used for ammonia manufacture.

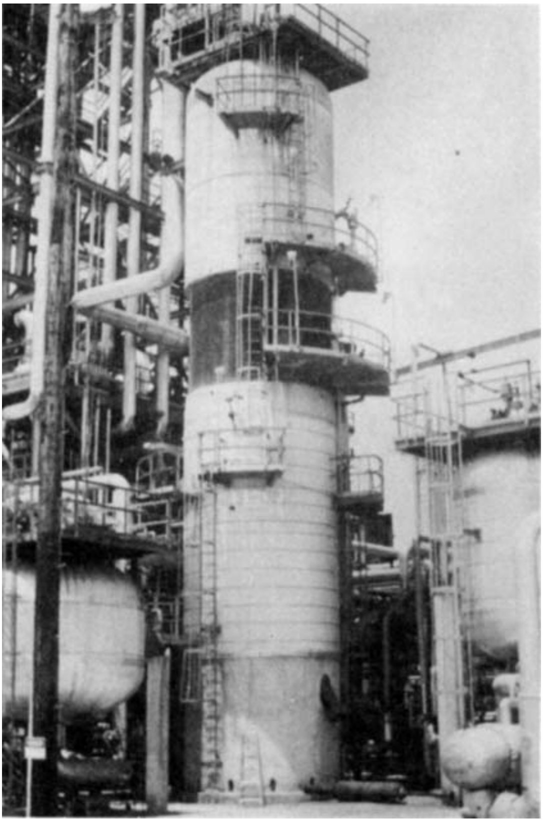


Figure 3.5 A shift converter reacts carbon monoxide and water to give carbon dioxide and more hydrogen. (Courtesy of Solutia Inc., Luling, LA)

3.2 Uses

Table 3.3 gives the total uses of hydrogen. Ammonia production is by far the most important application, followed by methanol manufacture. Hydrogenations in petroleum refineries are an important use. Many other industries utilize hydrogen. Miscellaneous uses include hydrogenation of fats and oils in the food industry, reduction of the oxides of metals to the free metals, pure hydrogen chloride manufacture, and liquid hydrogen as rocket fuel.

Table 3.3 Total Uses of Hydrogen

Ammonia	40%
Methanol	10
Other chemicals	6
Petroleum refining	4
Miscellaneous	40

Source: Chemical Economics Handbook

4. CARBON DIOXIDE

4.1 Manufacture

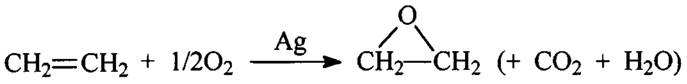
Over 90% of all carbon dioxide is made by steam-reforming of hydrocarbons, and much of the time natural gas is the feedstock. It is an important by-product of hydrogen and ammonia manufacture.

$$CH_4 + 2H_2O \longrightarrow 4H_2 + CO_2$$

A small amount (1%) of carbon dioxide is still made from fermentation of grain. Ethyl alcohol is the main product.

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2C_2H_5OH + 2CO_2$$

Another 1% is recovered as a by-product of ethylene oxide manufacture from ethylene and oxygen. When the oxidation goes too far some carbon dioxide is formed.



Other small amounts are obtained from coke burning, the calcination of lime, and in the manufacture of sodium phosphates from soda ash and phosphoric acid.

Table 3.4 Uses of Carbon Dioxide

Liquid and Solid:	
Food industry	51%
Beverage carbonation	18
Oil and gas recovery	11
Chemical manufacture	10
Metalworking	4
Miscellaneous	6
Gas:	
Oil and gas recovery	83
Chemical manufacture	17

Source: Chemical Economics Handbook

$$\text{C(coke)} + O_2 \longrightarrow CO_2$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$Na_2CO_3 + H_3PO_4 \longrightarrow Na_2HPO_4 + CO_2 + H_2O$$

4.2 Uses

Carbon dioxide is a gas at room temperature. Below -78°C it is a solid and is commonly referred to as "dry ice." At that temperature it sublimes and changes directly from a solid to a vapor. Because of this unique property, as well as its non-combustible nature, it is a common refrigerant and inert blanket. Table 3.4 shows the uses of carbon dioxide in all its forms: liquid, solid, and gas. Refrigeration using dry ice is especially important in the food industry. Beverage carbonation for soft drinks is a very big application. In oil and gas recovery carbon dioxide competes with nitrogen as an inert atmosphere for oil wells.

5. ECONOMICS OF INDUSTRIAL GASES

U.S. production of industrial gases is given in Fig. 3.6. Hydrogen is not included because so much of its production is captive, so as to make its production profile meaningless. Nor is the amount of nitrogen used to make ammonia included. Even without this captive nitrogen, notice the much steeper nitrogen production curve, especially in the late '70s and '80s. In 1980 nitrogen was ranked fifth in chemical production. It is now second.

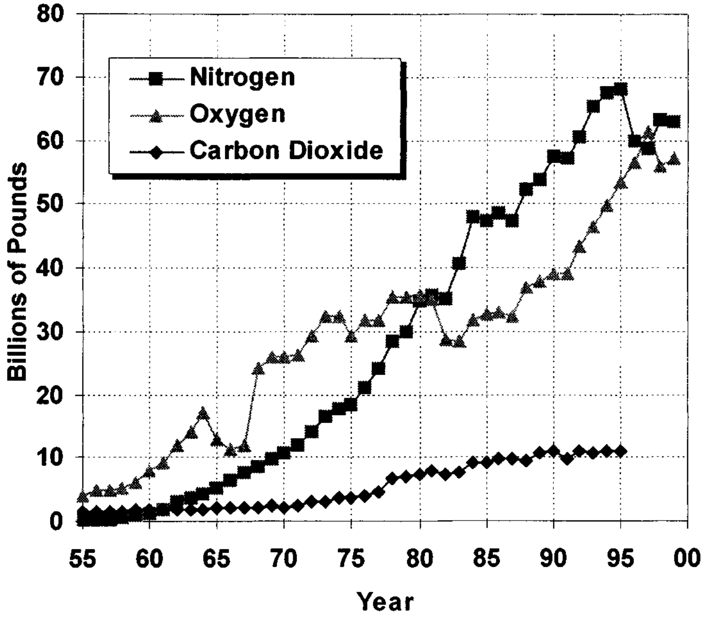


Figure 3.6 U.S. production of gases. (*Source*: Lowenheim and Moran and *Chemical and Engineering News*)

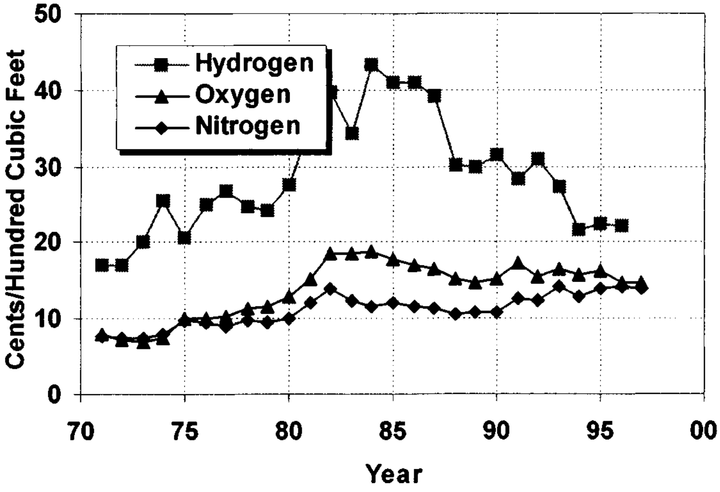


Figure 3.7 U.S. prices of gases. (*Source*: *Chemical Economics Handbook*)

Nitrogen and carbon dioxide were two of the fastest growing chemicals in the 1970s and 1980s especially because of their uses in oil and gas recovery. Oxygen on the other hand had a more linear growth, no doubt due to the suffering steel industry, in these years. Nitrogen passed oxygen in production in 1982, but oxygen is once again very close to nitrogen production in the 1990s and has made a comeback in this decade. Prices for nitrogen, oxygen, and hydrogen are given in Fig. 3.7. Carbon dioxide varies considerably in price depending on its form, dry ice or gaseous. Note that hydrogen is much more expensive, coming from expensive hydrocarbons, compared to nitrogen and oxygen, which share equivalent prices because of being manufactured together. Hydrogen prices were especially high in the 1970s and '80s, as were all petrochemicals derived from oil. The key in gas pricing is the important shipping charges, which are not included here. They are very expensive since a heavy container must be used to withstand the high pressures of even light weights of gases.

Suggested Readings

Austin, *Shreve's Chemical Process Industries*, pp. 106-124.
Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 442-457, 1073-1084.
Thompson, *Industrial Inorganic Chemicals: Production and Uses*, pp. 233-256.
Wiseman, *Petrochemicals*, pp. 141-148.

Chapter 4

Inorganic Nitrogen Compounds

Next, we consider ammonia and its derivatives in the top 50 chemicals. We have completed a study of the number one inorganic chemical sulfuric acid and its derivatives and have also studied industrial gases from which ammonia is made. Ammonia is in the top 10 chemicals and some important ammonia derivatives are listed in the top 50: ammonium nitrate, nitric acid, urea, and ammonium sulfate. Most ammonia eventually ends up in fertilizers of one type or another. The manufacturing chemistry for these chemicals is outlined below.

$$N_2 + 3H_2 \rightleftharpoons \underset{\text{ammonia}}{2NH_3}$$

$$NH_3 + 2O_2 \longrightarrow \underset{\text{nitric acid}}{HNO_3} + H_2O$$

$$NH_3 + HNO_3 \longrightarrow \underset{\text{ammonium nitrate}}{NH_4NO_3}$$

$$2NH_3 + CO_2 \longrightarrow \underset{\text{urea}}{NH_2CONH_2} + H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow \underset{\text{ammonium sulfate}}{(NH_4)_2SO_4}$$

It might also be argued that ammonia and its derivatives are all petrochemicals since the hydrogen is derived from methane or natural gas. Many ammonia plants are near oil refineries. Urea even contains carbon and is considered an organic chemical. But because all these nitrogen derivatives have been traditionally thought of as being inorganic, we will consider them at this time.

1. AMMONIA

$$NH_3$$

1.1 Manufacture

The process for ammonia manufacture will vary somewhat with the source of hydrogen, but 90% of ammonia plants generate the hydrogen by steam-reforming of natural gas. This has been the primary source of hydrogen since the early 1930s. Steam-reforming has already been discussed in the previous chapter and the process will not be repeated here, even though most of the design of an ammonia plant is concerned with the generation of hydrogen by steam-reforming.

If the hydrogen is made by steam-reforming, air is introduced at the secondary reformer stage. This provides nitrogen for the ammonia reaction. The oxygen of the air reacts with the hydrocarbon feedstock in combustion and helps to elevate the temperature of the reformer. Otherwise nitrogen can be added from liquefaction of air. In either case a hydrogen-nitrogen mixture is furnished for ammonia manufacture.

1.1.1 Reaction

$$N_2 + 3H_2 \xrightleftharpoons{Fe} 2NH_3$$

85-90% yield

1.1.2 Description

Fig. 4.1 outlines the Haber process to make ammonia. The reaction of nitrogen and hydrogen gases was first studied by Haber with Nernst and Bosch in the period 1904-1916. The two gases are adjusted to a 3:1 $H_2:N_2$ mixture and compressed to 2,000-10,000 psi (150-600 atm). The mixture is filtered to remove traces of oil, joined to recycled gases, and is fed to the reactor at 400-600 °C. The reactor (Fig. 4.2) contains an iron oxide catalyst that reduces to a porous iron metal in the $H_2:N_2$ mixture. Ruthenium on

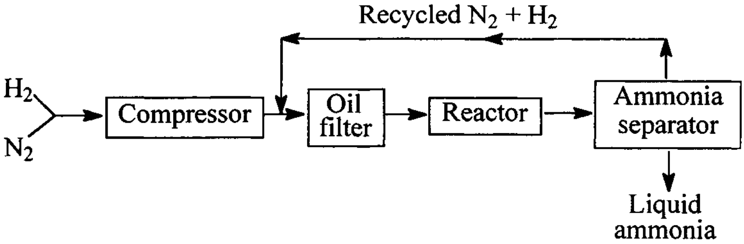


Figure 4.1 Haber process for making ammonia.

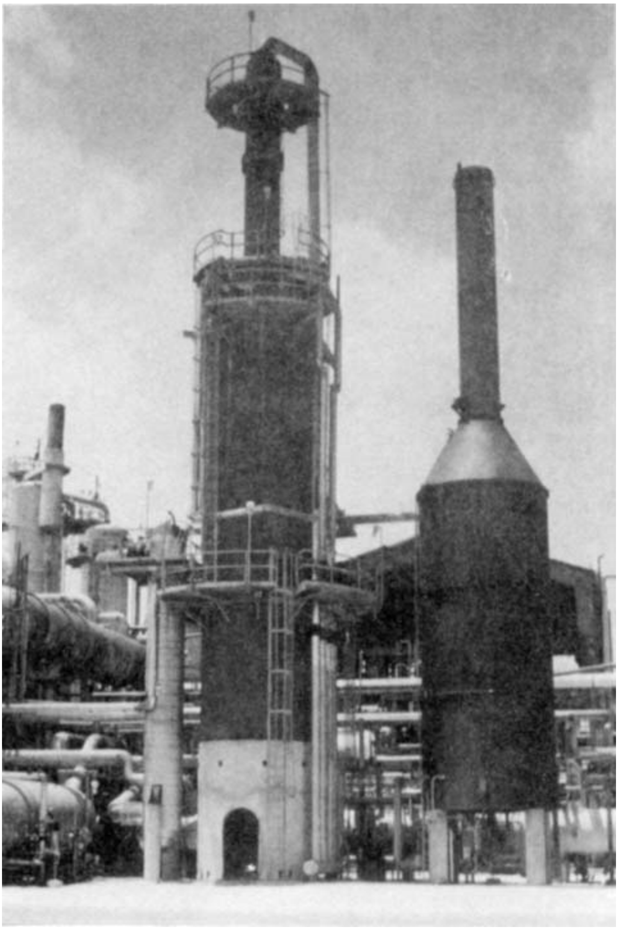


Figure 4.2 In the reactor for ammonia synthesis, nitrogen and hydrogen gases are used. (Courtesy of Solutia Inc., Luling, LA)

carbon is a new catalyst and is much more active than iron, but also more expensive. Exit gases are cooled to -10 or -20 °C and part of the ammonia liquefies. The remaining gases are recycled. The conversion to ammonia per pass is 20-22%. The overall yield is 85-90%.

This is our first distinction between conversion and yield, and it is important to know the difference. Conversion is the amount of product made per pass in a given reaction and can at times be small. With recycling of a raw material, however, the final percent yield, the overall transformation of reactants into products, can be very high.

1.2 Properties

Anhydrous ammonia is a colorless gas with a pungent odor, bp -33 °C. It can be liquefied at 25 °C under 175 psi. The gas is usually shipped as a liquid under pressure. It is very soluble in water. The water solution can be called ammonia water, aqua ammonia, ammonium hydroxide, or sometimes just "ammonia" misleadingly.

1.3 Uses

Table 4.1 gives the use profile for ammonia. It can be applied directly for fertilizer or made into other nitrogen-containing compounds used for fertilizer such as urea, ammonium nitrate, ammonium phosphate, ammonium sulfate, and nitric acid. Overall approximately 80% of ammonia has an end use as fertilizer. Explosives, a second important end use, made from ammonia are ammonium nitrate and, via nitric acid, the nitroglycerin used in dynamite. Chemical intermediates include acrylonitrile and caprolactam, which eventually go into fibers.

1.4 Economics

Fig. 2.2 in Chapter 2, Section 1, includes a production profile for ammonia. Ammonia production is tied to agriculture. Although the agricultural industry is quite variable, overall ammonia production is more

Table 4.1 Uses of Ammonia

Direct application fertilizer	20%
Other fertilizer materials	60
Chemical intermediates	19
Miscellaneous	1

Source: Chemical Profiles

constant. The great demand for fertilizers since World War II has spurred production. In this country there is now a slumping demand, and increased capacity in other countries has hurt exports. An average plant will manufacture 900-1500 tons/day. There are over 20 manufacturers in this country. Many of them are in the oil-rich Gulf region and are connected with oil refineries. Much ammonia is captive and used on site or internally within the company. Ammonia's price is very dependent on that of natural gas. Since it is one of the largest volume petrochemicals, its price has varied similarly to that of organic chemicals with a large increase in the 1970s. Its commercial value is high. At $155/ton and a production of 37.9 billion lb its worth is calculated as $2.9 billion.

2. NITRIC ACID

$$HNO_3$$

2.1 Manufacture

For many years nitric acid was made by the reaction of sulfuric acid and saltpeter (sodium nitrate), but this method is no longer used.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

Direct oxidation of ammonia is now the only process.

2.1.1 Reactions

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

$$\text{overall: } NH_3 + 2O_2 \longrightarrow HNO_3 + H_2O$$

94-95% yield

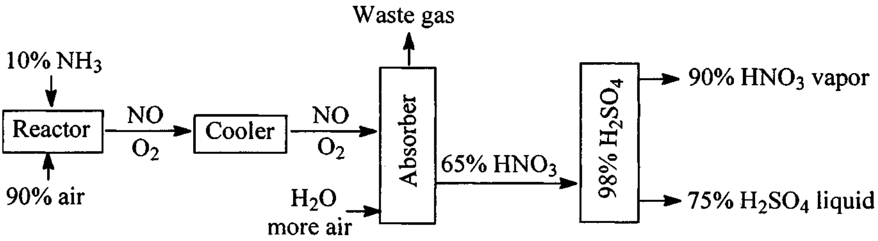


Figure 4.3 Manufacture of nitric acid by ammonia oxidation.

2.1.2 Description

Fig. 4.3 describes nitric acid manufacturing. A high-pressure process is most often used. It involves lower capital costs, increased acid strength obtained, increased rate of reaction, and a smaller tower volume required. The reactor contains a rhodium-platinum catalyst (2-10% rhodium) as wire gauzes in layers of 10-30 sheets at 750-920°C, 100 psi, and a contact time of 3×10^{-4} sec. After cooling, it enters the absorption tower with water and more air to oxidize the nitric oxide and hydrate it to 61-65% nitric acid in water. Waste gases contain nitric oxide or nitrogen dioxide. These are reduced with hydrogen or methane to ammonia or nitrogen gas. Traces of nitrogen oxides can be expelled. Concentration of the nitric acid in a silicon-iron or stoneware tower containing 98% sulfuric acid will give 90% nitric acid off the top and 70-75% sulfuric acid as the bottoms. This last step is necessary because simple distillation of nitric acid is not applicable; it forms an azeotrope with water at 68% acid. An alternative drying agent is magnesium nitrate, which can concentrate the acid to 100% HNO_3.

2.2 Properties

Pure 100% nitric acid is a colorless, highly corrosive liquid and a very powerful oxidizing agent, bp 86°C. It gradually yellows because of decomposition to nitrogen dioxide. Solutions containing more than 80% nitric acid are called "fuming nitric acids." The azeotrope is 68% HNO_3, 15 M, and has a bp of 110°C.

2.3 Uses

Nitric acid has a 65:25 fertilizer:explosive end use ratio. The production of ammonium nitrate makes up nearly all of these two uses. The other 10% is made into miscellaneous compounds: adipic acid, nitroglycerin, nitrocellulose, ammonium picrate, trinitrotoluene, nitrobenzene, silver nitrate, and various isocyanates.

3. AMMONIUM NITRATE

$$NH_4NO_3$$

3.1 Manufacture

Ammonium nitrate is made easily from ammonia and nitric acid.

$$NH_3 + HNO_3 \xrightarrow{} NH_4NO_3$$

99% yield

Although the basic reaction is the same, there are many modifications in ammonium nitrate manufacture and product form. Crystals, granules, and prills are made with the same chemistry but different engineering. The prilling technique is described here. In a stainless steel reactor the heat of neutralization boils the mixture, concentrating it to 85% nitrate. Vacuum evaporation at 125-140°C further concentrates the solution to 95%. The last water of this hygroscopic material is very difficult to remove. The hot solution is pumped to the top of a spray or prilling tower 60-70 m high. It is discharged through a spray head and solidifies as it falls in the air to form small spherical pellets, prills, of 2 mm diameter. The prills are screened, further dried, and dusted with clay to minimize sticking.

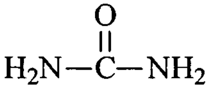
There are two alternative processes to prilling. In vacuum crystallization a rotating crystallizer forms crystals in a good size for fertilizer. These are centrifuged from the water and dried. In the Stengel process water is removed by heating. The molten mass solidifies with cooling into a solid sheet, which is ground into granular form mechanically.

Ammonium nitrate is a white hygroscopic solid, mp 169.6°C, is relatively unstable, and forms explosive mixtures with combustible materials or when contaminated with certain organic compounds. It is very soluble in water, 55% at 0°C.

3.2 Uses

Ammonium nitrate has an 82:18 fertilizer:explosive end use ratio. The chief use of ammonium nitrate until after World War II was as an explosive. Although it still accounts for more than 75% of all explosives, its major use is now as a fertilizer because of its high nitrogen content, 33.5% N.

4. UREA



$$H_2N-\overset{\overset{\large O}{\|}}{C}-NH_2$$

4.1 Manufacture

Although urea is an organic compound, it is best discussed with other ammonia-derived synthetic nitrogen compounds, especially in view of its importance to the fertilizer industry like the other compounds in this chapter. It is made easily from ammonia and carbon dioxide.

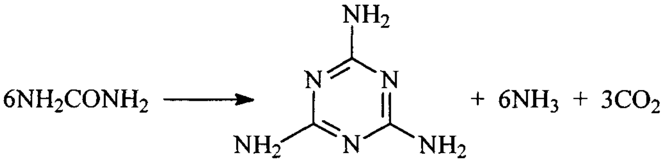
$$2NH_3 + CO_2 \longrightarrow \underset{\substack{\text{ammonium}\\ \text{carbamate}}}{NH_2COO^-NH_4^+} \longrightarrow \underset{\substack{\text{urea}\\ \text{80\% yield}}}{NH_2CONH_2} + H_2O$$

A 3:1 molar ratio of ammonia and carbon dioxide (excess ammonia) are heated in the autoclave for 2 hr at 190°C, and 1500-3000 psi. The mixture formed is approximately 35% urea, 8% ammonium carbamate, 10% water, and 47% ammonia. It is cooled and the ammonia is distilled at 60°C. The residue from the ammonia still enters a crystallizer at 15°C. More ammonia is removed by vacuum. The resulting slurry is centrifuged to get solid urea. All excess nitrogenous materials from the liquid are combined and processed into liquid fertilizer, which contains a mixture of all these materials.

Urea is a white solid, somewhat hygroscopic, mp 135°C, solubility 108 g/100 g water at 20°C.

4.2 Uses

Urea is used in solid fertilizer (54%), liquid fertilizer (32%), livestock feed (7%), urea-formaldehyde resins (5%), melamine (1%), and miscellaneous applications (1%). Presently, the most popular nitrogen fertilizer is a urea-ammonium nitrate solution. Urea-formaldehyde resins have large use as foam insulation. Melamine-formaldehyde resins are used as dinnerware and for extra-hard surfaces (Formica®). The melamine is synthesized by condensation of urea molecules.



melamine

5. AMMONIUM SULFATE

$$(NH_4)_2SO_4$$

Although not nearly so important as the other nitrogen compounds, ammonium sulfate is still in the top 50 and is important in the fertilizer industry. Most of it is synthesized by the direct reaction of ammonia and sulfuric acid. Water is removed by evaporation and the product is crystallized to large, white uniform crystals, mp 513 °C dec.

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

The ammonium sulfate is used to the extent of 97% in fertilizer. Other uses include water treatment, fermentation processes, fireproofing agents, and leather tanning.

Suggested Readings

Austin, *Shreve's Chemical Process Industries*, pp. 313-318.
Chemical Profiles in *Chemical Marketing Reporter*, 11-29-99 and 12-13-99.
Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 1084-1107.
Thompson, *Industrial Inorganic Chemicals: Production and Uses*, pp. 149-173.
Wiseman, *Petrochemicals*, pp. 141-148.

Chapter 5

Chemicals from Limestone

The next major raw material for which we discuss the derived chemicals is calcium carbonate, common limestone. It is the source of some carbon dioxide, but, more importantly, it is used to make lime (calcium oxide) and slaked lime (calcium hydroxide). Limestone, together with salt and ammonia, are the ingredients for the Solvay manufacture of sodium carbonate, soda ash. Soda ash is also mined directly from trona ore. The Solvay process manufactures calcium chloride as an important by-product. Soda ash in turn is combined with sand to produce sodium silicates to complete the chemicals in the top 50 that are derived from limestone. Since lime is the highest-ranking derivative of limestone in terms of total amount produced, we discuss it first. Refer to Fig. 2.1, Chapter 2, Section 1, for a diagram of limestone derivatives.

1. LIME

$$\mathrm{CaO}$$

Before going further, let us clarify the various common names of limestone and lime. The following is a summary of the nomenclature and the chemicals referred to. Industrial chemists quite often use the common names for these substances rather than the chemically descriptive names.

$\mathrm{CaCO_3}$: Limestone, calcite, calcium carbonate, marble chips, chalk
CaO: Lime, quicklime, unslaked lime, calcium oxide

$Ca(OH)_2$:	Slaked lime, hydrated lime, calcium hydroxide. A saturated solution in water is called limewater. A suspension in water is called milk of lime.

1.1 Manufacture

Lime is one of the oldest materials known to humankind. It was used by Romans, Greeks, and Egyptians for the production of cement and was employed in agriculture as well. One of the first things done by American settlers was to set up a lime kiln for the "calcining" or heating of limestone.

1.1.1 Reaction

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

Common temperatures used in converting limestone into lime are 1200-1300°C. For this reason lime is a very energy-intensive product. It takes the energy from a third of a ton of coal to produce 1 ton of lime.

1.1.2 Description

Fig 5.1 outlines lime production. The limestone is crushed and screened to a size of approximately 4-8 in. There are different heating techniques and kiln styles. The one diagrammed is a vertical Dorrco Fluo Solids system. The limestone enters the top. Air entering the bottom "fluidizes" the solids to get better circulation and reaction. Approximately 98% decarbonation is typical. When a kiln is used in conjunction with the Solvay process and the manufacture of soda ash, coke can be fired in the kiln along with limestone to give the larger percentages of carbon dioxide needed for efficient soda ash production by the reaction of the carbon with oxygen to give carbon dioxide. If a purer lime product is desired, the fine lime can be taken from area 4. A less pure product is obtained from the bottom kiln section. Another kind of kiln is the rotating, nearly horizontal type. These kilns can be as much as 12 ft. in diameter and 450 ft. long. Limestone enters one end. It is heated, rotated, and slowly moves at a slight decline to the other end of the kiln, where lime is obtained.

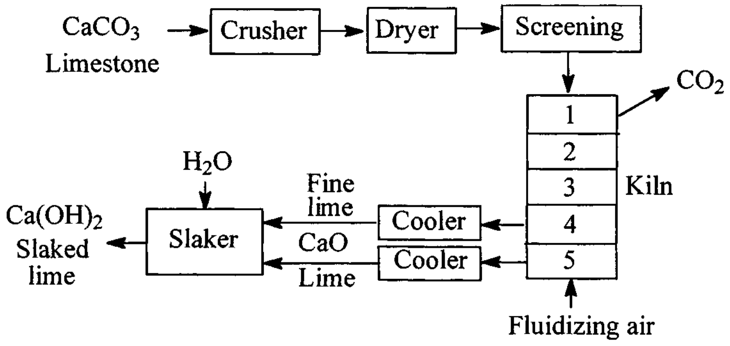


Figure 5.1 Lime manufacture.

1.2 Uses

For most applications slaked lime is sold. The hydration of lime is very exothermic and could ignite paper or wood containers of the unslaked material. Slaked lime is slightly soluble in water to give a weakly basic solution.

Table 5.1 summarizes the uses of lime. Lime is used as a basic flux in the manufacture of steel. Silicon dioxide is a common impurity in iron ore that cannot be melted unless it combines with another substance first to convert it to a more fluid lava called slag. Silicon dioxide is a Lewis acid and therefore it reacts with the Lewis base lime. The molten silicate slag is less dense than the molten iron and collects at the top of the reactor, where it can be drawn off. Over 100 lb of lime must be used to manufacture a ton of steel.

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

Table 5.1 Uses of Lime

Metallurgy	40%
Pollution control	15
Water treatment	10
Chemical manufacture	10
Pulp paper	5
Construction	5
Miscellaneous	15

Source: Key Chemicals

The uses of lime in chemical manufacture are too numerous to discuss since over 150 important chemicals are made with this basic material. In fact, only five other raw materials are used more frequently than lime for chemical manufacture: salt, coal, sulfur, air, and water. The most important chemical derivative of lime is soda ash, although the synthetic product has been a small percentage of all soda ash in recent years.

A growing use of lime is in pollution control, where lime scrubbers placed in combustion stacks remove sulfur dioxide present in combustion gases from the burning of high sulfur coal.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$Ca(OH)_2 + H_2SO_3 \longrightarrow CaSO_3 + 2H_2O$$

Lime is used in water treatment to remove calcium and bicarbonate ions.

$$Ca(OH)_2 + Ca^{+2} + 2HCO_3^- \longrightarrow 2CaCO_3 + 2H_2O$$

Lime is employed in the kraft pulping process to be discussed in detail in Chapter 22, Section 3.1. Most of it is recycled. Without this recycling the pulp and paper industry would be the largest lime user. The main reaction of lime in the kraft process is for the purpose of regenerating caustic soda (sodium hydroxide).

$$Na_2CO_3 + CaO + H_2O \longrightarrow CaCO_3 + 2NaOH$$

The caustic soda is then used in the digestion of wood. The lime is regenerated from the limestone by heating in a lime kiln.

A large part of Portland cement is lime-based. Sand, alumina, and iron ore are mixed and heated with limestone to 1500°C. Average percentages of the final materials in the cement and their structures are given here.

21%	$2CaO \bullet SiO_2$	Dicalcium silicate
52	$3CaO \bullet SiO_2$	Tricalcium silicate
11	$3CaO \bullet Al_2O_3$	Tricalcium aluminate
9	$4CaO \bullet Al_2O_3 \bullet Fe_2O_3$	Tetracalcium aluminoferrite
3	MgO	Magnesium oxide

The percentage of dicalcium silicate, sometimes abbreviated as C_2S in the industry, determines the final strength of the cement. The amount of tricalcium silicate, C_3S, is related to the early strength (7-8 days) required of the cement. Tricalcium aluminate, C_3A, relates to the set in the cement.

Tetracalcium aluminoferrite, C_4AF, reduces the heat necessary in manufacture.

1.3 Economics

The production history of lime is given with other chemicals in Fig. 2.2, Chapter 2, Section 1. Production dropped more for lime than most other chemicals in the 1980s, 2.4% per year. Lime production is very dependent on the steel industry, which in turn fluctuates directly with automobile and housing demand. But production rose again in the 1990s. Lime, being an energy intensive chemical because of the high temperatures required to make it from limestone, fluctuates more with energy prices than most other inorganic chemicals. From 1970-1975 the price rose from $12/ton to $28/ton, mainly because the oil embargo increased energy costs. Presently it sells for $57/ton or about 2.9¢/lb and the commercial value of its 45.2 billion lb is $1.3 billion.

2. SODA ASH (SODIUM CARBONATE)

$$Na_2CO_3$$

2.1 Manufacture

The LeBlanc process for the manufacture of soda ash was discovered in 1773 and was used universally for many years in Europe. Salt cake (sodium sulfate) reacts with limestone to give soda ash and a troublesome side product gypsum (calcium sulfate). The process is no longer used.

$$Na_2SO_4 + CaCO_3 \xrightarrow{\Delta} Na_2CO_3 + CaSO_4$$

In 1864 Ernest Solvay, a Belgian chemist, invented his ammonia-soda process. A few years later the soda ash price was reduced one third. The Solvay process had completely replaced the LeBlanc method by 1915. The Solvay method is still very popular worldwide. However, in this country large deposits of natural trona ore were found in the 1940s in Green River, Wyoming. In the last few years there has been a tremendous conversion from synthetic to natural soda ash. The first and last Solvay plant in the U.S. closed in 1986 (a large Allied Chemical plant in Solvay, NY). Trona ore is found about 500 m below the surface. It is called sodium sesquicarbonate and is mostly $2Na_2CO_3 \bullet NaHCO_3 \bullet 2H_2O$ (45% Na_2CO_3, 36% $NaHCO_3$, 15% water + impurities). Heating this ore gives soda ash. The conversion from the Solvay process to natural soda ash has been called one of the most successful chemical industry transformations of the late 1970s and early 1980s. The ratio of production for selected years certainly proves this point.

Year	1948	1974	1981	1985	1986
Solvay	94	46	9	6	0
Natural	6	54	91	94	100

Despite the fact that no new Solvay plants have been started since 1934 in this country, it is still an important method worldwide. There is some fascinating chemistry in this involved process and we will discuss it.

2.1.1 Solvay Reactions

$$\left[\begin{array}{l} CaCO_3 \longrightarrow CaO + CO_2 \\ CaO + H_2O \longrightarrow Ca(OH)_2 \end{array}\right] \text{source of } CO_2$$

$$2NH_3 + 2H_2O \rightleftharpoons 2NH_4OH \quad \text{source of } NH_4OH$$

$$\left[\begin{array}{l} 2NH_4OH + 2CO_2 \longrightarrow 2NH_4HCO_3 \\ 2NH_4HCO_3 + 2NaCl \longrightarrow 2NaHCO_3 + 2NH_4Cl \\ 2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O \end{array}\right] \begin{array}{c}\text{main Solvay}\\ \text{reactions}\end{array}$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + CaCl_2 + 2H_2O \quad \text{recycle of } NH_3$$

$$CaCO_3 + 2NaCl \longrightarrow Na_2CO_3 + CaCl_2 \quad \text{overall reaction}$$

2.1.2 Description

A detailed description of salt mining will be postponed until the next chapter, but it is important to note that soda ash is made from both limestone and salt, the two major raw materials. As outlined in Fig. 5.2, the brine (salt solution) is mixed with ammonia in a large ammonia absorber. A lime kiln, using technology similar to that discussed earlier, serves as the source of carbon dioxide, which is mixed with the salt and ammonia in carbonation towers to form ammonium bicarbonate and finally sodium bicarbonate and ammonium chloride. Filtration separates the less soluble sodium bicarbonate from the ammonium chloride in solution.

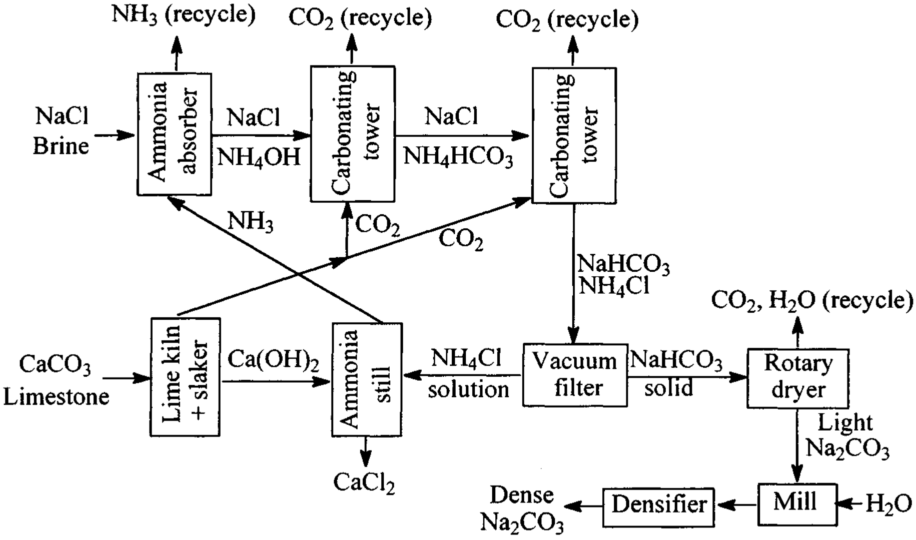


Figure 5.2 Manufacture of soda ash.

The sodium bicarbonate is heated to 175 °C in rotary dryers to give light soda ash. The carbon dioxide is recycled. Light soda ash is less dense than the natural material because holes are left in the crystals of sodium bicarbonate as the carbon dioxide is liberated. Dense soda ash, used by the glass industry, is manufactured from light ash by adding water and drying.

The ammonium chloride solution goes to an ammonia still where the ammonia is recovered and recycled. The remaining calcium chloride solution is an important by-product of this process, although in large amounts it is difficult to sell and causes a disposal problem.

2.2 Uses

Table 5.2 outlines the uses of soda ash. Glass is the biggest industry using soda ash. The 49% used by this industry is divided into 44% bottles and containers, 38% flat glass, 9% fiberglass, and 9% other. The glass industry is very complex and would take some time to discuss at length. There are about 500 different kinds of glass. However, 90% of all glass made is soda-lime-silica glass, which incorporates ingredients to be heated to give an approximate weight ratio of 70-74% SiO_2, 10-13% CaO, and 13-16% Na_2O. These glasses can be used for windows, containers, and many transparent fixtures. The sand must be nearly pure quartz, a crystalline form of silicon dioxide. These deposits often determine the location of glass

Table 5.2 Uses of Soda Ash

Glass	49%
Chemical manufacture	27
Soaps/detergents	11
Flue gas desulfurization	3
Pulp and paper	2
Water treatment	2
Miscellaneous	6

Source: Chemical Profiles

factories. Sodium oxide is principally supplied from dense soda ash, but other sources of the oxide include sodium bicarbonate, sodium sulfate, and sodium nitrate. Some nitrate is generally used because it will oxidize iron impurities and avoid coloration of the glass. Limestone is the source of lime. When these substances are heated the following reactions occur.

$$Na_2CO_3 + aSiO_2 \longrightarrow Na_2O \cdot aSiO_2 + CO_2$$
$$CaCO_3 + bSiO_2 \longrightarrow CaO \cdot bSiO_2 + CO_2$$

For common window glass the mole ratio may be 2 mol Na_2O, 1 mol CaO, and 5 mol SiO_2. Glass is essentially an amorphous, multicomponent solid mixture. Specific CaO-SiO_2 or Na_2O-SiO_2 compounds do not exist. The addition of borax increases the glass resistance to acids and thermal shock. This is called Pyrex® glass.

In many other uses soda ash competes directly with caustic soda as an alkali. The chemical of choice is then dependent on price and availability of the two.

3. CALCIUM CHLORIDE

$CaCl_2$

Calcium chloride is no longer in the top 50, but it is very high in the second 50 chemicals (see Chapter 13). Because it is an important by-product of the Solvay process, we will mention it here. Besides being a Solvay by-product it is also obtained from natural brines (especially in Michigan). A typical brine contains 14% NaCl, 9% $CaCl_2$, and 3% $MgCl_2$. Evaporation

Table 5.3 Uses of Calcium Chloride

Road Deicing	40%
Road dust control	20
Industrial processing	20
Oil and gas wells	10
Concrete	5
Miscellaneous	5

Source: Chemical Profiles

precipitates the sodium chloride. The magnesium chloride is removed by adding slaked lime to precipitate magnesium hydroxide.

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$$

The uses of calcium chloride are given in Table 5.3. A large amount of calcium chloride is used on roads for dust control in the summer and deicing in the winter. The dust control use percentage includes some for roadway base stabilization. It is less corrosive to concrete than is sodium chloride. A debate on which is worse environmentally on local plant life because of high salt concentrations remains to be resolved. The home ice-melt market for calcium chloride has grown recently. Local governments are also using more calcium chloride. Another recent competitor in the market is calcium magnesium acetate, made by reaction of high-magnesium content lime with acetic acid. This salt could prove to be a noncorrosive alternative to the chlorides. Calcium chloride is used for some industrial refrigeration applications. Saturated calcium chloride does not freeze until - 50°C, whereas saturated sodium chloride has a freezing point of - 20°C.

4. SODIUM SILICATE (SILICA GEL)

Soda ash is heated with sand at 1200-1400°C to form various sodium silicates (over 40 of them), which collectively are produced at levels sufficient to rank in the top 50. Some common ones are listed here.

$$Na_2CO_3 + nSiO_2 \longrightarrow Na_2O \cdot nSiO_2 + CO_2$$

Table 5.4 Uses of Sodium Silicate

Soaps and detergents	38%
Silica gel and catalysts	15
Pulp and paper	12
Rubber and elastomers	7
Food and health care	5
Agriculture	3
Paints and coatings	3
Miscellaneous	17

Source: Chemical Profiles

		Ratio of SiO_2/Na_2O
Sodium tetrasilicate	$Na_2Si_4O_9$	4
Sodium metasilicate	Na_2SiO_3	1
Sodium sesquisilicate	$Na_3HSiO_4 \cdot 5H_2O$	0.67
Sodium orthosilicate	Na_4SiO_4	0.50

Table 5.4 gives the uses of sodium silicate. It is a partial replacement for phosphates in detergents as a builder (see Chapter 24, Section 6) that does not pollute rivers and lakes. This is a growing use of sodium silicate. As a fine *silica gel* with a large surface area it is used for catalysis and column chromatography. In the pulp and paper industry it is used as a hydrogen peroxide stabilizer. Hydrogen peroxide is a pulp bleaching agent that is growing in use, replacing chlorine. In rubber tires it is replacing some of the carbon as a reinforcing agent, yielding the so-called "green tire."

Suggested Readings

Austin, *Shreve's Chemical Process Industries*, pp. 181-185.
Chemical Profiles in *Chemical Marketing Reporter*, 1-18-99, 2-1-99, and 6-5-00.
Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 409-414.
Thompson, *Industrial Inorganic Chemicals: Production and Uses*, pp. 123-148.

Chapter 6

Sodium Chloride Derivatives and Miscellaneous Inorganics

1. SODIUM CHLORIDE

NaCl

This very important chemical, which is known by many names such as salt, common salt, rock salt, grainer salt, and brine solution, is not included in the top 50 because it is really a naturally occurring mineral. We sometimes forget this because, although it is a mineral, it occurs as a very pure chemical and is readily isolated. If it were included in the top 50 list, it would be near number 1 with sulfuric acid, since close to 90 billion lb are processed each year in the United States. Salt mining must be nearly as old as humankind. It has been used as an object of worship, as a medium of exchange, and as a political weapon with a distribution dependent on high taxes. It is the oldest inorganic chemical industry. Sodium hydroxide, chlorine, hydrochloric acid, and titanium dioxide are all top 50 chemicals that are made from salt or salt derivatives.

1.1 Isolation

There are three important methods of salt isolation and purification: brine solution, rock salt mining, and the open pan or grainer process. The percentages of these methods have not changed dramatically in the last few years and are 54% brine, 32% rock salt, and 14% grainer salt.

1.1.1 Brine

In this method water is pumped into the salt deposit and the saturated salt solution is removed containing 26% salt, 73.5% water, and 0.5% impurities. Hydrogen sulfide is removed by aeration and oxidation with chlorine. Ca^{+2}, Mg^{+2}, and Fe^{+3} are precipitated as the carbonates using soda ash. These are removed in a settling tank. The brine solution can be sold directly or it can be evaporated to give salt of 99.8% purity. Huge deposits of salt, some four miles in diameter and eight miles deep, can be mined by this method.

1.1.2 Rock Salt

Deep mines averaging 1000 ft are used to take the solid material directly from the deposit. Salt obtained by this method is 98.5-99.4% pure. Leading states producing rock salt and their percentages are Louisiana (30%), Texas (21%), Ohio (13%), New York (13%), and Michigan (10%). Over one fourth of the world's salt is produced in the U.S.

1.1.3 Open Pan or Grainer Salt

Hot brine solution is held in an open pan approximately 4-6 m wide, 45-60 m long, and 60 cm deep at 96°C. Flat, pure sodium chloride crystals form on the surface and fall to the bottom. The crystals are raked to a centrifuge, separated from the brine, and dried. A purity of 99.98% is obtained. Grainer salt dissolves more readily and is preferred in some applications, such as the butter and cheese industries. It is more expensive because of energy use for the hot brine. Its cost can be as much as six times that of rock salt and 20 times that of brine.

1.2 Uses and Economics

Table 6.1 summarizes the uses of salt. Nearly half is consumed in the important electrolysis of brine to form two top 50 chemicals, sodium hydroxide and chlorine. One fourth is used on highways for deicing and competes with calcium chloride in this application. The food industry and animal feeds make up other important uses. Salt is surpassed only by phosphate rock in total production of all minerals. Its annual production is nearly 90 billion lb.

Table 6.1 Uses of Sodium Chloride

Sodium hydroxide—chlorine	44%
Highway ice control	24
Industrial	4
Food processing	3
Feeds and mixes	3
Other chemicals	2
Miscellaneous	20

Source: Kent

2. CAUSTIC SODA (SODIUM HYDROXIDE, CAUSTIC)

NaOH

2.1 Manufacture

For many years since its discovery in 1853 the "lime causticization" method of manufacturing caustic soda was used, which involves reaction of slaked lime and soda ash.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + CaCO_3$$

In 1892 the electrolysis of brine was discovered as a method for making both sodium hydroxide and chlorine. This rapidly grew in importance and since the 1960s it has been the only method of manufacture. Among electrolytic industries it is the second largest consumer of electricity, aluminum manufacture being the largest.

Year	% of NaOH by Electrolysis
1935	44
1940	50
1954	85
1962	100

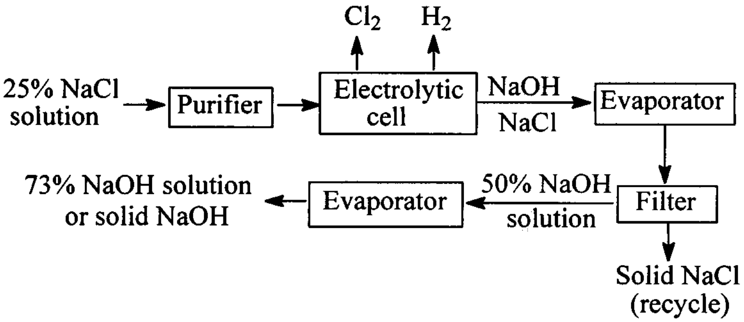


Figure 6.1 Electrolysis of brine.

2.1.1 Reaction

$$2NaCl + 2H_2O \xrightarrow{e^-} 2NaOH + H_2 + Cl_2$$

95-97% current efficiency

2.1.2 Description

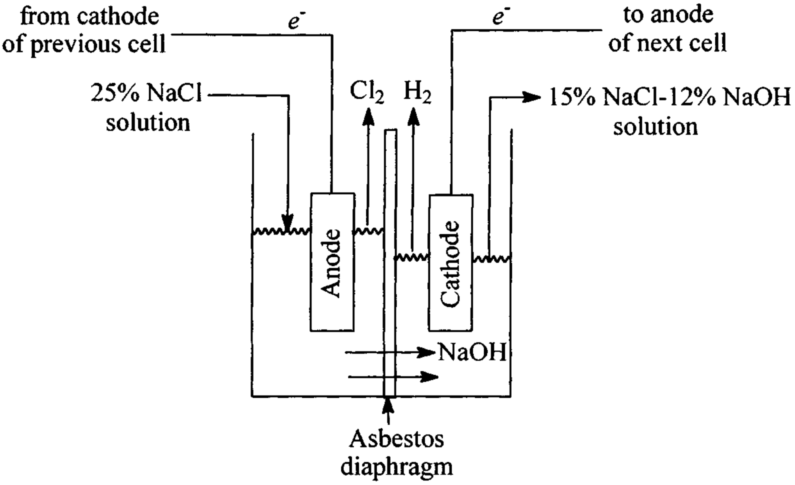
Fig. 6.1 shows the basics of an electrolysis plant. The brine that is used must be purified for this electrolytic process. Calcium, sulfate, and magnesium ions are removed by precipitation reactions.

$$Na_2CO_3 + CaCl_2 \longrightarrow CaCO_3 + 2NaCl$$

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$$

$$2NaOH + MgCl_2 \longrightarrow Mg(OH)_2 + 2NaCl$$

Different types of electrolytic cells are employed and will be discussed in the next section. Details of chlorine gas purification will be covered later. The hydrogen that is generated can be used as fuel or can be combined with some of the chlorine to give high-purity hydrogen chloride gas. There are cheaper methods for making hydrochloric acid. The hydrogen can also be used in a neighboring ammonia manufacturing plant. Evaporation and filtration of the basic solution after electrolysis gives solid salt, which can be



Anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Overall: $2Na^+ + 2Cl^- + 2H_2O \longrightarrow 2Na^+ + 2OH^- + Cl_2 + H_2$

Figure 6.2 Simplified diaphragm cell.

recycled, and an industrially popular 50% caustic solution. Further evaporation gives the solid caustic product.

2.2 Types of Electrolytic Cells

Two important types of cells are employed, the diaphragm cell (75% of all production) and the mercury cell (17%). Membrane cells account for 5% of production, other cells 3%.

2.2.1 Diaphragm Cell

A simple diaphragm cell and the reactions occurring at the anode and cathode are summarized in Fig. 6.2.

The diaphragm prevents the diffusion of sodium hydroxide toward the anode. This wall allows for the slow passage of solution and the free passage of sodium ions. It is made of asbestos fibers supported on an iron screen. The anode solution level is maintained higher than in the cathode compartment to retard back migration. If sodium hydroxide built up near the anode it would react with chlorine to give sodium hypochlorite as a side product.

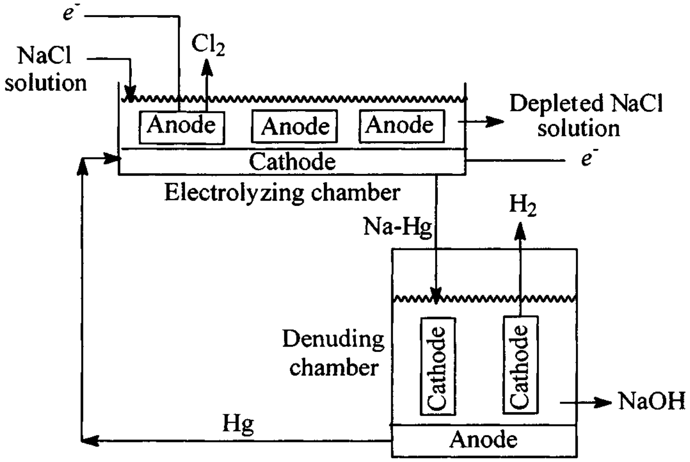
$$Cl_2 + 2NaOH \longrightarrow NaOCl + NaCl + H_2O$$

The anodes formerly were made of graphite but had to be replaced approximately every 250 days. New dimensionally stable anodes (DSA) are made of titanium with a coating of platinum, ruthenium, or iridium. They were developed around 1970 and have replaced graphite anodes in the U.S. The cathodes are steel boxes with perforated steel plates. There are advantages of the diaphragm cell. They are much less polluting than the mercury cells. They are probably more economical to run. Most new installations are diaphragms. They are definitely less expensive to operate in terms of electrical usage. Finally, the brine system is simpler and is a more economical operation. Each cell is about 6 ft square and may contain 100 anodes and cathodes. A typical plant would have several circuits with approximately 90 cells in each circuit.

2.2.2 Mercury Cell

The mercury cell has no diaphragm but is made of two separate compartments, as shown in Fig. 6.3. In the electrolyzing chamber the dimensionally stable anodes of ruthenium-titanium cause the chloride ion oxidation which is identical to that of a diaphragm cell. However, the cathode is simply a sodium amalgam flowing across the steel bottom of the cell at a slight angle from the horizontal. Notice that the cathode reaction, unlike the diaphragm cell cathode, involves the reduction of sodium ions to the metal.

This sodium amalgam enters a separate denuding chamber, sometimes called an amalgam decomposer, where the sodium metal reacts with water. Here the amalgam is the anode and the cathodes are graphite or iron. Hydrogen and caustic soda are the products here. The overall reaction, however, is identical to that of the diaphragm cell. The mercury is recycled into the electrolyzing chamber. Typical electrolyzing chambers measure 4 x 50 ft and are 1 ft high. The decomposers, one for each cell, are 2 x 16 ft high cylinders. The main advantage of the mercury cell is the low contamination of sodium chloride in the final caustic soda. This caustic has only 230 ppm NaCl impurity as compared to the diaphragm cell's caustic at 1,000 ppm NaCl Also, the sodium hydroxide solution does not require evaporation, and the chlorine is produced separately from the hydrogen and caustic, minimizing the hypochlorite side reaction and potential explosions.



Electrolyzing Chamber:

Anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode: $2Na^+ + 2e^- \longrightarrow 2Na$

Denuding Chamber:

Anode: $2Na \longrightarrow 2Na^+ + 2e^-$

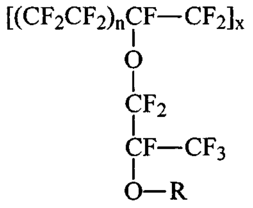
Cathode: $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

Overall: $2Na^+ + 2Cl^- + 2H_2O \longrightarrow 2Na^+ + 2OH^- + Cl_2 + H_2$

Figure 6.3 Simplified mercury cell.

2.2.3 Newer Cell Membranes

Recently, a new type of diaphragm has impacted the industry for a few new plants. The new membranes are perfluorinated polymers with occasional sulfonate and/or carboxylate groups. They have the general structure outlined here.



$$[(CF_2CF_2)_nCF{-}CF_2]_x \quad CF{-}O{-}CF_2{-}CF(CF_3){-}O{-}R$$

$R = \text{—}CF_2CF_2CF_2CO_2^-Na^+$ or $\text{—}CF_2CF_2SO_3^-Na^+$

Table 6.2 Uses of Caustic Soda

Direct application	55%
Organic chemicals	36
Inorganic chemicals	9

Source: Chemical Profiles

The anionic groups almost completely inhibit transport of hydroxide ions from the cathode, at the same time letting current flow in the form of sodium ions. The resulting caustic is purer and more concentrated while still avoiding the potential pollution of mercury cells. These cells have larger power requirements than asbestos diaphragm cells.

2.3 Uses of Caustic Soda

Table 6.2 shows the important applications of sodium hydroxide. Direct applications can be further broken down into pulp and paper (24%), soaps and detergents (10%), alumina (6%), petroleum (7%), textiles (5%), water treatment (5%), and miscellaneous (43%). Organic chemicals manufactured with sodium hydroxide are propylene oxide (23%), polycarbonate (5%), ethyleneamines (3%), epoxy resins (3%), and miscellaneous (66%). Inorganic chemicals manufactured are sodium and calcium hypochlorite (24%), sodium cyanide (10%), sulfur compounds (14%), and miscellaneous (52%). As you can see from the number of applications listed, and still the high percentages of miscellaneous uses, sodium hydroxide has a very diverse use profile. It is the chief industrial alkali.

3. CHLORINE

Cl_2

3.1 Manufacture

The electrolysis reaction and types of cells were described adequately under caustic soda. The chlorine gas, contaminated with water from the electrolytic cell, is cooled to 12-14°C to liquefy most of the water, then dried in a tower of sulfuric acid. The pure chlorine gas is compressed to 40 psi and condensed by cooling at -20 to -40°C to liquefy the gas.

Table 6.3 Uses of Chlorine

Ethylene dichloride	38%
Polyurethanes	14
Organics	8
Solvents	6
Pulp and paper bleaching	6
Water treatment	5
Titanium dioxide	3
Miscellaneous	20

Source: Chemical Profiles

3.2 Properties

Chlorine is a toxic, greenish-yellow gas with a pungent, irritating odor, bp -35°C at atmospheric pressure. It is very corrosive when wet, and is soluble in water to the extent of 177 ml/100 g at 30°C.

3.3 Uses of Chlorine

Table 6.3 outlines the diverse uses of chlorine. Many important organic chemicals are made by chlorinations, some of which are in the top 50 list such as ethylene dichloride. Propylene oxide does not contain chlorine, but a chlorohydrin process is used to make it from propylene. This is followed by loss of hydrogen chloride. Propylene oxide eventually is used to manufacture polyurethanes. These chemicals, together with various other chlorinated organics and solvents, combine to require nearly two thirds of all chlorine for the organic chemicals sector. The pulp and paper industry is using much less chlorine than a few years ago. In 1990 this used 18% of all chlorine, and now it is only 6%. The shift from chlorine bleaching of pulp to chlorine dioxide and non-chlorine bleaching has made this possible.

4. ECONOMICS OF CAUSTIC SODA AND CHLORINE

Fig. 6.4 very dramatically demonstrates the complete dependence of sodium hydroxide and chlorine production on each other. The production problem continually facing this industry is that two key chemicals are

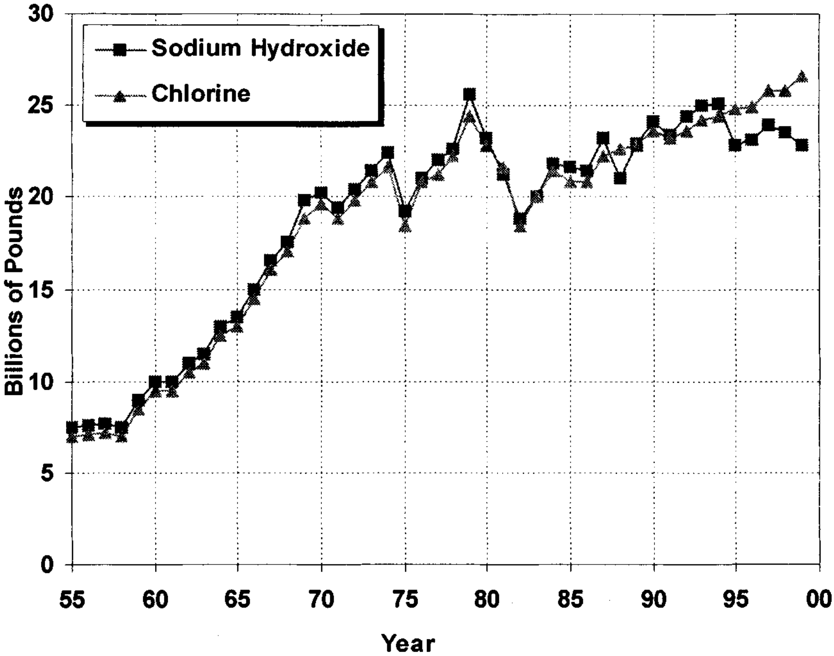


Figure 6.4 U.S. production of sodium hydroxide and chlorine. (*Source*: Lowenheim and Moran and *Chemical and Engineering News*)

produced in nearly the same amounts while the demand for the two chemicals fluctuates. The result is that one or the other is in tight supply and the price takes a jump in some years (1974, 1982, and 1991 for caustic soda, 1984 and 1998 for chlorine), as shown in Fig. 6.5. What the industry really needs is an alternate method of economically making both compounds to more easily meet the diverging demands for the two chemicals.

5. HYDROCHLORIC ACID (MURIATIC ACID, AQUEOUS HYDROGEN CHLORIDE)

HCl

Remember not to confuse hydrogen chloride, a colorless, poisonous gas with a pungent odor and a bp of -35 °C, with hydrochloric acid, an aqueous solution of HCl typically with 24-36% HCl by weight. The principal manufacture of hydrochloric acid is as a by-product from the chlorination of

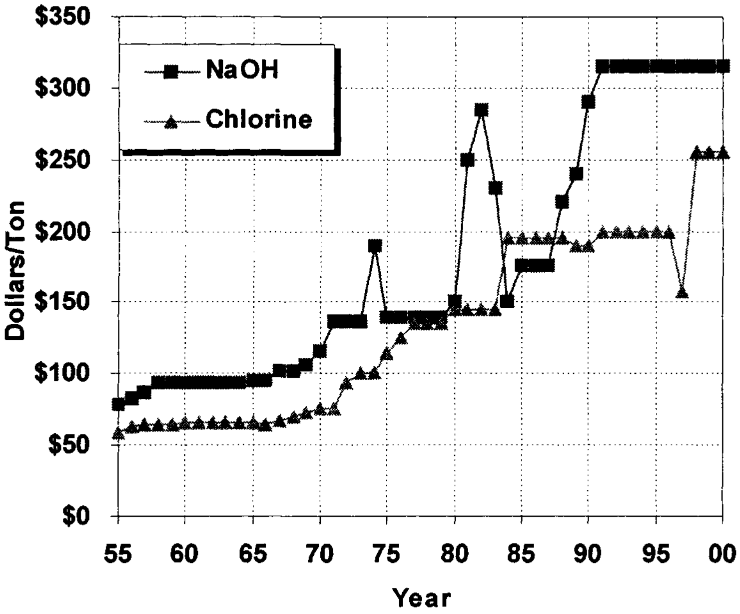
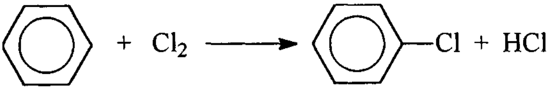


Figure 6.5 U.S. prices of sodium hydroxide and chlorine. (*Source*: Lowenheim and Moran and *Chemical Marketing Reporter*)

many organic compounds. We will be discussing these processes under organic chemicals, but a single example here would be the chlorination of benzene.



Thus hydrochloric acid is a derivative of chlorine. About 93% of it is made by various reactions including the cracking of ethylene dichloride and tetrachloroethane, the chlorination of toluene, fluorocarbons, and methane, and the production of linear alkylbenzenes. It is also a by-product of the reaction of phosgene and amines to form isocyanates.

Pure anhydrous hydrogen chloride gas is made in much smaller amounts by combining chlorine and hydrogen directly.

$$Cl_2 + H_2 \longrightarrow 2HCl$$

The uses of hydrochloric acid are given in Table 6.4. It is used in chemical manufacture especially for phenol and certain dyes and plastics.

Table 6.4 Uses of Hydrochloric Acid

Chemical production	30%
Steel pickling	20
Oil well acidifying	19
Food processing	17
Miscellaneous	14

Source: Chemical Profiles

Hydrochloric acid, being a by-product, is very cheap and is replacing sulfuric acid in some applications such as steel pickling, which is the cleaning of metal surfaces by acid etching. It leaves a cleaner surface than sulfuric acid, reacts more slowly, and can be recycled more easily. In oil well drilling it increases the permeability of limestone by acidifying the drilling process. Miscellaneous uses include swimming pools, brine treatment, semiconductors, and regeneration of ion exchange resins for water treatment.

6. TITANIUM DIOXIDE

TiO_2

Presently there are two main processes for manufacturing this important white pigment. The main one involves reaction of rutile ore (about 95% TiO_2) with chlorine to give titanium tetrachloride. For this reason we have chosen to group this key chemical under chlorine and sodium chloride. The titanium tetrachloride is a liquid and can be purified by distillation, bp 136°C. It is then oxidized to pure titanium dioxide and the chlorine is regenerated. Approximately 94% of all titanium dioxide is made by this process.

$$3TiO_2 + 4C + 6Cl_2 \xrightarrow{900^\circ C} 3TiCl_4 + 2CO + 2CO_2$$

$$TiCl_4 + O_2 \xrightarrow{1200\text{-}1400^\circ C} TiO_2 + 2Cl_2$$

The other 6% of the product is made by taking ilmenite ore (45-60% TiO_2) and treating it with sulfuric acid for digestion and filtration. Hydrolysis of the sulfate and final heating gives pure titanium dioxide.

Table 6.5 Uses of Titanium Dioxide

Surface coatings	52%
Paper coatings and filler	21
Plastics	19
Miscellaneous	8

Source: Chemical Profiles

$$FeO \cdot TiO_2 + 2H_2SO_4 \longrightarrow FeSO_4 + TiOSO_4 + 2H_2O$$

$$TiOSO_4 + 2H_2O \longrightarrow TiO_2 \cdot H_2O + H_2SO_4$$

$$TiO_2 \cdot H_2O \xrightarrow{\Delta} TiO_2 + H_2O$$

The iron sulfate crystallizes out from the $TiOSO_4$ solution and can be recycled to make more sulfuric acid.

The use profile of titanium dioxide is given in Table 6.5. Titanium dioxide has been the best selling white pigment since 1939. We will discuss why this is so later when we study coatings as a unit.

7. MISCELLANEOUS INORGANIC CHEMICALS

There are two inorganic chemicals in the top 50 that we have not yet covered: potash and carbon black, which are difficult to classify under a previous category.

7.1 Potash

$$KCl$$

The industrial term *potash* can be very misleading. It can refer to potassium carbonate (K_2CO_3), potassium hydroxide (KOH), potassium chloride (KCl), potassium sulfate (K_2SO_4), potassium nitrate (KNO_3), or collectively to all potassium salts and to the oxide K_2O. More correctly KOH is called caustic potash and KCl is called muriate of potash. Production is recorded in weight equivalents of K_2O since almost all potash is used as fertilizer and this industry quotes weight percentages of K_2O in its trade.

Large deposits of sylvinite (42.7% KCl, 56.6% NaCl) near Carlsbad, New Mexico, account for 85% of the potassium products produced in the U.S. The potassium chloride can be separated by either fractional crystallization or flotation. Potassium chloride is also obtained from the brines of Searles Lake, California. All these sources give potash (97% potassium chloride) with a 60% K_2O equivalent for fertilizer use. A chemical-grade product can be obtained to a purity of 99.9% potassium chloride. Almost all potash produced is potassium chloride. Potash is used mainly as fertilizer (88%) with a small amount (12%) used in chemical manufacture.

A small amount of potassium sulfate is isolated from natural deposits. Potassium nitrate is made by two synthetic processes.

$$NaNO_3 + KCl \longrightarrow KNO_3 + NaCl$$

$$2KCl + 2HNO_3 + \tfrac{1}{2}O_2 \longrightarrow 2KNO_3 + Cl_2 + H_2O$$

Potassium hydroxide is made by electrolysis of potassium chloride solutions in cells that are exactly analogous to sodium hydroxide production.

$$2KCl + 2H_2O \xrightarrow{e^-} 2KOH + H_2 + Cl_2$$

A large amount of potash is imported, in contrast to other mineral production in the United States. In 1999 2.8 billion lb of potash were processed in the U.S., but 10.2 billion lb were imported. This is a good time to compare some important minerals that we use to make various key inorganic chemicals, shown in Fig. 6.6. Phosphate rock leads in production. Salt is near it in production (not shown), followed by lime, sulfur, soda ash, and potash.

7.2 Carbon Black

$$C$$

This includes furnace black, colloidal black, thermal black, channel black, and acetylene black.

We will not debate whether carbon black is best treated as an inorganic or organic chemical. Both approaches have merit. Although certainly derived from petroleum, carbon black has uses similar to some inorganics;

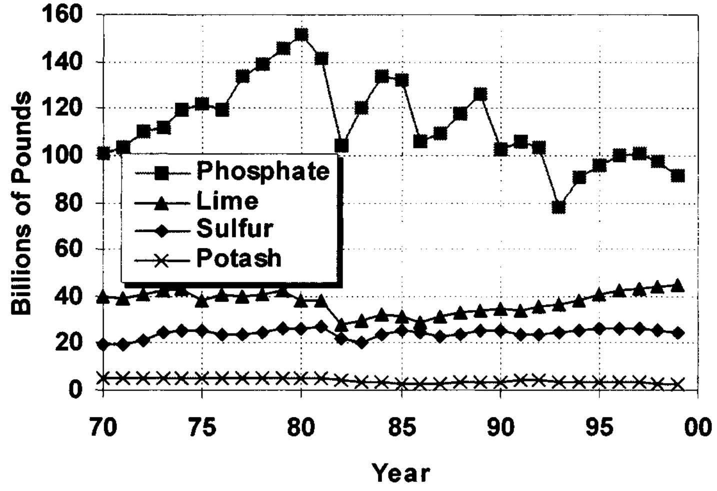


Figure 6.6 U.S. production of minerals. (*Source*: *Chemical and Engineering News*)

for example, it is the most widely used black pigment. Perhaps it is an appropriate bridge to complete our discussion of inorganics and to introduce petrochemicals. Almost all of the amount produced is furnace black involving partial combustion or a combination of combustion and thermal cracking of hydrocarbons, and to a lesser extent natural gas, at 1200-1400°C.

$$\text{—CH}_2\text{—} \longrightarrow C + H_2$$

$$\text{—CH}_2\text{—} + 1\tfrac{1}{2}O_2 \longrightarrow CO_2 + H_2O$$

or

$$CH_4 \longrightarrow C + 2H_2$$

$$CH_4 + 2O_2 \longrightarrow 2CO_2 + H_2O$$

Carbon is an important reinforcing agent for various elastomers. It is used in tires (71%) and other elastomers (22%). Miscellaneous applications (7%) include its use as a black pigment in inks and paints.

Suggested Readings

Austin, *Shreve's Chemical Process Industries*, pp. 213-215, 231-239.

Chemical Profiles in *Chemical Marketing Reporter*, 5-25-98, 6-1-98, 11-22-99, 5-1-00, 5-22-00, and 5-29-00

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 408-409, 421-436.

Chapter 7

Petroleum Refining Processes

1. INTRODUCTION

Before beginning our study of pure organic chemicals, we need to obtain some background into the chemistry of petroleum, since it is from this source that nearly all the major organic chemicals are derived. Table 7.1 lists the seven important organic chemicals, all of which are obtained by petroleum refining processes: ethylene, propylene, the butylenes, benzene, toluene, xylene, and methane. From these are made all 31 highest volume organic chemicals (some have more than one source and are listed twice). It seems appropriate that we study petroleum and its major refining processes in detail before discussing these chemicals.

Petroleum refining is not a part of our usual definition of the chemical industry, which includes Chemical Manufacturing (NAICS 325). However, the chemical process industries include those sectors of manufacturing as shown in Fig. 7.1: Paper Manufacturing (NAICS 322), Petroleum and Coal Products Manufacturing (324), Chemical Manufacturing (325), Plastics and Rubber Products Manufacturing (326), and Nonmetallic Mineral Product Manufacturing (327). All of these are important to the chemical industry. Petroleum refining is the largest part of Petroleum and Coal Products Manufacturing. It provides the raw materials for a large portion of the chemical industry and employs many chemists. NAICS 324 was down to \$125 billion of shipments in 1986 after a record \$224 billion in 1981. The slump was due mainly to decreased prices rather than production. In 1998 it still had not bounced back and was at \$137 billion. It has suffered compared to Chemical Manufacturing, which has grown faster than the other classes.

Table 7.1 Highest Volume Organic Chemicals Listed by Source

Ethylene	**C_4 Fraction**	**Benzene**
Ethylene dichloride	Butadiene	Ethylbenzene
Vinyl chloride	Acetic acid	Styrene
Ethylbenzene	Vinyl acetate	Cumene
Styrene	Isobutylene	Acetone
Acetic acid	Methyl *t*-butyl ether	Phenol
Vinyl acetate		Bisphenol A
Ethylene oxide	**Methane**	Cyclohexane
Ethylene glycol		Adipic acid
	Methanol	Nitrobenzene
Propylene	Formaldehyde	
	Dimethyl terephthalate	**Toluene**
Acrylonitrile	Methyl *t*-butyl ether	
Propylene oxide	Acetic acid	Benzene
Cumene	Vinyl acetate	
Acetone	*n*-Butyraldehyde	**Xylene**
Phenol	Urea	
Bisphenol A		*p*-Xylene
n-Butyraldehyde		Terephthalic acid
		Dimethyl terephthalate

By far the major product of this industry is the gasoline fraction from petroleum. Fig. 7.2 demonstrates this, since U.S. shipments of gasoline were down in 1986 as well. Gasoline in Fig. 7.2 follows a curve similar to Petroleum and Coal Products Manufacturing in Fig. 7.1. Other products such as jet fuel, kerosene, and fuel oils contribute substantially less to the total value of petroleum.

The olefins—ethylene, propylene, and the butylenes—are derived from natural gas and petroleum. Methane is the major constituent in natural gas. The aromatics—benzene, toluene, and the xylenes—are derived from petroleum. About 90% by weight of the organic chemicals in the world comes from natural gas and petroleum. But actually only 3% of this crude oil and 6% of refinery output in the U.S. is processed into chemicals, with the rest going as various fuels. Although we are a small user of the petroleum industry, this 3-6% going to petrochemical feedstock is important to us!

The petrochemical industry had its birth in the early 1900s. In 1913 propylene, a by-product of cracking, was introduced. In 1920 isopropyl alcohol was made from petroleum. In 1923 the first derivatives of ethylene were commercialized: ethylene chlorohydrin, ethylene glycol, and dichloroethane. By the 1940s petrochemicals were fully developed in the

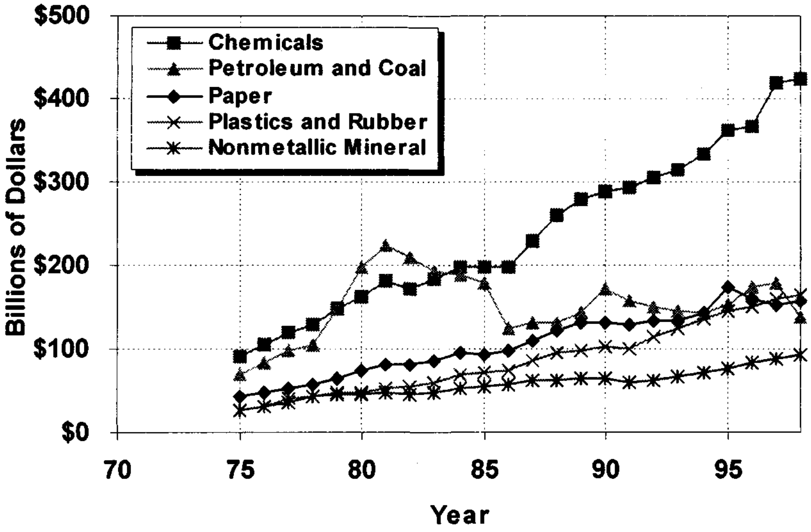


Figure 7.1 U.S. Shipments in the Chemical Process Industries. (*Source: Annual Survey of Manufactures*)

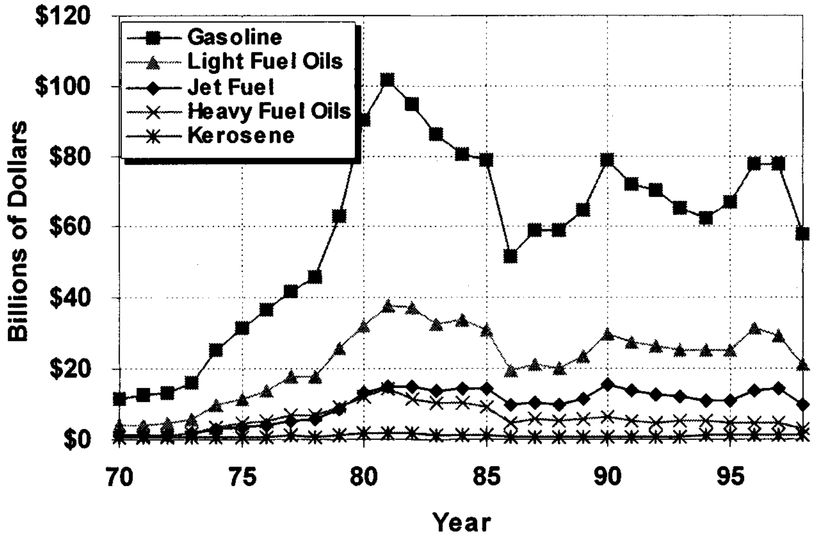


Figure 7.2 U.S. Shipments of petroleum products. (*Source: Annual Survey of Manufactures* and *Chemical Economics Handbook*)

Table 7.2 World Reserves and Production

Area	Known World Reserves, %	Oil Production, %
Middle East	66	31
United States	2	10
North America other than U.S.	5	7
Africa	7	11
Western Europe	2	10
Asia-Pacific	4	11
South and Central America	8	9
Eastern Europe	6	11

Source: Chemical Economics Handbook

U.S. and the 1950s and '60s saw rapid production increases. The oil crisis of 1973 caused huge increases in prices. The 1980s were characterized by much slower growth rates than the '50s and '60s, and we still did not rebound completely in the 1990s.

Oil is the largest segment of our energy raw materials use, being 40%, while coal use accounts for 27%, gas 21%, and hydroelectric/nuclear 12%. Table 7.2 summarizes the known world reserves of oil and the production by region. We immediately see that most countries, including the U.S., outside the Middle East region import oil in large amounts for their production and

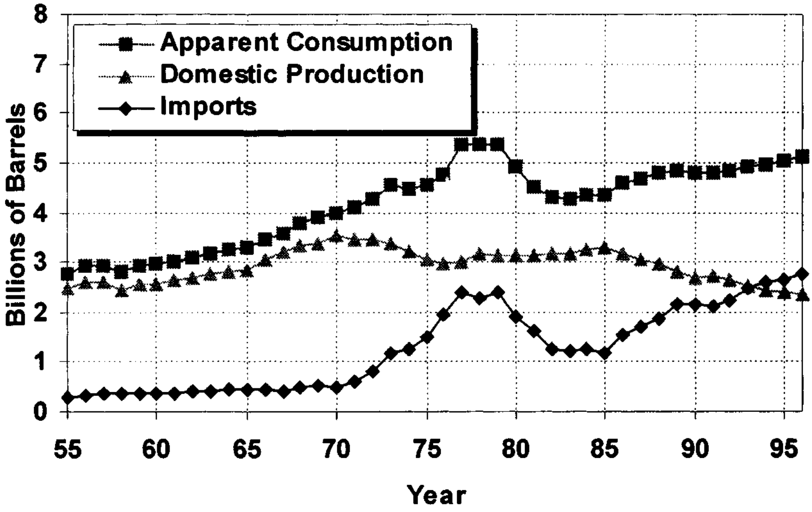


Figure 7.3 U.S. supply/demand for crude petroleum. (*Source: Chemical Economics Handbook*)

use. Two thirds of the known reserves in the world are in the Middle East. Fig. 7.3 demonstrates the growing dependence of the U.S. on imports. While our domestic production has not grown since the 1950s, imports have grown dramatically from 0.3 billion barrels of oil in 1955 to 3.0 billion barrels in 1997. We have increased our percentage of imports from approximately 13% in 1970 to 55% in 2000. A barrel (bbl) of crude oil is 42 gallons and 1 ton of crude oil is approximately 7.3 bbl. More meaningful figures of our tremendous use of oil can be quoted in terms of bbl used per day. We use approximately 18 million bbl/day of oil in this country. Worldwide production is about 56 million bbl/day. With only known reserves, this level of worldwide production could remain constant for only 43 years.

The reserves of coal are much greater than those for oil, and coal technology could be resurrected if necessary and if the industry and public want to pay the price for this development.

Finally we look at the price of oil. Fig. 7.4 shows the average U.S., domestic wholesale price for a barrel of oil. Note the very low prices in the early 1970s, the large increases in the late 1970s after the oil embargo, and the gradual levelling and final drop of prices in the late 1980s, with 1990s prices being fairly constant. The highest price of oil thus far has been $32 in 1981, an average for a whole year, but a brief period at $40 /bbl in late 1990, immediately after Iraq entered Kuwait, did occur. In parts of 2000 the price was back up to $34/bbl. An uncertain future lies ahead.

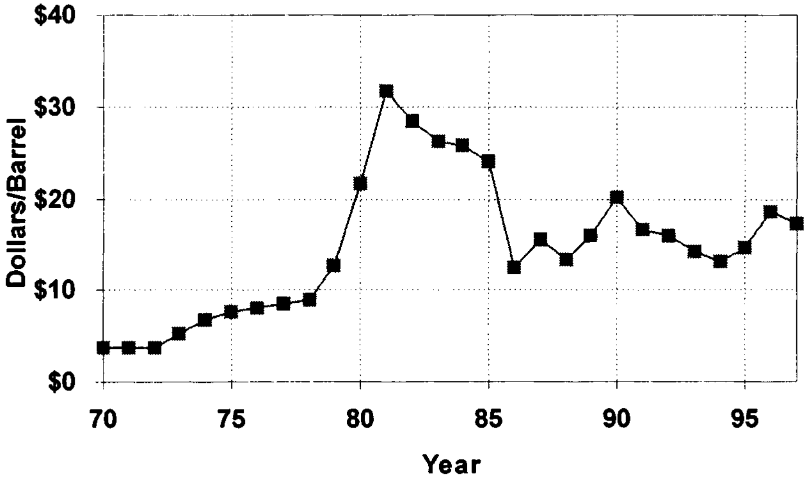


Figure 7.4 U.S. prices of crude oil. (*Source: Chemical Economics Handbook*)

Table 7.3 Fractions of Petroleum

Approximate bp (°C)	Name	Uses
<20°C	Gases	CH_4, C_2H_6, C_3H_8, C_4H_{10}—similar to natural gas and useful for fuel and chemicals.
20-150°C	Light naphtha (mainly C_5-C_6)	C_4-C_{10} aliphatic and cycloaliphatic compounds. May contain some aromatics. Useful for both fuel and chemicals.
150-200°C	Heavy naphtha (mainly C_7-C_9)	C_4-C_{10} aliphatic and cycloaliphatic compounds. May contain some aromatics. Useful for both fuel and chemicals.
175-275°C	Kerosene	Contains C_9-C_{16} compounds useful for jet, tractor, and heating fuel.
200-400°C	Gas oil	Contains C_{15}-C_{25} compounds useful for diesel and heating fuel. Catalytically cracked to naphtha and steam-cracked to olefins.
>350°C	Lubricating oil	Used for lubrication. May be catalytically cracked to lighter fractions.
>350°C	Heavy fuel oil	Boiler fuel. May be catalytically cracked to lighter fractions.
	Asphalt	Paving, coating, and structural uses.

Source: Wittcoff & Reuben

2. DISTILLATION

Several thousand compounds are present in petroleum. Few are separated as pure substances. Many of the uses of petroleum can be served by certain fractions from the distillation of crude oil. Typical distillation fractions and their uses are given in Table 7.3 and a distillation unit is shown in Fig. 7.5. The complexity of the molecules, molecular weight, and carbon number increase with the boiling point. The higher boiling fractions are usually distilled *in vacuo* at lower temperature than their atmospheric boiling points to avoid excessive decomposition to tars.

Each fraction of distilled petroleum still contains a complex mixture of chemicals but they can be somewhat categorized. A certain sample of straight-run gasoline (light naphtha) might contain nearly 30 aliphatic, noncyclic hydrocarbons, nearly 20 cycloaliphatic hydrocarbons (mainly cyclopentanes and cyclohexanes) sometimes called naphthenes, and 20 aromatic compounds.

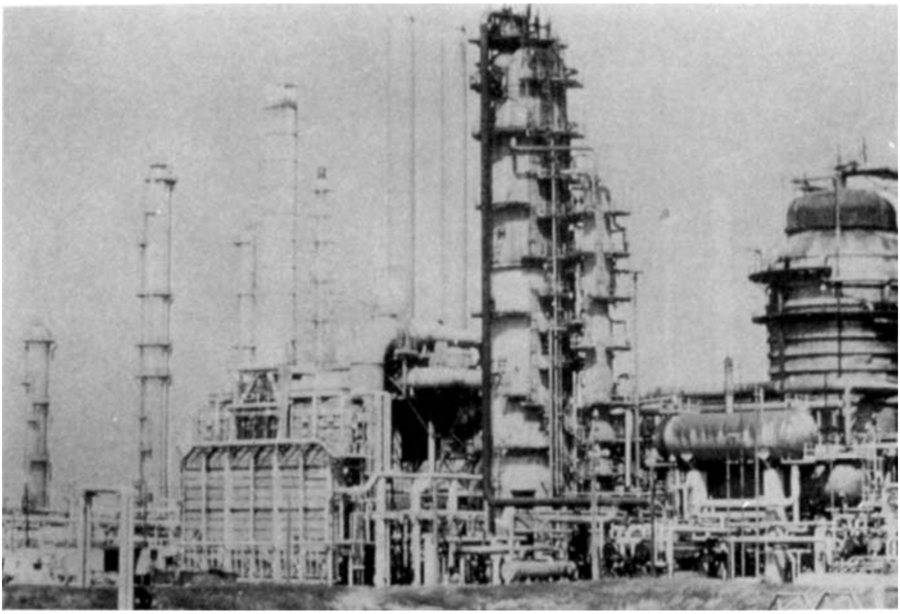
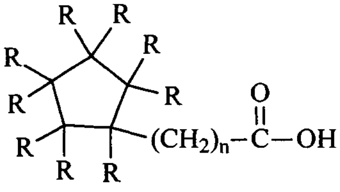


Figure 7.5 Large petroleum distillation columns like this one in the foreground can process over 400,000 barrels of crude oil per day into nearly 210,000-230,000 barrels of gasoline. That is enough to fill 678,000 13-gallon automobile tanks or 441,000 20-gallon automobile tanks. (Courtesy of BP Amoco, Texas City, TX)

Although petroleum basically consists of hydrocarbons, there are smaller amounts of other types of materials. For example, carboxylic acids occur to the extent of about 0.1-3%. These can be isolated quite easily by base extraction and the mixture is known as naphthenic acid, which can be used



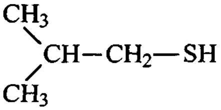
naphthenic acid

n = 1-5

R = H or alkyl

as its metal salt for paint drying, catalysts, lube additives, wood preservatives, and tire adhesion promoters. Approximately 20 million lb are used each year. A smaller amount of cyclohexyl derivatives are included in the mixture as well.

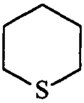
A small percentage of petroleum consists of compounds containing sulfur in one form or another. Examples of such compounds follow.



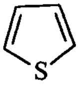
isobutyl mercaptan

$CH_3-S-CH_2-CH_3$

methyl ethyl sulfide



pentamethylene sulfide



thiophene

When gas or heating oil is used as a source of energy and burned to CO_2 and H_2O, the sulfur ends up as SO_2 in the air. The SO_2 is a major air contaminant, especially in larger cities. With air moisture it can form H_2SO_4 and H_2SO_3. Much of the sulfur-containing compounds must be taken out of petroleum before it can be used for this purpose. The current maximum percentage allowable in gasoline is 0.10% S. Nitrogen-containing compounds are present in petroleum and form NO_2 upon combustion. Most crude petroleum contains only 0.008% N, but some crudes can run to 0.25% N, although even the smaller percentage causes environmental concerns. Inorganic compounds are also present (sand, clay, and salt) but are more easily removed. Metals such as arsenic, lead, copper, nickel, and vanadium are present.

3. OCTANE NUMBER

The petroleum fraction that is the most important for the United States is gasoline. Let us take a closer look at some of the important aspects of gasoline. U.S. production was approximately 2.84 billion bbl in 1997. This is about 46% of the 6.12 billion bbl of refinery products and is way ahead of all other products, as shown in Table 7.4. In Europe the proportion of petroleum going to gasoline is considerably less, about 26%.

One cannot talk about the chemistry of gasoline without understanding octane number. When gasoline is burned in an internal combustion engine to CO_2 and H_2O, there is a tendency for many gasoline mixtures to burn unevenly. This is caused basically by ignition before the piston of the engine is in the proper position. Such nonconstant and unsmooth

Table 7.4 U.S. Production of Petroleum Products

Product	Billions of bbl/yr
Gasoline	2.84
Distillate Fuel Oils	1.24
Jet Fuels	0.57
Residual Fuel Oils	0.26
Liquefied Refinery Gases	0.25
Petroleum Coke	0.25
Still Gases	0.24
Asphalt	0.16
Petrochemical Feedstock	0.16
Other	0.15
Total	**6.12**

Source: Chemical Economics Handbook

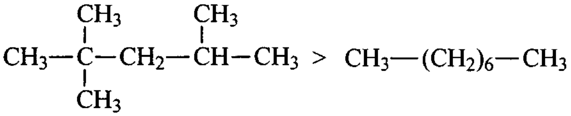
combustion creates a "knocking" noise in the engine. It has been found that certain hydrocarbons burn more smoothly than others in a gasoline mixture. In 1927 a scale was set up that attempted to define the "antiknock" properties of gasolines. At the time, 2,2,4-trimethylpentane (commonly called "isooctane") was the hydrocarbon that, when burned pure in an engine, gave the best antiknock properties (caused the least knocking). This compound was assigned the number 100, meaning it was the best hydrocarbon to use. The worst hydrocarbon they could find in gasoline that when burned pure gave the most knocking was *n*-heptane, assigned the number 0. When isooctane and heptane were mixed together they gave different amounts of knocking depending on their ratio: the higher the percentage of isooctane in the mixture, the lower was the amount of knocking. Then gasoline mixtures obtained from petroleum were burned for comparison. If a certain gasoline has the same amount of knocking as a 90% isooctane, 10% heptane (by volume) mixture, we now say that its octane number is 90. *Hence the octane number of a gasoline is the percent isooctane in an isooctane-heptane mixture that gives the same amount of knocking as the gasoline being measured.* Thus a *high* octane number means a *low* amount of knocking. The development of very high compression engines, especially for jet airplanes, now makes it necessary to extend the octane number scale beyond 100 with the use of additives.

Now there are two octane scales, a research octane number (RON) and a motor octane number (MON). RON values reflect performance at 600 rpm, 125°F, and low speed. MON is a performance index of driving with 900 rpm, 300°F, and high speed. Before 1973 RON values were the ones usually quoted to the public, but since 1973 the octane values posted on station pumps have been RON-MON averages. The average value better relates to the actual performance of the gasoline in an automobile engine. Concurrently, with the introduction of this new average scale, refiners also lowered the octane quality of their gasolines by about two units. As a result, some motorists began noticing knocking noises in their engines, even though they thought they were using the same gasoline they had always used. The MON is about six units lower than the RON. The pump now gives the (R + M)/2 value. Regular is usually 87-89 and premium about 92 on this scale.

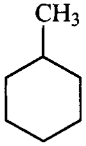
Certain rules have been developed for predicting the octane number of different types of gasoline, depending on the ratio of different types of hydrocarbons in the mixtures:

1. The octane number increases as the amount of branching or number of rings increases. Example: 2,2,4-trimethylpentane causes a higher octane number than *n*-octane; methylcyclohexane causes a higher octane number than *n*-heptane.

Octane number:



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_2-\overset{\displaystyle CH_3}{CH}-CH_3 > CH_3-(CH_2)_6-CH_3}$$

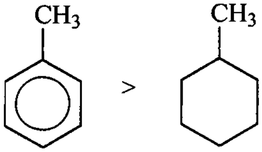


> $\mathrm{CH_3-(CH_2)_5-CH_3}$

Some typical RON values are *n*-heptane, 0; *n*-octane, -19; ethylcyclohexane, 46; methylcyclohexane, 75.

2. The octane number increases as the number of multiple bonds increases. Example: toluene causes a higher octane number than does methylcyclohexane.

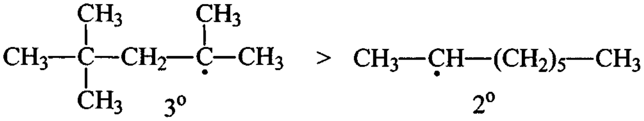
Octane number:



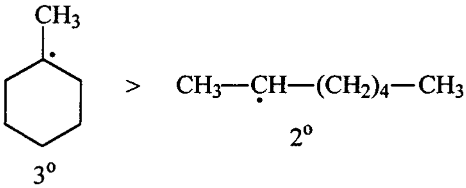
RONs:	
Ethylbenzene	107
Toluene	120
Xylenes	116-120

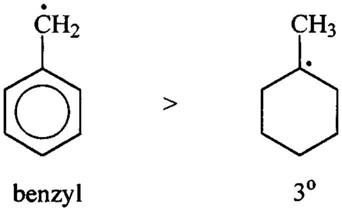
3. Summary of octane number: aromatics, alkenes, and alkynes > cyclic alkanes and branched alkanes > straight-chain alkanes.

If you recall that combustion is a free radical process, we can easily see why cyclic and branched alkanes burn more easily (and more smoothly) than straight-chain alkanes. The reason is that more stable free radicals are formed. This results in less knocking and a higher octane rating. Examples of free radical stability are the following:



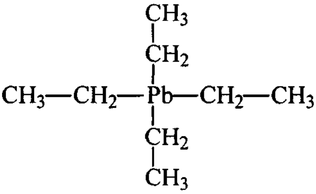
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{\bullet}{C}}-CH_3 \;>\; CH_3-\underset{\bullet}{C}H-(CH_2)_5-CH_3$$





4. ADDITIVES

In 1922 two chemists working at General Motors, Midgley and Boyd, were looking at different substances that would aid combustion of gasoline and help the knocking problems of engines. In other words, they were seeking methods of increasing the octane rating of gasoline without altering the hydrocarbon makeup. They were also interested in cleaning up the exhaust of automobiles by eliminating pollutants such as unburned hydrocarbons and carbon monoxide through more complete combustion. By far the best substance that they found was tetraethyllead.



$$\begin{array}{c} CH_3 \\ | \\ CH_2 \\ | \\ CH_3{-}CH_2{-}Pb{-}CH_2{-}CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{array}$$

This relatively inexpensive material was made from a Pb-Na alloy and ethyl chloride:

$$4Pb{-}Na + 4Et{-}Cl \longrightarrow \underset{bp = 202^{\circ}C}{Pb(Et)_4} + 4NaCl + 3Pb$$

The material added to gasoline to increase octane was called "ethyl" fluid. A typical mixture contained the following: 63% $PbEt_4$, 26% $Br{-}CH_2{-}CH_2{-}Br$, 9% $Cl{-}CH_2{-}CH_2{-}Cl$, 2% dye (as a warning of its toxicity). About 1-6 ml of ethyl fluid was added per gallon of gasoline, depending on the octane number desired. Tetraethyllead apparently burns to form lead dioxide.

$$Pb(Et)_4 \xrightarrow{O_2} PbO_2 + CO_2 + H_2O$$

Lead in this form complexes with hydrocarbons and aids in breaking carbon-carbon and carbon-hydrogen bonds.

$$PbO_2 + \text{hydrocarbons} \longrightarrow PbO_2 + CO_2 + H_2O$$

The lead oxide is not volatile and would accumulate in the engine if dibromoethane and dichloroethane were not added. These substances react with PbO_2 and form a volatile compound, $PbBr_2$ or $PbCl_2$, which is eliminated in the exhaust.

$$Br{-}CH_2{-}CH_2{-}Br + PbO_2 \xrightarrow{O_2} PbBr_2 + CO_2 + H_2O$$

In the environment the lead dihalide undergoes oxidation-reduction by sunlight to elemental lead and halogen, both of which are serious pollutants.

$$PbBr_2 \xrightarrow{h\upsilon} Pb^{o} + Br_2$$

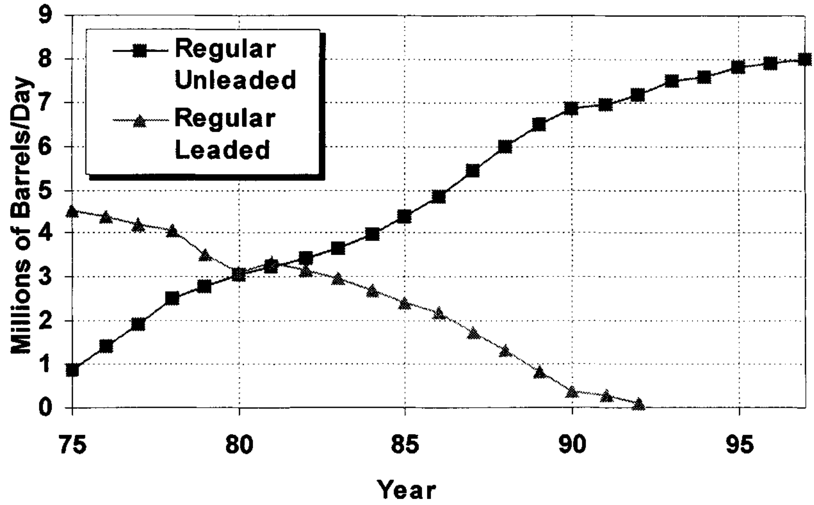
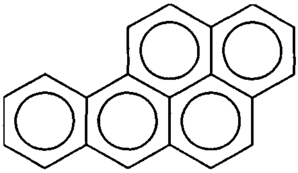


Figure 7.6 U.S. consumption of gasoline. (*Source: Chemical Economics Handbook*)

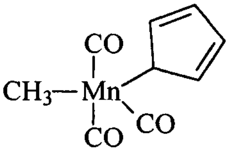
Before 1970 there was very little unleaded gasoline on the market, but by 1974 all gas stations were offering it. In 1974, unleaded fuel had become a necessity for most new cars because of their catalytic converters placed in the exhaust system. These contain platinum or palladium compounds that act as a surface catalyst to burn the hydrocarbons more completely. But lead coats the platinum and palladium and deactivates the converters, so unleaded gas must be used. Up to 4 g/gal of lead could be used in the 1970s, but this was decreased to 0.1 g by 1986. Since 1995 no leaded gas could be used in the U.S. Fig. 7.6 shows the dramatic shift from leaded to unleaded gas between 1975 and 1992.

This change to unleaded gasoline may or may not have been a wise decision. Unleaded gasoline requires the much larger and more extensive use of modern refining processes such as cracking and reforming of straight-run or natural gasoline. These processes increase the percentage of aromatic, olefins, and branched hydrocarbons and thus increase the octane number. These new gasolines do *not* solve the pollution problem. They solve the lead pollution problem, but unleaded gasolines show larger emissions of other contaminants. Of particular importance to the environment is the increase of certain *hydrocarbon emissions,* especially *carbon monoxide.* Certain unburned aromatic hydrocarbons and alkenes absorb sunlight readily and cause *smog.* Other aromatic hydrocarbons, such as benzopyrene, have been identified as known *carcinogens.* The effect of having these types of contaminants in the atmosphere has not yet been thoroughly studied.



benzopyrene

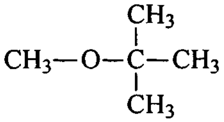
For the past several years other additives have been tried. Methylcyclopentadienyl manganese tricarbonyl (MMT) has been used in Canada for many years but is not presently added in the U.S. because it was thought to be a potential health hazard. But in Canada it has not changed the manganese concentration in air since 1977. Interestingly, in 1995 the U.S. approved its use, but no one has begun to include it in gasoline yet. In Canada it was briefly banned in 1997 because it was thought to decrease the effectiveness of auto emission control systems, but in 1998 it was started up again.



methylcyclopentadienyl
manganese tricarbonyl (MMT)

In 1977 the U.S. EPA began allowing the use of *t*-butyl alcohol up to 7%. More recently 50:50 mixtures of *t*-butyl alcohol and methyl alcohol are being used, and ethyl alcohol has also become popular. When 10% ethyl alcohol is mixed with gasoline it is called gasohol and it is popular in states with good corn crops, since the alcohol can be made from corn fermentation.

The most attractive alternative to tetraethyllead is now methyl *t*-butyl ether (MTBE). MTBE has been approved at the 7% level since 1979. In 1984 MTBE broke into the top 50 chemicals for the first time and from 1984-95 its production grew 25% per year, the largest increase by any of the



$$\begin{array}{c} \qquad\qquad\quad CH_3 \\ \qquad\qquad\quad | \\ CH_3-O-C-CH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_3 \end{array}$$

MTBE

top 50 chemicals. Note that all these additives would be expected to be good free radical initiators. A weak bond (especially the carbon-metal bond) or a stable free radical formed after breaking a bond is the important feature of these additives.

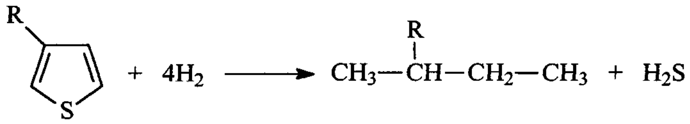
The Clean Air Act of 1991 required the benzene content of gasoline to decrease from 3 to 1%. In certain metro areas of the U.S. total aromatics had to be reduced from 36 to 25% by 1995. Since these contribute to high octane number, alternative methods had to be used to increase octane. The Clean Air Act specifies that the gasoline must be at the 2.0% oxygen level. Thus MTBE, ethyl *t*-butyl ether (ETBE), ethanol, methanol, and other ethers and alcohols had to be added at higher levels. This is called reformulated gasoline (RFG) and it may cut carbon monoxide levels and may help alleviate ozone depletion. But improved emission control systems may make this high level unnecessary. Currently MTBE accounts for 85% of the additive market, with 7% being ethanol and the remaining 8% split by the other chemicals. In 1999 California banned MTBE. In 2000 some factions called for a U.S. ban on MTBE and for increased use of ethanol to meet the oxygenate requirement. MTBE has been found in drinking water.

But ethanol cannot be blended into gasoline at the refinery because it is hygroscopic and picks up traces of water in pipelines and storage tanks. Also, ethanol shipped away from the Midwest, where it is made by corn fermentation, would add to the cost of gasoline. Gasohol may increase air pollution because gasoline containing ethanol evaporates more quickly. Studies and debate continue.

5. HYDROTREATING

Before other processes such as cracking and reforming are used to increase the octane rating, hydrotreating must occur. The distilled petroleum fractions are reacted with hydrogen at 285-340°C with a cobalt or nickel oxide/molybdenum oxide catalyst. The main reason for this reaction is to decrease the percentages of nitrogen- and sulfur-containing compounds, not only to lower pollution caused by these compounds when they were burned, but also to assure that no poisoning of catalysts in further refinery operations occurs. Sulfur compounds are notorious for this poisoning. Examples of hydrotreating reactions of molecules typically found in most oil feeds are the following:

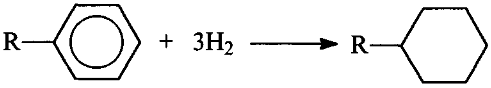
$$R{-}CH_2{-}CH_2{-}CH_2{-}NH_2 + H_2 \longrightarrow R{-}CH_2{-}CH_2{-}CH_3 + NH_3$$



The hydrogen sulfide and ammonia can be removed by amine extraction and acid washes respectively. Hydrotreating also removes metals from the feed that would otherwise poison the reforming and cracking catalysts.

As side reactions to this hydrotreating, some carbon-carbon double bonds are hydrogenated. Olefins are converted partially into alkanes, and aromatics into cyclic alkanes. These reactions actually decrease the octane rating of the gasoline somewhat, but further refinery operations such as cracking and reforming will restore and increase the percentage of olefin and aromatic compounds. The temporary formation of more saturated compounds is necessary to get the sulfur and nitrogen percentages down.

$$R-CH_2-CH=CH_2 + H_2 \longrightarrow R-CH_2-CH_2-CH_3$$



6. CRACKING

There are other processes that are used to refine petroleum into useful products. These are important processes for the gasoline fraction because they increase the octane rating. Some are used to increase the percentage of crude oil that can be used for gasoline. These processes are also important in the production of the key organic chemicals shown in Table 7.1, so we should be familiar with them.

One such process is cracking (Fig. 7.7). In catalytic cracking, as the name implies, petroleum fractions of higher molecular weight than gasoline can be heated with a catalyst and cracked into smaller molecules. This material can then be blended into the refinery gasoline feed.

$$\underset{(C_{12}\text{ and higher})}{\text{gas oil}} \xrightarrow[\text{silica-alumina}]{450\text{-}550^\circ C} \underset{(C_5\text{-}C_{10})}{\text{cracked gasoline}}$$

A simple example would be the following:

$$C_8-CH_2-CH_2-CH_2-CH_3 \longrightarrow C_8-CH=CH_2 + CH_3-CH_3$$

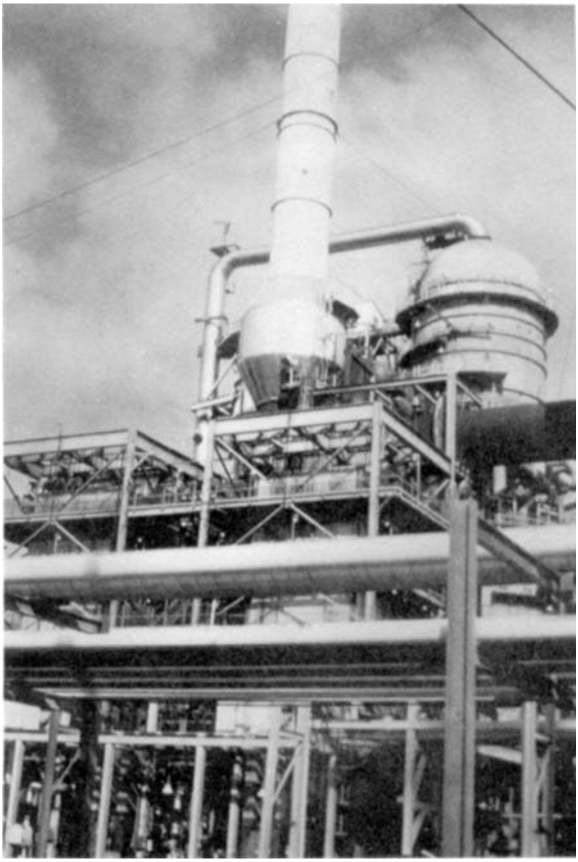
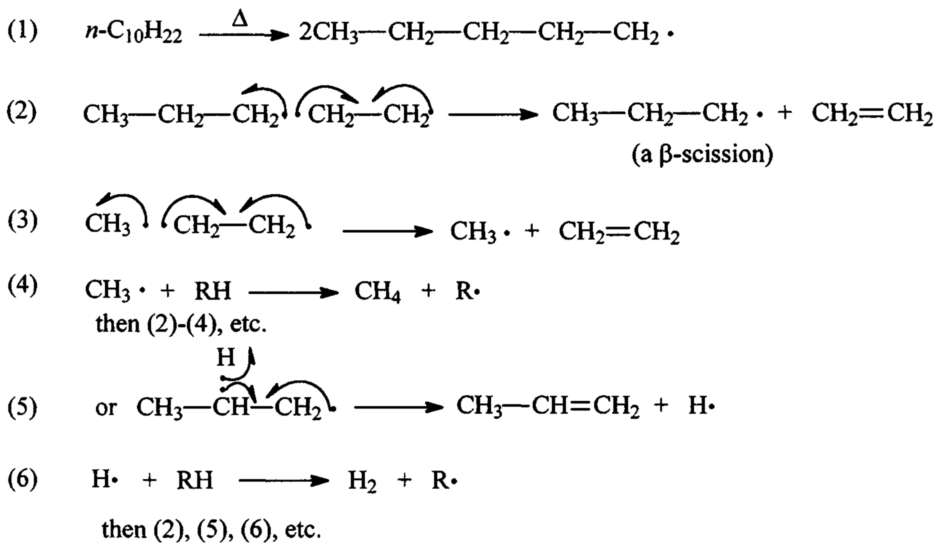


Figure 7.7 A typical large catalytic cracking unit (on the right in this picture) can process 110,000 barrels/day. (Courtesy of BP Amoco, Texas City, TX)

Catalytic cracking usually involves carbocations, but the mechanism is uncertain.

Although important to the gasoline industry, catalytic cracking is not a major route to petrochemicals. Thermal cracking involves higher temperatures of 850-900°C in the absence of a catalyst. It gives much higher percentages of C_2, C_3, and C_4 olefins and relatively low yields of gasoline. It was superseded for gasoline production by catalytic cracking and was only revived with the demand for ethylene production in the chemical industry. Only 9% of total U.S. refinery cracking is thermal, but this is the only way in which olefins for the chemical industry are made. The lighter petroleum fractions such as naphtha are cracked thermally to give mixtures rich in ethylene, propylene, butadiene, and BTX (benzene, toluene, and the



$$\text{(1)}\quad n\text{-}C_{10}H_{22} \xrightarrow{\Delta} 2CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2\cdot$$

$$\text{(2)}\quad CH_3{-}CH_2{-}CH_2\cdot\ \cdot CH_2{-}CH_2\cdot \longrightarrow CH_3{-}CH_2{-}CH_2\cdot + CH_2{=}CH_2$$

(a β-scission)

$$\text{(3)}\quad CH_3\cdot\ \cdot CH_2{-}CH_2\cdot \longrightarrow CH_3\cdot + CH_2{=}CH_2$$

$$\text{(4)}\quad CH_3\cdot + RH \longrightarrow CH_4 + R\cdot$$

then (2)-(4), etc.

$$\text{(5)}\quad \text{or}\ CH_3{-}\overset{H}{CH}{-}CH_2\cdot \longrightarrow CH_3{-}CH{=}CH_2 + H\cdot$$

$$\text{(6)}\quad H\cdot + RH \longrightarrow H_2 + R\cdot$$

then (2), (5), (6), etc.

Figure 7.8 Mechanism of thermal cracking.

xylenes). Even ethane and propane are cracked. When ethane is "cracked" to ethylene it of course loses no carbons, but it does lose two hydrogens. More examples:

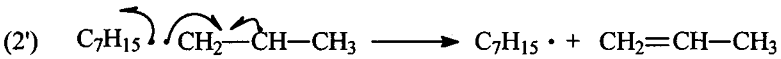
$$CH_3{-}CH_2{-}CH_3 \longrightarrow CH_2{=}CH_2 + CH_4$$

$$CH_3\text{-}CH_3 \longrightarrow CH_2{=}CH_2 + H_2$$

Thermal cracking is a free radical chain reaction. The mechanism is given in Fig. 7.8.

An alternative to step (1) for n-$C_{10}H_{22}$ involves a C-H bond to give a 2° radical, which then can undergo its own β-scission. Although β-scissions of C-H bonds can also happen, C-C bonds are weaker so these are preferred.

$$\text{(1')}\quad n\text{-}C_{10}H_{22} \longrightarrow C_7H_{15}{-}CH_2{-}\dot{C}H{-}CH_3 + H\cdot$$



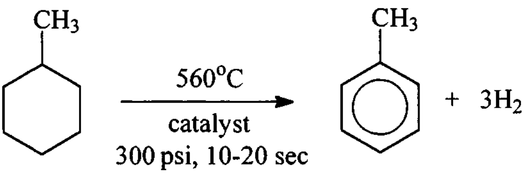
$$\text{(2')}\quad C_7H_{15}\cdot\ \cdot CH_2{-}\dot{C}H{-}CH_3 \longrightarrow C_7H_{15}\cdot + CH_2{=}CH{-}CH_3$$

$$\text{(3')}\quad C_7H_{15}\cdot \longrightarrow C_5H_{11}\cdot + CH_2{=}CH_2$$

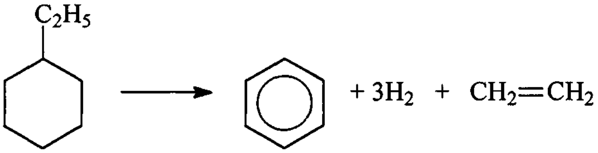
To maximize the amount of ethylene in the product, which is the idea in an olefin plant, the number of β-scissions are maximized. Higher temperatures favor this, because β-scissions have a high energy of activation. Also, since the β-scission is a unimolecular process, whereas other possible reactions are bimolecular, a low concentration of hydrocarbon is preferred. Thus steam is used as a diluent. When thermal cracking is used, ethylene percentages can be as high as 76%; in catalytic cracking the percentage is less than 1%.

In thermal free radical cracking, fragmentation to small molecules occurs readily. In catalytic cracking carbocations rearrange more because the differences in carbocation stabilities are greater than the differences in free radical stabilities.

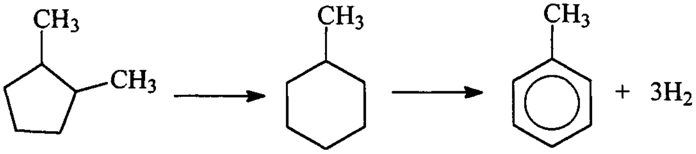
Dehydrogenation



Dealkylation and Dehydrogenation



Rearrangement and Dehydrogenation



Cyclization and Dehydrogenation

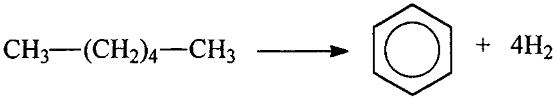


Figure 7.9 Examples of catalytic reforming.

7. REFORMING

Catalytic reforming (Fig. 7.9) leaves the number of carbon atoms in the feedstock molecules usually unchanged but the mixture contains a higher number of double bonds and aromatic rings. Reforming has become the principal process for upgrading gasoline. High temperatures with typical catalysts of platinum and/or rhenium on alumina and short contact times are used. A typical example is the reforming of methylcyclohexane to toluene. It is done in the presence of hydrogen (hydroforming) to control the rate and extent of this dehydrogenation process. Straight-run gasoline can be reformed to as high as 40-50% aromatic hydrocarbons, of which 15-20% is toluene. Reformed petroleum is our main BTX source.

The Platforming® process of UOP, where reforming occurs with a platinum catalyst and the surface of this catalyst acts as a "platform" for the reaction, has been well named (Fig. 7.10).

Figure 7.10 An aerial view of a catalytic reforming processing plant. The reactors are the 21-ft spherical objects in the middle. These contain platinum and are in a series so that the octane is increased a little more in each reactor. (Courtesy of BP Amoco, Texas City, TX)

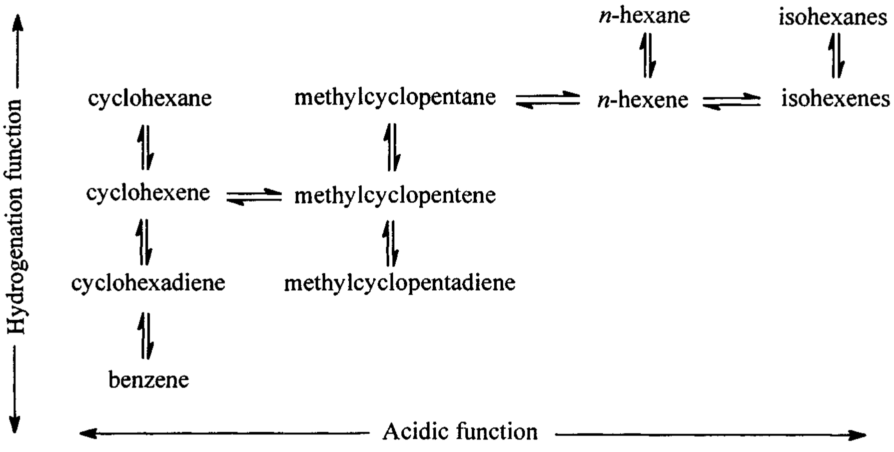


Figure 7.11 Functions of a dual catalyst. (*Source: C & E News*)

Although the mechanism of the platinum catalysis is by no means completely understood, chemists do know a lot about how it works. It is an example of a dual catalyst: platinum metal on an alumina support. Platinum, a transition metal, is one of many metals known for its hydrogenation and dehydrogenation catalytic effects. Recently bimetallic platinum/rhenium catalysts are now the industry standard because they are more stable and have higher activity than platinum alone. Alumina is a good Lewis acid and as such easily isomerizes one carbocation to another through methyl shifts.

Thus there is a hydrogenation function and an acidic function present in the catalyst, as diagrammed in Fig. 7.11. Simple aliphatics can be converted into aromatics. The mechanism for the conversion of hexane into benzene is given in Fig. 7.12. Basically it is a series of alternating dehydrogenations and carbocation rearrangements. Note that this conversion requires a 3° to 1° carbocation rearrangement to expand the ring size. Although this is unusual since 3° carbocations are more stable than 1° ions, we must remember that this occurs catalytically. Complexation to the Lewis acid catalytic surface makes the 1° carbocation stable enough to form, albeit as a reactive intermediate. The driving force for this rearrangement is the resonance stabilization of the final aromatic ring.

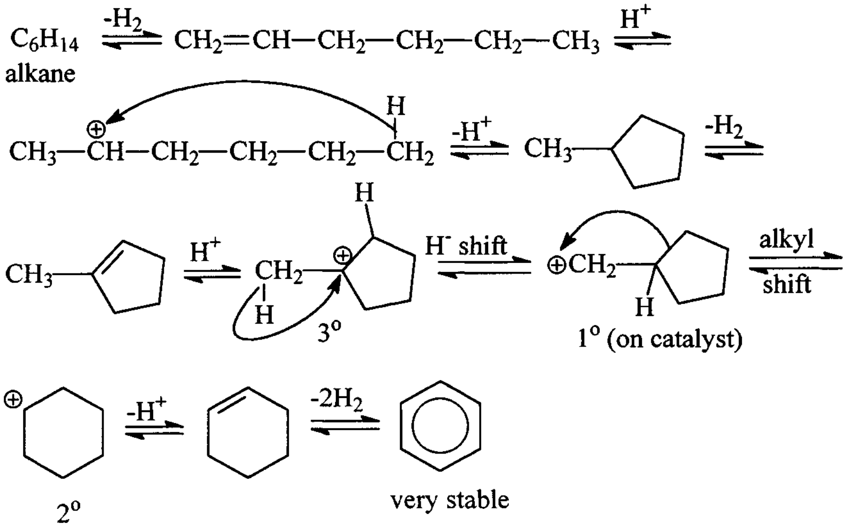


Figure 7.12 Mechanism of catalytic reforming. (*Source:* Wiseman)

8. ALKYLATION AND POLYMERIZATION

Although cracking and reforming are by far the most important refinery processes, especially for the production of petrochemicals, two other processes deserve mention. In alkylation paraffins react with olefins in the presence of an acid catalyst to give highly branched alkanes. Isobutylene and isobutane can react to give 2,2,4-trimethylpentane ("isooctane") which can be added to straight-run gasoline to improve the octane. The mechanism is well understood as a carbocation chain process involving a hydride shift, shown in Fig. 7.13.

In polymerization an olefin can react with another olefin to generate dimers, trimers, and tetramers of the olefin. As a simple example, isobutylene reacts to give a highly branched C_8 olefin.

In general, polymerization gives an average RON of 94; alkylation gives 95.

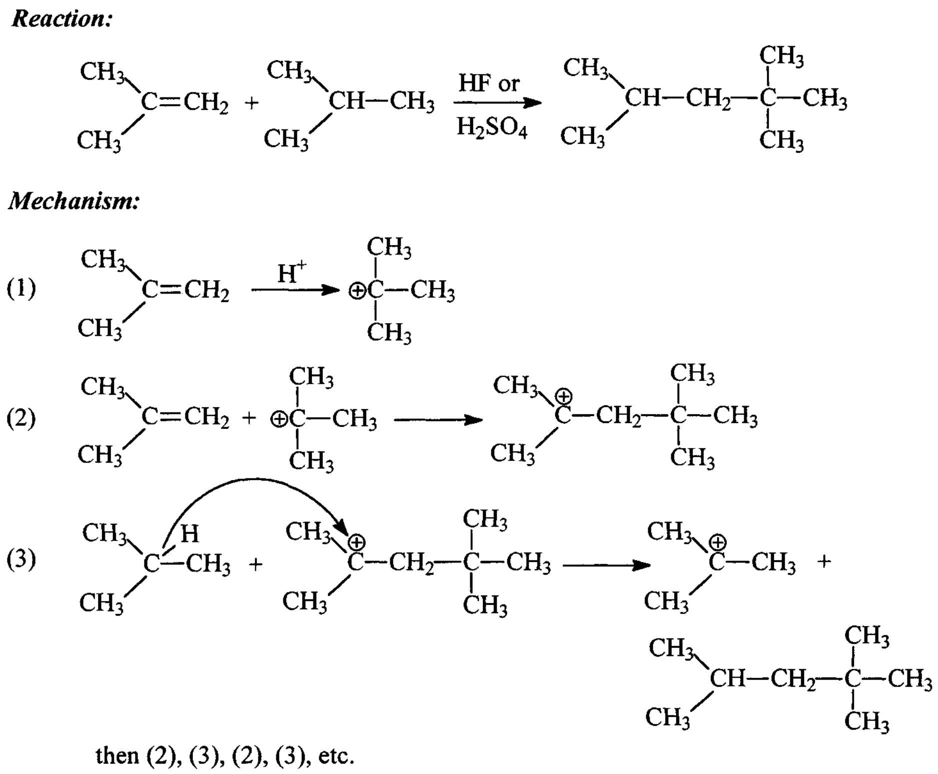


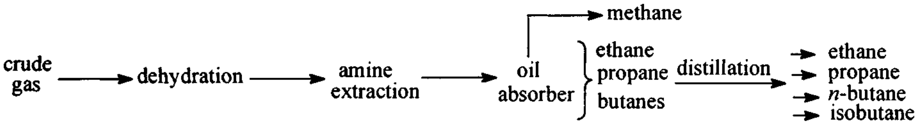
Figure 7.13 Reaction and mechanism of alkylation of gasoline.

9. SEPARATION OF NATURAL GAS: METHANE PRODUCTION

You may have noticed that, of the seven basic organic building blocks given in Table 7.1, only six of them are considered "chemicals" and are included in the *C & E News* Top 50. Methane is certainly an important substance, but it is really not commercially made by a chemical reaction as are the other six, which we will study in more detail in the next chapter. Methane is naturally occurring and can be as high as 97% of natural gas, the remainder being hydrogen, ethane, propane, butane, nitrogen, hydrogen sulfide and heavier hydrocarbons. A typical mixture contains 85% methane, 9% ethane, 3% propane, 1% butanes, and 1% nitrogen. Most of the natural gas is used as fuel, but about 28% of the 25 trillion cu ft (TCF) per year in the United States are used by the chemical industry. If we estimate natural gas consumption in mass rather than volume, the 25 trillion cubic feet is approximately a trillion lb of methane. Of this, the one fourth used for chemical manufacture is about 250 billion lb of methane. So the methane used by the chemical industry does compare to other raw materials such as phosphate rock in amount consumed. A typical price is 7-9¢/lb. Uses of natural gas by all industry include fuel (72%), inorganic chemicals including ammonia (15%), organic chemicals (12%), and carbon black (1%). The ethane and propane are converted to ethylene and propylene. The methane is purified and used to make a number of chemicals.

Figure 7.14 Storage tanks for crude oil can be huge. These handle 750,000 barrels, about the size of one oil tanker and perhaps two days supply for the oil refinery. A floating, expandable top enables minimal pressure variation with temperature. (Courtesy of BP Amoco, Texas City, TX)

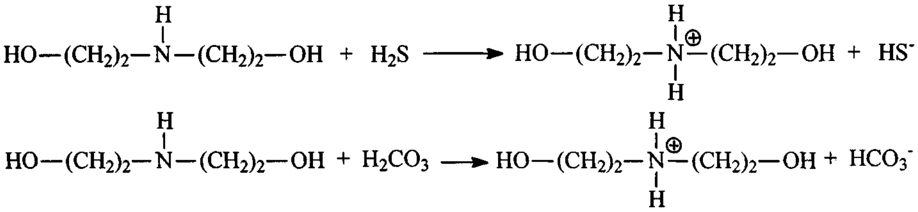
A simplified schematic for natural gas separation is given here and consists of the following steps.



1. Dehydration by passing through diethylene glycol, in which water is very soluble.

$$HO-(CH_2)_2-O-(CH_2)_2-OH$$

2. Elimination of hydrogen sulfide and carbon dioxide with aqueous mono- or diethanolamine.



$$HO-(CH_2)_2-\overset{H}{\overset{|}{N}}-(CH_2)_2-OH + H_2S \longrightarrow HO-(CH_2)_2-\overset{H}{\underset{H}{N^{\oplus}}}-(CH_2)_2-OH + HS^-$$

$$HO-(CH_2)_2-\overset{H}{\overset{|}{N}}-(CH_2)_2-OH + H_2CO_3 \longrightarrow HO-(CH_2)_2-\overset{H}{\underset{H}{N^{\oplus}}}-(CH_2)_2-OH + HCO_3^-$$

3. Dissolution of the higher boiling gases in an oil absorber of hexane, leaving the methane separated.
4. Fractional distillation of the oil to recover the oil and to collect the ethane, propane, *n*-butane, and isobutane separately.

Suggested Readings

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 480-509.
Wiseman, *Petrochemicals*, pp. 13-42, 90-95.
Wittcoff & Reuben, *Industrial Organic Chemicals*, pp. 46-87.
Szmant, *Organic Building Blocks of the Chemical Industry*, pp. 33-35, 64-66.

Chapter 8

Basic Organic Chemicals

As we saw in Table 7.1 the major organic chemicals are all derived from seven basic ones: ethylene, propylene, the C_4 fraction, benzene, toluene, xylene and methane. The production of methane, the major constituent in natural gas, has already been examined. We now consider in detail the manufacture, uses, and economic aspects of the other basic six organics. This will lead us into a discussion of the derivatives of each of them and their technology. We treat the basic ones first because, in addition to their importance, there is some similarity in their manufacture. Ethylene, propylene, and the C_4 fraction are all made by steam (thermal) cracking of hydrocarbons. Benzene, toluene, and the xylenes are made by catalytic reforming. Just how significant are these seven basic organics? Nearly all organic chemicals and polymers are derived from them.

1. ETHYLENE (ETHENE)

$$CH_2{=}CH_2$$

1.1 Manufacture

Most ethylene and propylene is made by the *thermal cracking*, sometimes called *steam cracking*, of hydrocarbons at high temperatures with no catalyst. In contrast to the catalytic cracking used by the petroleum industry to obtain large amounts of gasoline, thermal cracking is used since it yields larger percentages of C_2, C_3, and C_4 olefins. Originally the feedstock for this process was mostly ethane and propane from natural gas. But naphtha and gas oil fractions from petroleum can be used, and recently their use has increased dramatically with the high price and scarcer supply of natural gas. Relative costs of running ethylene plants vary with the type of feed and are cheaper for natural gas feeds: ethane, 1.0; propane, 1.2; naphtha, 1.4; gas oil, 1.5. This must be weighed against the difference in prices of the feedstocks themselves. The shift to heavier feedstocks is predicted to continue but at a slower rate than before.

1.1.1 Reactions

$$CH_3{-}CH_3 \longrightarrow CH_2{=}CH_2 + H_2$$

$$2CH_3{-}CH_2{-}CH_3 \longrightarrow CH_3{-}CH{=}CH_2 + CH_2{=}CH_2 + H_2 + CH_4$$

1.1.2 Description

Steam cracking is pictured in Fig. 8.1. The furnace in which the cracking takes place is at 815-870°C (1600°F). Sometimes as many as 6 to 20 furnaces are in parallel to increase production (see Fig. 8.2). Steam is used as a diluent to inhibit coking in the tubes and to increase the percentage of ethylene formed. The amount of steam changes with the molecular weight of the hydrocarbon and varies from 0.3 kg steam/kg ethane to 0.9 kg steam/kg gas oil. Contact time is 1 sec or less in the furnace. The exit gases are immediately cooled in the quench tower, then placed under 500 psi pressure by a compressor (Fig. 8.3). Monoethanolamine or caustic is used to remove hydrogen sulfide and carbon dioxide (see the natural gas discussion, Chapter 7, Section 9).

The demethanizer, deethanizer, and debutanizer are fractionating columns that separate the lighter and heavier compounds from each other. Traces of triple bonds are removed by catalytic hydrogenation with a palladium catalyst in both the C_2 and C_3 stream. Cumulated double bonds are also hydrogenated in the C_3 fraction. These are more reactive in hydrogenation than ethylene or propylene. The C_2 and C_3 splitters (Fig. 8.4) are distillation columns that can be as high as 200 ft. The mechanism of cracking was previously discussed in Chapter 7, Section 6.

Lower molecular weight feedstocks, such as ethane and propane, give a high percentage of ethylene; higher molecular weight feedstocks, such as naphtha and gas oil, are used if propylene demand is up. The following table summarizes the typical yields of olefins obtained from various feeds.

	Feed			
Product	**Ethane**	**Propane**	**Naphtha**	**Gas Oil**
Ethylene	76	42	31	23
Propylene	3	16	16	14
C_4	2	5	9	9

1.2 Properties

Ethylene is a colorless, flammable gas with a faint, pleasant odor and a bp of -103.8°C. The *flash point*, the lowest temperature at which the vapors of a liquid decompose to a flammable gaseous mixture, is -136.1°C. The *ignition temperature*, the temperature at which a substance begins to burn, is 450°C. Ethylene is sold from 95% purity (technical) to 99.9% purity. It can be transported by pipeline or by tank car. Smaller amounts come in 100-lb cylinders. Much of it is used on site by the company to make other products.

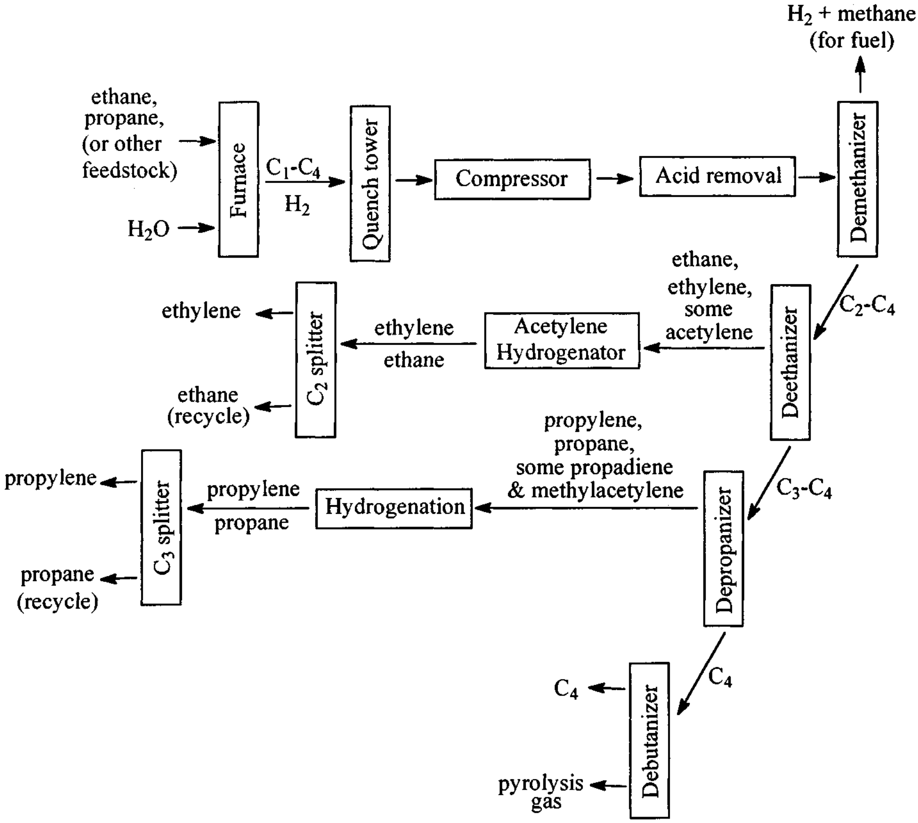


Figure 8.1 Manufacture of olefins by thermal cracking.

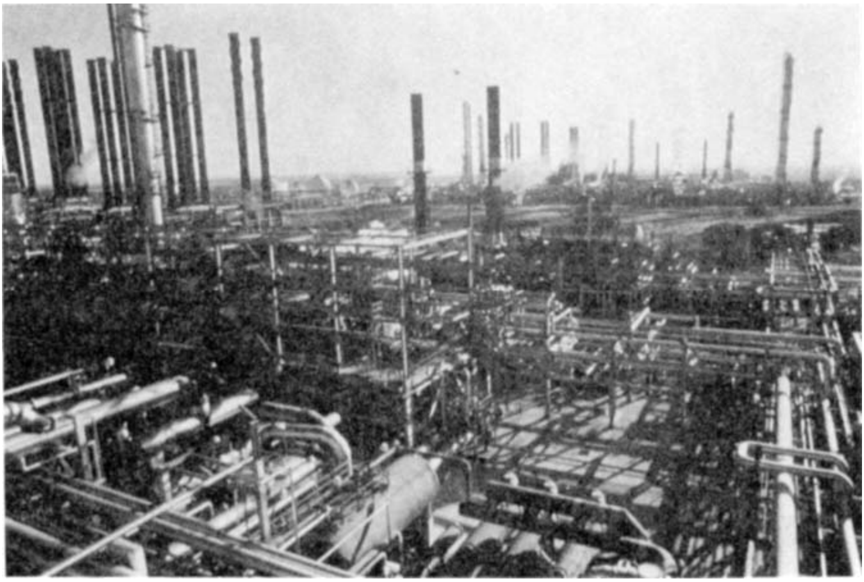


Figure 8.2 Distance view of two olefin plants. Note the furnace stacks and the large distillation columns. (Courtesy of BP Chemicals, Alvin, Texas)

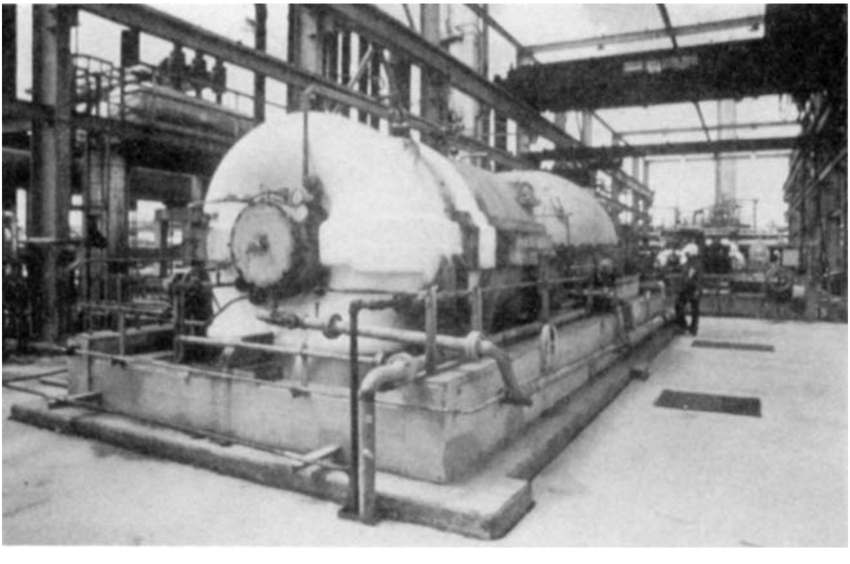


Figure 8.3 Exit gases from the furnace and quench tower of an olefin plant enter a compressor before distillation. Ice forms on the outside of the compressor even on warm days because of the cooling effect. (Courtesy of BP Chemicals, Alvin, Texas)

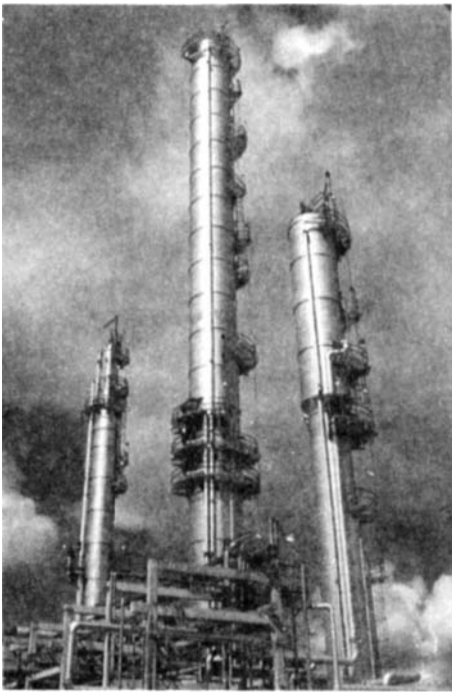


Figure 8.4 Distillation columns used in a large olefin plant. The middle one is the C_2 splitter and the highest at 200 ft, separating ethane and ethylene. (Courtesy of BP Chemicals, Alvin, Texas)

1.3 Uses

Table 8.1 shows the breakdown in uses of ethylene. Over half is

Table 8.1 Uses of Ethylene

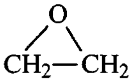
Polyethylene, LD and LLD	29%
Polyethylene, HD	26
Ethylene dichloride/vinyl chloride	16
Ethylene oxide/ethylene glycol	13
Ethylbenzene/styrene	6
Linear alcohols	4
Acetic acid/vinyl acetate	2
Miscellaneous	4

Source: Chemical Profiles

polymerized directly to polyethylene, both high and low density, which are used in thousands of plastics applications. Major organic chemicals made from ethylene are ethylene oxide, which is in turn converted into ethylene glycol for antifreeze and polyester fibers; ethylene dichloride, which is processed into vinyl chloride and polymerized to poly(vinyl chloride), another important plastic; ethylbenzene followed by styrene, polymerized to polystyrene plastic and foam; and linear alcohols and olefins, whose important end-uses are in soaps, detergents, and plastics. We will be covering these derivatives and specific uses in more detail in later chapters.

$(CH_2-CH_2)_n$

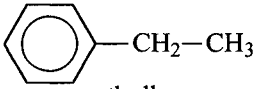
polyethylene



ethylene oxide

$Cl-CH_2-CH_2-Cl$

ethylene dichloride



ethylbenzene

$CH_3-(CH_2-CH_2)_n-OH$

linear alcohols

2. PROPYLENE (PROPENE)

$$CH_3-CH=CH_2$$

2.1 Manufacture

Propylene is manufactured by steam cracking of hydrocarbons as discussed under ethylene. The best feedstocks are propane, naphtha, or gas oil, depending on price and availability. About 50-75% of the propylene is consumed by the petroleum refining industry for alkylation and polymerization of propylene to oligomers that are added to gasoline. A smaller amount is made by steam cracking to give pure propylene for chemical manufacture.

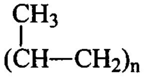
$$2CH_3-CH_2-CH_3 \longrightarrow CH_3-CH=CH_2 + CH_2=CH_2 + H_2 + CH_4$$

2.2 Properties

Propylene is a colorless, flammable gas with a slightly sweet aroma, bp -47.7°C, flash point -107.8°C, and ignition temperature 497.2°C. It is available in cylinders and tank cars and by pipeline.

2.3 Uses

Table 8.2 outlines the merchant uses of propylene. The biggest use, polymerization to polypropylene, is growing since this polymer is competing in many plastics applications with high density polyethylene. Acrylonitrile is polymerized to plastics and fibers. Propylene oxide is used in polyurethane plastic and foam. Cumene is made from propylene and benzene. It is an important intermediate in the manufacture of two top 50 chemicals, phenol and acetone. Oxo chemicals are made by reacting

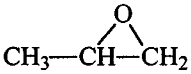


$(\overset{CH_3}{\overset{|}{C}}H-CH_2)_n$

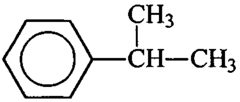
polypropylene

$CH_2{=}CH-C{\equiv}N$

acrylonitrile



propylene oxide



cumene

Table 8.2 Merchant Uses of Propylene

Polypropylene	39%
Acrylonitrile	14
Propylene oxide	11
Cumene	10
Oxo chemicals	8
Oligomers	5
Linear alcohols	4
Acrylic acid	3
Miscellaneous	3

Source: Chemical Profiles

Table 8.3 Percent Composition of a Typical C_4 Stream

n-butane	3%
isobutane	1
isobutene	23
1-butene	14
2-butene	11
butadiene	47
other	1

Source: Wittcoff & Reuben

propylene with synthesis gas (CO/H_2) to form C_4 alcohols. Small amounts of propylene are made into oligomers, where 3-5 propylene units are added to each other. These have importance in soaps and detergents, besides the very large captive use they have as mentioned above for petroleum refining.

3. THE C_4 STREAM

Besides ethylene and propylene, the steam cracking of naphtha and catalytic cracking in the refinery produce appreciable amounts of C_4 compounds. This C_4 stream includes butane, isobutane, 1-butene (butylene), *cis-* and *trans*-2-butene, isobutene (isobutylene), and butadiene. The C_4 hydrocarbons can be used to alkylate gasoline. Of these, only butadiene and isobutylene appear in the top 50 chemicals as separate pure chemicals. The other C_4 hydrocarbons have specific uses but are not as important as butadiene and isobutylene. A typical composition of a C_4 stream from steam cracking of naphtha is given in Table 8.3.

4. BUTADIENE (1,3-BUTADIENE)

$$CH_2{=}CH{-}CH{=}CH_2$$

4.1 Manufacture

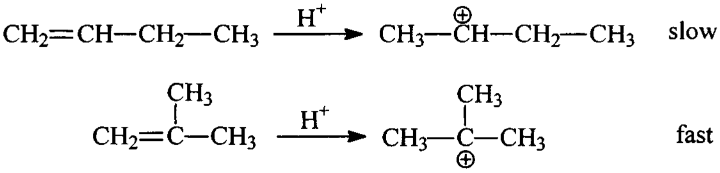
In the last ten years not enough butadiene could be made by steam-cracking alone. Thus about 70% is now made by dehydrogenation of butane or the butenes.

$$n\text{-}C_4H_8 \xrightarrow{Fe_2O_3} CH_2{=}CH{-}CH{=}CH_2 + H_2$$

$$CH_3{-}CH_2{-}CH_2{-}CH_3 \xrightarrow{Fe_2O_3} CH_2{=}CH{-}CH{=}CH_2 + 2H_2$$

57-63% yield

The crude C_4 fraction is extracted with acetone, furfural, or other solvents to remove alkanes such as *n*-butane, isobutane, and small amounts of pentanes, leaving only 1- and 2-butenes and isobutene. The isobutene is removed by reaction with sulfuric acid and water because it reacts more easily, being able to form a tertiary carbocation.



$$CH_2{=}CH{-}CH_2{-}CH_3 \xrightarrow{H^+} CH_3{-}\overset{\oplus}{C}H{-}CH_2{-}CH_3 \quad \text{slow}$$

$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH_3 \xrightarrow{H^+} CH_3{-}\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH_3 \quad \text{fast}$$

The product of hydrolysis, *t*-butyl alcohol, may be dehydrated to isobutylene for increased yields of this important C_4 compound.

The straight-chain 1- and 2-butenes can be converted into more butadiene when they are preheated in a furnace, mixed with steam as a diluent to minimize carbon formation, and passed through a reactor with a bed of iron oxide pellets. The material is cooled and purified by fractional distillation or extraction with solvents such as furfural, acetonitrile, dimethylformamide (DMF), and N-methylpyrrolidone (NMP). The conjugated π system of butadiene is attracted to these polar solvents more than the other C_4 compounds. *Extractive distillation* is used, where the C_4 compounds other than butadiene are distilled while the butadiene is complexed with the solvent. The solvent and butadiene pass from the bottom of the column and are then separated by distillation.

4.2 Properties

Butadiene is a colorless, odorless, flammable gas, with a bp of –4.7 °C. As of 2000 butadiene has been on the "Known to Be a Human Carcinogen" list of the Department of Health and Human Services. It has a time-weighted average threshold limit value (TLV) of 2 ppm. TLVs and carcinogens will be discussed more fully under benzene. Butadiene is expensive to store because it polymerizes easily and must be refrigerated.

Table 8.4 Uses of Butadiene

SBR	30%
Polybutadiene	20
Adiponitrile, HMDA	15
SB latex	10
Nitrile rubber	5
Chloroprene	5
Linear alcohols	4
Miscellaneous	10

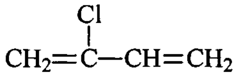
Source: Chemical Profiles

4.3 Uses

In Table 8.4 we see that most butadiene is polymerized either by itself or with styrene or acrylonitrile. The most important synthetic elastomer is styrene-butadiene rubber (SBR). SBR, along with polybutadiene, has its biggest market in automobile tires. Specialty elastomers are polychloroprene and nitrile rubber, and an important plastic is acrylonitrile/butadiene/styrene (ABS) terpolymer. Butadiene is made into adiponitrile, which is converted into hexamethylenediamine (HMDA), one of the monomers for nylon.

$(CH_2—CH{=}CH—CH_2)_n$

polybutadiene



$$CH_2{=}\overset{\displaystyle Cl}{\overset{|}{C}}—CH{=}CH_2$$

chloroprene

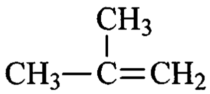
$N{\equiv}C—(CH_2)_4—C{\equiv}N$

adiponitrile

$H_2N—(CH_2)_6—NH_2$

hexamethylenediamine (HMDA)

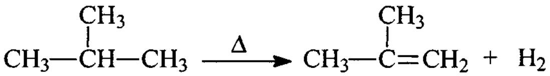
5. ISOBUTYLENE (ISOBUTENE)



$$CH_3—\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$$

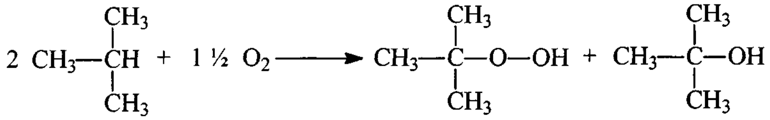
5.1 Manufacture

Isobutylene has had a tremendous increased production in the last few years because of the dynamic growth of the gasoline additive MTBE. About two thirds of it is made from isobutane by dehydrogenation in thermal cracking.

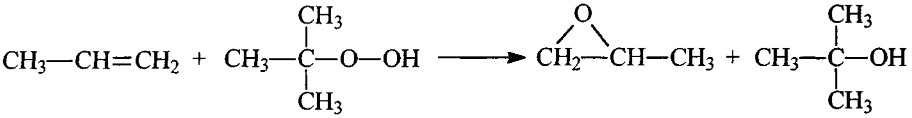


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3 \xrightarrow{\Delta} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 + H_2$$

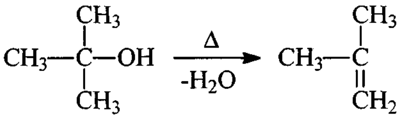
The other third comes from *t*-butyl alcohol by dehydration, with the *t*-butyl alcohol being made available as a by-product by oxidation of isobutane followed by epoxidation of propylene with *t*-butyl hydroperoxide.



$$2\ CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}H + 1\tfrac{1}{2}\ O_2 \longrightarrow CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-O-OH + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH$$



$$CH_3-CH=CH_2 + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-O-OH \longrightarrow \overset{\overset{\displaystyle O}{\diagup\ \diagdown}}{CH_2-CH}-CH_3 + CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH$$



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-OH \xrightarrow[-H_2O]{\Delta} CH_3-\underset{\underset{\displaystyle CH_2}{\|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}$$

The epoxidation of propylene is discussed in Chapter 10, Section 2. Some isobutane can be made by isomerizing *n*-butane. The isomerization of *n*-butenes to isobutylene is also being commercialized.

5.2 Uses

The major uses of isobutylene are estimated in Table 8.5. Much of isobutylene is a captive market used by refineries in alkylation or polymerization of gasoline. The remainder goes into the octane enhancer MTBE, polyisobutylene, and butyl rubber. Some is burned for fuel.

Table 8.5 Uses of Isobutylene

Alkylate gasoline	68%
MTBE	9
Fuel	8
Butyl rubber	5
Polyisobutylene	5
Linear alcohols	4
Miscellaneous	3

Source: Chemical Profiles

6. ECONOMIC ASPECTS OF OLEFINS

Fig. 8.5 shows the U.S. production of ethylene, propylene, and butadiene over the years. Ethylene has shown a good, steady increase for many years since the 1950s, as it has replaced ethanol as the major C_2 raw material and is now used in nearly half of all organic polymers and chemicals produced by volume. Some would argue that it should be used in place of sulfuric acid as the main economic indicator of the chemical industry. Certainly for organic chemicals it has top billing. Propylene shows a similar but lower trend. Although the official production of propylene is usually about half that of ethylene, it is probably near ethylene if captive refinery-made

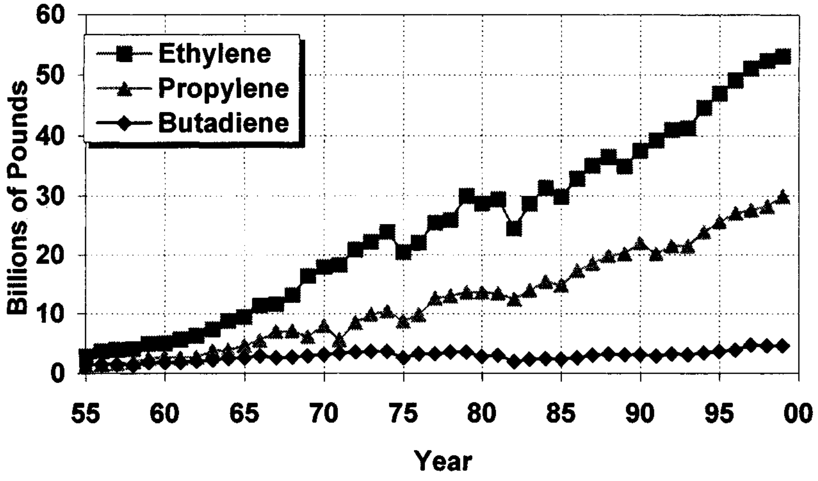


Figure 8.5 U.S. production of olefins. (*Source:* Lowenheim & Moran, *Chemical and Engineering News*, *Chemical Economics Handbook*, and *Chemical Profiles*)

Table 8.6 Ethylene Capacity

Year	Capacity, Billion lb	Production as a % of Capacity
1981	39	75
1984	37	84
1990	42	89
1997	53	94

Source: Chemical Profiles

material could be included accurately. Butadiene has definitely levelled off with the major slump in the automobile and tire industries during the 1980s, the only one of the three to drop in production during this decade. It is not doing very well in the 1990s either. Three fourths of all butadiene ends up in tires. Butadiene is about one tenth of ethylene production. The estimates of production for 2003 are 58.6 billion lb for ethylene, 35.3 billion lb for propylene, and 5.1 billion lb for butadiene.

Ethylene production as a percentage of capacity has become very tight in the last few years. The figures for four selected years are given in Table 8.6. Note that production and capacity are now nearly even, because of increasing polyethylene demand for the most part. There has been a reluctance to open new ethylene plants because of present questions on this market future. There are 35 ethylene plants in the U.S. representing 17 companies. Many of the plants are owned by oil company subsidiaries and are located in Texas and Louisiana near the oil fields of the Gulf region. A

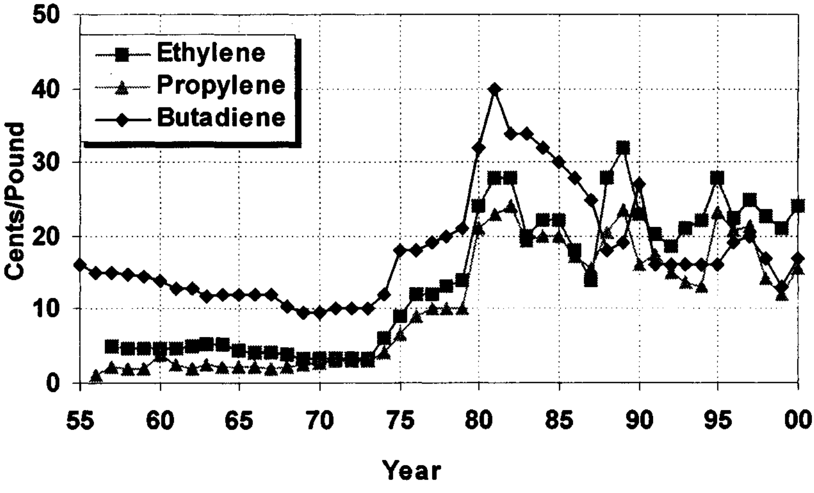
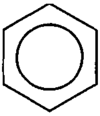


Figure 8.6 U.S. prices of olefins. (*Source:* Lowenheim & Moran and *Chemical Marketing Reporter*)

typical large plant will manufacture 1.0-2.0 billion lb/yr of ethylene and 0.5-1.5 billion lb/yr of propylene. There are over 60 plants of propylene from 30 companies. The manufacture of propylene is a more diversified business.

Fig. 8.6 summarizes price trends for the olefins. This is perhaps one of the most startling examples of all price charts shown in this text. Note that prices were amazingly steady or decreasing for many years through the 1950s, '60s, and early '70s. Then the oil embargo caused a record steep incline for most organics, and double-digit inflationary years until the early 1980s caused a jump in ethylene from 4¢/lb in 1973 to 28¢/lb in 1981, a 700% increase for an eight-year span. The ups and downs of the 1980s economy are also evident in the chart, and to some extent in the 1990s. Trends for propylene and butadiene follow a similar pattern. The commercial value ethylene is approximately $13 billion, that for propylene $5 billion, and that for butadiene $0.8 billion.

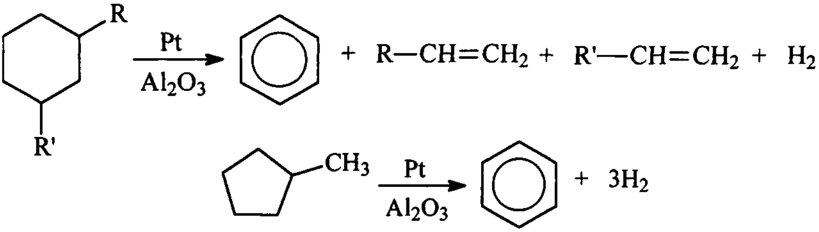
7. BENZENE (BENZOL)



7.1 Manufacture: Catalytic Reforming

For many years benzene was made from coal tar even as late as 1949, when all of it was made by this old process. New processes began to take over in the 1950s, which were used for 50% of the benzene in 1959, 94% in 1972, 96% in 1980, and near 100% in the 1990s. These new processes consist of catalytic reforming of naphtha and hydrodealkylation of toluene in a 70:30 capacity ratio.

7.1.1 Reactions



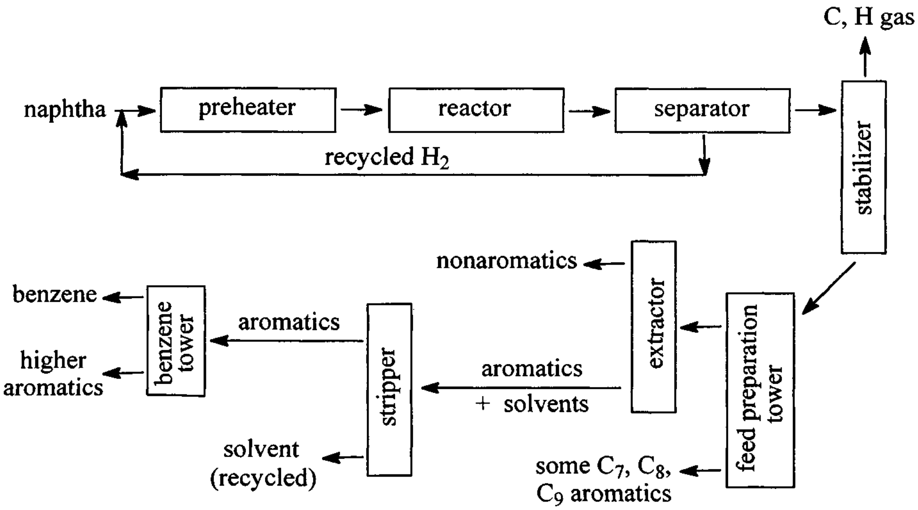


Figure 8.7 Manufacture of benzene, toluene, and xylenes by catalytic reforming.

7.1.2 Description

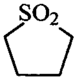
As seen in Fig. 8.7, the naphtha is preheated in a hydrogen atmosphere (to suppress coke formation) at 450-510°C, and 120-200 psi. The reactor is filled with 3-6 mm pellets of a platinum catalyst. In one pass 80% of the C_6 naphthenes form benzene. Natural benzene (1-9% of the feedstock) remains unchanged. Since hydrogen is present as the recycle gas, this is often called *hydroforming*. When platinum is the catalyst it is called the Platforming® process. For the mechanism of catalytic reforming see Chapter 7, Section 7. The hydrogen is separated; the stabilizer removes light hydrocarbon gases. The feed preparation tower increases the benzene percentage via distillation and collection of the overhead cut. The overhead fraction enters the Udex extraction process, which utilizes diethylene glycol as a solvent. Other solvents are tetraethylene glycol and sulfolane.

$$HO{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}OH$$

diethylene glycol

$$HO{-}CH_2{-}CH_2{-}(O{-}CH_2{-}CH_2)_2{-}O{-}CH_2{-}CH_2{-}OH$$

tetraethylene glycol



sulfolane

These solvents have high solubility for aromatics but not for nonaromatics. They also have high boiling points for later separation from the aromatics. Fractionation separates the benzene from the solvent and other aromatics. A typical Udex extraction starting with a reformed feed of 51.3% aromatic content gives 7.6% benzene, 21.5% toluene, 21%, xylenes, and 1.2% C_9 aromatics. The recovery rate is 99.5% of the benzene, 98% of the toluene, 95% of the xylene, and 80% of the C_9 aromatics.

7.2 Manufacture: Hydrodealkylation of Toluene

More toluene is formed than is needed in the catalytic reforming of naphtha. Benzene is always in tight supply. Table 8.7 shows the catalytic reformate production percentages of benzene, toluene, and xylene vs. the U.S. chemical demand. When the price is right it is economical to hydrodealkylate (add hydrogen, lose the methyl) toluene to benzene. This is best done on pure toluene, where the yield can be as high as 98.5%. The reaction can be promoted thermally or catalytically. As much as 30-50% of all benzene is made this way.

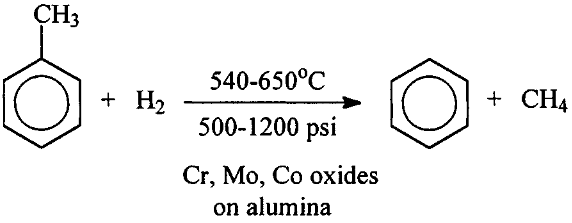


Table 8.7 BTX Production and Demand Percentage

Chemical	Reformate Production %	Chemical Demand %
Benzene	11	56
Toluene	55	10
Xylene	34	34

Source: Wittcoff & Reuben

7.3 Properties

Benzene is a clear, colorless, flammable liquid with a pleasant characteristic odor, bp 80.1°C, flash point -11.1°C, and ignition temperature 538°C. Benzene has been found to be very toxic and is on the list of "Known to Be Human Carcinogens" published every two years by the Department of Health and Human Services under the National Toxicology Program (NTP). There are four top 50 chemicals on this "worst" carcinogen list: benzene; 1,3-butadiene; ethylene oxide; and vinyl chloride. There are also four chemicals in the top 50 on the "Reasonably Anticipated to Be Human Carcinogens" list: acrylonitrile, ethylene dichloride, formaldehyde, and propylene oxide.

Benzene has a low threshold limit value or TLV. The time weighted average TLV (TWA) is the allowable exposure for an average 8 hr day or a 40 hr week. The short-term exposure limit TLV (STEL) is the maximum allowable exposure for any 15-min period. For benzene the TWA = 0.5 ppm and the STEL is 2.5 ppm, as given by the American Conference of Governmental Industrial Hygienists (ACGIH). This allowable exposure is much lower than those for toluene and xylene, probably because these latter two compounds have benzylic positions that are easily oxidized *in vivo* to compounds that can be eliminated from the body.

In 1989 the Environmental Protection Agency ordered a 90% reduction of industrial benzene emissions over the next several years at a cost of $1 billion. The new standard leaves more than 99% of the exposed population with risks of cancer less than one in 1 million, or one cancer case in the U.S. every 10 years. Hardest hit are the iron and steel industry, where benzene emissions from coke by-product recovery plants are large. Chemical industry plants have already reduced their benzene emissions 98%. EPA estimates that the 390,000 or so gasoline service stations in the U.S. will all have to be fitted with devices to eliminate the escape vapors when fuel is put into underground storage tanks.

7.4 Uses

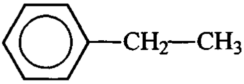
The important derivatives of benzene are shown in Table 8.8. Ethylbenzene is made from ethylene and benzene and then dehydrogenated to styrene, which is polymerized for various plastics applications. Cumene is manufactured from propylene and benzene and then made into phenol and acetone. Cyclohexane, a starting material for some nylon, is made by hydrogenation of benzene. Nitration of benzene followed by reduction gives

Table 8.8 Uses of Benzene

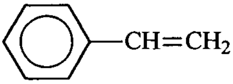
Ethylbenzene, styrene	53%
Cumene, phenol	22
Cyclohexane	12
Nitrobenzene, aniline	5
Linear alcohols	4
Miscellaneous	5

Source: Chemical Profiles

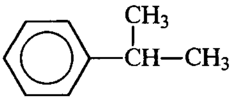
aniline, important in the manufacture of polyurethanes.



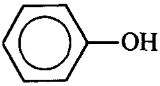
ethylbenzene



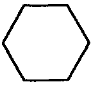
styrene



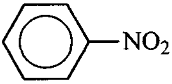
cumene



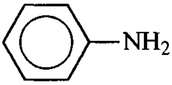
phenol



cyclohexane

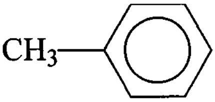


nitrobenzene



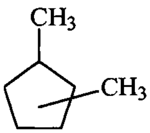
aniline

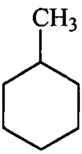
8. TOLUENE (TOLUOL)

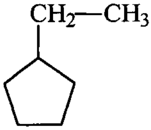


8.1 Manufacture

The Platforming-Udex process for catalytic reforming of naphtha is also used for toluene. The feedstock should be rich in seven carbon naphthenes such as dimethylcyclopentanes, methylcyclohexane, and ethylcyclopentane







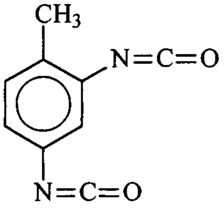
for higher toluene percentages. *n*-Heptane and dimethylhexane remain unchanged and contaminate the product. About 80-90% conversion of naphthenes into toluene is usually realized. Shell has an extraction process using sulfolane as the solvent. It has higher solvent power, solvent circulation is reduced, and the equipment can be smaller. The toluene is purified by azeotropically distilling the nonaromatics with methyl ethyl ketone (MEK, 90%) and water (10%). The excess MEK is then distilled from the toluene.

8.2 Properties

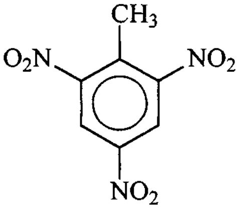
Toluene is a colorless, flammable liquid with a benzene-like odor, bp 110.8°C, flash point 4.4°C, ignition temperature 552°C, and TLV (TWA) = 50 ppm.

8.3 Uses

Table 8.9 shows the non-fuel uses of toluene. Some of the toluene goes into gasoline depending on its supply and price compared to other octane enhancers. Of the other uses of toluene about half is converted into benzene by hydrodealkylation, though this amount varies with the price difference between benzene and toluene. 2,4-Toluene diisocyanate (TDI) is a monomer for polyurethanes. Included in miscellaneous uses is 2,4,6-trinitrotoluene (TNT) as an explosive.



2,4-toluene diisocyanate(TDI)



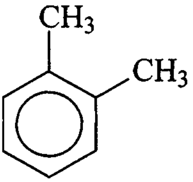
2,4,6-trinitrotoluene (TNT)

Table 8.9 Uses of Toluene

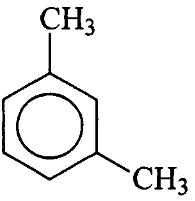
Benzene	57%
Solvent	22
Toluene diisocyanate	8
Miscellaneous	13

Source: Chemical Economics Handbook

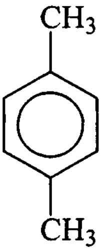
9. XYLENES (XYLOLS)



ortho



meta



para

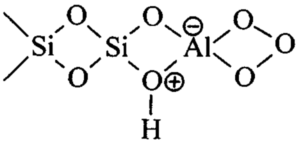
9.1 Manufacture

The xylenes can be used as a mixture or separated into pure isomers, depending on the application. The mixture is obtained from catalytic reforming of naphtha and separated from benzene and toluene by distillation.

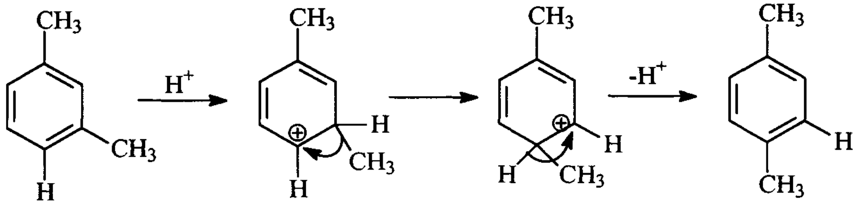
9.2 Separation of *p*-Xylene

The C_8 mixture is cooled to -70°C in the heat exchanger refrigerated by ethylene. Because of the difference in melting points (ortho, -25.0°C; meta, -47.9°C; para, 13.2°C), the para isomer crystallizes preferentially. The other two remain liquid as a mixture. The solid para isomer is centrifuged and separated. A second cooling cycle needs only propane as coolant and 95% purity results. Complete separation is accomplished with an optional third cooling cycle.

Because of the large demand for *p*-xylene, another method is now being used by Amoco to increase the percentage of the para isomer in mixed xylenes. They are heated at 300°C with an acidic zeolite catalyst, which equilibrates the three xylenes to an *o,m,p* ratio of 10:72:18%. The para isomer is separated by fractional crystallization, whereas the *o,m* mixture is reisomerized with the catalyst to produce more para product. Theoretically, all the xylenes could be transformed into the desired para isomer. The zeolite catalyst has the following structure.



The rearrangements of the methyl groups occur via a carbocationic process induced by protonation from the zeolite.



A third possibility of separating the para isomer has been used. This isomer can be selectively adsorbed on zeolites, then desorbed after the ortho and meta isomers have passed through.

9.3 Separation of *o*-Xylene by Fractional Distillation

The slightly different boiling point of the o-xylene is the basis for separation from the other two isomers through an elaborate column.

Isomer	**Boiling Point, °C**
Ortho	144.0
Meta	139.1
Para	138.5

9.4 Properties

The xylenes are colorless, flammable liquids, flash point 17.2°C, ignition temperature 359°C, TLV (TWA) = 100 ppm, and TLV (STEL) = 150 ppm.

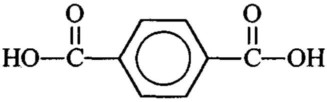
9.5 Uses

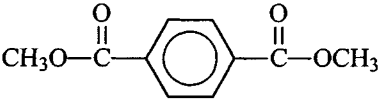
9.5.1 Mixed Xylenes

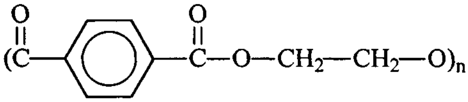
Pure para	39%
Pure ortho	18
Gasoline, benzene, solvent	37

9.5.2 Pure *p*-Xylene

p-Xylene is made into pure terephthalic acid (PTA or TA) or dimethyl terephthalate (DMT), which in turn is polymerized to polyester. About half of polyester is made from terephthalic acid and half from dimethyl terephthalate. Either is reacted with ethylene glycol to give poly(ethylene terephthalate). Large amounts of this polyester are used in textile fibers, photographic film, and soft drink bottles.

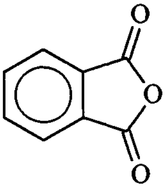

terephthalic acid (TA)


dimethyl terephthalate (DMT)


polyester

9.5.3 Pure *o*-Xylene

o-Xylene is converted into phthalic anhydride. About 53% of phthalic anhydride is an intermediate in the synthesis of plasticizers, substances that make plastics more flexible. A common plasticizer is dioctyl phthalate. Phthalic anhydride is also used to make unsaturated polyester resins (21%) and alkyd resins (15%).


phthalic anhydride

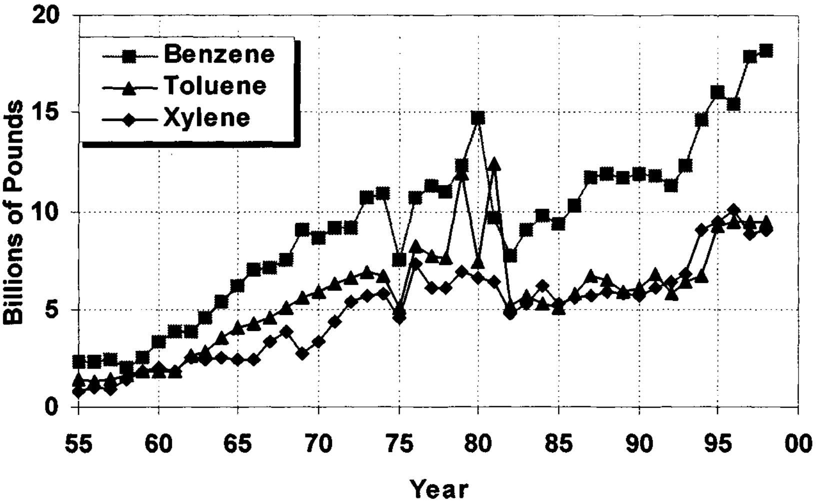


Figure 8.8 U.S. production of aromatics. (*Source:* Lowenheim & Moran, *Chemical and Engineering News*, *Chemical Economics Handbook*, and *Chemical Profiles*)

10. ECONOMIC ASPECTS OF AROMATICS

In Fig. 8.8 the production of benzene, toluene, and xylene are summarized. Healthy gains over the years with a steady incline until 1975 occurred, when the oil embargo dipped the production of all three deeply for the first time. More erratic years followed. Note that in some years such as 1980 and 1981, benzene went up when toluene went down and *vice versa.* In those years more toluene may or may not have been converted into benzene by hydrodealkylation. A common unit used in industry for BTX production is gallons rather than pounds. For benzene at 20°C, 1 gal = 7.320 lb; for toluene, 1 gal = 7.210 lb; for *p*-xylene, 1 gal = 7.134 lb; and for *o*-xylene, 1 gal = 7.300 lb. For many years toluene was in between benzene and xylene production. More recently the increasing demand for *p*-xylene has made xylene production similar to toluene, with both about half that of benzene. The estimate for benzene production in 2002 is 20 billion lb. Capacity of plants for benzene (Table 8.10) has remained relatively constant for the 1980s and increased for the 1990s, but production as a percentage of capacity is near 75% for many years. There are 22 plants making benzene, mostly in Texas.

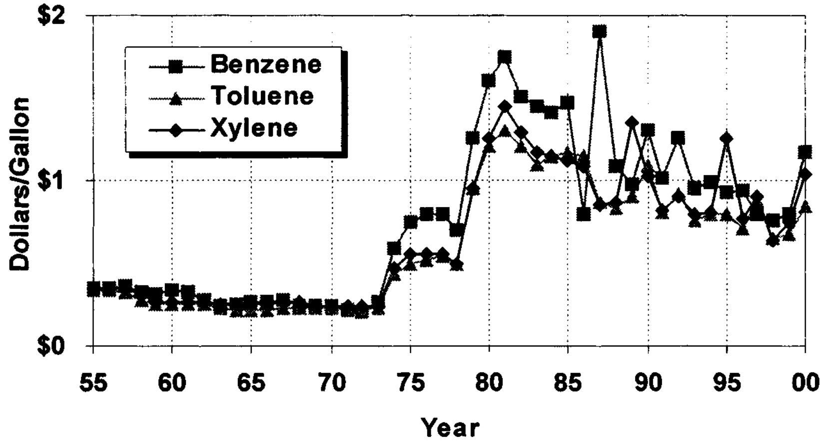


Figure 8.9 U.S. prices of aromatics. (*Source:* Lowenheim & Moran and *Chemical Marketing Reporter*)

Table 8.10 Benzene Capacity

Year	Capacity, Million gal.	Production as a % of Capacity
1981	2500	70
1987	2100	78
1990	2400	75
1999	3300	75

Source: Chemical Profiles

Fig. 8.9 shows U.S. prices for the aromatics in dollars per gallon. As in the olefins we see very steady pricing to the mid '70s, then heavy increases through the late '70s because of the oil embargo and early '80s because of higher inflation rates, followed by ups and downs, especially for benzene. For the hydrodealkylation of toluene to be profitable as a production method for benzene the price of toluene must be 50¢/gal lower than that for benzene. Sometimes this happens, sometimes not. *p*-Xylene is the more expensive isomer of the two commercial xylenes because of the crystallization process required. The commercial value of benzene is approximately $2 billion.

Suggested Readings

Chemical Profiles in *Chemical Marketing Reporter*, 6-9-97, 5-11-98, 5-18-98, 12-6-99, 1-24-00, and 1-31-00.

Lowenheim and Moran, *Faith, Keyes, and Clark's Industrial Chemicals*, pp. 126-137, 376-384, 874-881.
Wiseman, *Petrochemicals*, pp. 30-42, 80-88.
Wittcoff and Reuben, *Industrial Organic Chemicals*, pp. 59-70, 196-199.

Chapter 9

Derivatives of Ethylene

Over 100 billion lb of chemicals and polymers per year are made from ethylene, by far the most important organic chemical. Over 40% of all organic chemicals by volume are derived from ethylene. Unfortunately, we cannot describe the interesting chemistry and uses for all the important derivatives of ethylene. We will limit our detailed discussion to those chemicals made from ethylene that appear in the top 50, which amount to 8 important organic chemicals. These are listed in Table 9.1.

Again we are faced with the question of what order to treat these chemicals: by rank, alphabetically, and so on. Some of these chemicals can be grouped by manufacturing process, since one may be made from another, and both originally from ethylene, in a multistep synthetic sequence. We take advantage of this manufacturing relationship in our choice of order since it groups these chemicals together in one important feature that we wish to emphasize: their chemistry of manufacture. The discussions of these chemicals will be different from that for inorganics. For inorganics the

Table 9.1 Ethylene Derivatives in the Top 50

Ethylene dichloride
Vinyl chloride
Acetic acid
Vinyl acetate
Ethylbenzene
Styrene
Ethylene oxide
Ethylene glycol

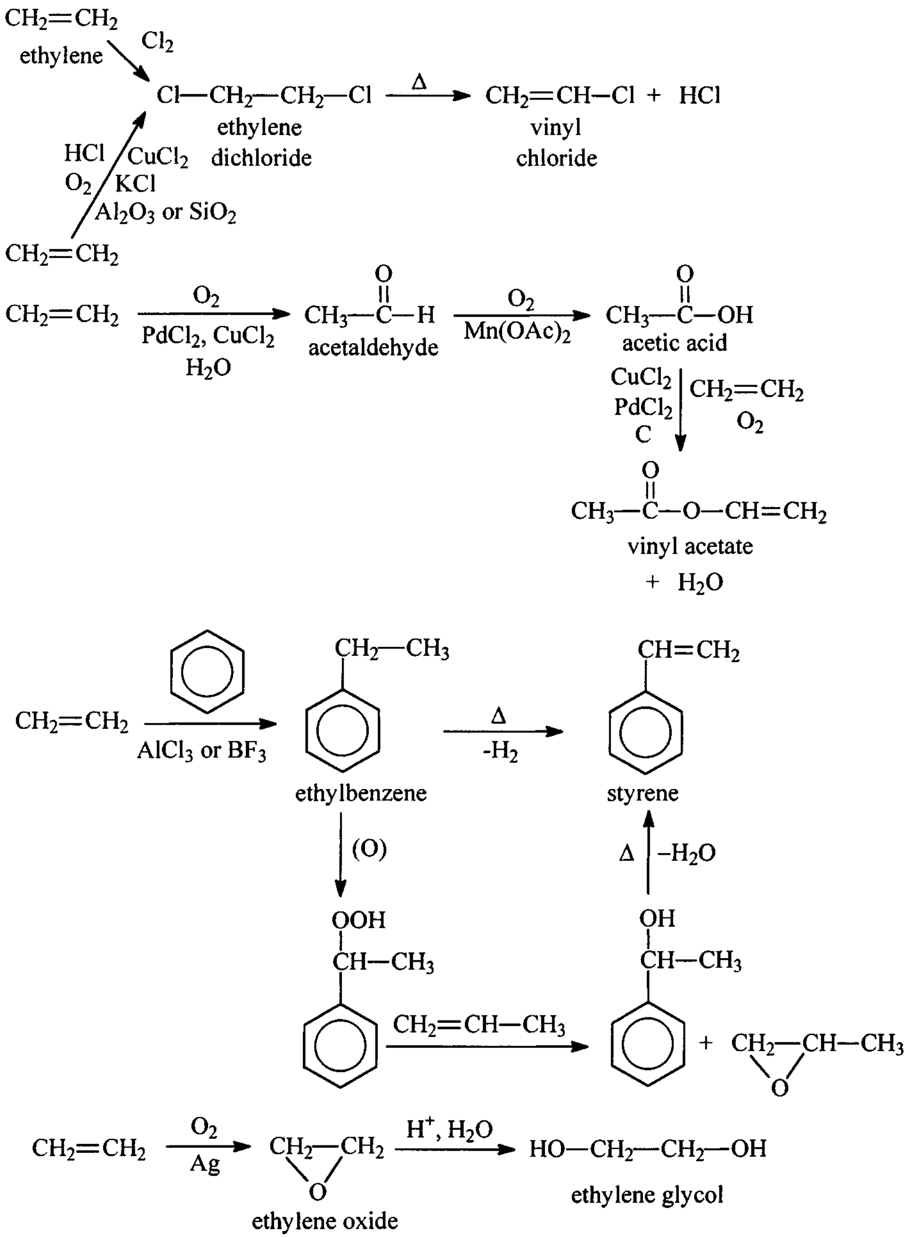


Figure 9.1 Synthesis of ethylene derivatives in the top 50 chemicals.

emphasis was on the simple reaction, the engineering aspects of the chemical's manufacture, uses, and economics. Because there are more organics than inorganics in the top 50, we must sacrifice some details in engineering and economics but still stress the chemistry of manufacture (including mechanism when known) and uses of the chemicals. Let us recall at this point that nearly half of all ethylene is polymerized to polyethylene. This process and the polymer will be discussed in a later chapter. Other than this the main large-scale industrial reactions of ethylene are summarized in this chapter. Fig. 9.1 gives an outline of this chemistry with the order that we will use to consider these chemicals. They are in four pairs, since vinyl chloride is made from ethylene dichloride, vinyl acetate is made from acetic acid, styrene is processed from ethylbenzene, and ethylene glycol is manufactured from ethylene oxide.

1. ETHYLENE DICHLORIDE (EDC)

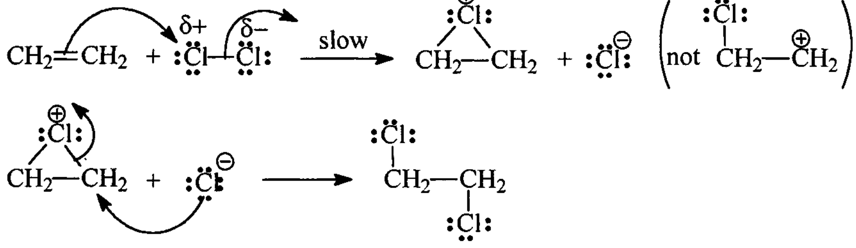
$$Cl—CH_2—CH_2—Cl$$

Ethylene dichloride is one of the highest-ranked derived organic chemicals and is made in excess of 20 billion lb/yr. There are two major manufacturing methods for this chemical, each of which contributes about 50% to the total production of EDC. The classical method for EDC manufacture is the electrophilic addition of chlorine to the double bond of ethylene. The yield is good (96-98%); it can be done in vapor or liquid phase at 40-50°C using ethylene dibromide as a solvent, and the product is easily purified by fractional distillation. The mechanism is well understood and is a good example of the very general addition of an electrophile to a double bond. Here the intermediate is the bridged chloronium ion, since in this structure all atoms have a complete octet. A primary carbocation is less stable. Polarization of the chlorine-chlorine bond occurs as it approaches the π cloud of the double bond. Backside attack of chloride ion on the bridged ion completes the process.

Reaction:

$$CH_2{=}CH_2 + Cl_2 \xrightarrow{FeCl_3} Cl—CH_2—CH_2—Cl$$

Mechanism:



In contrast to this direct chlorination there is the oxychlorination of ethylene using hydrogen chloride and oxygen, the other major method now used. Since the chlorine supply is sometimes short and it is difficult to balance the caustic soda and chlorine demand (both are made by the electrolysis of brine), hydrogen chloride provides a cheap alternate source for the chlorine atom. Most of the ethylene dichloride manufactured is converted into vinyl chloride by eliminating a mole of HCl, which can then be recycled and used to make more EDC by oxychlorination. EDC and vinyl chloride plants usually are physically linked. Most plants are 50:50 direct chlorination:oxychlorination to balance the output of HCl.

$$50\%\quad CH_2{=}CH_2 + 2HCl + \tfrac{1}{2}O_2 \longrightarrow Cl{-}CH_2{-}CH_2{-}Cl + H_2O$$

$$Cl{-}CH_2{-}CH_2{-}Cl \longrightarrow CH_2{=}CH{-}Cl + HCl\ \text{(recycle)}$$

$$50\%\quad CH_2{=}CH_2 + Cl_2 \longrightarrow Cl{-}CH_2{-}CH_2{-}Cl$$

$$Cl{-}CH_2{-}CH_2{-}Cl \longrightarrow CH_2{=}CH{-}Cl + HCl\ \text{(recycle)}$$

What probably happens in the oxychlorination process is that chlorine is formed in situ. The reaction of hydrogen chloride and oxygen to give chlorine and water was discovered by Deacon in 1858. Once the chlorine is formed, it then adds to ethylene as in the direct chlorination mechanism. Cu^{+2} is the catalyst and helps to more rapidly react HCl and O_2 because of its ability to undergo reduction to Cu^{+1} and reoxidation to Cu^{+2}. KCl is present to reduce the volatility of $CuCl_2$.

$$2HCl + 2Cu^{+2} \longrightarrow Cl_2 + 2Cu^{+} + 2H^{+}$$

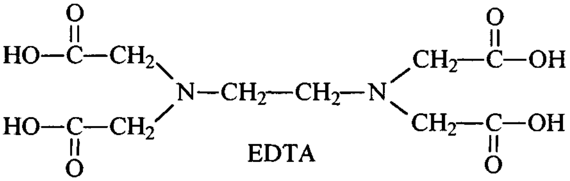
$$2Cu^{+} + \tfrac{1}{2}O_2 + 2H^{+} \longrightarrow 2Cu^{+2} + H_2O$$

Ethylene dichloride is a colorless liquid with a bp of 84 °C. As with many chlorinated hydrocarbons, it is quite toxic and has a TLV value of 10 ppm (TWA). It is on the list of "Reasonably Anticipated to Be Human Carcinogens."

Nearly all ethylene dichloride is made into vinyl chloride, which is polymerized to the important plastic poly(vinyl chloride) (PVC). Perchloroethylene (perc) is used as a dry cleaning agent (55%), a chemical intermediate (29%), and a metal cleaning agent (11%). Perc has a 75% share of the dry cleaning business. Methyl chloroform is one of a few chlorinated compounds that has low toxicity, but it is being phased out because of its ozone depleting potential. Sometimes called "1,1,1," it is used as a chemical intermediate (60%), a metal cleaning agent (25%), and as an ingredient in adhesives, coatings, and inks (8%). Vinylidene chloride is polymerized to a plastic (Saran®). The ethylenediamines are used as chelating agents, the most important being ethylenediaminetetracetic acid (EDTA).

$CH_2{=}CH{-}Cl$	$Cl_2C{=}CCl_2$	$CH_3{-}CCl_3$
vinyl chloride	perchloroethylene	methyl chloroform

$CH_2{=}CCl_2$	$NH_2{-}CH_2{-}CH_2{-}NH_2$
vinylidene chloride	ethyleneamines



EDTA

Despite these minor uses, the economics of EDC is linked to the demand for PVC plastic.

2. VINYL CHLORIDE (VINYL CHLORIDE MONOMER, VCM)

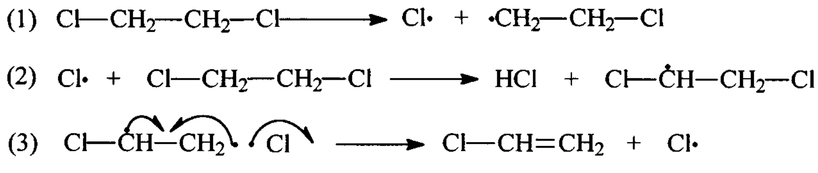
$$CH_2{=}CH{-}Cl$$

Although there are two manufacturing methods for ethylene dichloride, all the vinyl chloride is made by a single process, thermal dehydrochlorination of EDC. This takes place at temperatures of 480-510°C under a pressure of 50 psi with a charcoal catalyst to give a 99% yield. Vinyl chloride is a gas at ambient pressure with a bp of -13°C. It is separated from ethylene dichloride by fractional distillation. Vinyl chloride readily polymerizes so it is stabilized with inhibitors to prevent polymerization during storage. The mechanism of formation is a free-radical chain process as shown below. Although the conversion is low, 50-60%, recycling the EDC allows an overall 99% yield.

Reaction:

$$Cl{-}CH_2{-}CH_2{-}Cl \xrightarrow{\Delta} CH_2{=}CH{-}Cl + HCl$$

Mechanism:



(1) $Cl{-}CH_2{-}CH_2{-}Cl \longrightarrow Cl\cdot + \cdot CH_2{-}CH_2{-}Cl$

(2) $Cl\cdot + Cl{-}CH_2{-}CH_2{-}Cl \longrightarrow HCl + Cl{-}\dot{C}H{-}CH_2{-}Cl$

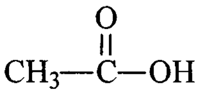
(3) $Cl{-}\dot{C}H{-}CH_2{-}Cl \longrightarrow Cl{-}CH{=}CH_2 + Cl\cdot$

then (2), (3), (2), (3), etc.

The largest use of vinyl chloride is in the manufacture of poly(vinyl chloride) plastic, which finds diverse applications in the building and construction industry as well as in the electrical, apparel, and packaging industries. Poly(vinyl chloride) does degrade relatively fast for a polymer, but various heat, ozone, and ultraviolet stabilizers make it a useful polymer. A wide variety of desirable properties can be obtained by using various amounts of plasticizers, such that both rigid and plasticized PVC have large markets. PVC takes up 98% of all vinyl chloride with only 2% being used for chlorinated solvents and poly(vinylidene chloride).

After some tough years in the 1970s vinyl chloride had a good economic gain in the 1980s. The 1997 production of approximately 15 billion lb is expected to increase by about 3% per year in the near future. At a price of 21¢/lb that gives a total commercial value of $3.2 billion. One of the reasons vinyl chloride has had some bad years is the recent findings of toxicity. It causes liver cancer and is on the list of chemicals that are "Known to Be Human Carcinogens." In 1973 its TLV was 200 ppm. This was reduced in 1974 to 50 ppm and in 1980 the TWA was 5 ppm. In 2000 it is 1 ppm. However, apparently this causes no health problems for poly(vinyl chloride) uses. Only the monomer is a health hazard. As a result, the economic situation looks good.

3. ACETIC ACID (ETHANOIC ACID, GLACIAL ACETIC ACID)



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

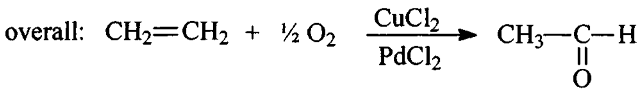
If there is a prime example of an organic chemical that is in a state of flux and turnover in regards to the manufacturing method, it is probably acetic acid. There are now three industrial processes for making acetic acid. Domestic capacity in 1978 was almost equal among acetaldehyde oxidation, *n*-butane oxidation, and methanol carbonylation. In 1980 methanol carbonylation exceeded 40% of the capacity and will continue to increase in its share of capacity because of economic advantages. In 1998 methanol carbonylation was 64% of capacity. Acetic acid will also be covered in the derivatives of methane chapter, but it is appropriate to cover it here since both it and vinyl acetate are still made from ethylene.

Ethylene is the exclusive organic raw material for making acetaldehyde, 70% of which is further oxidized to acetic acid or acetic anhydride. The Wacker process, named after a German company, for making acetaldehyde involves cupric chloride and a small amount of palladium chloride in aqueous solution as a catalyst. The inorganic chemistry of this reaction is understood: (1) A π complex between ethylene and palladium chloride is formed and decomposes to acetaldehyde and palladium metal; (2) the palladium is reoxidized to palladium chloride by the cupric chloride; and (3) the cuprous chloride thus formed is reoxidized to the cupric state by oxygen fed to the system. The three equations that follow indicate the series of redox reactions that occur. When added together they give the overall reaction. The yield is 95%.

$$(1)\quad CH_2{=}CH_2 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd^o + 2HCl$$

$$(2)\quad Pd^o + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$$

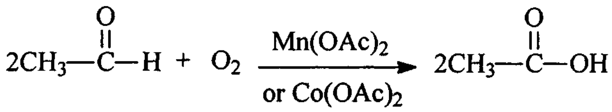
$$(3)\quad 2CuCl + \tfrac{1}{2}O_2 + 2HCl \longrightarrow 2CuCl_2 + H_2O$$



$$\text{overall:}\quad CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow[PdCl_2]{CuCl_2} CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-H$$

The details of the organic chemistry of the reaction of ethylene with $PdCl_2$ (equation (1) above) are also known and are shown in Fig. 9.2. The palladium ion complexes with ethylene and water molecules and the water adds across the bond while still complexed to palladium. The palladium then serves as a hydrogen acceptor while the double bond reforms. Keto-enol tautomerism takes place, followed by release of an acetaldehyde molecule from the palladium.

When it was a major source for acetic acid, acetaldehyde was in the top 50 at about 1.5 billion lb. Now it is under a billion pounds but it is still used to manufacture acetic acid by further oxidation. Here a manganese or cobalt acetate catalyst is used with air as the oxidizing agent. Temperatures range from 55-80°C and pressures are 15-75 psi. The yield is 95%.



$$2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + O_2 \xrightarrow[\text{or } Co(OAc)_2]{Mn(OAc)_2} 2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

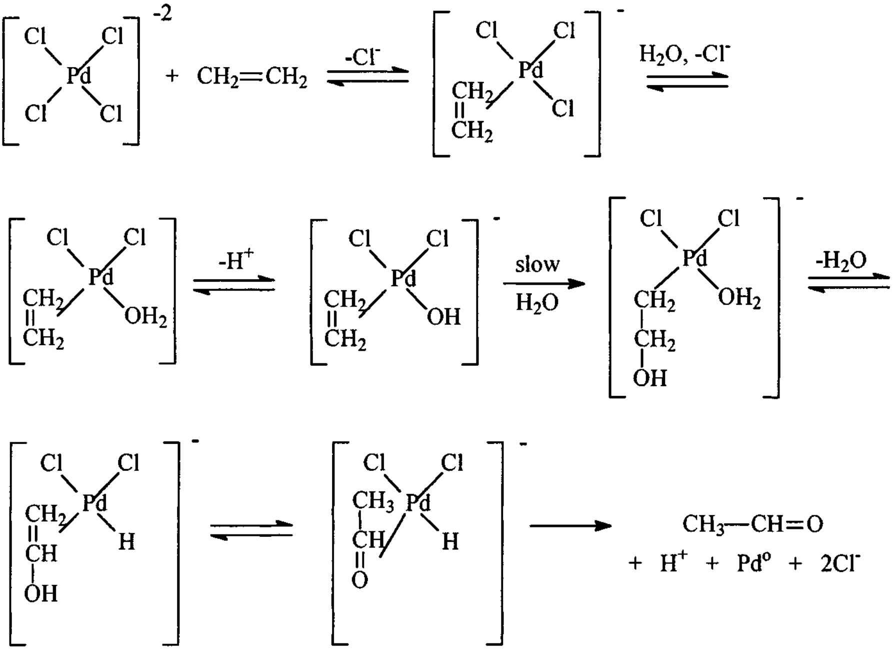
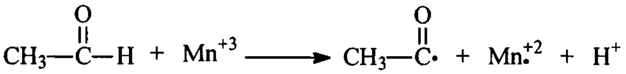


Figure 9.2 Mechanism of the Wacker reaction. (*Source:* White)

Although the oxidation reaction is simple, the mechanism is quite complex and involves the formation of peracetic acid first.

(1) 

$$CH_3-\overset{O}{\overset{\|}{C}}-H + Mn^{+3} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}\cdot + Mn^{\cdot +2} + H^+$$

(2) 

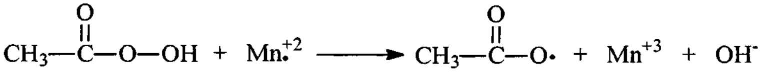
$$CH_3-\overset{O}{\overset{\|}{C}}\cdot + O_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-O\cdot$$

(3) 

$$CH_3-\overset{O}{\overset{\|}{C}}-O-O\cdot + CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-OH + CH_3-\overset{O}{\overset{\|}{C}}\cdot$$

then (2), (3), (2), (3), etc.

Some of the peracetic acid decomposes with the help of the catalyst and the catalyst is regenerated by this process.

(4) 

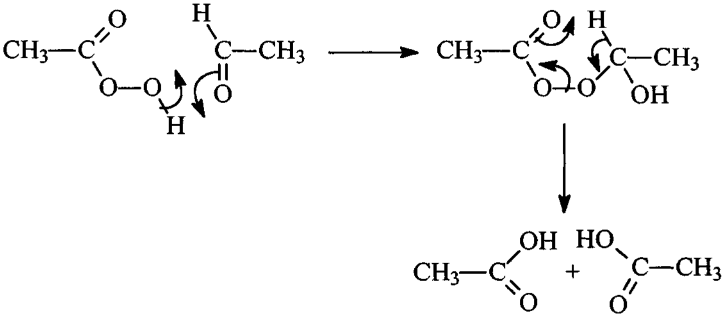
$$CH_3-\overset{O}{\overset{\|}{C}}-O-OH + Mn^{+2} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O\cdot + Mn^{+3} + OH^-$$

(5) 

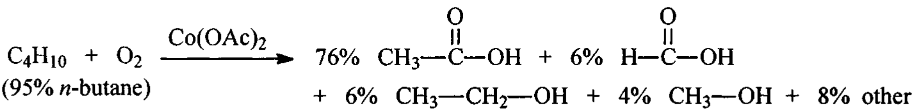
$$CH_3-\overset{O}{\overset{\|}{C}}-O\cdot + CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}\cdot$$

then (2), (3), (2), (3), etc.

Most of the peracetic acid decomposes via a cyclic reaction with acetaldehyde to form two moles of acetic acid.



A second manufacturing method for acetic acid utilizes butane from the C_4 petroleum stream rather than ethylene. It is a very complex oxidation with a variety of products formed, but conditions can be controlled to allow a large percentage of acetic acid to be formed. Cobalt (best), manganese, or chromium acetates are catalysts with temperatures of 50-250°C and a pressure of 800 psi.



$$\underset{(95\%\ n\text{-butane})}{C_4H_{10}} + O_2 \xrightarrow{Co(OAc)_2} 76\%\ CH_3-\overset{O}{\overset{\|}{C}}-OH + 6\%\ H-\overset{O}{\overset{\|}{C}}-OH + 6\%\ CH_3-CH_2-OH + 4\%\ CH_3-OH + 8\%\ \text{other}$$

The mechanism of this reaction involves free radical oxidation of butane to butane hydroperoxide, which decomposes to acetaldehyde via β scissions. It is similar to the oxidation of cyclohexane to cyclohexanol and cyclohexanone, which will be discussed in Chapter 11, Section 4.

The third and now preferred method of acetic acid manufacture is the carbonylation of methanol (Monsanto process), involving reaction of methanol and carbon monoxide (both derived from methane). This is discussed in Chapter 12, Section 3.

Table 9.2 Uses of Acetic Acid

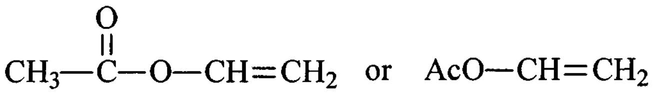
Vinyl acetate	60%
Cellulose acetate	10
Acetic esters	10
Solvent for TA/DMT	10
Miscellaneous	10

Source: Chemical Profiles

Although we have included acetic acid manufacture under ethylene derivatives, as you can see it is made from three of the seven basic organics: ethylene, C_4 hydrocarbons, and methane, with the most important method being from methane. Pure 100% acetic acid is sometimes called glacial acetic because when cold it will solidify into layered crystals similar in appearance to a glacier. It is a colorless liquid with a pungent, vinegar odor and sharp acid taste, bp 118 °C, and mp 17 °C.

Table 9.2 summarizes the uses of acetic acid. Vinyl acetate is another top 50 chemical. Acetic anhydride is used to make cellulose acetate and at times has been in the top 50 chemicals itself. Cellulose acetate is a polymer used mainly as a fiber in clothing and cigarette filters. Ethyl acetate is a common organic solvent. Acetic acid is used as a solvent in the manufacture of terephthalic acid (TA) and dimethyl terephthalate (DMT), which are monomers for the synthesis of poly(ethylene terephthalate), the "polyester" of the textile industry. A minor household use of acetic acid is as a 3-5% aqueous solution, which is called vinegar.

4. VINYL ACETATE

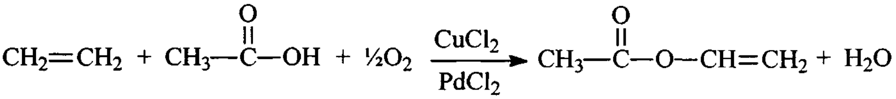


$$CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—O—CH{=}CH_2 \quad \text{or} \quad AcO—CH{=}CH_2$$

Vinyl acetate is one of many compounds where classical organic chemistry has been replaced by a catalytic process. It is also an example of older acetylene chemistry becoming outdated by newer processes involving other basic organic building blocks. Up to 1975 the preferred manufacture of this important monomer was based on the addition of acetic acid to the triple bond of acetylene using zinc amalgam as the catalyst, a universal reaction of alkynes.

$$\mathrm{CH{\equiv}CH + HOAc \xrightarrow[Hg]{Zn} CH_2{=}CH{-}OAc}$$

In 1969, 90% of vinyl acetate was manufactured by this process. By 1975 only 10% was made from acetylene, and in 1980 it was obsolete. Instead, a newer method based on ethylene replaced this old acetylene chemistry. A Wacker catalyst is used in this process similar to that for acetic acid. Since the acetic acid can also be made from ethylene, the basic raw material is solely ethylene, in recent years very economically advantageous as compared to acetylene chemistry. An older liquid-phase process has been replaced by a vapor-phase reaction run at 70-140 psi and 175-200°C. Catalysts may be (1) C—$PdCl_2$—$CuCl_2$, (2) $PdCl_2$—Al_2O_3, or (3) Pd—C, KOAc. The product is distilled; water, acetaldehyde, and some polymer are separated. The acetaldehyde can be recycled to acetic acid. The pure colorless vinyl acetate is collected at 72°C. It is a lachrymator (eye irritant). The yield is 95%. The mechanism of this reaction is the same as the Wacker process for ethylene to acetic acid, except that acetic acid attacks rather than water. You should develop this mechanism similar to Fig. 9.2, subtituting acetic acid for water.



$$\mathrm{CH_2{=}CH_2 + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + \tfrac{1}{2}O_2 \xrightarrow[PdCl_2]{CuCl_2} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}CH{=}CH_2 + H_2O}$$

Table 9.3 gives the uses of vinyl acetate. Poly(vinyl acetate) is used primarily in adhesives, coatings, and paints, especially those that are water-based. This percentage of use has increased dramatically in recent years. The shift to water-based coatings has certainly helped vinyl acetate production. Copolymers of poly(vinyl acetate) with poly(vinyl chloride) are used in flooring and PVC pipe. Poly(vinyl alcohol) is used in textile sizing, adhesives, emulsifiers, and paper coatings. Poly(vinyl butyral) is the plastic inner liner of most safety glass.

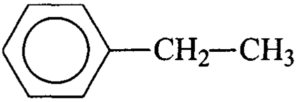
Table 9.3 Uses of Vinyl Acetate

Poly(vinyl acetate)	55%
Poly(vinyl alcohol)	19
Poly(vinyl butyral)	12
Copolymers	8
Miscellaneous	6

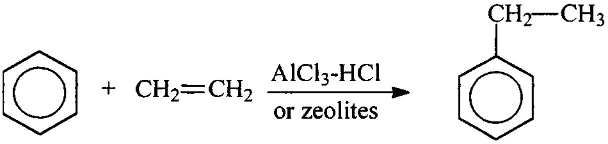
Source: Chemical Profiles

Vinyl acetate is a good example of an ethylene chemical with a high percentage of exports, sometimes near 30%. The United States now has a cost advantage in ethylene production and many ethylene derivatives have high export percentages.

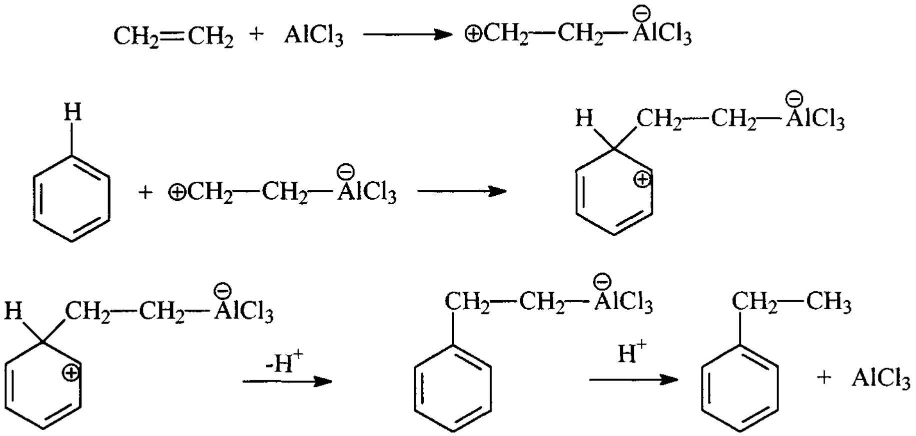
5. ETHYLBENZENE



Despite the use of new catalysts for manufacturing some industrial organic chemicals, many well-known classical reactions still abound. The Friedel-Crafts alkylation is one of the first reactions studied in electrophilic aromatic substitution. It is used on a large scale for making ethylbenzene.

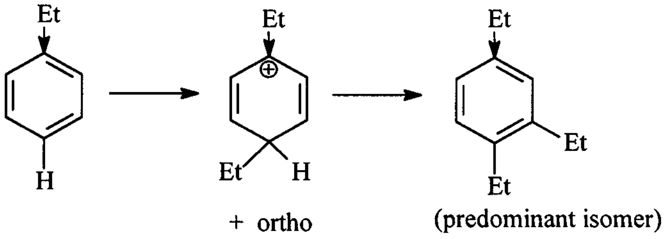


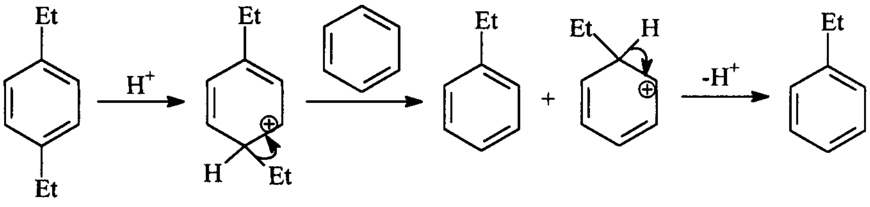
Note that ethylbenzene is a derivative of two basic organic chemicals, ethylene and benzene. A vapor-phase method with boron trifluoride, phosphoric acid, or alumina-silica as catalysts has given away to a liquid-phase reaction with aluminum chloride at 90 °C and atmospheric pressure. A new Mobil-Badger zeolite catalyst at 420 °C and 175-300 psi in the gas phase may be the method of choice for future plants to avoid corrosion problems. The mechanism of the reaction involves complexation of the



ethylene with the Lewis acid catalyst, attack of the electrophilic carbon on the aromatic ring, loss of the proton to rearomatize, and desorption of the catalyst with subsequent protonation in the side chain.

Excess benzene must be used. A common benzene:ethylene ratio is 1.0:0.6. This avoids the formation of di- and triethylbenzenes. The first ethyl group, being electron donating inductively as compared to hydrogen, will activate the benzene ring toward electrophilic attack by stabilizing the intermediate carbocation. The benzene when in excess prevents this since it increases the probability of the attack on benzene rather than on ethylbenzene, but some polyethylbenzenes are formed, and these can be separated in the distillation process and burned for fuel. Alternatively, disubstituted isomers can be transalkylated with benzene to give two moles of monosubstituted product. The benzene is recycled.

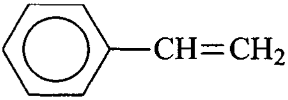




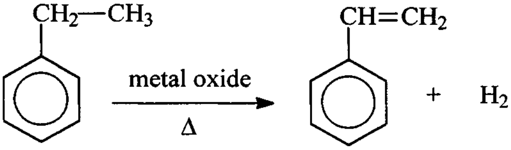
Ethylbenzene is a colorless liquid, bp 136°C. Despite the elaborate separations required, including washing with caustic and water and three distillation columns, the overall yield of ethylbenzene is economically feasible at 98%.

Almost all ethylbenzene (99%) is used to manufacture styrene. Only 1% is used as a solvent.

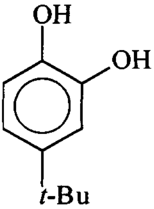
6. STYRENE (VINYLBENZENE, PHENYLETHENE)

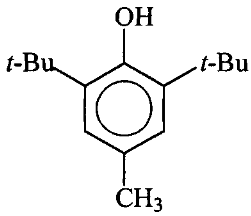


Approximately 79% of the styrene produced in the United States is made from ethylbenzene by dehydrogenation. This is a high-temperature reaction (630°C) with various metal oxides as catalysts, including zinc, chromium, iron, or magnesium oxides coated on activated carbon, alumina, or bauxite. Iron oxide on potassium carbonate is also used. Most dehydrogenations do not occur readily even at high temperatures. The driving force for this reaction is the extension in conjugation that results, since the double bond on the side chain is in conjugation with the ring. Conditions must be controlled to avoid polymerization of the styrene. Sulfur is added to prevent polymerization. The crude product has only 37% styrene but contains 61% ethylbenzene. A costly vacuum distillation through a 70-plate column at 90°C and 35 torr is needed to separate the two. The ethylbenzene is recycled. Usually a styrene plant is combined with an ethylbenzene plant when designed. The yield is 90%.



Because styrene readily polymerizes it is immediately treated with an antioxidant such as *p*-*t*-butylcatechol at 10 ppm.



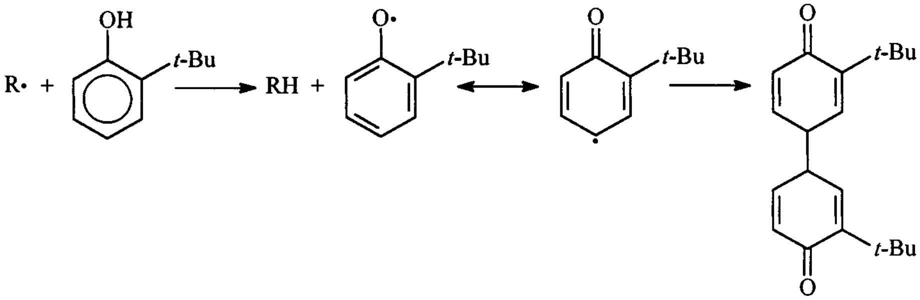


BHT

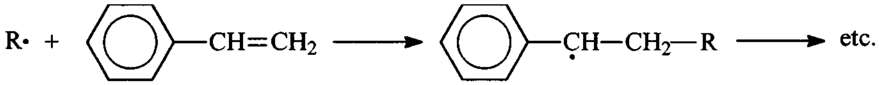
Many phenols, especially "hindered phenols" such as butylated hydroxy toluene (BHT), are good antioxidants. They act as radical scavengers by readily reacting with stray radicals to give very stable radicals via resonance.

The alkyl radicals then cannot initiate the polymerization of substances such as styrene.

This happens:



Instead of:



A new alternate method for the manufacture of styrene, called the oxirane process, now accounting for 21% of production, uses ethylbenzene. It is oxidized to the hydroperoxide and reacts with propylene to give phenylmethylcarbinol (or methyl benzyl alcohol, MBA) and propylene oxide, the latter being a top 50 chemical itself. The alcohol is then dehydrated at relatively low temperatures (180-400 °C) using an acidic silica gel or titanium dioxide catalyst, a much cleaner and less energy-dependent reaction than the dehydrogenation. Other olefins besides propylene could be used in the epoxidation reaction, but it is chosen because of the high demand for the epoxide. Some acetophenone is separated and hydrogenated back to MBA.

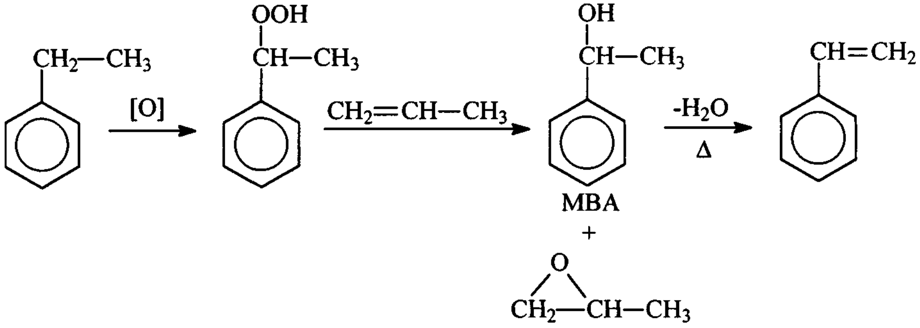


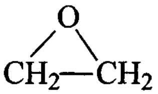
Table 9.4 Uses of Styrene

Polystyrene	62%
ABS resins	11
SB latex	8
Unsaturated polyester resins	7
SBR	6
Miscellaneous	6

Source: Chemical Profiles

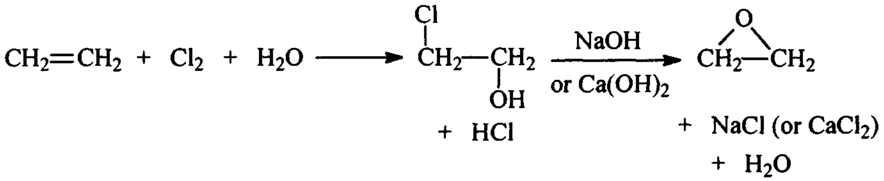
Table 9.4 shows the uses of styrene. These are dominated by polymer chemistry and involve polystyrene and its copolymers. We will study these in detail later, but the primary uses of polystyrene are in various molded articles such as toys, bottles, and jars, and foam for insulation and cushioning. Styrene manufacture is a large business. With a production of 11.4 billion lb and a price of 30¢/lb styrene has a commercial value of approximately $3.4 billion.

7. ETHYLENE OXIDE

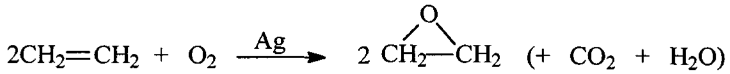


Another example of a famous organic chemical reaction being replaced by a catalytic process is furnished by the manufacture of ethylene oxide. For many years it was made by chlorohydrin formation followed by dehydrochlorination to the epoxide. Although the chlorohydrin route is still used to convert propylene to propylene oxide, a more efficient air epoxidation of ethylene is used and the chlorohydrin process for ethylene oxide manufacture has not been used since 1972.

Old method:



New method:



$$2CH_2{=}CH_2 + O_2 \xrightarrow{Ag} 2\,\overset{O}{CH_2{-}CH_2} \quad (+\ CO_2 + H_2O)$$

The higher yields (85%) in the chlorohydrin method are not enough to outweigh the waste of chlorine inherent in the process. Although the yields in the direct oxidation method (75%) are lower, the cheap oxidant atmospheric oxygen is hard to beat for economy. Some overoxidation to carbon dioxide and water occurs. Good temperature control at 270-290°C and pressures of 120-300 psi with a 1 sec contact time on the catalyst are necessary. Tubular reactors containing several thousand tubes of 20-50 mm diameter are used. Even though metallic silver is placed in the reactor, the actual catalyst is silver oxide under the conditions of the reaction. Ethylene oxide is a gas at room temperature with a bp of 14°C.

Table 9.5 lists the uses of ethylene oxide. Ethylene glycol is eventually used in two primary types of end products: polyesters and antifreeze. About half the ethylene glycol is used for each end product. Poly(ethylene terephthalate) is the leading synthetic fiber and has other important applications in plastic film and bottles. Ethylene glycol is a common antifreezing agent especially in automobile radiators.

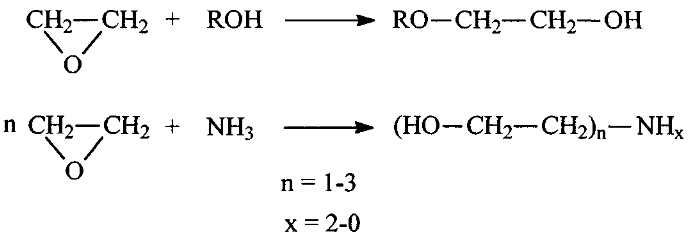
As a hospital sterilant for plastic materials, ethylene oxide was ideal since radiation or steam cannot be used. It is in this application that evidence of high miscarriage rates (3x normal) of women on hospital sterilizing staffs caused a lowering of the TLV to 1 ppm. The chemical was most often used in closed systems but in this application incidental exposures were said to go as high as 250 ppm. Since 1984 ethylene oxide is no longer used as a hospital sterilant. It is now on the "Known to Be Human Carcinogens" list. Ethylene oxide is important in the manufacture of many nonionic detergents to be discussed in a later chapter. It is a feedstock for synthesizing glycol ethers (solvents for paints, brake fluids) and ethanolamines (surfactants and

Table 9.5 Uses of Ethylene Oxide

Ethylene glycol	58%
Ethoxylate surfactants	12
Ethanolamines	10
Di, tri, & polyethylene glycols	9
Glycol ethers	6
Polyether polyols	3
Miscellaneous	2

Source: Chemical Profiles

gas scrubbing of refineries to remove acids). The manufacturing chemistry of these two materials is given below.



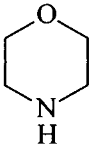
Diethylene and triethylene glycol (DEG and TEG) are produced as by-products of ethylene glycol. DEG and TEG are used in polyurethane and unsaturated polyester resins and in the drying of natural gas. DEG is also used in antifreeze and in the synthesis of morpholine, a solvent, corrosion inhibitor, antioxidant, and pharmaceutical intermediate.

$$HO—CH_2—CH_2—O—CH_2—CH_2—OH$$

diethylene glycol (DEG)

$$HO—CH_2—CH_2—O—CH_2—CH_2—O—CH_2—CH_2—OH$$

triethylene glycol (TEG)

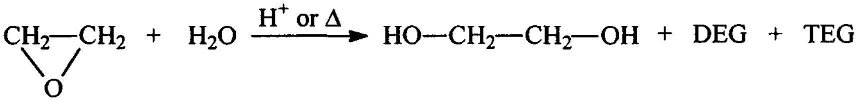


morpholine

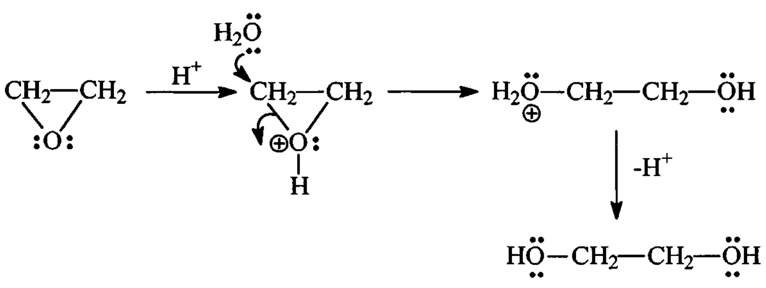
8. ETHYLENE GLYCOL (ETHAN-1,2-DIOL)

$$HO—CH_2—CH_2—OH$$

The primary manufacturing method of making ethylene glycol is from acid- or thermal-catalyzed hydration and ring opening of the oxide. Nearly all the glycol is made by this process. Either a 0.5-1.0% H_2SO_4 catalyst is used at 50-70°C for 30 min or, in the absence of the acid, a temperature of 195°C and 185 psi for 1 hr will form the diol. A 90% yield is realized when the ethylene oxide:water molar ratio is 1:5-8. The advantage of the acid-catalyzed reaction is no high pressure; the thermal reaction however needs no corrosion resistance and no acid separation step.



The ethylene glycol, bp 198 °C, is readily vacuum distilled and separated from the DEG, bp 246 °C, and TEG, bp 288 °C. The mechanism of the reaction follows the general scheme for acid-catalyzed ring openings of epoxides.



Research is being conducted on the direct synthesis of ethylene glycol from synthesis gas. In one process very high pressures of 5,000 psi with very expensive catalysts Rh_x (CO) are being studied. An annual loss of rhodium catalyst of only 0.000001% must be realized before this process will compete economically. At least five other alternate syntheses of ethylene glycol that bypass toxic ethylene oxide are being researched.

Table 9.6 shows the use profile for ethylene glycol. In 1950 only 48% of antifreeze was ethylene glycol, whereas in 1962 it accounted for 95% of all

Table 9.6 Uses of Ethylene Glycol

Antifreeze	30%
Polyester fiber	27
Polyester bottles	25
Industrial uses	10
Polyester film	4
Miscellaneous	4

Source: Chemical Profiles

antifreeze. Its ideal properties of low melting point, high boiling point, and unlimited water solubility make it a good material for this application. The polyester bottle market is rising rapidly. Ten years ago it was a small percentage of ethylene glycol use. Now one fourth of all glycol goes to this type of polyester market. The polyester bottle market is expected to increase >8% per year in the near future, while fiber grows only at 3-4% per year. A production of 6.5 billion lb and a price of 29¢/lb for ethylene glycol gives a commercial value of $1.8 billion.

Suggested Readings

Chemical Profiles in *Chemical Marketing Reporter*, 2-9-98, 2-16-98, 4-20-98, 11-2-98, and 11-9-98.
Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 809-830.
Szmant, *Organic Building Blocks of the Chemical Industry*, pp. 188-264.
White, *Introduction to Industrial Chemistry*, pp. 62-79.
Wiseman, *Petrochemicals*, pp. 43-63, 102-103, 151-152, and 163-164.
Wittcoff and Reuben, *Industrial Organic Chemicals*, pp. 88-148.

Chapter 10

Chemicals from Propylene and Butylene

As we learned in Chapter 8, the official production of propylene is usually about half that of ethylene, only because a large part of the propylene is used by petroleum refineries internally to alkylate gasolines. This captive use is not reported. Of the propylene used for chemical manufacture, nearly 40% is polymerized to polypropylene, to be discussed in a later chapter. Of the remaining amount of propylene, seven chemicals from the top 50 are manufactured. These are listed in Table 10.1. Their industrial manufacturing methods are summarized in Fig. 10.1. Note that four of these chemicals, cumene, phenol, acetone, and bisphenol A, are also derived from a second basic organic chemical, benzene.

1. ACRYLONITRILE (2-PROPENONITRILE)

$$CH_2{=}CH{-}C{\equiv}N$$

Table 10.1 Propylene Derivatives in the Top 50

Acrylonitrile
Propylene Oxide
Cumene
Phenol
Acetone
Bisphenol A
n-Butyraldehyde

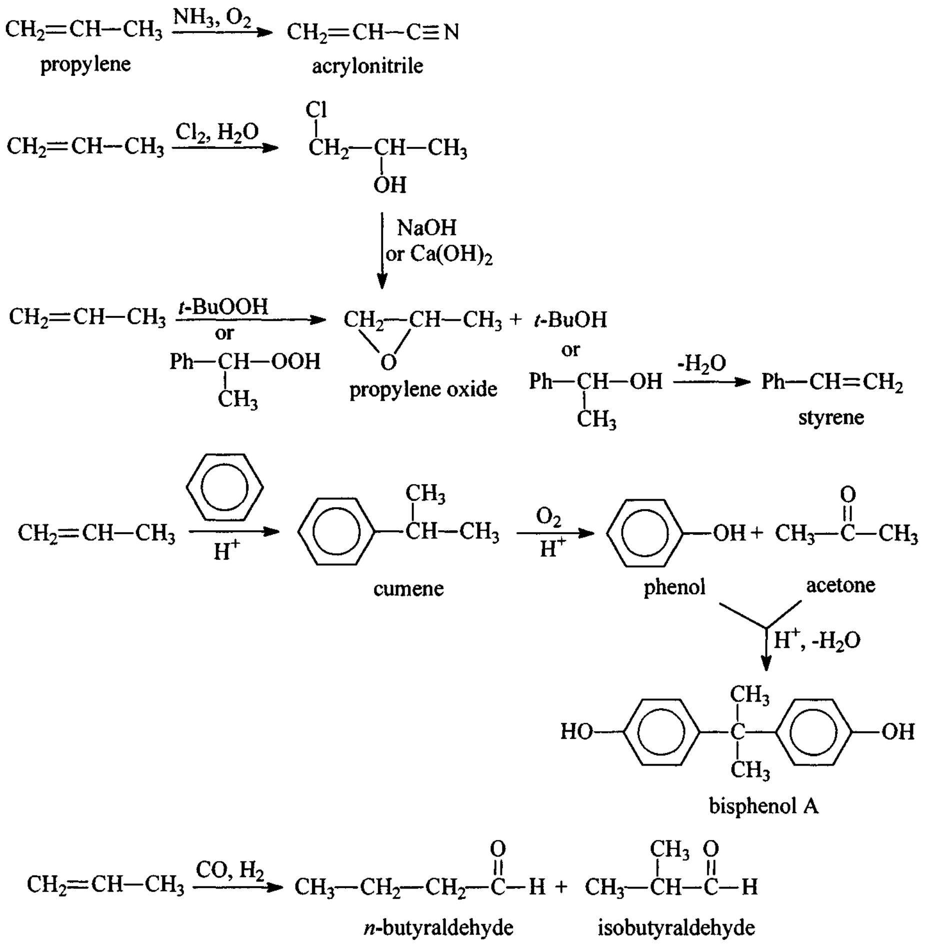
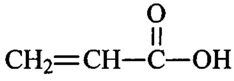


Figure 10.1 Synthesis of propylene derivatives in the top 50 chemicals.

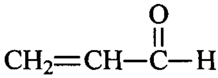
Acrylonitrile and other three-carbon analogs containing a double bond have a common name derived from the word *acrid*, meaning strong and disagreeable, in regard to the odor of most of these chemicals. Compounds in this family are given here with their common names.

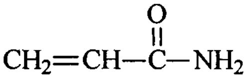
acrylonitrile $CH_2=CH-C\equiv N$

acrylic acid



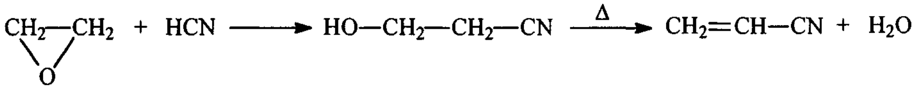
$CH_2=CH-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

acrolein 
$CH_2{=}CH{-}\overset{\overset{\Large O}{||}}{C}{-}H$

acrylamide 
$CH_2{=}CH{-}\overset{\overset{\Large O}{||}}{C}{-}NH_2$

Acrylonitrile was made completely from acetylene in 1960 by reaction with hydrogen cyanide. For some years ethylene oxide was the raw material for addition of HCN and elimination of H_2O.

$$CH{\equiv}CH + HCN \longrightarrow CH_2{=}CH{-}CN$$



Neither of these methods is used today. Around 1970 the industry switched from C_2 raw materials and classical organic chemical addition reactions to the ammoxidation of propylene. Now all acrylonitrile is made by this procedure, which involves reaction of propylene, ammonia, and oxygen at 400-450°C and 0.5-2 atm in a fluidized bed $Bi_2O_3{\cdot}nMoO_3$ catalyst. The yield is approximately 70%.

$$2CH_2{=}CH{-}CH_3 + 2NH_3 + 3O_2 \longrightarrow 2CH_2{=}CH{-}C{\equiv}N + 6H_2O$$

The mechanism is undoubtedly a free radical reaction that occurs very easily at the allyl site in propylene, forming the resonance-stabilized allyl radical.

$$CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2$$

By-products of this reaction are acetonitrile, $CH_3{-}C{\equiv}N$, and hydrogen cyanide. This is now a major source of these two materials. Interestingly, the C_2 by-product acetonitrile has a bp of 81.6°C, whereas acrylonitrile with three carbons has a lower bp of 77.3°C, quite an unusual reversal of this physical property's dependence on molecular weight. The TWA of acrylonitrile is 2 ppm and it is on the list of "Reasonably Anticipated to Be Human Carcinogens."

Table 10.2 outlines the uses of acrylonitrile. One important use of acrylonitrile is in the polymerization to polyacrylonitrile. This substance and its copolymers make good synthetic fibers for the textile industry. Acrylic is the fourth largest produced synthetic fiber behind polyester, nylon, and

Table 10.2 Uses of Acrylonitrile

Adiponitrile	33%
Acrylic fibers	25
ABS/SA resins	23
Acrylamide	9
Nitrile elastomers	3
Miscellaneous	7

Source: Chemical Profiles

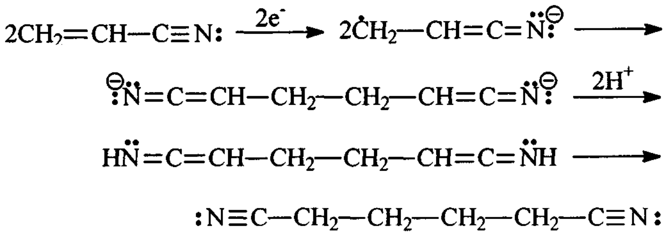
polyolefin. It is known primarily for its warmth, similar to the natural and more expensive fiber wool. Approximately 23% of the acrylonitrile is made into plastics, including the copolymer of styrene-acrylonitrile (SA) and the terpolymer of acrylonitrile, butadiene, and styrene (ABS). Acrylamide has a fast-growing use as a flocculent for water treatment units. Exports of acrylonitrile are over 1 billion lb/yr.

The largest use of acrylonitrile is the manufacture of adiponitrile, made by two different methods. One method is by the electrohydrodimerization of acrylonitrile. It is converted into hexamethylenediamine (HMDA), which is used to make nylon. The other adiponitrile synthesis is C_4 chemistry, which will be discussed later in this chapter, Section 8.

$$2CH_2{=}CH{-}C{\equiv}N \xrightarrow[2e^-]{2H^+} N{\equiv}C{-}(CH_2)_4{-}C{\equiv}N \xrightarrow{H_2} H_2N{-}(CH_2)_6{-}NH_2$$

acrylonitrile adiponitrile HMDA

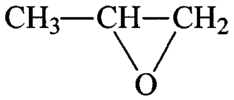
About one third of all adiponitrile is made from acrylonitrile. In the electrodimerization of acrylonitrile a two-phase system is used containing a phase transfer catalyst tetrabutylammonium tosylate [$(n\text{-}Bu)_4N^+OTs^-$]. The head-to-head dimerization may be visualized to occur in the following manner.



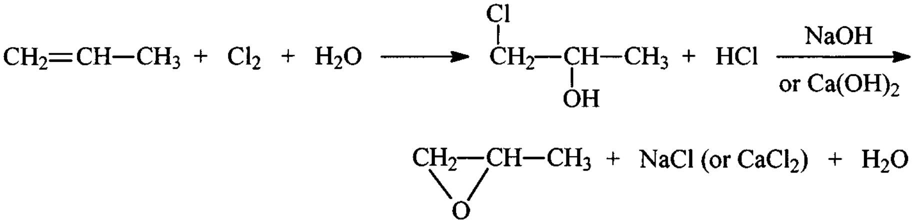
$$2CH_2{=}CH{-}C{\equiv}N{:} \xrightarrow{2e^-} 2\dot{C}H_2{-}CH{=}C{=}\ddot{N}{:}^{\ominus} \longrightarrow$$
$$^{\ominus}{:}\ddot{N}{=}C{=}CH{-}CH_2{-}CH_2{-}CH{=}C{=}\ddot{N}{:}^{\ominus} \xrightarrow{2H^+}$$
$$H\ddot{N}{=}C{=}CH{-}CH_2{-}CH_2{-}CH{=}C{=}\ddot{N}H \longrightarrow$$
$${:}N{\equiv}C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C{\equiv}N{:}$$

The by-product of acrylonitrile manufacture, HCN, has its primary use in the manufacture of methyl methacrylate by reaction with acetone. This is covered later in this chapter, Section 4.

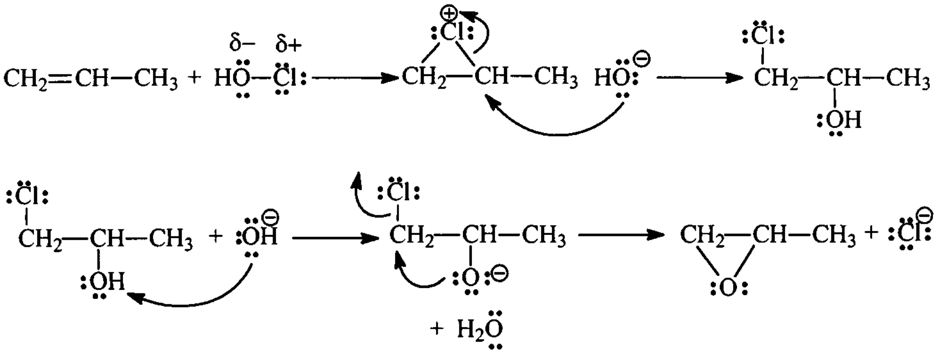
2. PROPYLENE OXIDE (1,2-EPOXYPROPANE)



There are two important methods for the manufacture of propylene oxide, each accounting for one half the total amount produced. The older method involves chlorohydrin formation from the reaction of propylene with chlorine water. Before 1969 this was the exclusive method. Unlike the analogous procedure for making ethylene oxide from ethylene, which now is obsolete, this method for propylene oxide is still economically competitive. Many old ethylene oxide plants have been converted to propylene oxide synthesis.



The mechanism in the first step involves an attack of the electrophilic chlorine on the double bond of propylene to form a chloronium ion, which is attacked by a hydroxide ion to complete the first reaction. The dilute

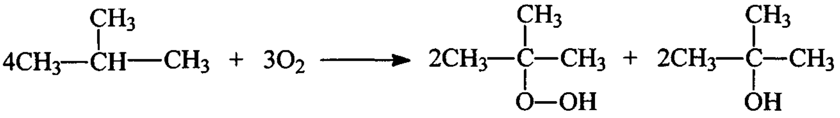


chlorohydrin solution is mixed with a 10% slurry of lime to form the oxide, which is purified by distillation, bp 34°C. The yield is 90%. Propylene oxide has a TWA of 20 ppm and is on the list of "Reasonably Anticipated to Be Human Carcinogens."

A new variation of the chlorohydrin process uses *t*-butyl hypochlorite as chlorinating agent. The waste brine solution can be converted back to chlorine and caustic by a special electrolytic cell to avoid the waste of chlorine.

The second manufacturing method for propylene oxide is via peroxidation of propylene, called the Halcon process after the company that invented it. Oxygen is first used to oxidize isobutane to *t*-butyl hydroperoxide (BHP) over a molybdenum naphthenate catalyst at 90°C and 450 psi. This oxidation occurs at the preferred tertiary carbon because a tertiary alkyl radical intermediate can be formed easily.

Reaction:



$$4CH_3-\overset{CH_3}{CH}-CH_3 + 3O_2 \longrightarrow 2CH_3-\underset{O-OH}{\overset{CH_3}{C}}-CH_3 + 2CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

BHP

Mechanism:

(1) $(CH_3)_3CH + X\cdot \longrightarrow (CH_3)_3C\cdot + HX$

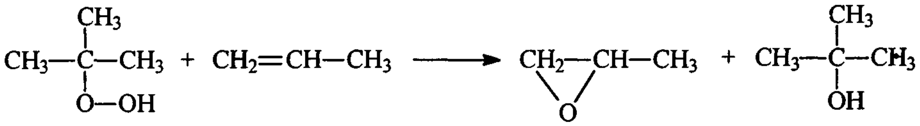
(2) $(CH_3)_3C\cdot + O_2 \longrightarrow (CH_3)_3COO\cdot$

(3) $(CH_3)_3COO\cdot + (CH_3)_3CH \longrightarrow (CH_3)_3COOH + (CH_3)_3C\cdot$

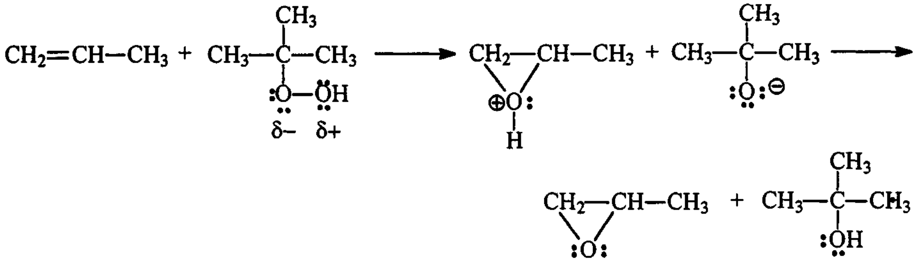
then (2), (3), (2), (3), etc.

The BHP is then used to oxidize propylene to the oxide. This reaction is ionic and its mechanism follows. The yield of propylene oxide from propylene is 90%.

Reaction:



Mechanism:



The *t*-butyl alcohol can be used to increase the octane of unleaded gasoline or it can be made into methyl *t*-butyl ether (MTBE) for the same application. The alcohol can also be dehydrated to isobutylene, which in turn is used in alkylation to give highly branched dimers for addition to straight-run gasoline.

Since approximately 2.2 lb of *t*-butyl alcohol would be produced per 1 lb of propylene oxide, an alternative reactant in this method is ethylbenzene hydroperoxide. This eventually forms phenylmethylcarbinol along with the propylene oxide. The alcohol is dehydrated to styrene. This chemistry was covered in Chapter 9, Section 6 as one of the syntheses of styrene. Thus the side product can be varied depending on the demand for substances such as *t*-butyl alcohol or styrene. Research is being done on a direct oxidation of propylene with oxygen, analogous to that used in the manufacture of ethylene oxide from ethylene and oxygen (Chapter 9, Section 7). But the proper catalyst and conditions have not yet been found. The methyl group is very sensitive to oxidation conditions.

As an aside to the manufacture of propylene oxide via the chlorohydrin process let us mention use of this type of chemistry to make epichlorohydrin.

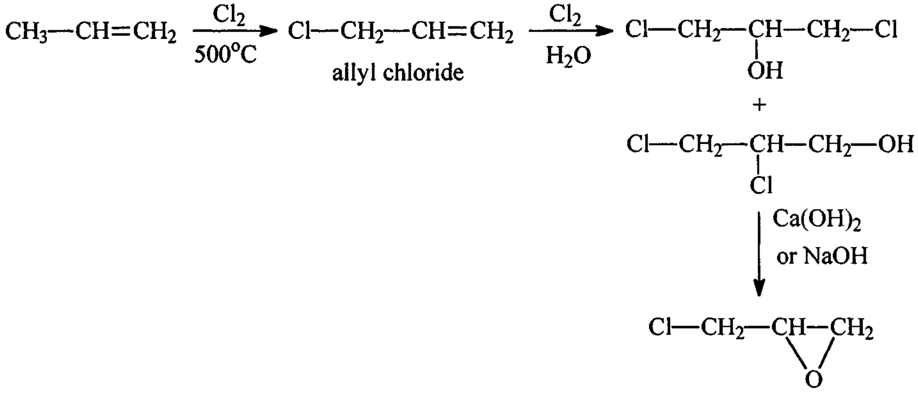


Table 10.3 Uses of Propylene Oxide

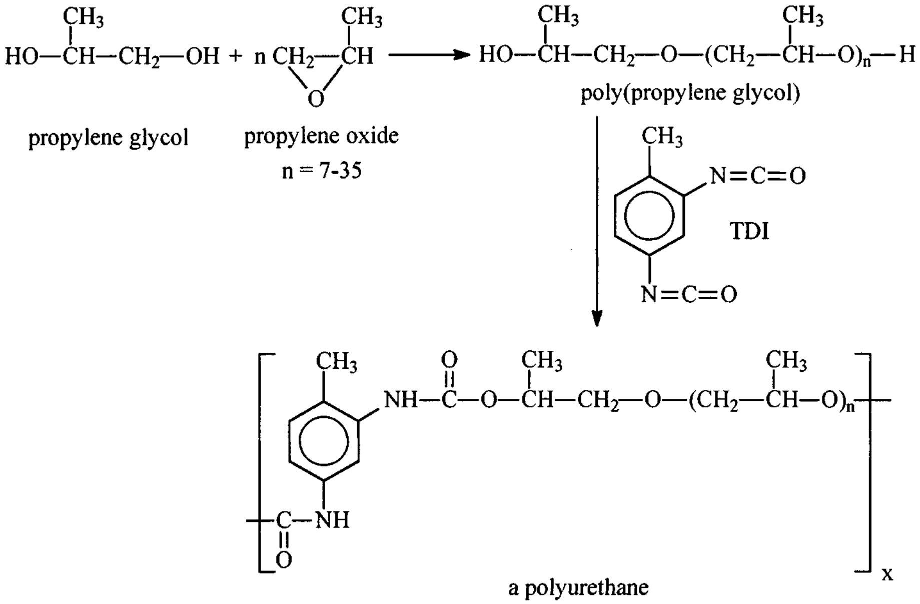
Polypropylene glycol	60%
Propylene glycol	25
Glycol ethers	4
Miscellaneous	11

Source: Chemical Profiles

Although not in the top 50, it is an important monomer for making epoxy adhesives as well as glycerine (HO-CH_2-CHOH-CH_2-OH). Propylene is first chlorinated free radically at the allyl position at 500°C to give allyl chloride, which undergoes chlorohydrin chemistry as discussed previously to give epichlorohydrin. The student should review the mechanism of allyl free radical substitution from a basic organic chemistry course and also work out the mechanism for this example of a chlorohydrin reaction.

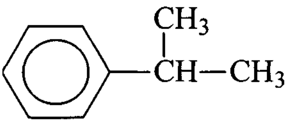
Table 10.3 summarizes the uses of propylene oxide. Propylene glycol is made by hydrolysis of propylene oxide. The student should develop the mechanism for this reaction, which is similar to the ethylene oxide to ethylene glycol conversion (Chapter 9, Section 8). Propylene glycol is a monomer in the manufacture of unsaturated polyester resins, which are used for boat and automobile bodies, bowling balls, and playground equipment.

But an even larger use of the oxide is its polymerization to poly(propylene glycol), which is actually a polyether, although it has

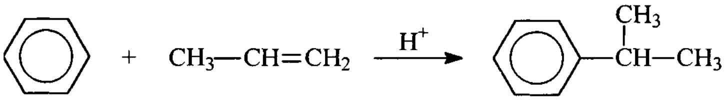


hydroxy end groups. These hydroxy groups are reacted with an isocyanate such as toluene diisocyanate (TDI) to form the urethane linkages in the high molecular weight polyurethanes, useful especially as foams for automobile seats, furniture, bedding, and carpets. Poly(propylene glycol) is used to make both flexible and rigid polyurethane in a 90:10 market ratio.

3. CUMENE (ISOPROPYLBENZENE)



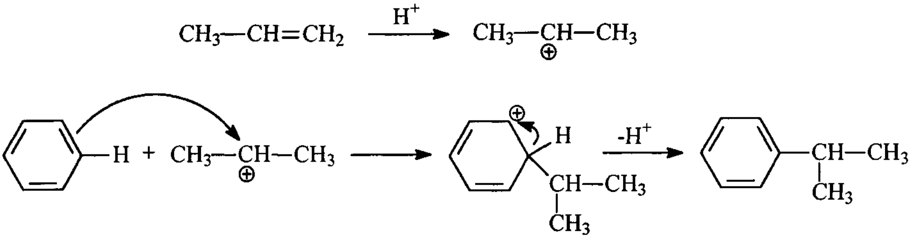
Cumene is an important intermediate in the manufacture of phenol and acetone. The feed materials are benzene and propylene. This is a Friedel-Crafts alkylation reaction catalyzed by solid phosphoric acid at 175-225 °C and 400-600 psi. The yield is 97% based on benzene and 92% on propylene. Excess benzene stops the reaction at the monoalkylated stage and prevents the polymerization of propylene. The benzene:propylene ratio is 8-10:1.



(excess)

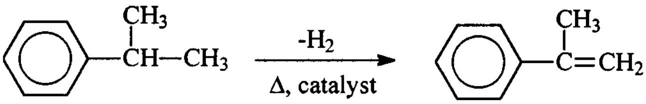
Interestingly, if benzene is left out similar conditions are used to manufacture the trimer and tetramer of propylene. The cumene is separated by distillation, bp 153 °C.

The mechanism of the reaction involves electrophilic attack of the catalyst on the double bond of propylene to form the more stable secondary cation, which reacts with the π cloud of benzene to give a delocalized ion. Deprotonation rearomatizes the ring.

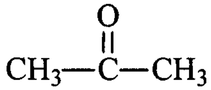


A major industry shift to zeolite-based catalyst systems is expected to lower production costs and improve product yield.

Approximately 95% of the cumene is used to make phenol and acetone. A small amount is used to make α-methylstyrene by dehydrogenation. This material is used in small amounts during the polymerization of styrene to vary the properties of the resulting copolymer.



4. ACETONE (2-PROPANONE)



$$CH_3—\overset{\overset{O}{||}}{C}—CH_3$$

Presently there are two processes that make acetone in large quantities. The feedstock for these is either isopropyl alcohol or cumene. In the last few years there has been a steady trend away from isopropyl alcohol and toward cumene, but isopropyl alcohol should continue as a precursor since manufacture of acetone from only cumene would require a balancing of the market with the co-product phenol from this process.

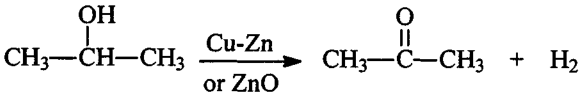
This is not always easy to do, so an alternate acetone source is required. In fact, isopropyl alcohol may become attractive again since cumene can be used to increase octane ratings in unleaded gasoline, and phenol, as a plywood adhesive, has its ups and downs with the housing industry. The percentage distribution of the two methods is given in Table 10.4.

In the minor route isopropyl alcohol, obtained from the hydrolysis of propylene, is converted into acetone by either dehydrogenation (preferred) or air oxidation. These are catalytic processes at 500°C and 40-50 psi. The acetone is purified by distillation, bp 56°C. The conversion per pass is 70-85% and the yield is over 90%.

Table 10.4 Manufacture of Acetone

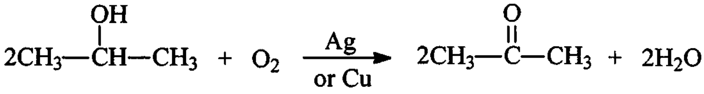
Year	From Isopropyl Alcohol	From Cumene
1959	80%	20%
1975	46	54
1985	15	85
1999	6	94

dehydrogenation



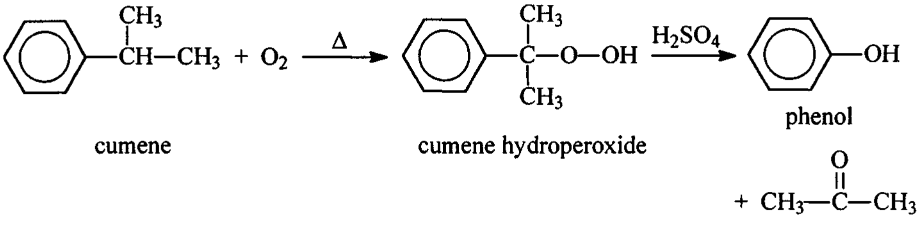
$$\mathrm{CH_3{-}\overset{\displaystyle OH}{\overset{|}{C}}H{-}CH_3} \xrightarrow[\text{or ZnO}]{\text{Cu-Zn}} \mathrm{CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3} + \mathrm{H_2}$$

air oxidation



$$\mathrm{2CH_3{-}\overset{\displaystyle OH}{\overset{|}{C}}H{-}CH_3} + \mathrm{O_2} \xrightarrow[\text{or Cu}]{\text{Ag}} \mathrm{2CH_3{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3} + \mathrm{2H_2O}$$

The main route, the formation of phenol and acetone from cumene hydroperoxide, involves a fascinating rearrangement of cumene hydroperoxide where a phenyl group migrates from carbon to an electron-deficient oxygen atom. This was discovered by German chemists Hock and Lang in 1944 and commercialized in 1953 in the U.S. and U.K. The hydroperoxide is made by reaction of cumene with oxygen at 110-115°C until 20-25% of the hydroperoxide is formed. The oxidation step is similar to that of cyclohexane to cyclohexane hydroperoxide and will be treated in Chapter 11, Section 4. Students should be able to work out this mechanism on their own with this help! Concentration of the hydroperoxide to 80% is followed by the acid-catalyzed rearrangement at 70-80°C. The overall yield is 90-92%.



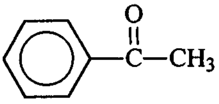
cumene

cumene hydroperoxide

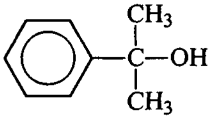
phenol

acetone

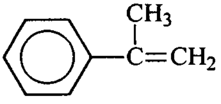
Side products are acetophenone, 2-phenylpropan-2-ol, and α-methylstyrene. Acetone is distilled first at bp 56°C. Vacuum distillation



acetophenone



2-phenylpropan-2-ol



α-methylstyrene

recovers the unreacted cumene and yields α-methylstyrene, which can be hydrogenated back to cumene and recycled. Further distillation separates phenol, bp 181°C, and acetophenone, bp 202°C. The weight ratio of acetone:phenol is 0.6:1.0.

The mechanism of the rearrangement is an excellent practical industrial example of a broad type of rearrangement, one occurring with an electron-deficient oxygen. The mechanism is given in Fig. 10.2.

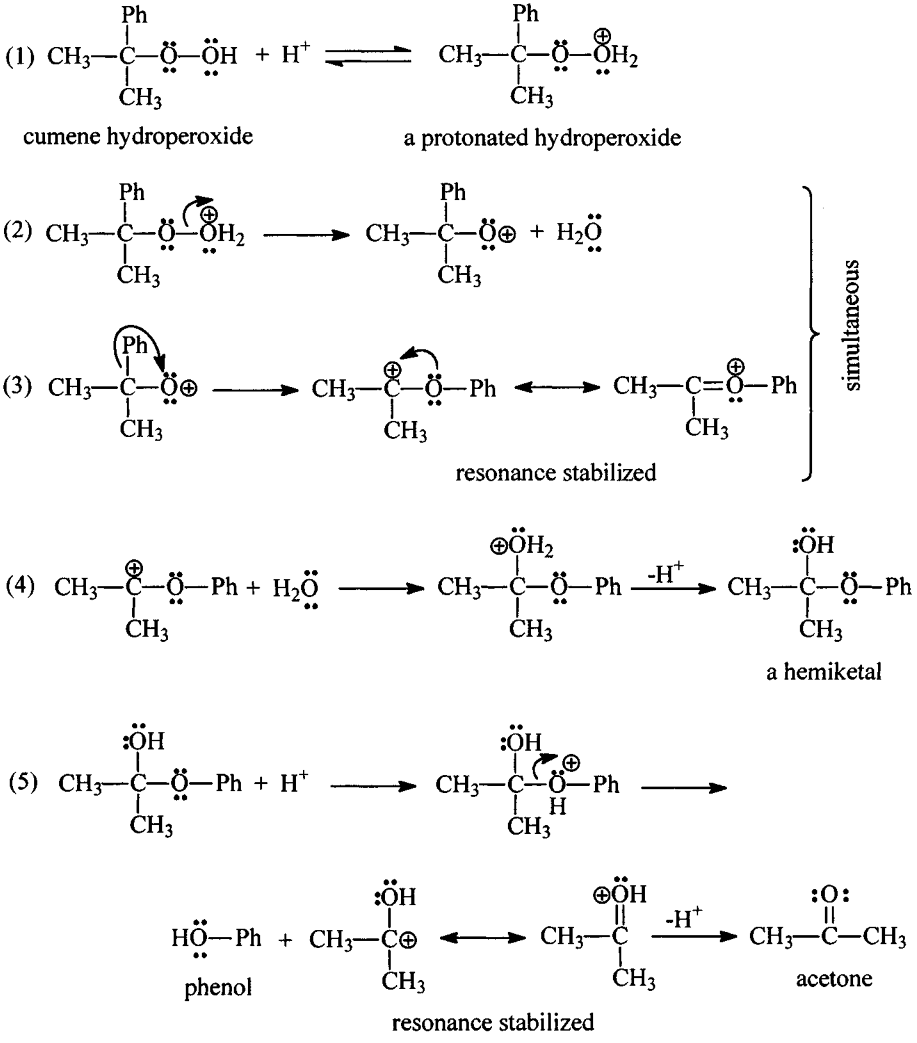


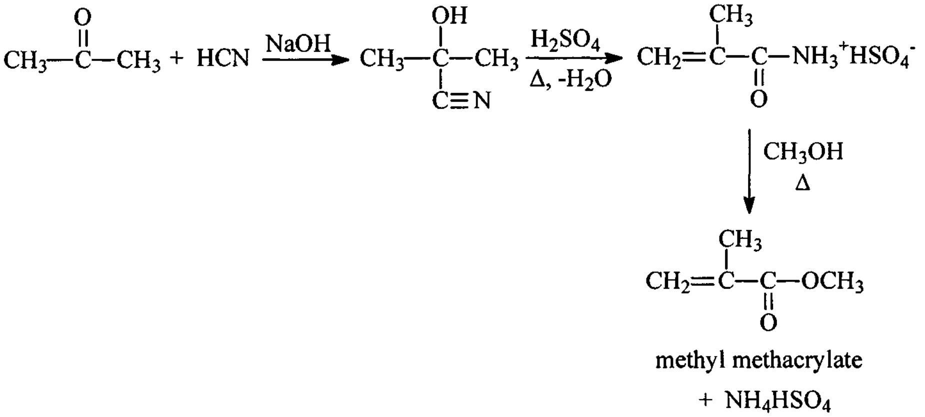
Figure 10.2 Mechanism of the cumene hydroperoxide rearrangement.

Table 10.5 Uses of Acetone

Acetone cyanohydrin	45%
Bisphenol A	20
Solvent	17
Aldol chemicals	8
Miscellaneous	10

Source: Chemical Profiles

Table 10.5 gives the uses of acetone. A very important organic chemical that just missed the top 50 list, methyl methacrylate, is made from acetone, methanol, and hydrogen cyanide. Approximately 1.2 billion lb of this compound is manufactured and then polymerized to poly(methyl methacrylate), an important plastic known for its clarity and used as a glass substitute. The synthesis is outlined as follows.

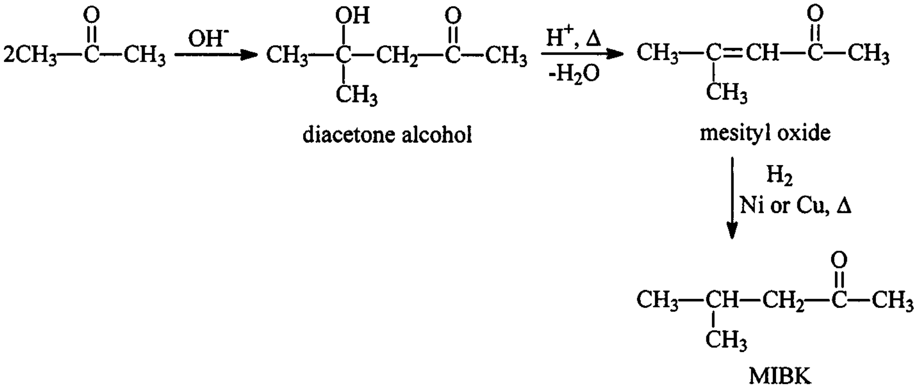


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + HCN \xrightarrow{NaOH} CH_3-\underset{\underset{\displaystyle C\equiv N}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CH_3 \xrightarrow[\Delta,\ -H_2O]{H_2SO_4} CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-NH_3^+HSO_4^-$$

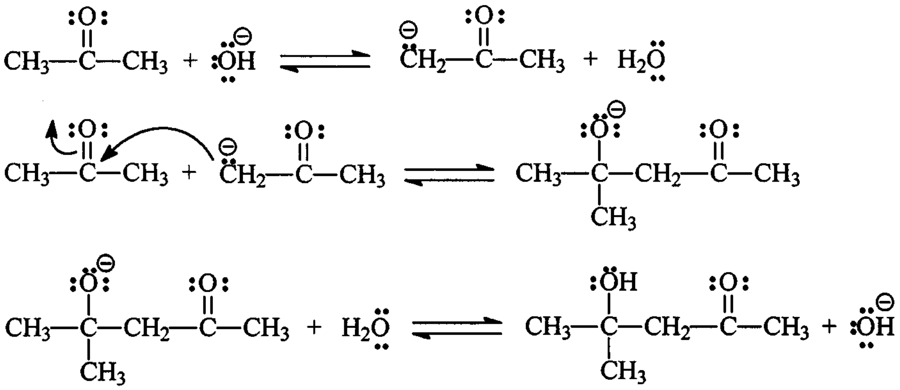
$$\xrightarrow[\Delta]{CH_3OH} CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-OCH_3 + NH_4HSO_4$$

The first reaction is a nucleophilic addition of HCN to a ketone, the second is a dehydration of an alcohol and hydrolysis of a nitrile, and the third is esterification by methanol.

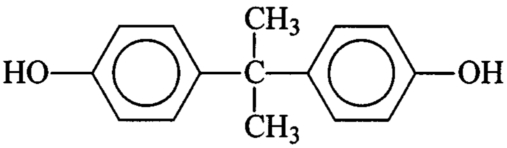
Aldol chemicals refer to a variety of substances desired from acetone involving an aldol condensation in a portion of their synthesis. The most important of these chemicals is methyl isobutyl ketone (MIBK), a common solvent for many coatings, pesticides, adhesives, and pharmaceuticals. Approximately 0.17 billion lb of MIBK were made in recent years. The synthesis is outlined on the next page.



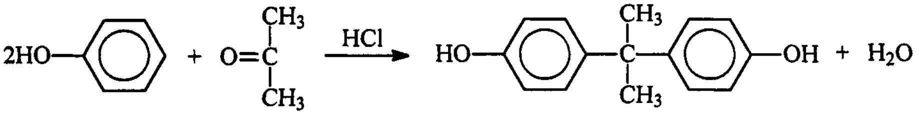
Diacetone alcohol is a solvent used in hydraulic fluids and printing inks. Recall that the aldol condensation is an example of a variety of carbanion reactions used to make large molecules from smaller ones. An aldehyde or a ketone with at least one hydrogen on the carbon next to the carbonyl will react to give the aldol condensation. The mechanism is given as follows.



5. BISPHENOL A (BPA)



Bisphenol A is manufactured by a reaction between phenol and acetone, the two products from the cumene hydroperoxide rearrangement. The temperature of the reaction is maintained at 50°C for about 8-12 hr. A slurry of BPA is formed, which is neutralized and distilled to remove excess phenol. Some *o,p* isomer is formed along with the predominance of *p,p* isomer.

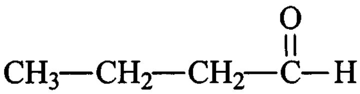


bisphenol A

The student should develop the mechanism of this reaction using the following stepwise information: (1) protonation of the carbonyl; (2) electrophilic attack on the aromatic ring; (3) rearomatization by proton loss; (4) another protonation, but then loss of a water molecule; and (5) electrophilic attack and rearomatization.

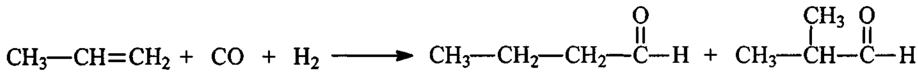
The major uses of BPA are in the production of polycarbonate resins (63%) and epoxy resins (27%). Polycarbonates have major outlets in automotive parts, compact discs, eyeglasses, and sheet and glazing applications, and have caused bisphenol A consumption to more than double during the past decade. Epoxy resins are two-component adhesives for very strong bonding. Miscellaneous uses include flame retardants (mostly tetrabromobisphenol A) and other polymer manufacture. Polycarbonate grade bisphenol A is >99% *p,p* isomer. The epoxy grade is 95% *p,p*. The *p,p* and *o,p* isomers can be separated by a combination of distillation and crystallization.

6. *n*-BUTYRALDEHYDE (BUTANAL)



$$CH_3{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}H$$

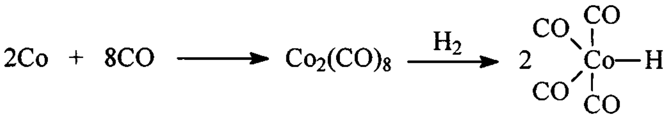
Butyraldehyde is made from propylene by the *oxo process*, also known as *hydroformylation*. Synthesis gas ($CO + H_2$) is catalytically reacted with propylene to the butyraldehydes. The approximate yields are 67% *n*-butyraldehyde and 15% isobutyraldehyde.



$$CH_3{-}CH{=}CH_2 + CO + H_2 \longrightarrow CH_3{-}CH_2{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}H + CH_3{-}\overset{CH_3}{\overset{|}{C}H}{-}\overset{O}{\overset{\|}{C}}{-}H$$

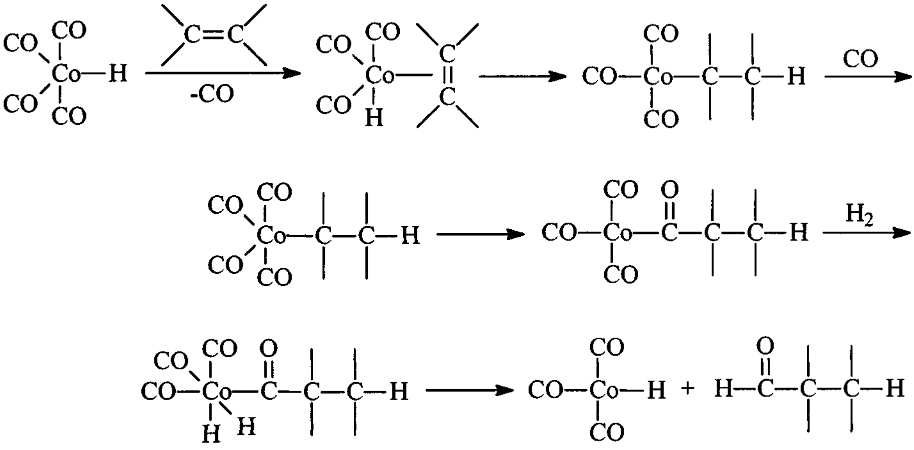
n-butyraldehyde isobutyraldehyde

The classic oxo catalyst is octacarbonyldicobalt at 130-175°C and 250 atm. This reacts with hydrogen to give hydridotetracarbonyl cobalt, the active catalyst in the oxo process.



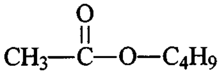
$$2Co + 8CO \longrightarrow Co_2(CO)_8 \xrightarrow{H_2} 2\,(CO)_4Co{-}H$$

The mechanism of carbonylation/hydrogenation involves addition of the alkene to form a π complex, followed by alternating additions of H, CO, and H.



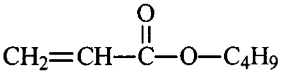
Newer catalysts are being studied to increase the ratio of *n*-butyraldehyde to isobutyraldehyde.

The main use of *n*-butyraldehyde is the production of *n*-butyl alcohol by hydrogenation. *n*-Butyl alcohol is used for ester synthesis, especially butyl acetate, acrylate, and methacrylate, common solvents for coatings.



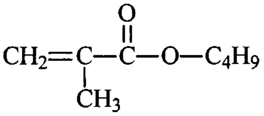
$CH_3{-}C(=O){-}O{-}C_4H_9$

butyl acetate



$CH_2{=}CH{-}C(=O){-}O{-}C_4H_9$

butyl acrylate



$CH_2{=}C(CH_3){-}C(=O){-}O{-}C_4H_9$

butyl methacrylate

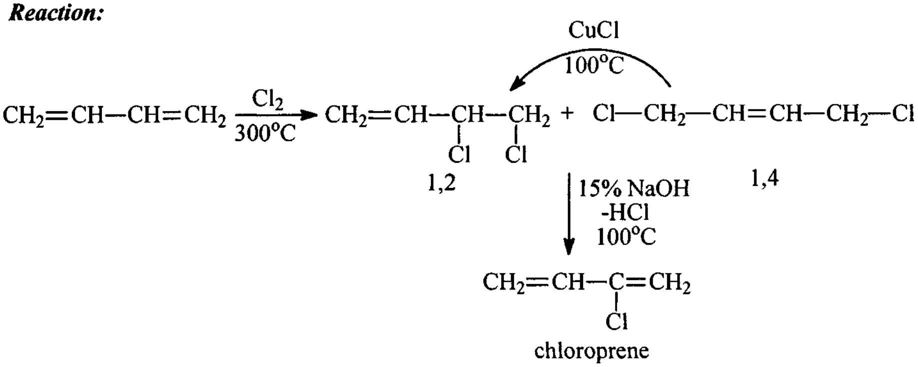
7. CHEMICALS FROM THE C_4 FRACTION

Chemicals obtained from petroleum having four carbons are manufactured at a considerably lower scale than ethylene or propylene derivatives. Only five C_4 compounds—butadiene, acetic acid, vinyl acetate, isobutylene, and methyl *t*-butyl ether (MTBE)—appear in the top 50. The manufacture of butadiene and isobutylene, as well as the separation of other C_4 compounds from petroleum, is described in Chapter 8, Sections 3-5. Acetic acid was discussed as a derivative of ethylene in Chapter 9, Section 3 and is discussed as a derivative of methane in Chapter 12, Section 3. Vinyl acetate was discussed in Chapter 9, Section 4. A few important derivatives of C_4 chemistry will be briefly mentioned here as well as MTBE.

8. BUTADIENE DERIVATIVES

Besides butadiene, another important monomer for the synthetic elastomer industry is chloroprene, which is polymerized to the chemically resistant polychloroprene. It is made by chlorination of butadiene follow by dehydrochlorination. As with most conjugated dienes, addition occurs either 1,2 or 1,4 because the intermediate allyl carbocation is delocalized. The 1,4-isomer can be isomerized to the 1,2-isomer by heating with cuprous chloride.

Reaction:

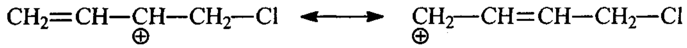


$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[300^\circ C]{Cl_2} \underset{1,2}{CH_2{=}CH{-}\underset{Cl}{CH}{-}\underset{Cl}{CH_2}} + \underset{1,4}{Cl{-}CH_2{-}CH{=}CH{-}CH_2{-}Cl}$$

$$\underset{1,4}{Cl{-}CH_2{-}CH{=}CH{-}CH_2{-}Cl} \xrightarrow[100^\circ C]{CuCl} \underset{1,2}{CH_2{=}CH{-}\underset{Cl}{CH}{-}\underset{Cl}{CH_2}}$$

$$\underset{1,2}{CH_2{=}CH{-}\underset{Cl}{CH}{-}\underset{Cl}{CH_2}} \xrightarrow[100^\circ C]{15\%\ NaOH,\ -HCl} \underset{\text{chloroprene}}{CH_2{=}CH{-}\underset{Cl}{C}{=}CH_2}$$

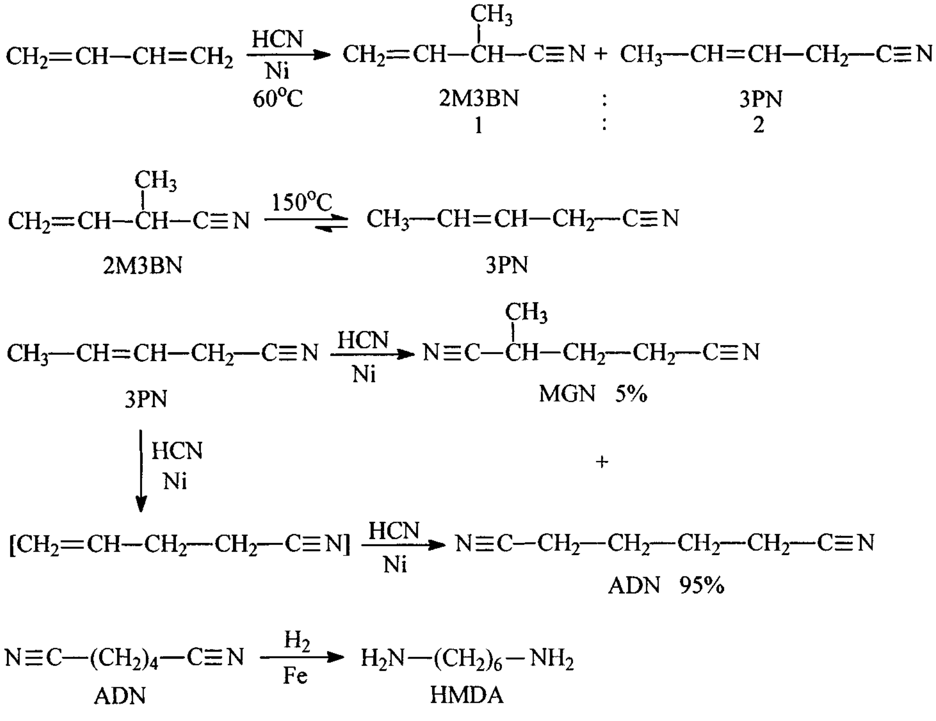
Intermediate:



$$CH_2{=}CH{-}\underset{\oplus}{CH}{-}CH_2{-}Cl \longleftrightarrow \underset{\oplus}{CH_2}{-}CH{=}CH{-}CH_2{-}Cl$$

Another derivative of butadiene, hexamethylenediamine (HMDA), is used in the synthesis of nylon. We have already met this compound earlier in this chapter since it is made from acrylonitrile through adiponitrile.

Approximately two thirds of all adiponitrile is made from 1,3-butadiene and 2 moles of hydrogen cyanide. This is an involved process chemically and it is summarized in Fig. 10.3. Butadiene first adds one mole of HCN at 60°C with a nickel catalyst via both 1,2- and 1,4-addition to give respectively 2-methyl-3-butenonitrile (2M3BN) and 3-pentenonitrile (3PN) in a 1:2 ratio. The 1,2-addition is the usual Markovnikov addition with a secondary carbocation intermediate being preferred. Fig. 10.4 shows an ADN reactor. Next isomerization of the 2M3BN to 3PN takes place at 150°C. Then more HCN, more catalyst, and a triphenylboron promoter react with 3PN to form 5% methylglutaronitrile (MGN) and mostly adiponitrile (ADN). The ADN is formed from 3PN probably through isomerization of 3PN to 4-pentenonitrile and then anti-Markovnikov addition of HCN to it. The nickel catalyst must play a role in this last unusual mode of addition, and a steric effect may also be operating to make CN^- attack at the primary carbon rather than a cationically preferred secondary carbon. A complicated set of extractions and distillations is necessary to obtain pure ADN. Even then the hexamethylenediamine (HMDA) made by hydrogenation of ADN must also be distilled through seven columns to purify it before polymerization to nylon. Fig. 10.5 pictures some HMDA distillation units.



$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[\text{Ni}]{\text{HCN}} CH_2{=}CH{-}\overset{CH_3}{\overset{|}{C}H}{-}C{\equiv}N + CH_3{-}CH{=}CH{-}CH_2{-}C{\equiv}N$$

60°C 2M3BN : 3PN

1 : 2

$$CH_2{=}CH{-}\overset{CH_3}{\overset{|}{C}H}{-}C{\equiv}N \xrightleftharpoons{150^\circ C} CH_3{-}CH{=}CH{-}CH_2{-}C{\equiv}N$$

2M3BN 3PN

$$CH_3{-}CH{=}CH{-}CH_2{-}C{\equiv}N \xrightarrow[\text{Ni}]{\text{HCN}} N{\equiv}C{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_2{-}CH_2{-}C{\equiv}N$$

3PN MGN 5%

HCN Ni +

$$[CH_2{=}CH{-}CH_2{-}CH_2{-}C{\equiv}N] \xrightarrow[\text{Ni}]{\text{HCN}} N{\equiv}C{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}C{\equiv}N$$

ADN 95%

$$N{\equiv}C{-}(CH_2)_4{-}C{\equiv}N \xrightarrow[\text{Fe}]{H_2} H_2N{-}(CH_2)_6{-}NH_2$$

ADN HMDA

Figure 10.3 Manufacture of adiponitrile and hexamethylenediamine from 1,3-butadiene.

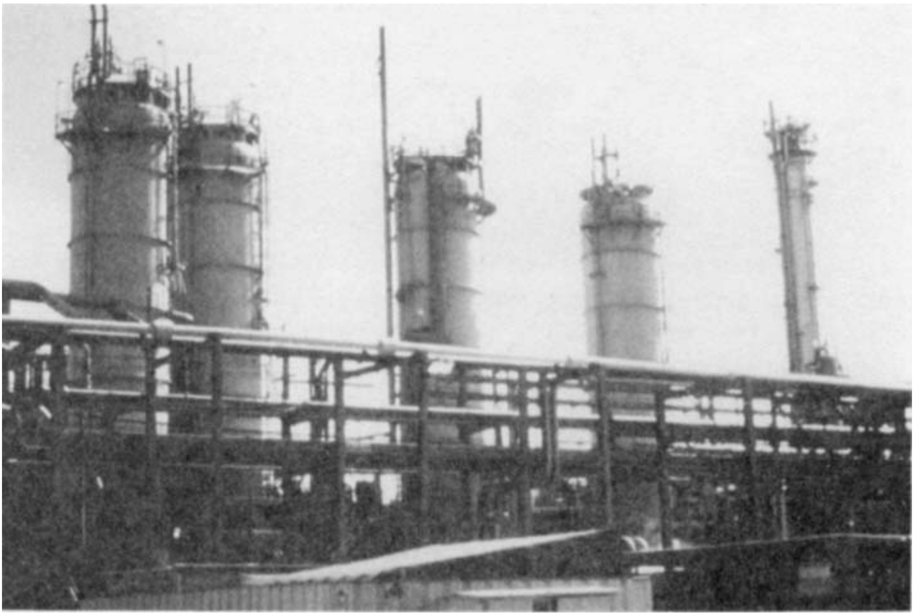


Figure 10.4 Reactors used in the conversion of 1,3-butadiene and HCN to adiponitrile. (Courtesy of Du Pont)

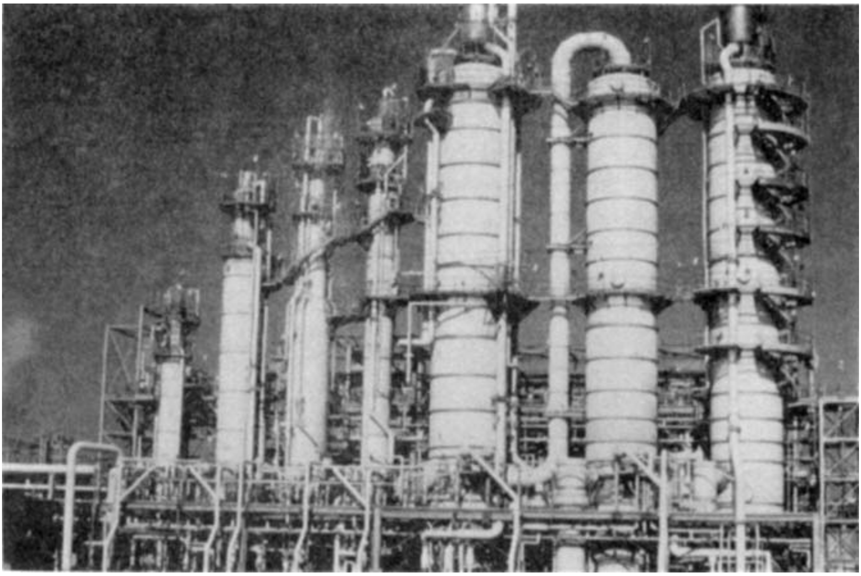
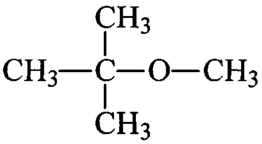


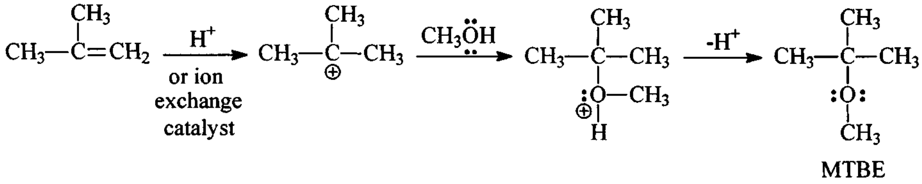
Figure 10.5 Distillation columns associated with the purification of hexamethylenediamine. (Courtesy of Du Pont)

9. METHYL *t*-BUTYL ETHER (MTBE)



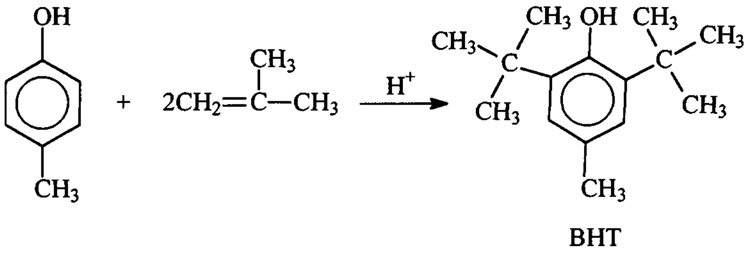
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3$$

In 1984 methyl *t*-butyl ether (MTBE) broke into the top 50 for the first time with a meteoric rise in production from 0.8 billion lb in 1983 to 1.47 billion lb in 1984 to be ranked 47th. In 1990 it was 24th with production over 6 billion lb, and in 1995 it was 12th at 18 billion lb. A full discussion of the current economic status of MTBE is given in Chapter 7, Section 4 as the important gasoline octane enhancer. That is its only major use. MTBE is manufactured by the acid catalyzed electrophilic addition of methanol to isobutylene.

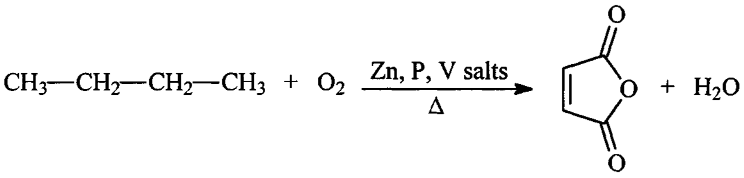


10. OTHER C₄ DERIVATIVES

An important antioxidant for many products is butylated hydroxytoluene (BHT), more properly named 4-methyl-2,6-di-*t*-butylphenol. Acid-catalyzed electrophilic aromatic substitution of a *t*-butyl cation at the activated positions ortho to the hydroxy group of *p*-cresol yields this product. *p*-Cresol is obtained from coal tar or petroleum.

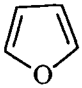


For many years maleic anhydride (MA) was made from benzene by oxidation and loss of two moles of CO_2. Even as late as 1978 83% of maleic anhydride was made from benzene. However, the new Occupational Safety and Health Administration (OSHA) standards for benzene plants required modifications in this process, and butane is also cheaper than benzene. As a result since 1989 all maleic anhydride is now made from butane. This has been a very rapid and complete switch in manufacturing method.



MA

The mechanism is not well understood, but the intermediates in the process are butadiene and furan. The uses of maleic anhydride are



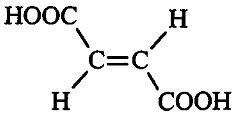
furan

summarized in Table 10.6. Unsaturated polyester resins are its prime use area. Food acidulants include fumaric and malic acids. Malic acid competes with citric acid as an acidulant for soft drinks, and it is added to products that contain aspartame, the artificial sweetener, because it makes aspartame taste more like sugar. Agricultural chemicals made from MA include daminozide (Alar®), a growth regulator for apples which in 1989 was found to be carcinogenic because of a breakdown product, unsymmetrical dimethylhydrazine (UMDH). Alar® is needed to keep the apple on the tree, to make a more perfectly shaped, redder, firmer apple, and to maintain firmness in stored apples by reducing ethylene production.

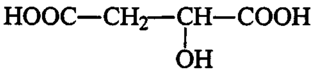
Table 10.6 Uses of Maleic Anhydride

Unsaturated polyester resins	62%
Lube oil additive	11
Copolymers	7
Agricultural chemicals	4
Fumaric acid	3
Malic acid	3
Miscellaneous	10

Source: Chemical Profiles

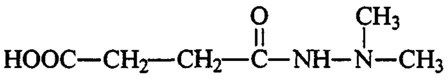


fumaric acid



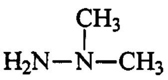
$HOOC-CH_2-\underset{OH}{\underset{|}{C}}H-COOH$

malic acid



$HOOC-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH-\overset{CH_3}{\overset{|}{N}}-CH_3$

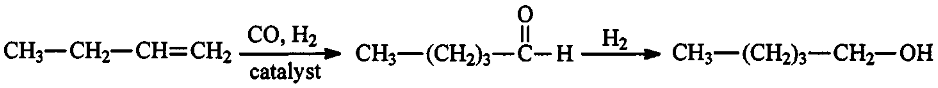
daminoazide (Alar®)



$H_2N-\overset{CH_3}{\overset{|}{N}}-CH_3$

UDMH

The oxo process is used to convert the C_4 fraction to C_5 derivatives. Synthesis gas is catalytically reacted with 1-butene to give pentanal which can be hydrogenated to 1-pentanol (*n*-amyl alcohol), giving a route to C_5 compounds in larger amounts than what would be available from C_5 alkanes in petroleum.



$$CH_3-CH_2-CH=CH_2 \xrightarrow[\text{catalyst}]{CO,\ H_2} CH_3-(CH_2)_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2} CH_3-(CH_2)_3-CH_2-OH$$

Suggested Readings

Chemical Profiles in *Chemical Marketing Reporter*, 7-29-96, 12-2-96, 3-20-98, 7-13-98, 1-4-99, 3-22-99, 4-5-99, 12-27-99, and 5-8-00.
Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 830-846.
Szmant, *Organic Building Blocks of the Chemical Industry*, pp. 265-378.
Wiseman, *Petrochemicals*, pp. 65-88.
Wittcoff and Reuben, *Industrial Organic Chemicals*, pp. 149-224.

Chapter 11

Derivatives of the Basic Aromatics

1. BENZENE DERIVATIVES

There are nine chemicals in the top 50 that are manufactured from benzene. These are listed in Table 11.1. Two of these, ethylbenzene and styrene, have already been discussed in Chapter 9, Sections 5 and 6, since they are also derivatives of ethylene. Three others—cumene, acetone, and bisphenol A—were covered in Chapter 10, Sections 3-5, when propylene derivatives were studied. Although the three carbons of acetone do not formally come from benzene, its primary manufacturing method is from cumene, which is made by reaction of benzene and propylene. These compounds need not be discussed further at this point. That leaves phenol, cyclohexane, adipic acid, and nitrobenzene. Figure 11.1 summarizes the synthesis of important chemicals made from benzene. Caprolactam is the monomer for nylon 6 and is included because of it importance.

Table 11.1 Benzene Derivatives in the Top 50

Ethylbenzene
Styrene
Cumene
Phenol
Acetone
Bisphenol A
Cyclohexane
Adipic acid
Nitrobenzene

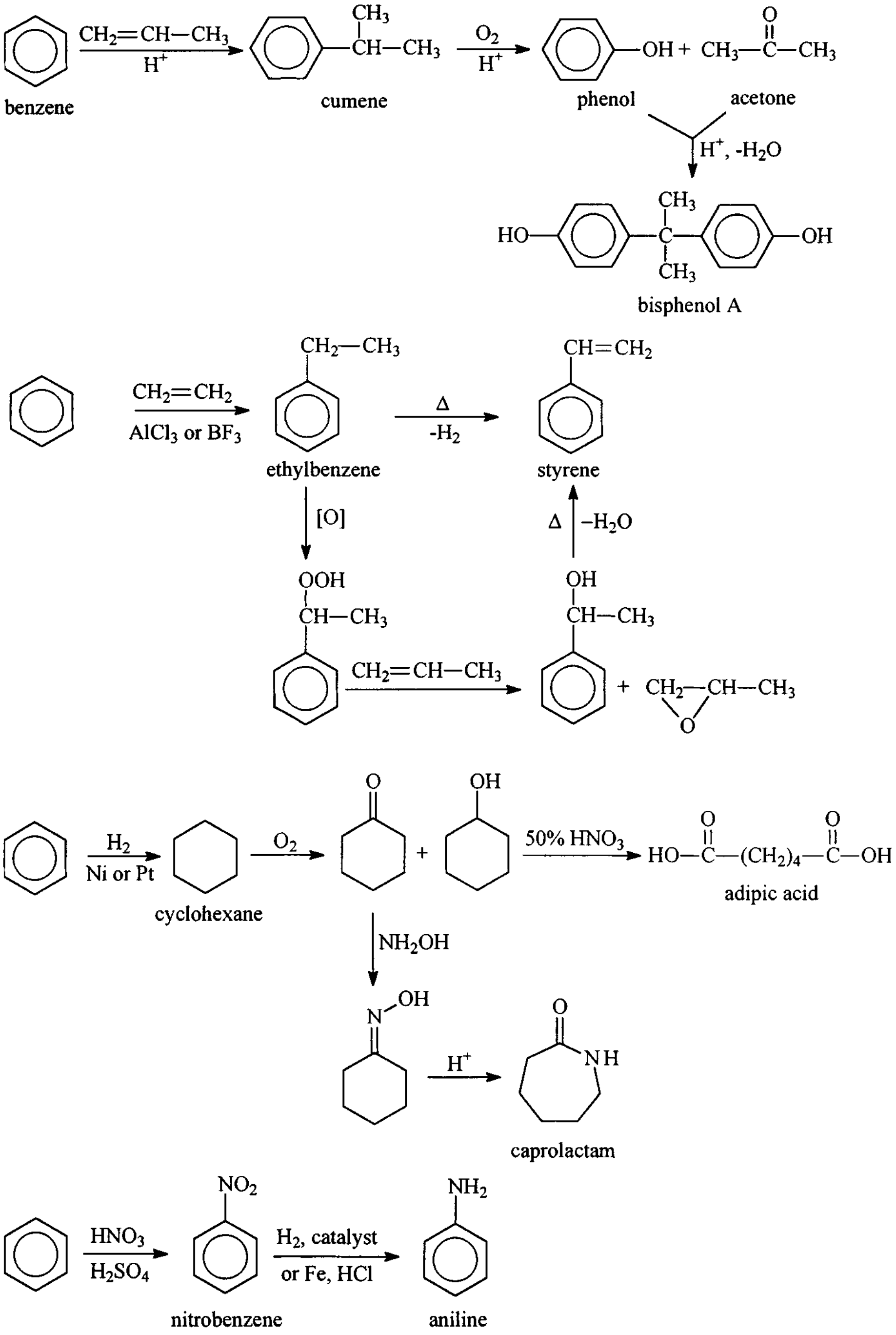
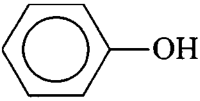


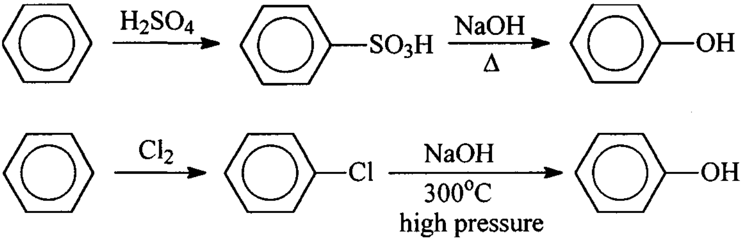
Figure 11.1 Synthesis of benzene derivatives.

2. PHENOL (CARBOLIC ACID)



The major manufacturing process for making phenol was discussed in Chapter 10, Section 4, since it is the co-product with acetone from the acid-catalyzed rearrangement of cumene hydroperoxide. The student should review this process. It accounts for 95% of the total phenol production and has dominated phenol chemistry since the early 1950s. But a few other syntheses deserve some mention.

A historically important method, first used about 1900, is sulfonation of benzene followed by desulfonation with caustic. This is classic aromatic chemistry. In 1924 a chlorination route was discovered. Both the sulfonation and chlorination reactions are good examples of electrophilic aromatic substitution on an aromatic ring. Know the mechanism of these reactions. These routes are no longer used commercially.



A minor route, which now accounts for 2% of phenol, takes advantage of the usual surplus of toluene from petroleum refining. Oxidation with a number of reagents gives benzoic acid. Further oxidation to *p*-hydroxybenzoic acid and decarboxylation yields phenol. Here phenol competes with benzene manufacture, also made from toluene when the surplus is large. The last 2% of phenol comes from distillation of petroleum and coal gasification.

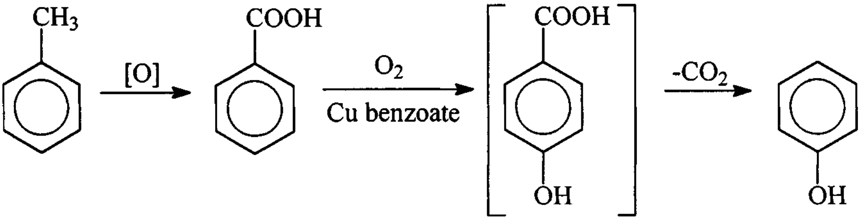


Table 11.2 Uses of Phenol

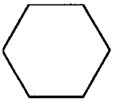
Bisphenol A	35%
Phenolic resins	34
Caprolactam	15
Aniline	5
Xylenols	5
Alkylphenols	5
Miscellaneous	1

Source: Chemical Profiles

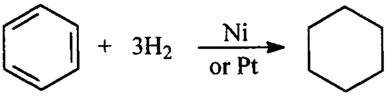
Table 11.2 outlines the uses of phenol. We will consider the details of phenol uses in later chapters. Phenol-formaldehyde polymers (phenolics) have a primary use as the adhesive in plywood formulations. We have already studied the synthesis of bisphenol A from phenol and acetone. Phenol's use in detergent synthesis to make alkylphenols will be discussed later. Caprolactam and aniline are mentioned in the following sections in this chapter.

Although phenol ranked thirty-fourth in 1995, it is still the highest ranked derivative of benzene other than those using ethylene or propylene along with benzene. Its 2000 price was 38¢/lb. That gives a total commercial value of $1.6 billion for the 4.2 billion lb produced.

3. CYCLOHEXANE (HEXAHYDROBENZENE, HEXAMETHYLENE)



Benzene can be quantitatively transformed into cyclohexane by hydrogenation over either a nickel or platinum catalyst. This reaction is carried out at 210°C and 350-500 psi, sometimes in several reactors placed in series. The yield is over 99%.



Although many catalytic reactions are not well understood, a large amount of work has been done on hydrogenations of double bonds. The metal surface acts as a source of electrons. The π bonds as well as hydrogen atoms are bound to this surface. Then the hydrogen atoms react with the complexed carbons one at a time to form new C—H bonds. No reaction occurs without the metal surface. The metal in effect avoids what would otherwise have to be a free radical mechanism that would require considerably more energy. The mechanism is outlined as follows.

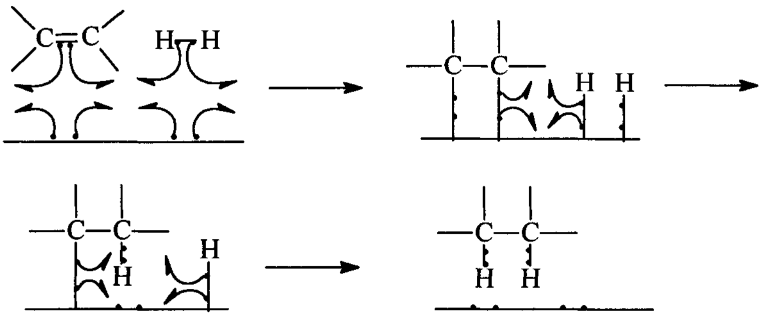
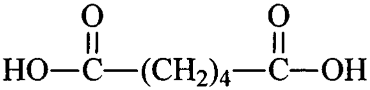


Table 11.3 shows the main uses of cyclohexane. Adipic acid is used to manufacture nylon 6,6, the major nylon used currently in the U.S. Caprolactam is the monomer for nylon 6, for which there is a growing market.

4. ADIPIC ACID (1,6-HEXANDIOIC ACID)



$$HO-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_4-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

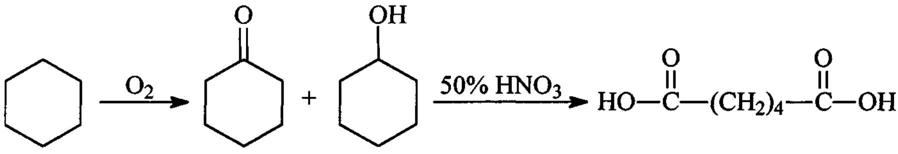
Nearly all the adipic acid manufactured, 98%, is made from cyclohexane by oxidation. Air oxidation of cyclohexane with a cobalt or manganese (II) naphthenate or acetate catalyst at 125-160°C and 50-250 psi pressures gives a mixture of cyclohexanone and cyclohexanol. Benzoyl peroxide is another

Table 11.3 Uses of Cyclohexane

Adipic acid	55%
Caprolactam	26
Miscellaneous	19

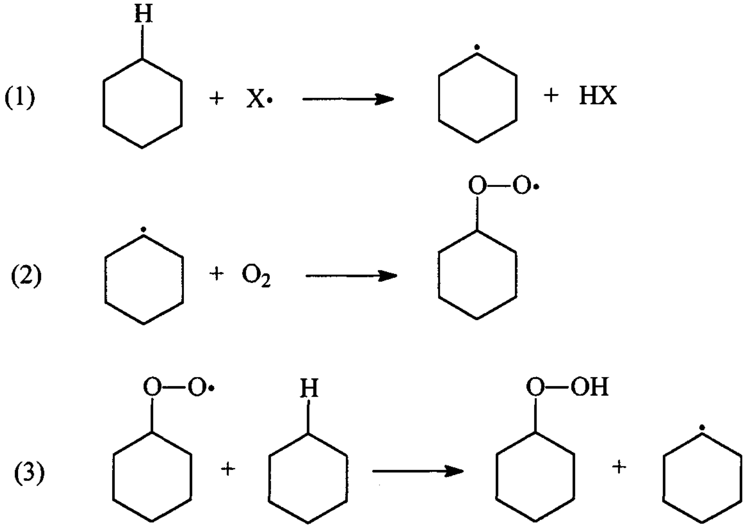
Source: Chemical Profiles

possible catalyst. The yield is 75-80% because of some ring opening and other further oxidation that takes place. The cyclohexanone/cyclohexanol mixture (sometimes referred to as ketone-alcohol, KA mixture, or "mixed oil") is further oxidized with 50% nitric acid with ammonium vanadate and copper present as catalysts at 50-90°C and 15-60 psi for 10-30 min.



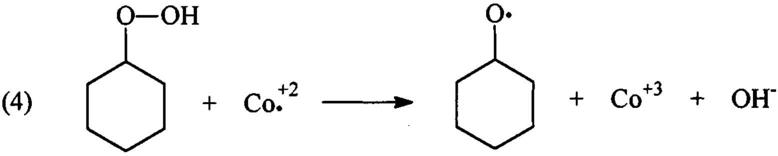
1:3 mixed oil

The mechanism of cyclohexane oxidation involves cyclohexane hydroperoxide as a key intermediate.



then (2), (3), (2), (3), etc.

The cyclohexane hydroperoxide then undergoes a one-electron transfer with cobalt or manganese (II). Chain transfer of the cyclohexyloxyl radical gives cyclohexanol or β-scission gives cyclohexanone.



to step (6) or (7)

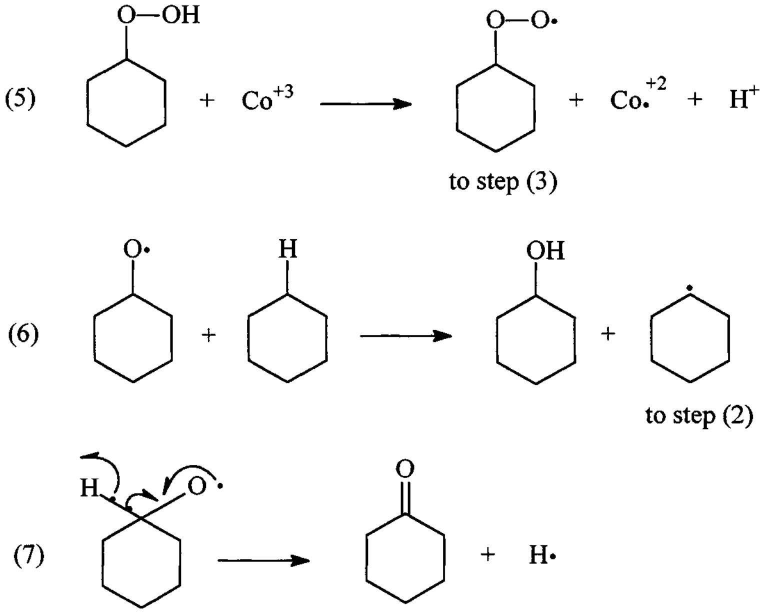
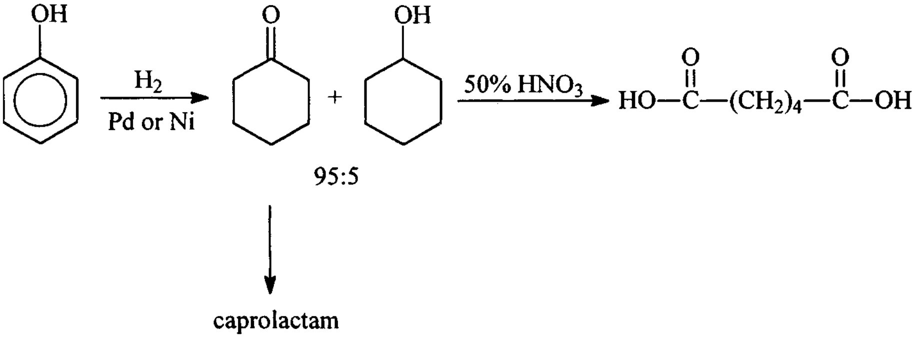


Figure 11.2 shows a cyclohexane oxidation reactor. The further oxidation of the ketone and alcohol to adipic acid is very complex but occurs in good yield, 94%, despite some succinic and glutaric acid by-products being formed because the adipic acid can be preferentially crystallized and centrifuged.

A small amount of adipic acid, 2%, is made by hydrogenation of phenol with a palladium or nickel catalyst (150°C, 50 psi) to the mixed oil, then nitric acid oxidation to adipic acid. If palladium is used, more cyclohexanone is formed. Although the phenol route for making adipic acid is not economically advantageous because phenol is more expensive than benzene, the phenol conversion to greater cyclohexanone percentages can be used successfully for caprolactam manufacture (see next section), where cyclohexanone is necessary.



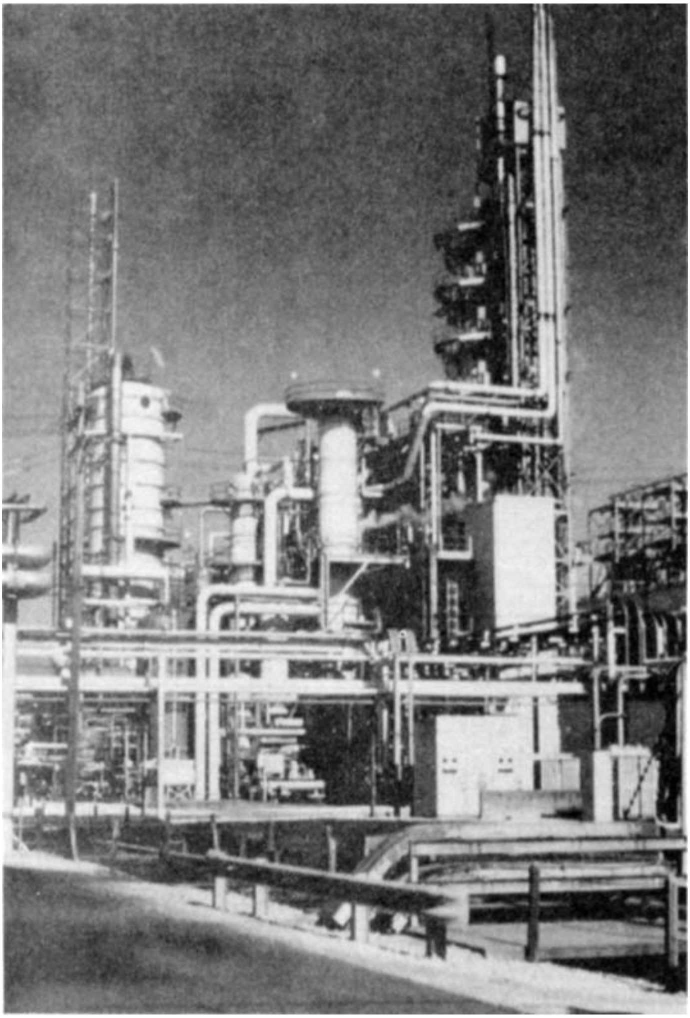


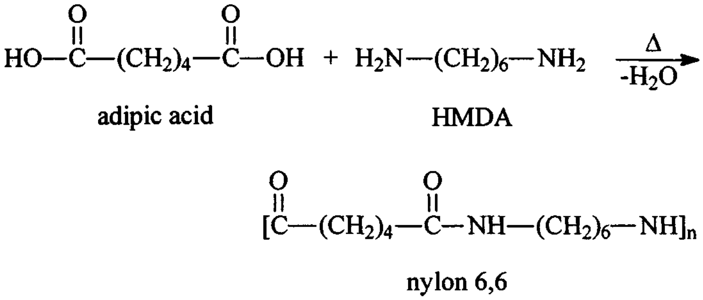
Figure 11.2 The large tower on the right is the cyclohexane oxidation chamber and purification unit to convert cyclohexane to the hydroperoxide and then to cyclohexanone/cyclohexanol. An elevator leads to the top platform of this narrow tower, where an impressive view of this and other surrounding plants can be obtained. (Courtesy of Du Pont)

Table 11.4 gives the uses of adipic acid. As will be seen later, nylon 6,6 has large markets in textiles, carpets, and tire cords. It is made by reaction of HMDA and adipic acid.

Table 11.4 Uses of Adipic Acid

Nylon 6,6 fibers	72%
Nylon 6,6 resins	18
Polyurethanes	5
Plasticizer	3
Miscellaneous	2

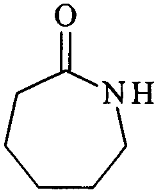
Source: Chemical Profiles



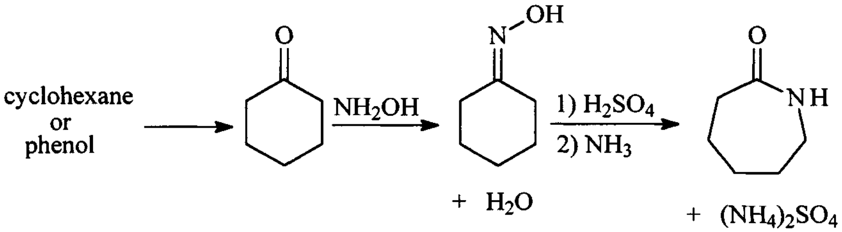
$$\underset{\text{adipic acid}}{HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{HMDA}}{H_2N-(CH_2)_6-NH_2} \xrightarrow[-H_2O]{\Delta}$$

$$\underset{\text{nylon 6,6}}{[\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH-(CH_2)_6-NH]_n}$$

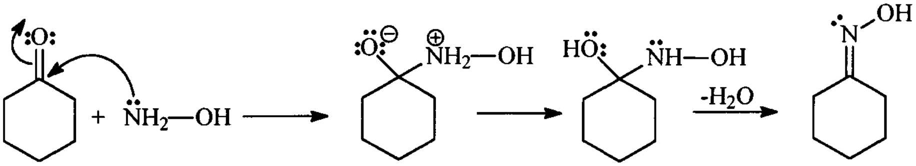
5. CAPROLACTAM



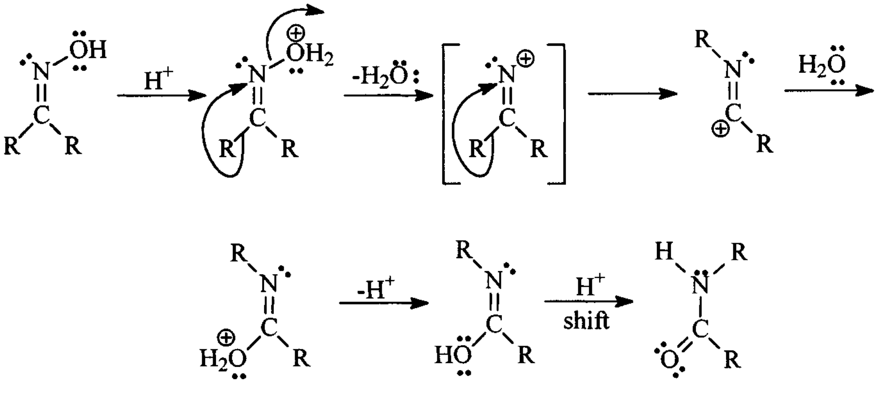
The common name caprolactam comes from the original name for the C_6 carboxylic acid, caproic acid. Caprolactam is the cyclic amide (lactam) of 6-aminocaproic acid. Its manufacture is from cyclohexanone, made usually from cyclohexane (58%), but also available from phenol (42%). Some of the cyclohexanol in cyclohexanone/cyclohexanol mixtures can be converted to cyclohexanone by a ZnO catalyst at 400°C. Then the cyclohexanone is converted into the oxime with hydroxylamine. The oxime undergoes a very famous acid-catalyzed reaction called the Beckmann rearrangement to give caprolactam. Sulfuric acid at 100-120°C is common but phosphoric acid is also used, since after treatment with ammonia the by-product becomes ammonium phosphate, which can be sold as a fertilizer. The caprolactam can be extracted and vacuum distilled, bp 139°C at 12 mm. The overall yield is 90%.



The first reaction, formation of the oxime, is a good example of a nucleophilic addition to a ketone followed by subsequent dehydration. Oximes are common derivatives of aldehydes and ketones because they are solids that are easily purified.

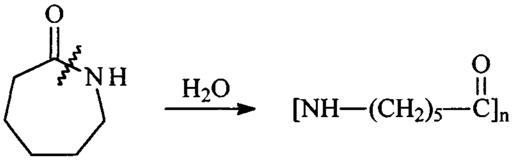


In the rearrangement of cumene hydroperoxide we saw an industrial example of a rearrangement of electron-deficient oxygen. The Beckmann rearrangement of caprolactam is a successful large-scale example of a rearrangement to electron-deficient nitrogen. Protonation of the hydroxyl followed by loss of a water molecule forms the positive nitrogen, but the R group can migrate while the water leaves, so the nitrenium ion may not be a discreet intermediate. Attack of water on the rearranged ion and a proton shift to form the amide completes the process.

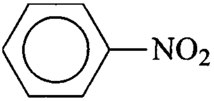


The student should adapt this general mechanism and work through the specific cyclic example of cyclohexanone oxime to caprolactam. Note that the result of the shift is an expansion of the ring size in the final amide product with the incorporation of the nitrogen atom as part of the ring.

All of the caprolactam goes into nylon 6 manufacture, especially fibers (80%) and plastic resin and film (20%). Although nylon 6,6 is still the more important nylon in this country (about 2:1) and in the U.K., nylon 6 is growing rapidly, especially in certain markets such as nylon carpets. In other countries, for example, Japan, nylon 6 is more predominant. Nylon 6 is made directly from caprolactam by heating with a catalytic amount of water.

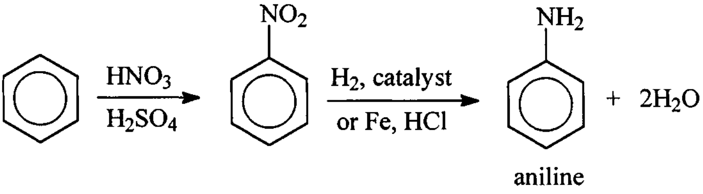


6. NITROBENZENE



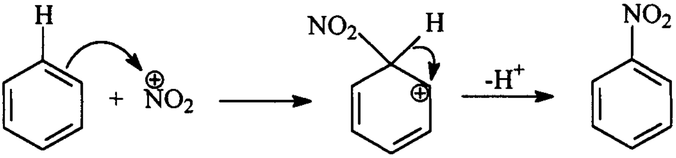
Aniline is an important derivative of benzene that can be made in two steps by nitration to nitrobenzene and either catalytic hydrogenation or acidic metal reduction to aniline. Both steps occur in excellent yield. Almost all nitrobenzene manufactured (97%) is directly converted into aniline. The nitration of benzene with mixed acids is an example of an electrophilic aromatic substitution involving the nitronium ion as the attacking species. The hydrogenation of nitrobenzene has replaced the iron-

Reaction:



Mechanism:

$$HNO_3 + 2H_2SO_4 \rightleftharpoons H_3O^+ + 2HSO_4^- + \overset{\oplus}{N}O_2$$



acid reduction process. At one time the special crystalline structure of the Fe_3O_4 formed as a by-product in the latter process made it unique for use in pigments. But the demand for this pigment was not great enough to justify continued use of this older method of manufacturing aniline.

The uses of aniline obtained from nitrobenzene are given in Table 11.5. Aniline's use in the rubber industry is in the manufacture of various vulcanization accelerators and age resistors. By far the most important and growing use for aniline is in the manufacture of *p,p*-methylene diphenyl diisocyanate (MDI), which is polymerized with a diol to give a polyurethane.

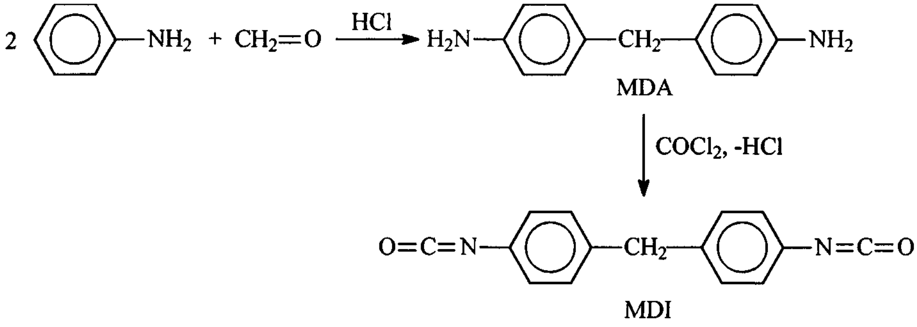


Table 11.5 Uses of Aniline

MDI	80%
Rubber-processing chemicals	11
Herbicides	3
Dyes and pigments	3
Specialty fibers	2
Miscellaneous	1

Source: Chemical Profiles

Two moles of aniline react with formaldehyde to give *p,p*-methylenedianiline (MDA). MDA reacts with phosgene to give MDI. The student should develop the mechanism of this electrophilic aromatic substitution.

We have already been introduced to polyurethane chemistry in Chapter 10, Section 2, where we used toluene diisocyanate (TDI) reacting with a diol to give a polyurethane. Polyurethanes derived from MDI are more rigid than those from TDI. New applications for these rigid foams are in home insulation and exterior autobody parts. The intermediate MDA is now on the "Reasonably Anticipated to Be Human Carcinogens" list and the effect of this action on the market for MDI remains to be seen. The TLV-TWA values for MDA and MDI are some of the lowest of the chemicals we have discussed, being 0.1 and 0.005 ppm respectively.

7. TOLUENE DERIVATIVES

Other than benzene, 30% of which is made from toluene by the hydrodealkylation process, there are no other top 50 chemicals derived from

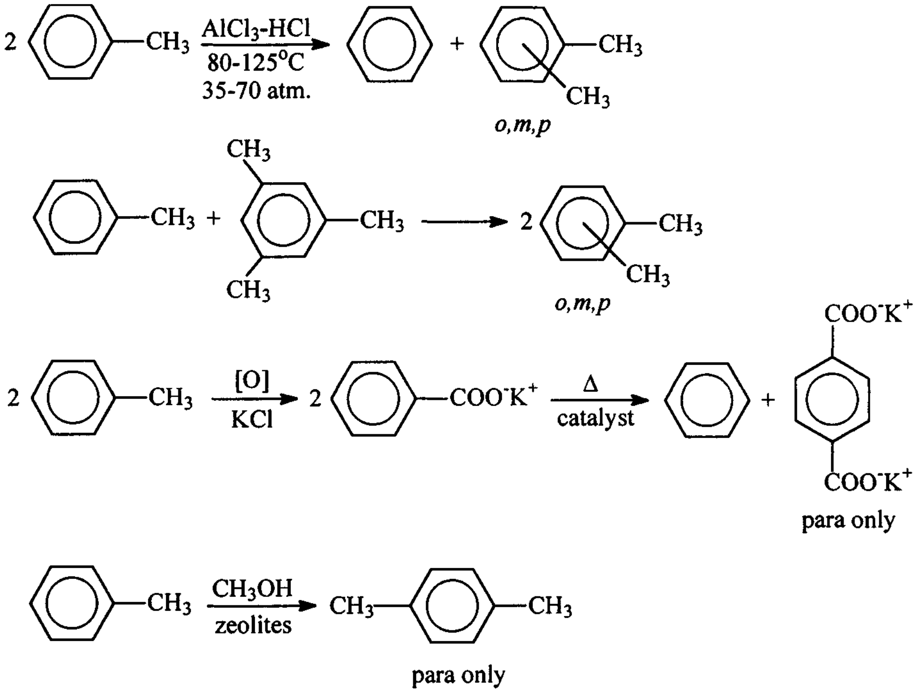
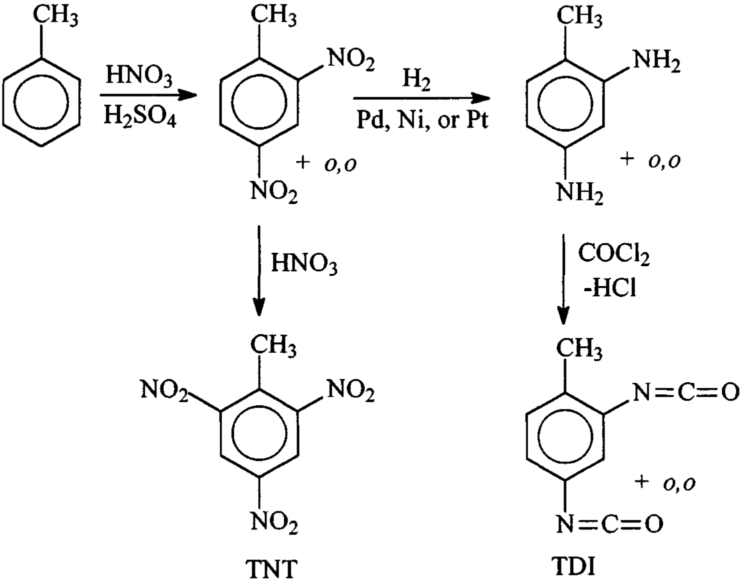


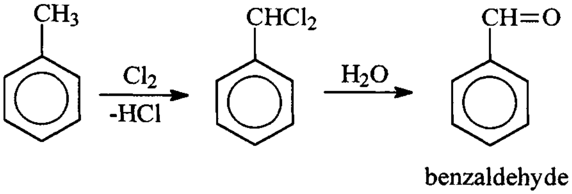
Figure 11.3 Conversion of toluene to other aromatic compounds.

toluene in large amounts. However, a few important chemicals are made from toluene. As we learned earlier in this chapter, Section 2, a very small amount of phenol is made from toluene. Toluene also provides an alternate source that is becoming more popular for the xylenes, especially *p*-xylene. These routes are indicated in Fig. 11.3. The first example, the disproportionation of toluene to benzene and the xylenes, is being used in the U.S. to the extent of 3-4 billion lb of benzene and xylenes. The last two examples provide routes respectively to terephthalic acid and *p*-xylene without the need for an isomer separation, a very appealing use for toluene that is often in excess supply as compared to the xylenes.

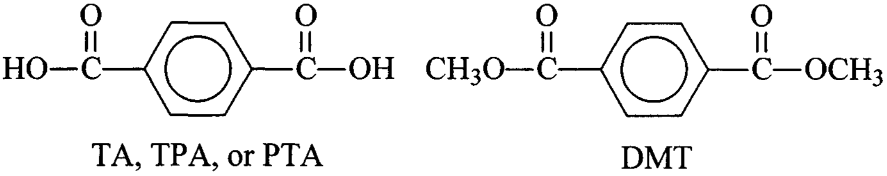
Two other derivatives of toluene are the important explosive trinitrotoluene (TNT) and the polyurethane monomer toluene diisocyanate (TDI). TNT requires complete nitration of toluene. TDI is derived from a mixture of dinitrotoluenes (usually 80% *o,p* and 20% *o,o*) by reduction to the diamine and reaction with phosgene to the diisocyanate. TDI is made into flexible foam polyurethanes for cushioning in furniture (35%), transportation (25%), carpet underlay (20%), and bedding (10%). A small amount is used in polyurethane coatings, rigid foams, and elastomers.



Finally, benzaldehyde, an ingredient in flavors and perfumes, is made by dichlorination of toluene (free radically via the easily formed benzyl radical) followed by hydrolysis.

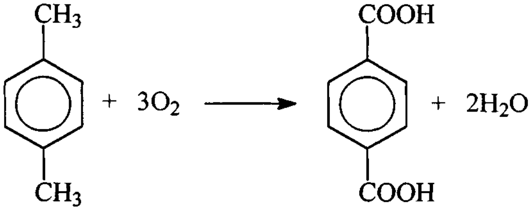


8. TEREPHTHALIC ACID AND DIMETHYL TEREPHTHALATE

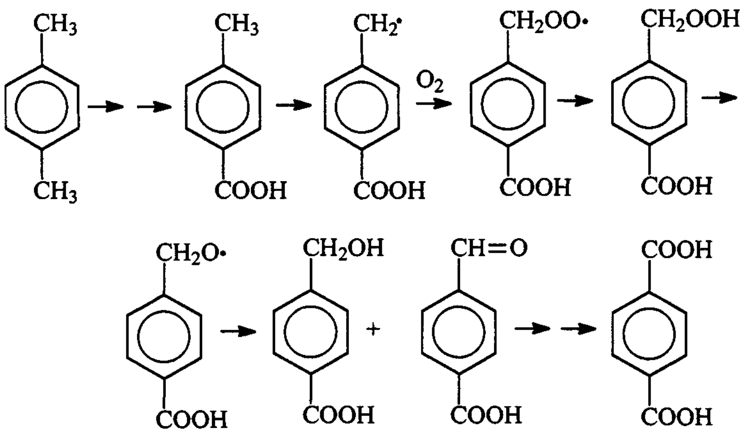


There are only two top 50 chemicals, terephthalic acid and dimethyl terephthalate, derived from *p*-xylene and none from *o*- or *m*-xylene. But phthalic anhydride is made in large amounts from *o*-xylene.

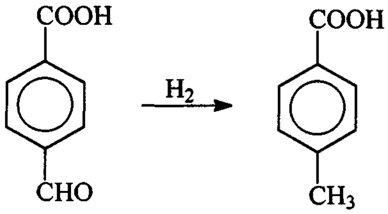
Terephthalic acid is commonly abbreviated TA or TPA. The abbreviation PTA (P = pure) is reserved for the product of 99% purity for polyester manufacture. For many years polyesters had to be made from dimethyl terephthalate (DMT) because the acid could not be made pure enough economically. Now either can be used. TA is made by air oxidation of *p*-xylene in acetic acid as a solvent in the presence of cobalt, manganese, and bromide ions as catalysts at 200°C and 400 psi. TA of 99.6% purity is formed in 90% yield. This is called the Amoco process.



A partial mechanism with some intermediates is given on the next page. Details are similar to the cyclohexane to cyclohexanone:cyclohexanol process discussed in this chapter, Section 4.



The crude TA is cooled and crystallized. The acetic acid and xylene are evaporated and the TA is washed with hot water to remove traces of the catalyst and acetic acid. Some *p*-formylbenzoic acid is present as an impurity from incomplete oxidation. This is most easily removed by hydrogenation to *p*-methylbenzoic acid and recrystallization of the TA to give 99.9% PTA, which is a polyester-grade product, mp > 300 °C.



p-formylbenzoic acid *p*-methylbenzoic acid

DMT can be made from crude TA or from *p*-xylene directly. Esterification of TA with methanol occurs under sulfuric acid catalysis. Direct oxidation of *p*-xylene with methanol present utilizes copper and manganese salt catalysis.

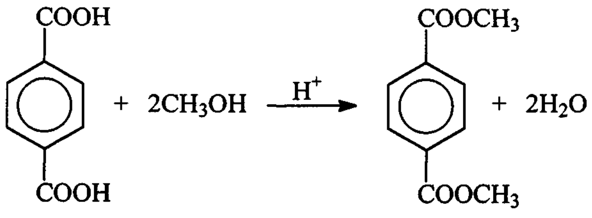
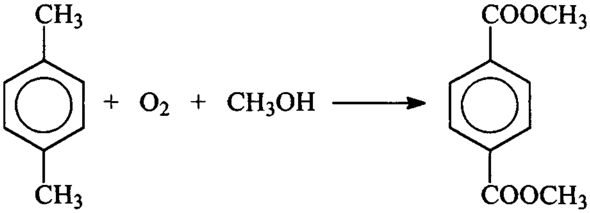


Table 11.6 Uses of TA/DMT

Polyester fiber	50%
Polyester resin	33
Polyester film	8
Miscellaneous	9

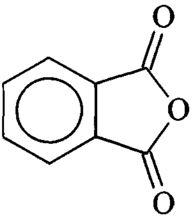
Source: Chemical Profiles



DMT must be carefully purified via a five-column distillation system, bp 288 °C, mp 141 °C. The present distribution of the TA/DMT market in the U.S. is 44:56. All new plants will probably make terephthalic acid.

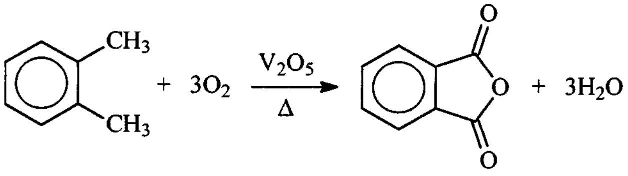
Table 11.6 shows the uses of TA/DMT. TA or DMT is usually reacted with ethylene glycol to give poly(ethylene terephthalate) (90%) but sometimes it is combined with 1,4-butanediol to yield poly(butylene terephthalate). Polyester fibers are used in the textile industry. Films find applications as magnetic tapes, electrical insulation, photographic film, and packaging. Polyester bottles, especially in the soft drink market, are growing rapidly in demand.

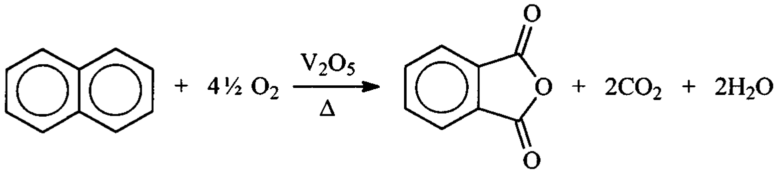
9. PHTHALIC ANHYDRIDE



The manufacturing method of making phthalic anhydride has been changing rapidly similar to the switchover in making maleic anhydride. In 1983 28% of phthalic anhydride came from naphthalene, 72% from *o*-

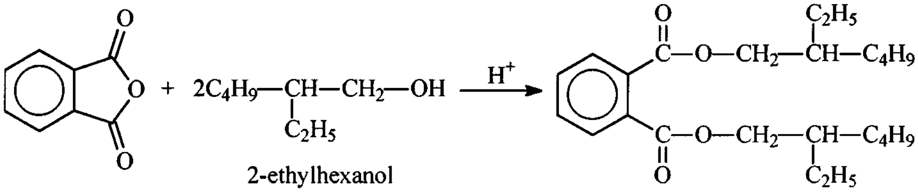
xylene. No naphthalene-based plants were open in 1989. In 1993 naphthalene rebounded and was used to make 20% of the phthalic anhydride again because of a price increase for *o*-xylene, but as of 1998 no phthalic anhydride is made from naphthalene. Despite the better yield in the naphthalene process, energetic factors make this less favorable economically compared to the *o*-xylene route.





The uses of phthalic anhydride include plasticizers (53%), unsaturated polyester resins (22%), and alkyd resins (15%).

Phthalic anhydride reacts with alcohols such as 2-ethylhexanol to form liquids that impart great flexibility when added to many plastics without hurting their strength. Most of these plasticizers, about 80%, are for poly(vinyl chloride) flexibility. Dioctyl phthalate (DOP), also called di-(2-ethylhexyl)phthalate (DEHP), is a common plasticizer.



DOP or DEHP

High doses of DEHP have been found to cause liver cancer in rats and mice and it is on the "Reasonably Anticipated to Be Human Carcinogens" list. In 2000 a report by the National Toxicology Program found serious concern that DEHP in vinyl medical devices may harm the reproductive organs of critically ill and premature male infants exposed during medical treatment. They also expressed concern that development of male unborn babies would be harmed by the pregnant mothers' exposure to DEHP or that the child would be harmed by other DEHP exposure during the first few years of life. Certain plasticizer applications, such as those in infants' pacifiers and squeeze toys, as well as blood bags, respiratory masks, oxygen tubing, and intravenous bags softened with DEHP, may be affected in the years ahead. Other diesters of phthalic anhydride do not seem to have the toxic effects of DEHP so substitutes should be easy to find.

Suggested Readings

Chemical Profiles in *Chemical Marketing Reporter*, 3-2-98, 4-13-98, 6-8-98, 6-15-98, 7-6-98, 2-8-99, 2-15-99, and 3-29-99.
Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 849-862.
Szmant, *Organic Building Blocks of the Chemical Industry*, pp. 407-574.
Wiseman, *Petrochemicals*, pp. 101-140.
Wittcoff and Reuben, *Industrial Organic Chemicals*, pp. 234-293.

Chapter 12

Chemicals from Methane

In previous discussions we studied a large percentage of important chemicals derived from methane. Those in the top 50 are listed in Table 12.1 and their syntheses are summarized in Fig. 12.1.

As we learned in Chapters 3 and 4, many inorganic compounds, not just ammonia, are derived from synthesis gas, made from methane by steam-reforming. In the top 50 this would include carbon dioxide, ammonia, nitric acid, ammonium nitrate, and urea. No further mention need be made of these important processes. We discussed MTBE in Chapter 7, Section 4, and Chapter 10, Section 9, since it is an important gasoline additive and C_4 derivative. In Chapter 10, Section 6, we presented *n*-butyraldehyde, made by the oxo process with propylene and synthesis gas, which is made from methane. In Chapter 11, Section 8, we discussed dimethyl terephthalate. Review these pertinent sections. That leaves only two chemicals, methanol and formaldehyde, as derivatives of methane that have not been discussed. We will take up the carbonylation of methanol to acetic acid, now the most important process for making this acid. Vinyl acetate is made from acetic

Table 12.1 Methane Derivatives in the Top 50

Ammonia Derivatives
Methyl *t*-butyl ether
n-Butyraldehyde
Dimethyl terephthalate
Methanol
Formaldehyde
Acetic acid
Vinyl acetate

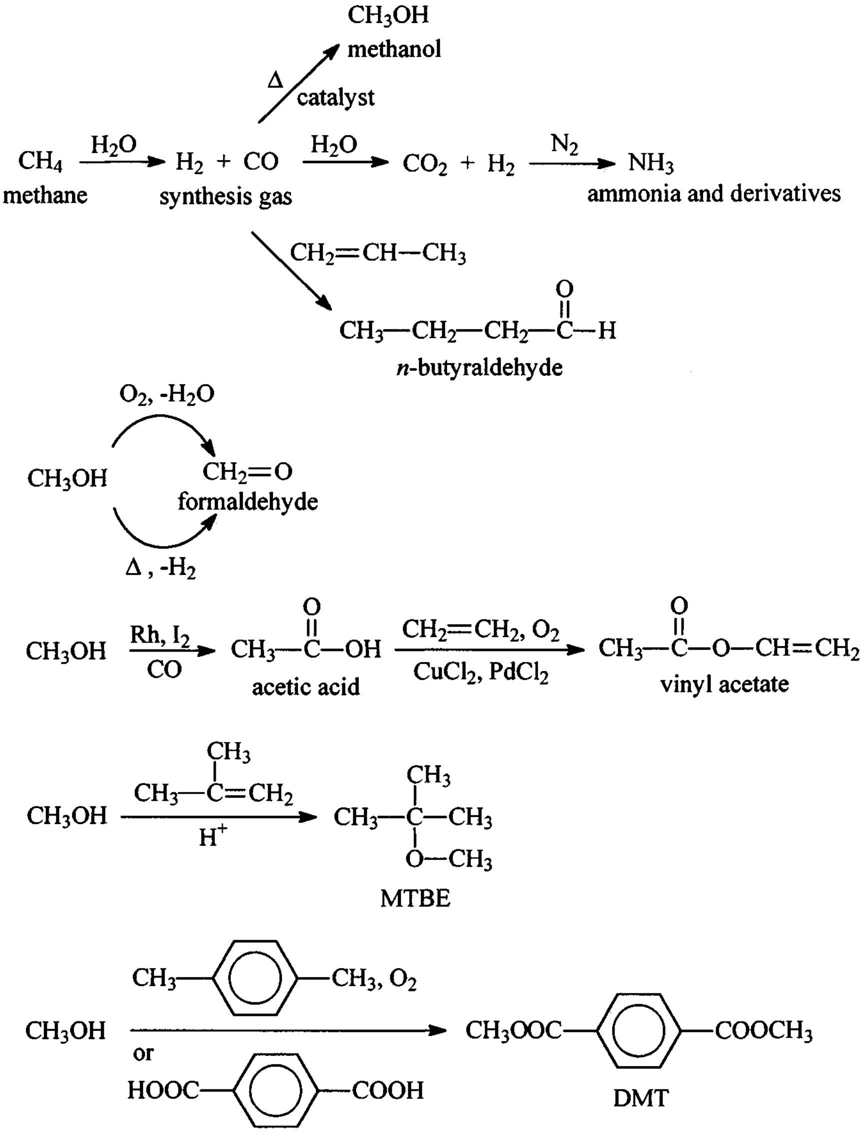


Figure 12.1 Synthesis of methane derivatives.

acid as seen in Chapter 9, Section 4. We will also discuss an important class of compounds, chlorofluorocarbons, some of which are derived from methane. Although not in the top 50, these have important uses and are making headlines these days.

1. METHANOL (WOOD ALCOHOL, METHYL ALCOHOL)

CH_3OH

Before 1926 all methanol was made by distillation of wood. Now it is all synthetic. Methanol is obtained from synthesis gas under appropriate conditions. This includes zinc, chromium, manganese, or aluminum oxides as catalysts, 300°C, 250-300 atm (3000-5000 psi), and most importantly a 1:2 ratio of $CO:H_2$. Newer copper oxide catalysts require lower temperatures and pressures, usually 200-300°C and 50-100 atm (750-1500 psi). A 60% yield of methanol is realized. As seen in Chapter 3, many synthesis gas systems are set to maximize the amount of hydrogen in the mixture so that more ammonia can be made from the hydrogen reacting with nitrogen. The shift conversion reaction aids the attainment of this goal. When synthesis gas is to be used for methanol manufacture, a 1:2 ratio $CO:H_2$ ratio is obtained by adding carbon dioxide to the methane and water.

$$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2$$

$$CO + 2H_2 \xrightarrow[\substack{\text{pressure} \\ \text{metal oxides}}]{\Delta} CH_3OH$$

Thus methanol and ammonia plants are sometimes combined since carbon dioxide, which must be removed from hydrogen to use it for ammonia production, can in turn be used as feed to adjust the $CO:H_2$ ratio to 1:2 for efficient methanol synthesis. The methanol can be condensed and purified by distillation, bp 65°C. Unreacted synthesis gas is recycled. Other products include higher boiling alcohols and dimethyl ether.

Table 12.2 gives the uses for methanol. The percentage of methanol used in the manufacture of formaldehyde has been fluctuating. It was 42% in 1981. It has decreased in part because of recent toxicity scares of formaldehyde. The percentage of methanol used in acetic acid manufacture is up from 7% in 1981 because the carbonylation of methanol has become the preferred acetic acid manufacturing method. MTBE is the octane enhancer and is synthesized directly from isobutylene and methanol. It was

Table 12.2 Uses of Methanol

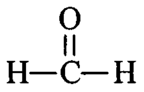
MTBE	40%
Formaldehyde	24
Acetic acid	12
Solvents	6
Chloromethanes	3
Methyl methacrylate	3
Methylamines	2
Dimethyl terephthalate	2
Miscellaneous	8

Source: Chemical Profiles

the fastest growing use for methanol for many years but it will drop dramatically if MTBE is banned. Many other important chemicals are made from methanol, although they do not quite make the top 50 list. Some of these can be found in Chapter 13 where the second 50 chemicals are summarized. With a U.S. production of 2.9 billion gal and a price of 47¢/gal, the commercial value of methanol is $1.4 billion.

Not mentioned in the table is the direct use of methanol as fuel for automobiles. It is added in small amounts to gasoline, sometimes as a blend with other alcohols such as *t*-butyl alcohol, to increase octane ratings and lower the price of the gasoline. Experimentation is even being done on vehicles that burn pure methanol. This fuel use is usually captive but a good estimate is that it may account for almost 10% of the methanol produced.

2. FORMALDEHYDE (METHANAL)



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

Formaldehyde is produced solely from methanol. The process can be air oxidation or simple dehydrogenation. Since the oxidation is exothermic and the dehydrogenation is endothermic, usually a combination is employed where the heat of reaction of oxidation is used for the dehydrogenation.

oxidation $2CH_3OH + O_2 \xrightarrow{\Delta} CH_2{=}O + 2H_2O$

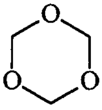
dehydrogenation $CH_3OH \xrightarrow{\Delta} CH_2{=}O + H_2$

Table 12.3 Uses of Formaldehyde

Urea-formaldehyde resins	23%
Phenol-formaldehyde resins	19
Acetylene chemicals	12
Polyacetal resins	11
MDI	6
Pentaerythritol	5
Urea-formaldehyde concentrates	4
HMTA	4
Melamine resins	4
Miscellaneous	12

Source: Chemical Profiles

Various metal oxides or silver metal are used as catalysts. Temperatures range from 450-900 °C and there is a short contact time of 0.01 sec. Formaldehyde is stable only in water solution, commonly 37-56% formaldehyde by weight. Methanol (3-15%) may be present as a stabilizer. Formaldehyde in the pure form is a gas with a bp of - 21 °C but is unstable and readily trimerizes to trioxane or polymerizes to paraformaldehyde.



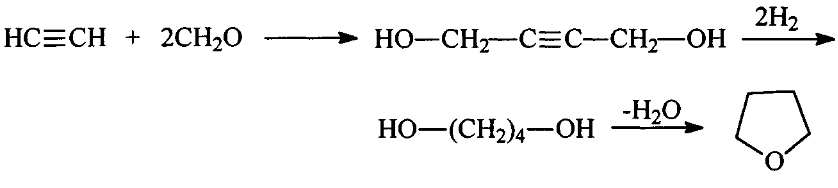
trioxane

$HO—(CH_2—O)_n—H$

paraformaldehyde

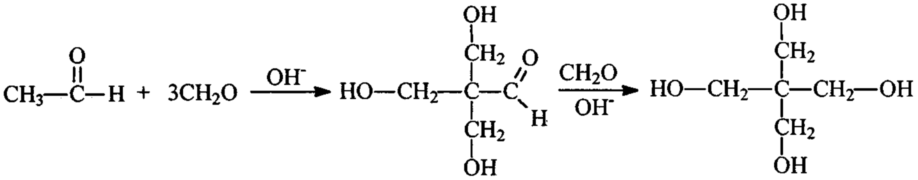
n = 8-50

Table 12.3 summarizes the uses of formaldehyde. Two important thermosetting plastics, urea- and phenol-copolymers, take nearly one half the formaldehyde manufactured. Urea-formaldehyde resins are used in particleboard, phenol-formaldehyde resins in plywood. 1,4-Butanediol is made for some polyesters and is an example of acetylene chemistry that has not yet been replaced. Tetrahydrofuran (THF) is a common solvent that is made by dehydration of 1,4-butanediol.



THF

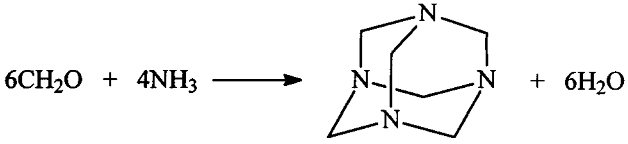
Polyacetal resins have a repeating unit of -O-CH_2-. They are strong, stiff polymers for valves, hoses, and tube connectors. Pentaerythritol finds end-uses in alkyd resins and explosives (pentaerythritol tetranitrate). To appreciate this synthesis, the student should review two condensation reactions, the crossed aldol and the crossed Cannizzaro. Acetaldehyde reacts with 3 mol of formaldehyde in three successive aldol condensations. This product then undergoes a Cannizzaro reaction with formaldehyde.



pentaerythritol

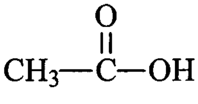
+ HCOOH

Hexamethylenetetramine (HMTA) has important uses in modifying phenolic resin manufacture and is an intermediate in explosive manufacture. Although it is a complex three-dimensional structure, it is easily made by the condensation of formaldehyde and ammonia.



Debate is continuing on the safety and toxicity of formaldehyde and its products, especially urea-formaldehyde foam used as insulation in construction and phenol-formaldehyde as a plywood adhesive. Presently the TLV-STEL of formaldehyde is 0.3 ppm. Formaldehyde is on the "Reasonably Anticipated to Be Human Carcinogens" list.

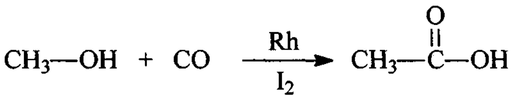
3. ACETIC ACID



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Two manufacturing methods and the uses of acetic acid were discussed in Chapter 9, Section 3, since it is made from ethylene and the C_4 stream.

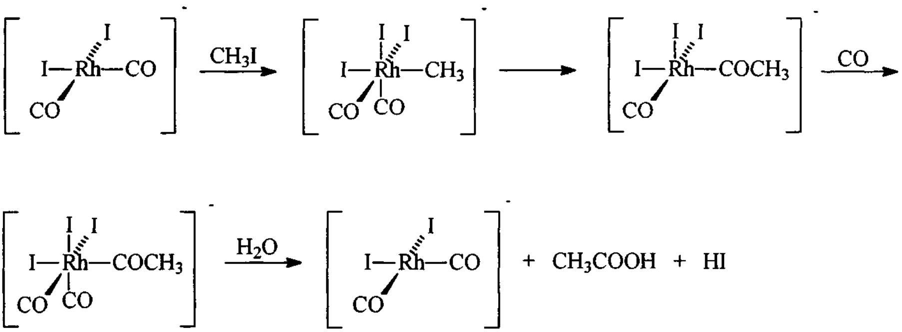
However, since 1970 the preferred method of acetic acid manufacture is carbonylation of methanol (Monsanto process), involving reaction of methanol and carbon monoxide (both derived from methane) with rhodium and iodine as catalysts at 175 °C and 1 atm. The yield of acetic acid is 99% based on methanol and 90% based on carbon monoxide.



$$CH_3{-}OH + CO \xrightarrow[I_2]{Rh} CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH$$

The mechanism is well understood, involving complexation of the rhodium with iodine and carbon monoxide, reaction with methyl iodide (formed from the methanol with hydrogen iodide), insertion of CO in the rhodium-carbon bond, and hydrolysis to give product with regeneration of the complex and more hydrogen iodide.

$$CH_3OH + HI \longrightarrow CH_3I + H_2O$$



Since acetic acid is used to make vinyl acetate (Chapter 9, Section 4) in large amounts, this top 50 chemical is also dependent on methanol as a major raw material.

4. CHLOROFLUOROCARBONS (CFCs AND HCFCs) AND FLUOROCARBONS (HFCs)

Because of the growing importance of CFCs in environmental chemistry, a basic understanding of the chemistry and uses of this diverse chemical family is necessary. Together they represent a production of over 800 million lb/yr that, at $1.00/lb, is a large commercial value.

This industry segment uses common abbreviations and a numbering system for CFCs and related compounds. The original nomenclature developed in the 1930s at Du Pont is still employed and uses three digits. When the first digit is 0, it is dropped. The first digit is the number of carbons minus 1, the second digit is the number of hydrogens plus 1, and the third digit is the number of fluorines. All other atoms filling the four valences of each carbon are chlorines. Important nonhydrogen-containing CFCs are given below. Originally these were called Freons.®

CCl_2F_2	CCl_3F	CCl_2FCClF_2
CFC-12	CFC-11	CFC-113

When some of the chlorines are replaced by hydrogens, CFCs become HCFCs, the now more common nomenclature for those chlorofluorocarbons containing hydrogen. The numbering is the same. When more than one isomer is possible, the most symmetrically substituted compound has only a number; letters a and b are added to designate less symmetrical isomers.

$CHClF_2$	CF_3CHCl_2	CF_3CHClF
HCFC-22	HCFC-123	HCFC-124

CCl_2FCH_3	$CClF_2CH_3$
HCFC-141b	HCFC-142b

When there is no chlorine and the chemical contains only hydrogen, fluorine, and carbon, they are called HFCs.

CF_3CHF_2	CH_2FCF_3	CH_3CHF_2
HFC-125	HFC-134a	HFC-152a

Halons, a closely related type of chemical that also contain bromine, are used as fire retardants. Numbering here is more straightforward: first digit, no. of carbons; second digit, no. of fluorines; third digit, no. of chlorines; and fourth digit, no. of bromines. Common Halons are the following: Halon 1211, CF_2BrCl; Halon 1301, CF_3Br; and Halon 2402, $C_2F_4Br_2$.

Most CFCs are manufactured by combining hydrogen fluoride and either carbon tetrachloride or chloroform. The hydrogen fluoride comes from fluorspar, CaF_2, reacting with sulfuric acid. The chlorinated methanes are manufactured from methane. Important reactions in the manufacture of CFC-11 and -12 and HCFC-22 are given in Fig. 12.2.

The current use pattern of CFCs is shown in Table 12.4. The classic CFCs that have been used for refrigeration and air conditioning are mostly CFC-11 and -12, with some -114 and -115. A large portion of this usage is

$$\begin{aligned}
&CCl_4\text{:} \quad CH_4 + 4S \longrightarrow CS_2 + 2H_2S\\
&\qquad CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2\\
&\qquad \text{or } CH_4 + 4Cl_2 \longrightarrow CCl_4 + 4HCl\\
&HF\text{:} \quad CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4\\
&CFCs\text{:} \; 3HF + 2CCl_4 \xrightarrow{SbCl_5} CCl_2F_2 + CCl_3F + 3HCl\\
&\qquad 2HF + CHCl_3 \longrightarrow CHClF_2 + 2HCl
\end{aligned}$$

Figure 12.2 Manufacture of Chlorofluorocarbons.

now for automobile air conditioning. Refrigerants and home air conditioning are switching to HCFC-22. Foam blowing agents use CFC-11 and -12. Solvent use, especially for cleaning of electronic circuit boards, employs CFC-113. A large previous use of CFCs was in aerosols and propellants. This has been outlawed. An estimated 3 billion aerosol cans/yr used CFCs in the early 1970s.

What are the properties of CFCs that make them unique for certain applications? Propellants for aerosols need high volatility and low boiling points. Interestingly, compared to the same size hydrocarbons, fluorocarbons have higher volatility and lower boiling points, unusual for halides. They are less reactive, more compressible, and more thermally stable than hydrocarbons. They also have low flammability, toxicity, and odor. They are used in air conditioners and refrigerators because they have high specific heats, high thermal conductivities, and low viscosities. Their nonflammability and low toxicity are also attractive in these applications.

What's the problem with CFCs? In the mid-1970s CFCs were determined to photodissociate in the stratosphere to form chlorine atoms. These chlorine atoms then react with ozone to deplete this protective layer in

Table 12.4 Uses of Chlorofluorocarbons

Refrigerants/air-conditioning	46%
Fluoropolymers	28
Foam blowing agents	20
Solvent cleaning	3
Miscellaneous	3

Source: Chemical Profiles

our atmosphere. The mechanism is a typical free radical chain process. Initiation in step (1) involves breaking a carbon-chlorine bond, weaker than a carbon-fluorine bond. Two propagation steps then can rapidly deplete ozone by reaction with the chlorine atoms.

$$(1)\quad CCl_2F_2 \xrightarrow{h\nu} Cl\cdot + \cdot CClF_2$$

$$\text{or}\quad CCl_3F \xrightarrow{h\nu} Cl\cdot + \cdot CCl_2F$$

$$(2)\quad Cl\cdot + O_3 \longrightarrow ClO\cdot + O_2$$

$$(3)\quad ClO\cdot + O \longrightarrow Cl\cdot + O_2$$

then (2), (3), (2), (3), etc.

Net reaction, (2) + (3): $O_3 + O \longrightarrow 2O_2$

Long-range effects of having less ozone in the stratosphere involve greater ultraviolet sunlight transmission, alteration of weather, and an increased risk of skin cancer. The ozone depletion potential for CFCs and other fluorocarbons have been measured and are given below relative to CFC-11 and -12. Notice that the HCFCs with lower chlorine content have lower depletion potentials than the CFCs, and the one HFC studied shows no depletion potential because it contains no chlorine.

CFC-11	1.0	HCFC-123	0.016
CFC-12	1.0	HCFC-141b	0.081
CFC-113	0.8	HCFC-22	0.053
CFC-114	1.0	HFC-134a	0
CFC-115	0.6		

HCFCs and HFCs, because of the hydrogen in the molecule, react with hydroxyl groups in the lower atmosphere. The HCFCs are being pushed as possible temporary replacements in some applications of CFCs, though HCFCs will be phased out early in the 21st century.

The manufacturing picture and the recent past and future of CFCs are rapidly changing. In 1988 annual CFC consumption was 2.5 billion lb. In the U.S. about 5,000 businesses at 375,000 locations produced goods and services valued in excess of $28 billion. More than 700,000 jobs were supported by these businesses. In 1999 the consumption of fluorocarbons was only 800 million lb. Obviously the CFC phaseout must be done properly to minimize the effects on these businesses and individuals. The following brief chronology will give the student an idea of the situation as of this writing.

1978 The EPA outlawed CFC-11 and -12 in aerosol and propellant applications because of fear of ozone depletion. They were replaced by propane and butane, highly flammable hydrocarbons.

1984 An ozone hole over Antarctica was discovered with especially low concentrations of ozone above that continent in their spring (Northern Hemisphere's fall). This was linked to CFCs.

1988 Du Pont, the largest producer of CFCs, called for a total CFC production phaseout. A possible arctic ozone hole was studied. The EPA called for a total ban of CFCs.

1989 The Montreal Protocol was completed. This asked for a worldwide production freeze at the 1986 levels, a 20% cut by 1993, and another 30% lowering of production by 1998 for CFC-11, -12, -113, -114, and -115.

1992 At a meeting in Copenhagen 80 nations set HCFC deadlines including a production freeze by 1996, a 35% reduction by 2004, 90% by 2015, and 100% by 2030.

1993 HCFC-141b replaced CFC-11 as the blowing agent in insulating foams.

1994 HFC-134a replaced CFC-12 in auto air-conditioners for all new cars. CFC-12 was to be used in old cars because of the high cost to switch. HFC-134a and HCFC-123 replaced CFC-12 and CFC-11 in large building cooling systems.

1995 The Nobel Prize in Chemistry went to Rowland, Mokina, and Crutzen for linking ozone depletion with NO_x and CFCs.

1997 Large doses of HCFC-123 were found to possibly cause liver damage.

1998 HFCs were found to possibly have an effect as long-lived greenhouse gases, increasing the average atmospheric temperature.

Suggested Readings

Chemical Profiles in *Chemical Marketing Reporter*, 6-22-98, 10-11-99, 7-31-00, and 8-28-00.

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 800-809.

Szmant, *Organic Building Blocks of the Chemical Industry*, pp. 61-187.

Wiseman, *Petrochemicals*, pp. 148-155.

Wittcoff and Reuben, *Industrial Organic Chemicals*, pp. 294-337.

Chapter 13

The Second Fifty Industrial Chemicals

1. INTRODUCTION AND BACKGROUND

The basis of most of our study of industrial chemicals thus far has been the top 50. These chemicals are produced utilizing some fascinating processes on a large scale, and an understanding and appreciation of these chemicals, their manufacture and uses, provides the student with a solid background in industrial chemicals. We might ask ourselves what comes next? What are some other important large-scale chemicals that, though not made quite at the volume of the top 50, nevertheless in their own right make important contributions to the chemical industry?

In 1988 we made the first attempt at developing a list of the second 50 chemicals arranged by approximate U.S. production. This list and the manufacture and uses of the chemicals were discussed in two papers. The list contains very interesting chemistry and can bring out many instructive features on the day-to-day importance of chemistry. The list was revised and incorporated into the text on industrial chemistry in 1992. We have again updated this list for this book to see what trends have occurred over a ten-year period. This is a valuable reference to those interested in studying commodity chemicals in greater detail than what the top 50 list offers. Indeed in previous chapters we have included some of these chemicals in our discussions, especially those that are monomers for important polymers to be mentioned later. Nearly half of the second 50 have been noted already in passing. This chapter will present these compounds as a unit, discuss the second 50 list in general terms, and summarize briefly each of the 50 chemicals in regard to manufacturing methods and use. The list of

Table 13.1 The Second 50 Chemicals

1999	1992	1988	Chemical	Prod. Bill. lb	Ave. % Ann. Growth	Ave. Price ¢/lb
51	51	84	Phosgene	2.60	4.0	74
52	53	51	Acetic anhydride	2.10	1.5	50
53	54	53	Linear alpha olefins	2.00	4.4	60
54	--	--	Tall oil	1.94	1.0	5
55	--	--	Calcium chloride	1.80	1.5	11
56	--	55	Caprolactam	1.60	2.3	93
57	--	--	Isopropyl alcohol	1.48	0.5	34
58	66	65	Acrylic acid	1.47	7.0	87
59	59	60	Hexamethylenediamine	1.45	4.5	116
60	60	57	Hydrogen cyanide	1.44	3.0	60
61	57	69	*n*-Butyl alcohol	1.40	2.5	51
62	--	--	Borates	1.39	0.5	25
63	64	63	Aniline	1.34	5.4	49
64	--	--	Sodium sulfate	1.28	-2.0	6
65	99	--	Hydrogen peroxide	1.26	9.0	42
66	91	52	Ethanol (synthetic)	1.22	2.0	32
67	58	61	Methyl methacrylate	1.18	2.0	70
68	69	90	Methylene diphenyl diisocy.	1.14	7.0	115
69	71	62	Phthalic anhydride	1.13	3.5	42
70	94	89	Methyl chloride	1.12	2.5	39
71	56	58	Acetone cyanohydrin	1.10	3.7	--
72	63	66	Cyclohexanone	1.10	8.3	73
73	73	71	*o*-Xylene	1.09	2.0	13
74	82	--	Sodium bicarbonate	1.08	3.5	46
75	--	--	Potassium sulfates	1.05	5.0	9
76	72	85	Propylene glycol	1.05	3.0	67
77	93	91	Butyl acrylate	1.00	5.5	82
78	75	75	Toluene diisocyanate	0.90	2.7	100
79	81	78	Linear alkylbenzenes	0.85	1.5	58
80	84	81	Ethanolamines	0.85	2.5	58
81	96	83	Diethylene glycol	0.78	2.5	39
82	98	--	Sulfur dioxide	0.78	2.0	12
83	85	80	2-Ethylhexanol	0.77	1.0	56
84	77	73	Acetaldehyde	0.73	4.0	46
85	74	70	*n*-Paraffins	0.71	0.5	21

Table 13.1 (Cont'd) The Second 50 Chemicals

1999	1992	1988	Chemical	Prod. Bill. lb	Ave. % Ann. Growth	Ave. Price ¢/lb
86	79	68	Phosphorus	0.70	1.2	125
87	89	96	Nonene	0.64	8.2	22
88	--	79	Methyl ethyl ketone	0.64	-0.5	46
89	--	95	1,4-Butanediol	0.62	4.6	116
90	88	87	Potassium hydroxide	0.58	3.2	186
91	--	98	Maleic anhydride	0.56	2.5	53
92	--	--	Sorbitol	0.52	3.5	37
93	65	--	Sodium tripolyphosphate	0.52	-5.0	45
94	95	--	Chloroform	0.52	2.0	30
95	--	--	Bromine	0.50	5.0	56
96	68	--	Isobutane	0.49	-1.9	8
97	87	--	Hydrofluoric acid	0.49	-2.0	65
98	90	100	1-Butene	0.48	7.0	48
99	--	93	Glycerol	0.46	3.0	60
100	--	--	Ferric chloride	0.45	5.0	54

Source: Chemical Profiles and *Chemical Prices* in *Chemical Marketing Reporter, Facts and Figures* in *Chemical and Engineering News,* and *Chemical and Economics Handbook*

chemicals with their rank, production, growth, and prices is given in Table 13.1.

Production figures are sometimes very difficult to obtain for chemicals. A number of sources have been examined in detail and recent production amounts were found for most chemicals in an attempt to generate the second 50. Generally, the guidelines for selection of the chemicals are similar to those for the top 50 list. A single chemical, or a commercially useful, closely related family of chemicals, is included. No polymers are listed. Some chemicals do not appear on the list, or are lower than what they might be due to a large captive use and unofficially reported production. We make no claim that the exact ranking is correct. Nevertheless we feel the list as developed is quite functional. Literature to 1999 is covered.

2. CHARACTERISTICS OF THE SECOND 50 CHEMICALS

The most immediate characteristic of the second 50 is the dominance of organic chemicals, a total of 38, leaving only 12 inorganics. But the number of organics has decreased from a 1992 total of 42 and a 1988 total of 47 of the second 50. Organics in the second 50 own 43 of a total of 52 billion pounds of chemical production for all 50. In grand total production, the second 50 list at 52 billion pounds shows an increase of 16% from the 45 billion pound total from 1992 and an increase of 53% from the 34 billion pound total of 1988. The 52 billion pound grand total is only a fraction of the top 50's 750 billion pounds, only 7% of the higher list. The current second 50 list ranges from phosgene at 2.60 billion pounds to ferric chloride at 0.45 billion pounds. As is obvious from the high production found for a few chemicals, there is an overlap with the *Chemical and Engineering News* top 50 list, but all important chemicals are on one list or the other.

Changes in specific chemicals can be noted. Four chemicals—calcium chloride, caprolactam, isopropyl alcohol, and sodium sulfate—all fell from the former top 50 list since 1992. In addition to these changes, six new chemicals that did not appear either in 1992 or 1988 have moved into the second 50 list. Some chemicals have changed rankings dramatically between 1992 and 1999. Hydrogen peroxide, ethanol, and methyl chloride have increased the most, while sodium tripolyphosphate and isobutane have decreased the most. Hydrogen peroxide is being used more in bleaching pulp and paper, which may have caused much of the increase. Sodium tripolyphosphate in detergents is being phased out because of environmental concerns. It was a top 50 chemical in the 1980s and it is now ranked only 93. Also included in Table 13.1 are long-term growth patterns for each of the second 50 chemicals. The percent average annual growth is given for approximately a ten-year duration, the exact years depending on the available source used. Positive growth is evident for 45 chemicals. The average annual growth rate for all the second 50 chemicals is +2.9%.

The average prices of commercial quantities in cents per pound are given in Table 13.1. Six chemicals are over $1.00/lb: hexamethylenediamine (59), methylene diphenyl diisocyanate (68), toluene diisocyanate (78), phosphorus (86), 1,4-butanediol (89), and potassium hydroxide (90). In 1992 only three chemicals, and in 1988 only two chemicals, were over $1.00/lb. The cheapest of the second 50 chemicals is tall oil, with sodium sulfate close. The average price for all the second 50 chemicals is $0.55/lb.

Table 13.2 The Second 50 Organic Chemicals
As Derivatives of the Seven Basic Organics

Ethylene	**C_4 Fraction**	**Benzene**
Acetaldehyde	Acetic anhydride	Aniline
Acetic anhydride	Hexamethylenediamine	Caprolactam
Diethylene glycol	Isobutane	Cyclohexanone
Ethanol	1-Butene	Linear alkylbenzenes
Ethanolamines	Maleic anhydride	Methylene diphenyl diisocy.
Linear alpha olefins	Methyl ethyl ketone	
		Xylene
Propylene	**Methane**	
		Phthalic anhydride
Acetone cyanohydrin	Acetic anhydride	*o*-Xylene
Acrylic acid	1,4-Butanediol	
Butyl acrylate	Butyl acrylate	**Other Sources**
n-Butyl alcohol	*n*-Butyl alcohol	
2-Ethylhexanol	Chloroform	1,4-Butanediol
Glycerol	2-Ethylhexanol	Glycerol
Hexamethylenediamine	Hydrogen cyanide	Linear alpha olefins
Hydrogen cyanide	Methyl chloride	Linear alkylbenzenes
Isopropyl alcohol	Methylene diphenyl diisocy.	Nonene
Methyl methacrylate	Methyl methacrylate	*n*-Paraffins
Propylene glycol	Phosgene	Sodium bicarbonate
	Toluene diisocyanate	Sorbitol
Toluene		Tall oil
Toluene diisocyanate		

3. DERIVATIVES OF THE SEVEN BASIC ORGANICS

The dominance of organic chemicals in the list has prompted us to separate them according to the seven basic organic chemicals (ethylene, propylene, the C_4 stream, benzene, toluene, xylene, and methane) on which they are based. Double counting is, of course, necessary since some derivatives are made from more than one basic organic chemical. Table 13.2 shows the organic chemicals in the second 50 separated by basic source. Compare Table 13.2 with Table 7.1. Larger numbers of chemicals in the second 50 are derived from propylene and methane than in the top 50. Unlike the organics in the top 50, the second 50 organics have some sources beside the seven basic organics.

Table 13.3 Second 50 Chemical Pairs

Precursor	Derivative
Acetaldehyde	Acetic anhydride
Acetone cyanohydrin	Methyl methacrylate
Acrylic acid	Butyl acrylate
Aniline	Methylene diphenyl diisocyanate
1-Butene	Methyl ethyl ketone
n-Butyl alcohol	Butyl acrylate
Hydrogen cyanide	Acetone cyanohydrin
Nonene	Linear alkylbenzenes
n-Paraffins	Linear alkylbenzenes
n-Paraffins	Linear alpha olefins
n-Paraffins	Nonene
Phosgene	Methylene diphenyl diisocyanate
Phosgene	Toluene diisocyanate
o-Xylene	Phthalic anhydride

4. SECOND 50 CHEMICAL PAIRS

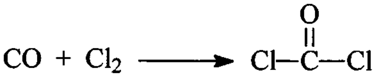
The second 50 chemicals commonly are made with another representative of this same list as one of its precursors, while only originally being derived from a more basic chemical. Table 13.3 gives 15 such paired chemicals. These second 50 pairs are one reason why an exact list of rank may not be possible, since so many production amounts are very close.

5. MANUFACTURE AND USES

The following sections briefly mention the one or two processes used to make the chemical on a large scale. Then the chemical's uses are given with approximate percentages. A close study of this chemistry uncovers many interesting relationships among all 100 top chemicals in the U.S. The section numbers below correspond to the ranking of chemicals from 51-100 in Table 13.1.

51. Phosgene

Phosgene is manufactured by reacting chlorine gas and carbon monoxide in the presence of activated carbon. Much of the market is captive. The merchant market is small.

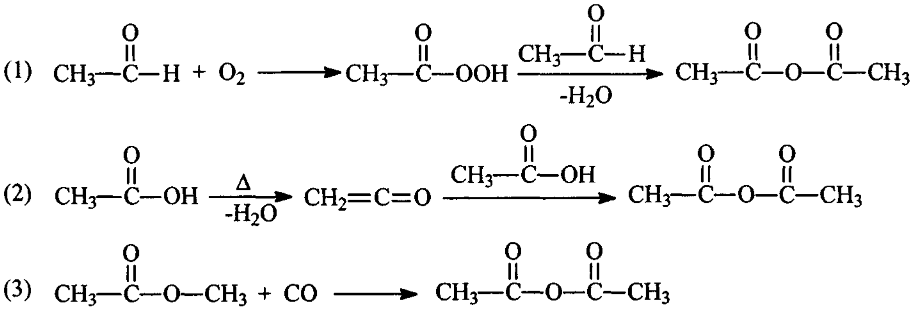


$$CO + Cl_2 \longrightarrow Cl-\overset{O}{\overset{\parallel}{C}}-Cl$$

Uses of phosgene include the manufacture of toluene diisocyanate (45%), methylene diphenyl diisocyanate and polymer diisocyanates (38%), and polycarbonate resins (12%).

52. Acetic Anhydride

Acetic anhydride may be produced by three different methods. The first procedure involves the *in situ* production from acetaldehyde of peracetic acid, which in turn reacts with more acetaldehyde to yield the anhydride. In the preferred process, acetic acid (or acetone) is pyrolyzed to ketene, which reacts with acetic acid to form acetic anhydride. A new process to make acetic anhydride involves CO insertion into methyl acetate. This may be the process of the future.



$$(1)\quad CH_3-\overset{O}{\overset{\parallel}{C}}-H + O_2 \longrightarrow CH_3-\overset{O}{\overset{\parallel}{C}}-OOH \xrightarrow[-H_2O]{CH_3-\overset{O}{\overset{\parallel}{C}}-H} CH_3-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-CH_3$$

$$(2)\quad CH_3-\overset{O}{\overset{\parallel}{C}}-OH \xrightarrow[-H_2O]{\Delta} CH_2=C=O \xrightarrow{CH_3-\overset{O}{\overset{\parallel}{C}}-OH} CH_3-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-CH_3$$

$$(3)\quad CH_3-\overset{O}{\overset{\parallel}{C}}-O-CH_3 + CO \longrightarrow CH_3-\overset{O}{\overset{\parallel}{C}}-O-\overset{O}{\overset{\parallel}{C}}-CH_3$$

Approximately 86% of acetic anhydride is used as a raw material in the manufacture of cellulose acetate.

53. Linear Alpha Olefins (LAO)

Linear hydrocarbons with a double bond at the end of the chain are made by oligomerization of ethylene. Compounds with 6-18 carbons are the most popular. Ziegler catalysts are used in this process. Note that certain olefins such as nonene and dodecene can also be made by cracking and dehydrogenation of *n*-paraffins.

$$CH_2{=}CH_2 \longrightarrow \underset{n = 3\text{ to }15}{CH_3{-}(CH_2)_n{-}CH{=}CH_2}$$

LAOs are copolymerized with polyethylene to form linear low density polyethylene (LLDPE). 1-Hexene and 1-octene are especially useful for this purpose. LLDPE accounts for the largest use (31%) of LAOs, while detergent alcohols (23%), lubricants and lube oil additives (17%), and oxo alcohols for plasticizers (10%) are other important uses.

54. Tall Oil

During the kraft pulping process, the first step in making hundreds of paper products, crude tall oil is obtained from the alkaline material by acidifying it with sulfuric acid. The crude tall oil is then converted through dehydration, dry distillation, and finally the fractionation of the vaporized tall oil compounds. Fatty acids, rosin acids, and neutral materials make up tall oil.

$$2R{-}COO^-Na^+ + H_2SO_4 \longrightarrow Na_2SO_4 + 2R{-}COOH$$

Examples of the fatty acids are oleic (*cis*-9-octadecenoic) and linoleic (*cis,cis*-9,12-octadecadienoic) acid. The major constituent of rosin acids is abietic acid. Uses of tall oil are tall oil rosin (31%, for paper size, protective coatings, adhesives, inks, and rubber), tall oil fatty acids (30%, in protective coatings, soaps, and inks), tall oil pitch (30%, in fuel, binders, coatings, rubber modifiers, asphalt, sizing, inks, and hardboard impregnation), and distilled tall oil (9%, in soaps, coatings, flotation, and board impregnation).

55. Calcium Chloride

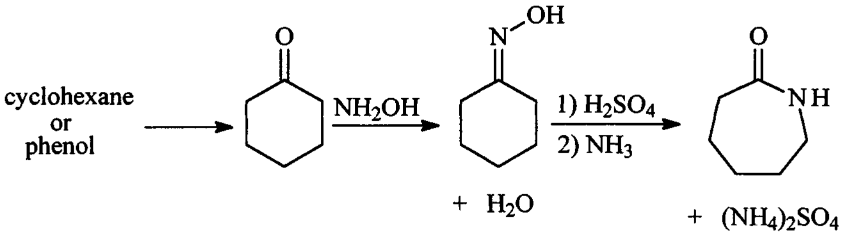
Calcium chloride is obtained from natural brines, typically containing 14% NaCl, 9% $CaCl_2$, and 3% $MgCl_2$. Evaporation precipitates the sodium chloride. The magnesium chloride is removed by adding slaked lime to precipitate magnesium hydroxide.

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$$

Uses of calcium chloride include road deicing (40%), where it competes with sodium chloride, road dust control and roadway base stabilization (20%), industrial processing (20%), oil and gas wells (10%), and concrete (5%).

56. Caprolactam

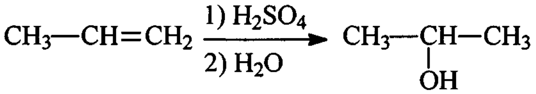
Caprolactam is discussed more completely in Chapter 11, Section 5. It is made from cyclohexane by oxidation to cyclohexanone-cyclohexanol mixture, formation of cyclohexanone oxime, and acid-catalyzed rearrangement.



All caprolactam goes into nylon 6 manufacture, including fibers (80%) and plastic resin and film (20%).

57. Isopropyl Alcohol

Esterification of propylene with 85% H_2SO_4 to isopropyl hydrogen sulfate, followed by hydrolysis to the alcohol, is the manufacturing method for isopropyl alcohol.



$$CH_3{-}CH{=}CH_2 \xrightarrow[2)\ H_2O]{1)\ H_2SO_4} CH_3{-}\underset{\substack{|\\ OH}}{CH}{-}CH_3$$

Isopropyl alcohol is used for a coatings solvent (30%), a processing solvent (25%), household and personal care products (15%), pharmaceuticals (15%), and acetone manufacture (7%).

58. Acrylic Acid

Acrylic acid is made by the oxidation of propylene to acrolein and further oxidation to acrylic acid. Another common method of production is acrylonitrile hydrolysis.

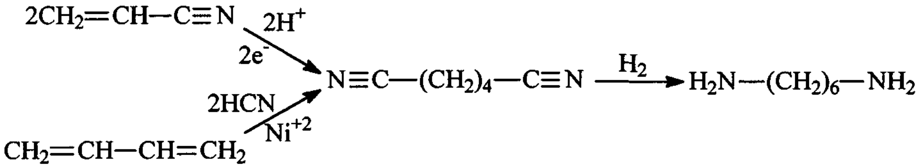
$$(1)\ CH_2{=}CH{-}CH_3 \xrightarrow{O_2} CH_2{=}CH{-}CHO \xrightarrow{O_2} CH_2{=}CH{-}COOH$$

$$(2)\ CH_2{=}CH{-}CN \xrightarrow[H^+]{H_2O} CH_2{=}CH{-}COOH$$

Acrylic acid and its salts are raw materials for an important range of esters, including methyl, ethyl, butyl, and 2-ethylhexyl acrylates. The acid and its esters are used in polyacrylic acid and salts (32%, including superabsorbent polymers, detergents, water treatment chemicals, and dispersants), surface coatings (18%), adhesives and sealants (15%), textiles and non-wovens (12%), plastic modifiers (5%), and paper coating (3%).

59. Hexamethylenediamine (HMDA)

Hexamethylenediamine is discussed in Chapter 10, Sections 1 and 8. It is produced from adiponitrile by hydrogenation. Adiponitrile comes from electrodimerization of acrylonitrile (32%) or from anti-Markovnikov addition of 2 moles of hydrogen cyanide to butadiene (68%).



HMDA is used exclusively in the production of nylon 6,6.

60. Hydrogen Cyanide

Approximately 80% of all hydrogen cyanide is manufactured by the reaction of air, ammonia, and natural gas over a platinum or platinum-rhodium catalyst at elevated temperature. The reaction is referred to as the Andrussow process. Hydrogen cyanide is also available as a by-product from acrylonitrile manufacture by ammoxidation (20%).

$$(1)\ 2CH_4 + 2NH_3 + 3O_2 \longrightarrow 2HCN + 6H_2O$$

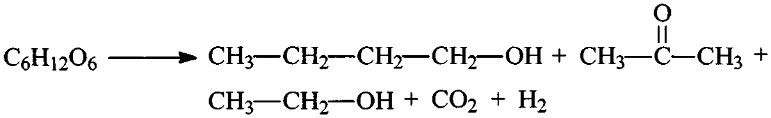
$$(2)\ CH_2{=}CH{-}CH_3 + 2NH_3 + 3O_2 \longrightarrow 2CH_2{=}CH{-}C{\equiv}N + 6H_2O\ (+\ HCN)$$

Adiponitrile production accounts for 41% of hydrogen cyanide use, methyl methacrylate for 32%. Other uses include sodium cyanide (14%, a fast-growing application in gold mining), methionine (4%), and chelating agents (3%).

61. *n*-Butyl Alcohol

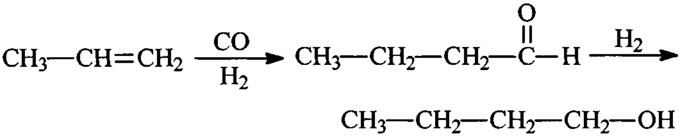
n-Butyl alcohol can be obtained from carbohydrates (such as molasses and grain) by fermentation. Acetone and ethanol are also produced. Synthetic processes account for the majority of current-day production. Propylene and synthesis gas give *n*-butyl alcohol. Isobutyl alcohol is a by-product.

(1)



$$C_6H_{12}O_6 \longrightarrow CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + CH_3{-}CH_2{-}OH + CO_2 + H_2$$

(2)



$$CH_3{-}CH{=}CH_2 \xrightarrow[H_2]{CO} CH_3{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H \xrightarrow{H_2} CH_3{-}CH_2{-}CH_2{-}CH_2{-}OH$$

n-Butyl alcohol is used for butyl acrylate and methacrylate (36%), glycol ethers (31%), solvent (13%), butyl acetate (12%), and plasticizers (4%).

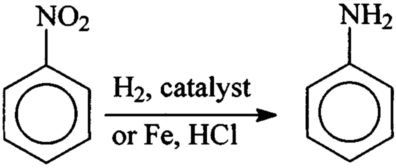
62. Borates

The principal chemicals that make up this general category are borax pentahydrate ($Na_2B_4O_7 \bullet 5H_2O$), anhydrous borax ($Na_2B_4O_7$), borax decahydrate ($Na_2B_4O_7 \bullet 10H_2O$), and boric acid ($H_3BO_3$ and HBO_2). These chemicals all begin with boron minerals from brines. The metal borates such as borax react with strong mineral acids to form boric acid. A large sodium borate deposit was discovered in California in 1913 and this has become the principal world source of sodium borates and boric acid.

Glass fiber insulation (30%) is the primary use of borates. Other uses include textile glass fiber (18%), soaps, detergents, and bleaches (10%), glass (10%), agriculture (7%), and flame retardants (6%).

63. Aniline

Aniline is discussed further in Chapter 11, Section 6. It is made by the reduction of nitrobenzene (83%) by either catalytic hydrogenation or acidic metal reduction. The reaction of ammonia and phenol is a newer process that shows promise and is being used (17%).



Major uses of aniline include *p,p'*-methylene diphenyl diisocyanate (MDI) (75%) and rubber chemicals (15%) production. It is also used to a smaller extent in herbicides (4%), dyes and pigments (3%), and specialty fibers (2%).

64. Sodium Sulfate

Approximately 73% of all North American sodium sulfate is obtained directly from natural salt sources in Searles Lake, California and in Texas, Mexico, and Canada. Miscellaneous methods of manufacture account for smaller percentages. This includes 5% as a by-product in the production of viscose rayon, where sulfuric acid and sodium hydroxide are used to degrade the cellulose. Sodium dichromate manufacture gives another 6% of sodium sulfate as a by-product.

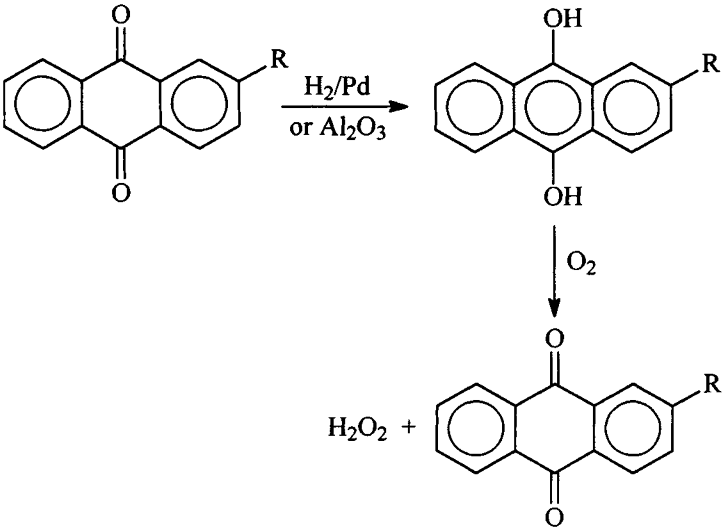
$$(1)\quad 2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$$

$$(2)\quad 2Na_2CrO_4 + H_2SO_4 + H_2O \longrightarrow Na_2Cr_2O_7 \cdot 2H_2O + Na_2SO_4$$

The current uses of sodium sulfate include detergents (45%, as a phosphate substitute), textiles (18%), kraft sulfate pulping (13%), and glass (10%).

65. Hydrogen Peroxide

The most important method of making hydrogen peroxide is by reduction of anthraquinone to the hydroquinone, followed by reoxidation to anthraquinone by oxygen and formation of the peroxide. R is usually ethyl but *t*-butyl and *sec*-amyl have also been used.



Hydrogen peroxide is used in pulp and paper (50%, as a replacement for chlorine in kraft bleaching); environmental control, including municipal and industrial water treatment (17%); chemical synthesis (15%); and textiles (9%).

66. Ethanol (Synthetic)

Synthetic ethanol is made by the hydration of ethylene over a phosphoric acid-on-celite catalyst and accounts for 8% of all ethanol.

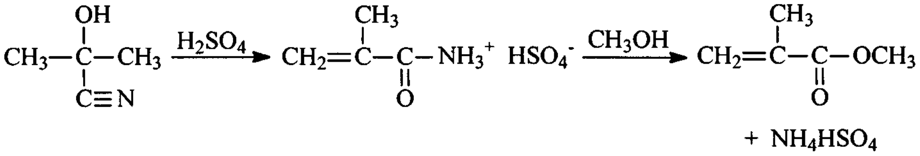
$$CH_2{=}CH_2 + H_2O \longrightarrow CH_3{-}CH_2{-}OH$$

The predominant method of ethanol manufacture, at one time, was by fermentation of sugars; this method went out of use in the 1930s. However, corn fermentation is now a source of 92% of all ethanol and is used for gasohol, a 10% alcohol:90% gasoline blend used for automobile fuel.

Industrial grade ethanol uses include solvents (60%) and chemical intermediates (40%). Fermentation uses include fuels (90%), solvents and chemicals (5%), and beverages (5%).

67. Methyl Methacrylate (MMA)

The only method used in the U.S. for the production of methyl methacrylate is the acetone cyanohydrin process. Acetone cyanohydrin (from the reaction of acetone with hydrogen cyanide) is reacted with sulfuric acid to yield methacrylamide sulfate, which is further hydrolyzed and esterified in a continuous process. Other processes using different raw materials have been tried in the U.S. and abroad, but the acetone cyanohydrin process has prevailed over the years.

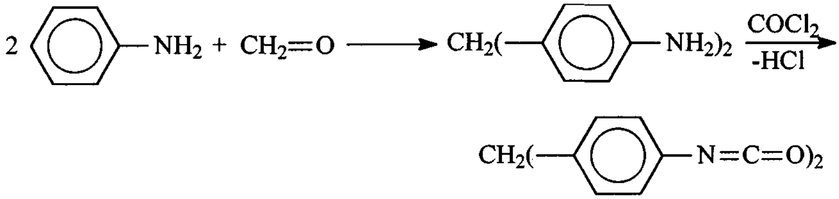


$$CH_3-\overset{OH}{\underset{C\equiv N}{C}}-CH_3 \xrightarrow{H_2SO_4} CH_2=\overset{CH_3}{C}-\underset{O}{\underset{\|}{C}}-NH_3^+\ HSO_4^- \xrightarrow{CH_3OH} CH_2=\overset{CH_3}{C}-\underset{O}{\underset{\|}{C}}-OCH_3 + NH_4HSO_4$$

Methyl methacrylate is polymerized to poly(methyl methacrylate), which is used in cast and extruded sheet (32%), surface coatings (24%), molding powder and resins (15%), impact modifiers (13%), and emulsion polymers (8%).

68. Methylene Diphenyl Diisocyanate (MDI)

Aniline is condensed with formaldehyde; reaction with phosgene gives MDI.

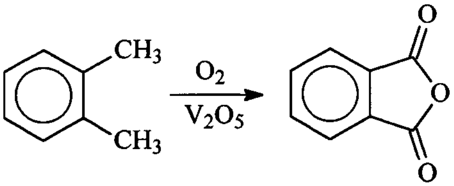


MDI

Rigid polyurethane foams account for 80% of MDI use, especially for construction (about half of this use), refrigeration, packaging, and tank and pipe insulation. Other uses are reaction-injection molding (RIM) applications (13%) and cast elastomers (2%).

69. Phthalic Anhydride

In 1983 about 72% of the phthalic anhydride made in the United States came from the reaction of *o*-xylene with air. The rest was made from naphthalene, which was isolated from coal tar and petroleum. In 1989 all plants used *o*-xylene.



Plasticizers such as dioctyl phthalate (51%), unsaturated polyester resins (24%), and alkyd resins (12%) account for the majority of phthalic anhydride use.

70. Methyl Chloride

The major method (65%) for the production of methyl chloride is by the reaction of methanol and hydrogen chloride, with the aid of a catalyst and either in the vapor or liquid phases. Approximately 35% is made by the chlorination of methane.

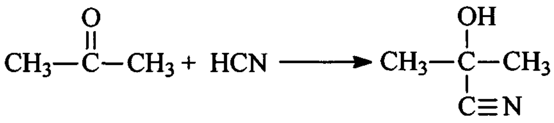
$$(1)\quad CH_3OH + HCl \longrightarrow CH_3Cl + H_2O$$

$$(2)\quad CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

The uses of methyl chloride are as follows: methyl chlorosilanes as intermediates for silicones (82%), methyl cellulose (6%), agricultural chemicals (4%), quaternary amines (4%), and butyl rubber (2%).

71. Acetone Cyanohydrin

Acetone cyanohydrin is manufactured by the direct reaction of hydrogen cyanide with acetone catalyzed by base, generally in a continuous process.

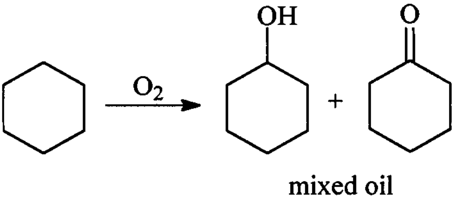


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + HCN \longrightarrow CH_3-\underset{\underset{C\equiv N}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

Acetone cyanohydrin is an intermediate in the manufacture of methyl methacrylate.

72. Cyclohexanol/Cyclohexanone

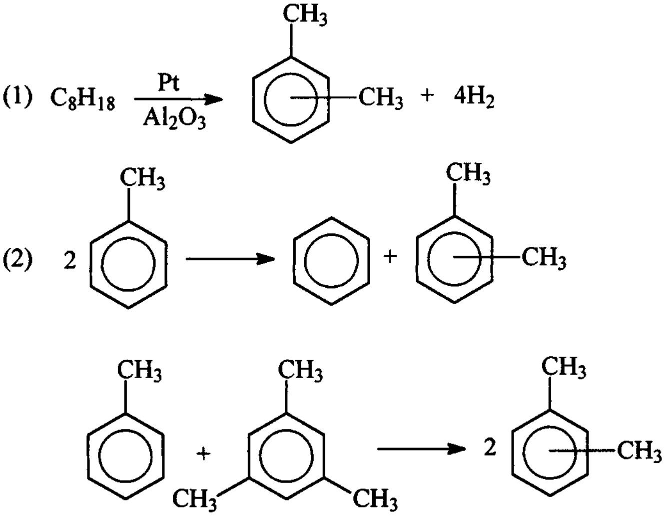
Cyclohexanol and cyclohexanone are made by the air oxidation of cyclohexane (81%) with a cobalt(II) naphthenate or acetate or benzoyl peroxide catalyst at 125-160°C and 50-250 psi. Also used in the manufacture of this mixture is the hydrogenation of phenol at elevated temperatures and pressures, in either the liquid or vapor phase (19%). The ratio of alcohol to ketone varies with the conditions and catalysts.



"Mixed oil" is used for the manufacture of caprolactam (53%, for nylon 6) and adipic acid (44%, for nylon 6,6). Cyclohexanol is favored if the use is for adipic acid; cyclohexanone is favored if the mixture is to be made into caprolactam.

73. *o*-Xylene

There are two methods of manufacture of the xylenes. The major one is from petroleum by catalytic reforming with a platinum-alumina catalyst. The second method (which has been developed recently) is by processes involving the disproportionation of toluene or the transalkylation of toluene



with trimethylbenzenes The ortho isomer is separated from the meta and para isomer by fractional distillation.

o-Xylene is used almost exclusively as feedstock for phthalic anhydride manufacture.

74. Sodium Bicarbonate

Sodium bicarbonate can be made by treating soda ash with carbon dioxide and water. Sodium bicarbonate is called bicarbonate of soda or baking soda. It is also mined from certain ores called nahcolite.

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2NaHCO_3$$

The uses of sodium bicarbonate include food (32%), animal feed (24%), cleaning products (9%), pharmaceuticals and personal care (9%), chemicals (8%), water treatment (6%), and fire extinguishers (2%).

75. Potassium Sulfates

Potassium sulfate (K_2SO_4) is produced from mixed minerals or brines such as langbenite ore, $K_2SO_4 \bullet 2MgSO_4$, found in Mexico. Reaction with potassium chloride gives pure potassium sulfate. In the Mannheim process potassium chloride reacts with sulfuric acid to give the sulfate.

$$(1)\quad K_2SO_4 \cdot 2MgSO_4 + 4KCl \longrightarrow 3K_2SO_4 + 2MgCl_2$$

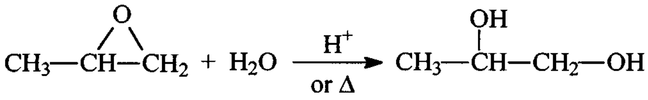
$$(2)\quad KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$$

$$KCl + KHSO_4 \longrightarrow K_2SO_4 + HCl$$

The major use of potassium sulfates is in agriculture as a fertilizer (97%). The other 3% is used in industry. Potassium sulfate accounts for about 5% of the potash industry. It is twice as expensive as potassium chloride and is only used as potash fertilizer where it performs better than potassium chloride.

76. Propylene Glycol

Propylene glycol is produced by hydration of propylene oxide in a process similar to that for the production of ethylene glycol by hydration of ethylene oxide.



Unsaturated polyester resins account for the majority of the commercial use of propylene glycol (40%). Other uses include liquid and laundry detergent (15%), cosmetics and pharmaceuticals (12%), antifreeze and deicers (10%), pet food (6%), functional fluids (6%), paint and coatings (4%), and tobacco humectants (3%).

77. Butyl Acrylate

Some acrylates are still produced by a modified Reppe process that involves the reaction of acetylene, the appropriate alcohol (in the case of butyl acrylate, butyl alcohol is used), and carbon monoxide in the presence of an acid. The process is continuous and a small amount of acrylates is made this way. The most economical method of acrylate production is that of the direct oxidation of propylene to acrylic acid, followed by esterification.

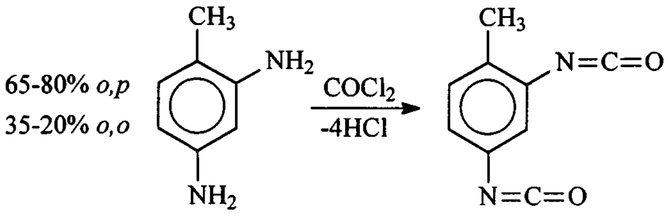
$$(1)\quad HC{\equiv}CH + ROH + CO \xrightarrow[HCl]{Ni(CO)_4} CH_2{=}CH{-}COOR$$

$$(2)\quad CH_2{=}CH{-}CH_3 \xrightarrow{O_2} CH_2{=}CH{-}COOH \xrightarrow[H^+]{ROH} CH_2{=}CH{-}COOR$$

Acrylates find major use in coatings (45%), textiles (25%), and fibers, polishes, paper, and leather (15% collectively).

78. Toluene Diisocyanate (TDI)

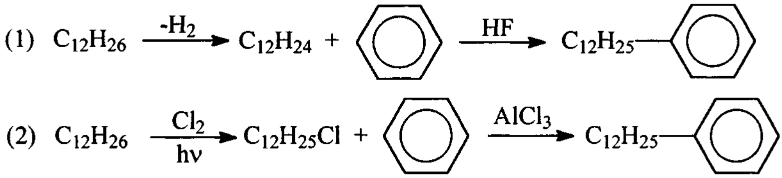
Toluene diisocyanate (TDI) is made from the reaction of 2,4-toluenediamine and phosgene. The diamine is made by reduction of dinitrotoluene, which in turn is manufactured by nitration of toluene. See Chapter 11, Section 7.



Polyurethanes account for the use of TDI. Approximately 85% of this goes toward flexible polyurethane foams (35% furniture, 25% transportation, 20% carpet underlay, 10% bedding), 6% toward coatings, 4% in elastomers, and 3% in rigid foams.

79. Linear Alkylbenzenes (LAB)

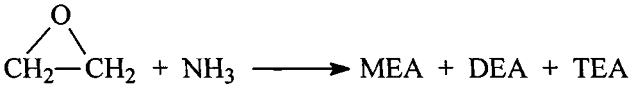
Linear alkylbenzenes are made from *n*-paraffins (C_{10}-C_{14}) by either partial dehydrogenation to olefins and addition to benzene with HF as catalyst (60%) or chlorination of the paraffins and Friedel-Crafts reaction with benzene and an aluminum chloride catalyst (40%). See Chapter 24 for more information.



The major uses of linear alkylbenzenes are in the manufacture of linear alkyl sulfonates, LAS, for laundry (70%), light duty dishwashing liquids (15%), industrial cleaners (12%), and household cleaners (3%).

80. Ethanolamines

Ethanolamines are made by reacting ethylene oxide and excess ammonia, followed by separation of unreacted ammonia and the three ethanolamines. The proportion of the three products depends on reaction conditions.



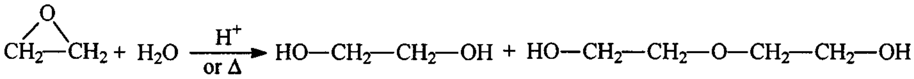
$$\overset{O}{CH_2{-}CH_2} + NH_3 \longrightarrow \text{MEA} + \text{DEA} + \text{TEA}$$

monoethanolamine (MEA)	$HO{-}CH_2{-}CH_2{-}NH_2$
diethanolamine (DEA)	$(HO{-}CH_2{-}CH_2)_2NH$
triethanolamine (TEA)	$(HO{-}CH_2{-}CH_2)_3N$

The breakdown of use of ethanolamines is surfactants (32%), ethylenediamines (20%), gas purification (17%), herbicides (10%), metal cleaning (10%), and textiles (5%).

81. Diethylene Glycol

Diethylene glycol is produced as a by-product in the manufacture of ethylene glycol from hydrolysis of ethylene oxide. It is separated from the ethylene glycol by vacuum distillation.



Breakdown of diethylene glycol use is as follows: unsaturated polyester resins (20%), polyester polyols (15%), antifreeze blending (12%), triethylene and tetraethylene glycol (9%), solvents (9%), morpholine (7%), and natural gas dehydration (4%). Much of the market is captive. The merchant market is small.

82. Sulfur Dioxide

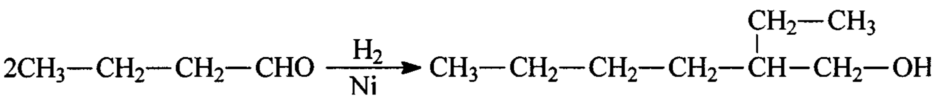
Sulfur dioxide is made as part of the contact process for making sulfuric acid (Chapter 2, Section 2.2). Sulfur and oxygen are burned at 1000°C. Sulfur dioxide can be made by oxidation of various metal sulfides or hydrogen sulfide, or it can be made from calcium sulfate or used sulfuric acid as well.

$$S + O_2 \longrightarrow SO_2$$

Uses include chemicals (40%), pulp and paper (23%), food and agriculture (14%), water and waste water treatment (9%), metal and ore refining (6%), and oil recovery and refining (4%).

83. 2-Ethylhexanol

2-Ethylhexanol is produced by aldol condensation of butyraldehyde followed by reduction. It can also be made in one step from propylene and synthesis gas converted to butanols and 2-ethylhexanol without isolating the butyraldehydes. See Chapter 10, Section 6.

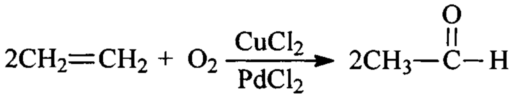


$$2CH_3{-}CH_2{-}CH_2{-}CHO \xrightarrow[Ni]{H_2} CH_3{-}CH_2{-}CH_2{-}CH_2{-}\underset{}{\overset{\displaystyle CH_2{-}CH_3}{\overset{|}{C}H}}{-}CH_2{-}OH$$

Plasticizers account for 60% of the use of 2-ethylhexanol (especially dioctyl phthalate, 34%; dioctyl adipate, 5%; and trioctyl trimellitate, 4%). About 17% goes toward the making of 2-ethylhexyl acrylate for adhesives and coatings, and 7% for 2-ethylhexylnitrate.

84. Acetaldehyde

Acetaldehyde may be made (1) from ethylene by direct oxidation, with the Wacker-catalyst containing copper(II) and palladium(II) salts; (2) from ethanol by vapor-phase oxidation or dehydrogenation; or (3) from butane by vapor-phase oxidation. The direct oxidation of ethylene is the most commonly used process, accounting for 80% of acetaldehyde production.



$$2CH_2{=}CH_2 + O_2 \xrightarrow[PdCl_2]{CuCl_2} 2CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H$$

The main use of acetaldehyde is in acetic acid and acetic anhydride production (70%); other uses include pyridine bases (8%), pentaerythritol (7%), peracetic acid (6%), and 1,3-butylene glycol (2%).

85. *n*-Paraffins

$$C_nH_{2n+2}$$

The production of the *n*-paraffins, especially C_{10}-C_{14}, involves the use of zeolites to separate straight chain compounds from the kerosene fraction of petroleum.

The main use of *n*-paraffins is in the production of linear alkylbenzenes (90%) for the detergent industry. The other uses are solvents and lubricants (7%) and chlorinated paraffins (3%).

86. Phosphorus

Yellow phosphorus (known also as white phosphorus) is produced by reducing phosphate rock (calcium phosphate or calcium fluorophosphate) with carbon in the presence of silica as flux; heat of reaction is furnished by an electric-arc furnace.

$$2Ca_3(PO_4)_2 + 10C + 6SiO_2 \longrightarrow P_4 + 6CaSiO_3 + 10CO$$

Phosphorus is used for the manufacture of thermal phosphoric acid (75%) and other chemicals (25%), including phosphorus trichloride, pentasulfide, and pentoxide.

87. Nonene

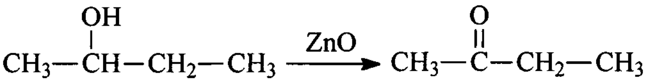
Originally made by the trimerization of propylene to give a branched nonene, this product now has limited use for detergents because of nonbiodegradability. Cracking and dehydrogenation of *n*-paraffins is now the preferred method, giving very linear chains. With good linear wax, an olefin product containing as much as 90% linear alpha olefins can be prepared.

$$C_9H_{20} \xrightarrow[\text{or catalyst}]{540\text{-}565^\circ C} C_9H_{18} + H_2$$

Nonene is used in the manufacture of nonylphenol (30%) and ethoxylated nonylphenol nonionic surfactants. It is also used in the oxo process to make isodecyl alcohol (34%) for esters as plasticizers.

88. Methyl Ethyl Ketone (MEK)

Methyl ethyl ketone is made mostly by the dehydrogenation of *sec*-butyl alcohol. A small amount is isolated as a by-product in acetic acid production by the oxidation of *n*-butane.



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH_3 \xrightarrow{ZnO} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

MEK is used for coatings solvents (62%), adhesives (12%), magnetic tapes (5%), lube oil dewaxing (5%), and printing inks (3%).

89. 1,4-Butanediol

1,4-Butanediol, also known as tetramethylene glycol, is produced by the hydrogenation of butynediol (made from acetylene and formaldehyde).

$$HC\equiv CH + 2HCHO \longrightarrow HO-CH_2-C\equiv C-CH_2-OH \xrightarrow{2H_2} HO-(CH_2)_4-OH$$

The major use of this chemical is in the manufacture of polyesters. It is also used to make an industrial solvent, tetrahydrofuran (THF).

90. Potassium Hydroxide

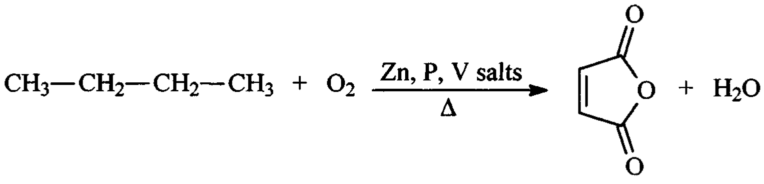
Potassium hydroxide is produced by the electrolysis of potassium chloride solutions.

$$2KCl + 2H_2O \xrightarrow{e^-} 2KOH + H_2 + Cl_2$$

The breakdown of the use of potassium hydroxide is as follows: potassium chemicals (35%), potassium carbonate (25%), liquid fertilizer (12%), soaps (12%), and potassium phosphates (7%).

91. Maleic Anhydride (MA)

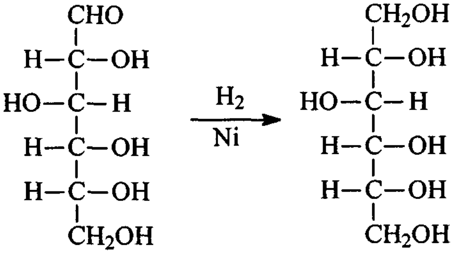
Maleic anhydride is made by the vapor-phase oxidation of *n*-butane. See Chapter 10, Section 10.



MA

Uses of MA include unsaturated polyester resins (63%), lubricating oil additives (11%), copolymers (8%), alkenyl succinic anhydrides (5%), malic acid (3%), fumaric acid (2%), and agricultural chemicals (2%).

92. Sorbitol



D-glucose D-sorbitol

Sorbitol is produced by high-pressure catalytic hydrogenation of glucose derived from cornstarch. It can also be produced as a co-product with mannitol if invert sugar (50% glucose, 50% fructose) is used as raw material.

Toothpaste, toiletries, and cosmetics make up the largest sorbitol use (35%). Others uses include confections and food (30%), ascorbic acid (15%), industrial surfactants (10%), and pharmaceuticals (7%).

93. Sodium Tripolyphosphate (STPP)

Sodium tripolyphosphate is made by the reaction of phosphoric acid and sodium carbonate in the proper amounts to give a 1:2 ratio of monosodium and disodium phosphates and then heating to effect dehydration at 300-500°C.

$$2H_3PO_4 + Na_2CO_3 \longrightarrow 2NaH_2PO_4 + H_2O + CO_2$$

$$4H_3PO_4 + 4Na_2CO_3 \longrightarrow 4Na_2HPO_4 + 4H_2O + 4CO_2$$

$$NaH_2PO_4 + 2Na_2HPO_4 \longrightarrow 2Na_5P_3O_{10} + 2H_2O$$

STPP is used primarily as a builder for detergents, including dishwashing detergents (45%) and industrial and institutional detergents (31%). It also has food uses (13%). Up to 1988 it was in the top 50 chemicals because of its powerful ability to sequester dipositive ions in hard water, but it causes eutrophication of lakes and has been replaced in most detergents by other compounds.

94. Chloroform

Chloroform is produced by the chlorination of methylene chloride, which in turn is made by the chlorination of methyl chloride and methane.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

The main use of chloroform is in the manufacture of HCFC-22 (98%, 70:30 refrigerants: polymers). See Chapter 12, Section 4.

95. Bromine

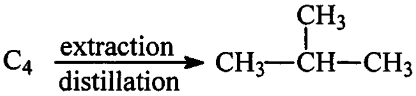
Bromine is present in brines as sodium bromide. The brines are heated to about 90°C and treated with chlorine to oxidize the bromide ions. The elemental bromine is then separated from the brine solution by blowing out with steam or air. The crude bromine—containing water, chlorine and organic matter—is purified, typically by a distillation process, and then dried with concentrated sulfuric acid. About 95% of the bromine is recovered from the brine.

$$2NaBr + Cl_2 \longrightarrow Br_2 + 2NaCl$$

Bromine is primarily used in flame-retardants (40%). It is also used in drilling fluids (24%), brominated agricultural chemicals (13%), and biocides/water treatment (7%).

96. Isobutane

Isobutane can be isolated from the petroleum C_4 fraction or from natural gas by extraction and distillation.



$$C_4 \xrightarrow[\text{distillation}]{\text{extraction}} CH_3{-}\overset{\overset{\large CH_3}{|}}{C}H{-}CH_3$$

There are two major uses of isobutane. Dehydrogenation to isobutylene is a large use. The isobutylene is then converted into the gasoline additive methyl *t*-butyl ether. Isobutane is also oxidized to the hydroperoxide and then reacted with propylene to give propylene oxide and *t*-butyl alcohol. The *t*-butyl alcohol can be used as a gasoline additive, or dehydrated to isobutylene. See Chapter 8, Section 5.

97. Hydrofluoric Acid

Fluorspar (CaF_2), 20% oleum, and sulfuric acid are heated in a horizontal rotating drum.

$$CaF_2 + H_2SO_4 \xrightarrow{250\text{-}300°C} 2HF + CaSO_4$$

Uses are for fluorocarbons (66%), alumina (14%), petroleum alkylation catalysis (4%), stainless steel pickling (4%), and uranium chemical production (2%).

98. 1-Butene

The steam-cracking of naphtha and catalytic cracking in the refinery produce the C_4 stream, which includes butane, l-butene (butylene), *cis*- and *trans*-2-butene, isobutylene, and butadiene. l-Butene can be separated by extracting the isobutylene with sulfuric acid and distilling the l-butene away from butane and butadiene. About 54% is made this way. See Chapter 8, Section 4.1. It is also made by Ziegler ethylene oligomerization with other longer linear alpha olefins (25%). Shell uses a proprietary non-Ziegler oligomerization (21%).

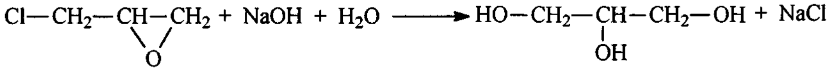
$$C_nH_{2n+2} \xrightarrow{\Delta} CH_3-CH_2-CH=CH_2 + H_2$$

l-Butene is used as a comonomer to make polyethylene. About 65% is used for both LLDPE and HDPE (93:7). It is also used to make polybutene-l (13%), valeraldehyde (pentanal) by the oxo process (12%), and butylene oxide (1%).

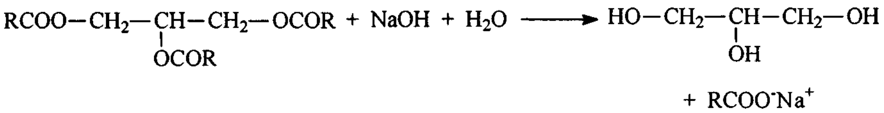
99. Glycerol

Approximately 27% of glycerol (glycerin) comes from a synthetic process, the hydrolysis of epichlorohydrin. The remaining 73% is made from fats as a by-product of soap manufacture.

(1)



(2)



$$\mathrm{RCOO-CH_2-\underset{OCOR}{CH}-CH_2-OCOR + NaOH + H_2O \longrightarrow HO-CH_2-\underset{OH}{CH}-CH_2-OH + RCOO^-Na^+}$$

Glycerol is used for drugs, personal care (including toothpaste), skin, and hair care products (42%), food and beverages (18%), tobacco (13%), polyether polyols for urethanes (11%), and alkyd resins (6%).

100. Ferric Chloride

Ferric chloride is largely produced as a by-product of pickling steel and of titanium dioxide pigment production. It can also be produced by direct methods. The traditional method, known as direct chlorination, produces anhydrous ferric chloride and involves the reaction of dry chlorine with red-hot iron.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

Municipal wastewater treatment (59%), municipal potable water treatment (22%), and industrial water treatment (8%) are the main applications for ferric chloride.

Suggested Readings

Chemical Economics Handbook gives production, uses, and prices for chemicals.

Chemical Profiles and *Chemical Prices* series in *Chemical Marketing Reporter* provide many production estimates, use patterns, and prices for chemicals.

Chenier, P.J.; Artibee, D.S. *J. Chem. Educ.* **1988**, *65*, 244-250.

Chenier, P.J.; Artibee, D.S. *J. Chem. Educ.* **1988**, *65*, 433-436.

Facts and Figures, an annual series in *Chemical and Engineering News*, gives production for some chemicals.

Chapter 14

Basic Polymer Chemistry: Thermoplastics

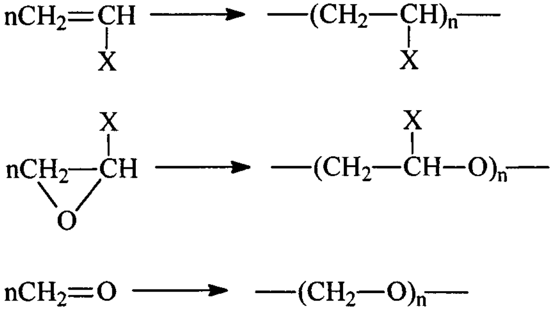
1. DEFINITIONS AND CLASSES

To begin our discussion of polymers we introduce some of the words used to describe different types of polymers. These terms will be used throughout our discussions of this subject, which will be quite detailed. The polymer industry stands out above all others as a consumer of heavy organic chemicals. The U.S. polymer industry produces over 100 billion lb of polymers and 50% of industrial chemists work with polymers. Thus we can see the importance of being acquainted with the polymers used in industry.

Polymers can be subdivided into a number of types. They may be specified as thermoplastic or thermoset, as linear or cross-linked depending on their structure. They may be step growth or chain growth, addition or condensation polymers depending on their mechanism of formation. They may be classed as block, graft, regular, random, and isotactic, syndiotactic, or atactic by their structures. Similarly, polymer processes may be free radical, cationic, anionic, metal complex, metal oxide, or metallocene catalyzed. The procedure or technique by which they are made may be bulk, solution, suspension, or emulsion polymerization. Finally, they may be classified by their end properties and uses as plastics, fibers, elastomers, coatings, or adhesives. In this and the next chapter we will try to clarify all these terms as we study polymers and give you numerous examples. Then we will be in position to study their end uses in detail by taking a separate look at plastics, fibers, elastomers, coatings, and adhesives.

To begin, *polymers* may be defined as substances that have repeating units and high molecular weight. *Polymerization* is the joining together of many small molecules to form very large ones with these repeating units. Perhaps the most important subdivision of polymerization is into chain growth or addition polymerization and step growth or condensation polymerization. The older designation of addition and condensation are not quite as accurate as chain and step growth.

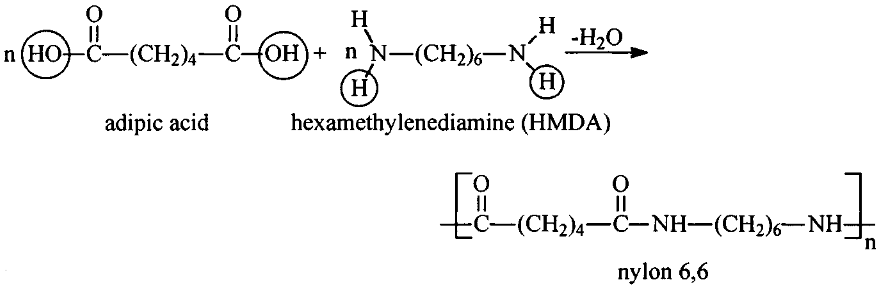
Chain growth polymerization is characterized by the fact that the intermediates in the process—free radicals, ions, or metal complexes—are transient and cannot be isolated. Once a chain is initiated, monomer units add on to growing chains very quickly, and the molecular weight of that unit builds up 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 low concentration of growing chains. Chain 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 this way. There is no net loss of atoms in the polymer.



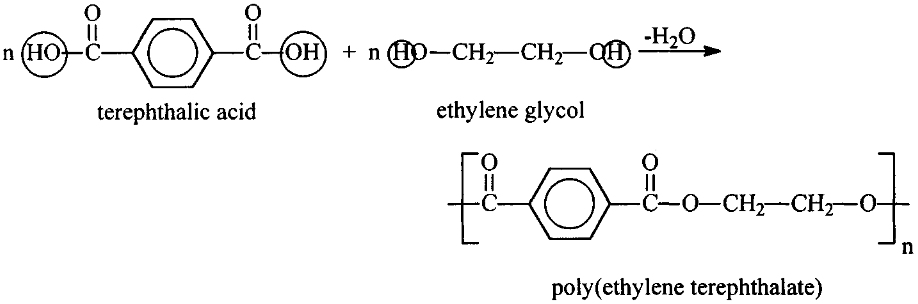
$$nCH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow -(CH_2-\underset{X}{\underset{|}{CH}})_n-$$

$$nCH_2{=}O \longrightarrow -(CH_2-O)_n-$$

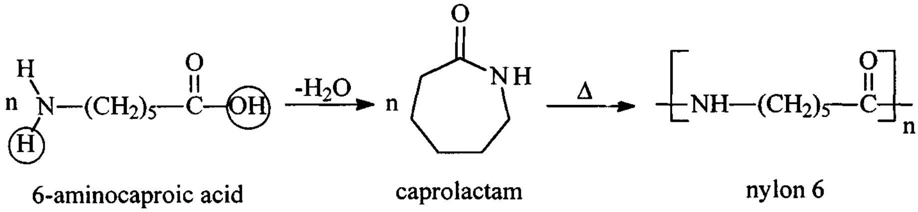
Step growth polymerization occurs because of reactions between molecules containing functional groups. This can be stopped at any time and low molecular weight products can be isolated (oligomers). The monomer does not decrease steadily in concentration; rather, it disappears early in the reaction because of the ready formation of oligomers. Long reaction times gradually 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. Usually in step polymerization a small molecule such as water is lost as two monomers combine, but this is not always so. Common examples of step growth or condensation polymers are polyamides (nylons) and polyesters.



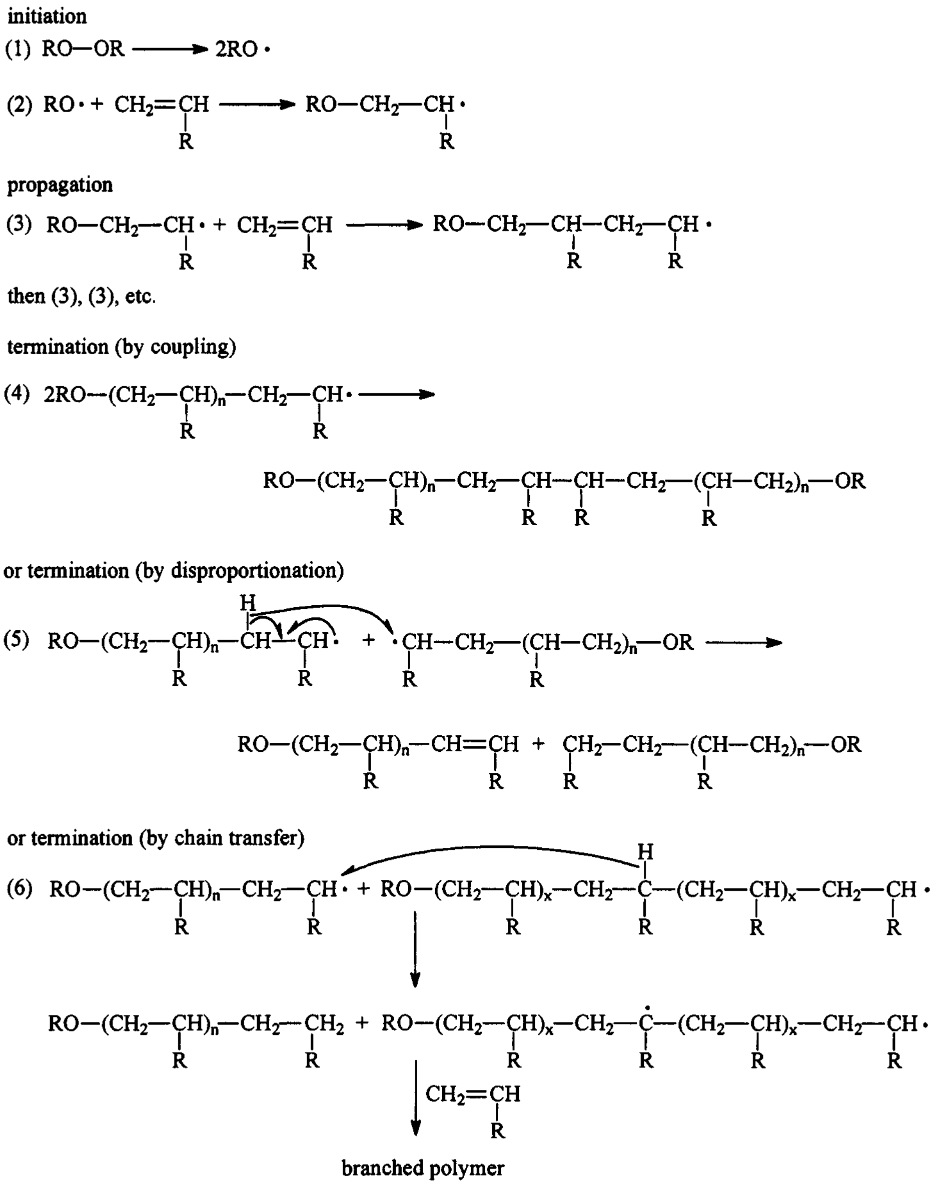
$$n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + n\,HN(H)-(CH_2)_6-N(H)H \xrightarrow{-H_2O} \left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\right]_n$$



The polymerization of caprolactam to nylon 6 is an example of a step polymerization that does not lose a molecule of water. Oligomers can be isolated at any time, which is clearly a step reaction. If we recall that it is actually the polymerization of 6-aminocaproic acid, then we can see that it is indeed a step polymerization with loss of water.



First, let us treat in more detail the different types of chain or addition polymerizations and then later discuss as a unit the step or condensation polymerizations.



$$(1)\ \mathrm{RO{-}OR} \longrightarrow \mathrm{2RO\cdot}$$

$$(2)\ \mathrm{RO\cdot} + \mathrm{CH_2{=}\underset{R}{CH}} \longrightarrow \mathrm{RO{-}CH_2{-}\underset{R}{CH}\cdot}$$

$$(3)\ \mathrm{RO{-}CH_2{-}\underset{R}{CH}\cdot} + \mathrm{CH_2{=}\underset{R}{CH}} \longrightarrow \mathrm{RO{-}CH_2{-}\underset{R}{CH}{-}CH_2{-}\underset{R}{CH}\cdot}$$

$$(4)\ \mathrm{2RO{-}(CH_2{-}\underset{R}{CH})_n{-}CH_2{-}\underset{R}{CH}\cdot} \longrightarrow \mathrm{RO{-}(CH_2{-}\underset{R}{CH})_n{-}CH_2{-}\underset{R}{CH}{-}\underset{R}{CH}{-}CH_2{-}(\underset{R}{CH}{-}CH_2)_n{-}OR}$$

$$(5)\ \mathrm{RO{-}(CH_2{-}\underset{R}{CH})_n{-}\overset{H}{CH}{-}\underset{R}{CH}\cdot} + \mathrm{\cdot\underset{R}{CH}{-}CH_2{-}(\underset{R}{CH}{-}CH_2)_n{-}OR} \longrightarrow \mathrm{RO{-}(CH_2{-}\underset{R}{CH})_n{-}CH{=}\underset{R}{CH}} + \mathrm{\underset{R}{CH_2}{-}CH_2{-}(\underset{R}{CH}{-}CH_2)_n{-}OR}$$

$$(6)\ \mathrm{RO{-}(CH_2{-}\underset{R}{CH})_n{-}CH_2{-}\underset{R}{CH}\cdot} + \mathrm{RO{-}(CH_2{-}\underset{R}{CH})_x{-}CH_2{-}\underset{R}{\overset{H}{C}}{-}(CH_2{-}\underset{R}{CH})_x{-}CH_2{-}\underset{R}{CH}\cdot} \longrightarrow \mathrm{RO{-}(CH_2{-}\underset{R}{CH})_n{-}CH_2{-}\underset{R}{CH_2}} + \mathrm{RO{-}(CH_2{-}\underset{R}{CH})_x{-}CH_2{-}\underset{R}{\overset{\bullet}{C}}{-}(CH_2{-}\underset{R}{CH})_x{-}CH_2{-}\underset{R}{CH}\cdot} \xrightarrow{\mathrm{CH_2{=}\underset{R}{CH}}} \text{branched polymer}$$

Figure 14.1 Mechanism of olefin free radical polymerization.

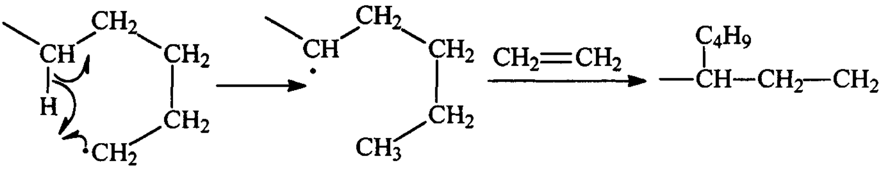
2. CHAIN GROWTH POLYMERIZATION

2.1 Free Radical Initiation

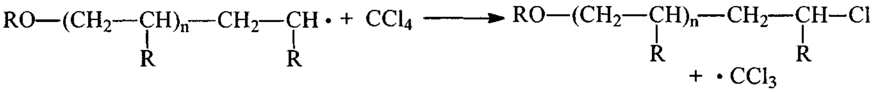
Many polymerizations are initiated by free radicals, especially alkoxy radicals formed by thermal decomposition of peroxides. A general mechanism for olefin free radical polymerization with initiation, propagation, and termination is given in Fig. 14.1.

After the initial reaction of a radical with the first monomer unit, a series of propagation steps follows, rapidly building up the molecular weight and degree of polymerization. The important part of this mechanism is therefore the (3), (3), etc. noted. This is what makes the polymer! With unsymmetrical monomers the "head-to-tail" addition is preferred because whatever it is in the R group that stabilized the radical once will do so each time a propagation step happens.

Chain termination can occur via coupling of two radicals. It may occur by disproportionation, that is, a hydrogen atom transfer from a carbon neighboring one radical site to another radical site, forming one saturated and one unsaturated end group. It may also be brought about by a chain transfer. This is simply a hydrogen atom transfer from an "internal" carbon site from a so-called "finished" chain. If this happens, not only does it terminate the growing chain, but it also induces a branch in what was the "finished" chain. Reaction of this new radical will therefore occur nonlinearly. Branching can have a marked effect on polymer properties. It can also occur by hydrogen atom abstraction from a carbon atom in the same chain as the radical site, provided a stable, nonstrained six-membered ring transition state can be maintained. Low-density polyethylene (LDPE) is therefore characterized by C_4 branches.



Finally, chain transfer is undesirable except when it is used intentionally to limit molecular weight by adding good chain transfer agents such as carbon tetrachloride. Here transfer of a chlorine atom limits the size of one chain and at the same time initiates formation of a new chain by the trichloromethyl radical. Instead of (3), (3), (3), etc., we get (3), (3), (7), (8), (3), (3), (7), (8), etc., with a lower average chain length.

(7) 

$$RO{-}(CH_2{-}\underset{R}{CH})_n{-}CH_2{-}\underset{R}{CH}\cdot + CCl_4 \longrightarrow RO{-}(CH_2{-}\underset{R}{CH})_n{-}CH_2{-}\underset{R}{CH}{-}Cl + \cdot CCl_3$$

(8) 

$$\cdot CCl_3 + CH_2{=}\underset{R}{CH} \longrightarrow Cl_3C{-}CH_2{-}\underset{R}{CH}\cdot$$

Mercaptans (R—S—H) and phenols (Ar—O—H) also make good chain transfer agents by breaking the S—H or O—H bonds.

A wide variety of monomer olefins can be used in free radical polymerization. Common examples are given in Fig. 14.2. You should be able to furnish the starting monomer given the structure of the polymer or vice versa.

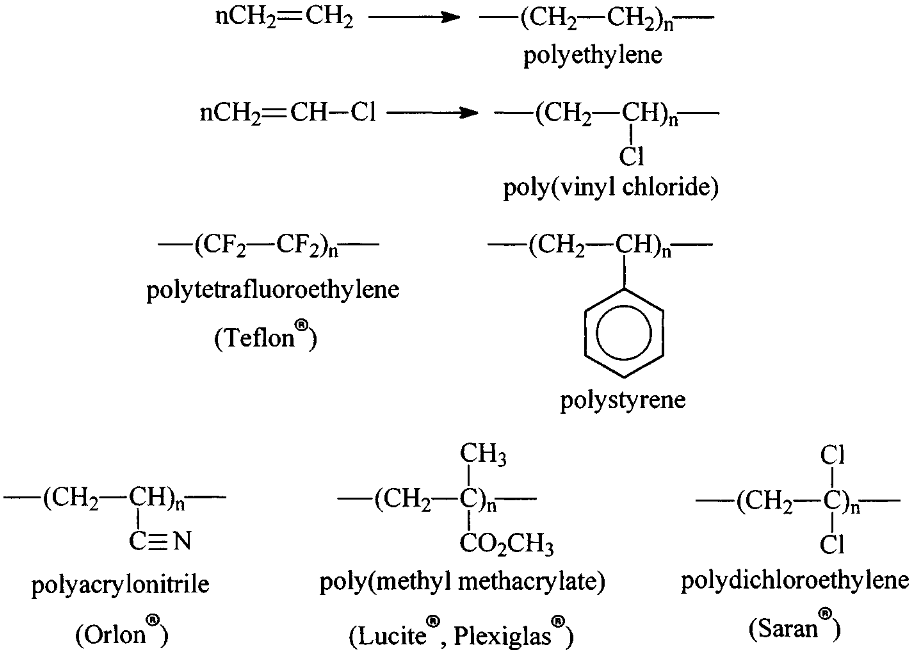
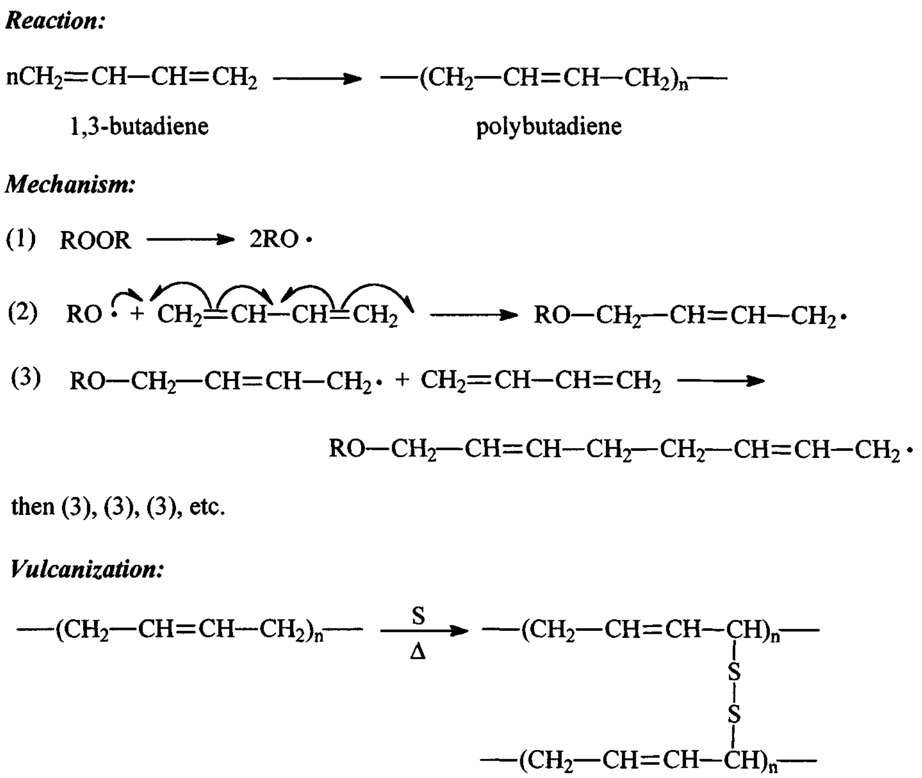


Figure 14.2 Examples of polymers from free radical processes.



Reaction:

$$n\mathrm{CH_2{=}CH{-}CH{=}CH_2} \longrightarrow \mathrm{{-}(CH_2{-}CH{=}CH{-}CH_2)_n{-}}$$

1,3-butadiene polybutadiene

Mechanism:

$$(1)\quad \mathrm{ROOR} \longrightarrow \mathrm{2RO\cdot}$$

$$(2)\quad \mathrm{RO\cdot + CH_2{=}CH{-}CH{=}CH_2} \longrightarrow \mathrm{RO{-}CH_2{-}CH{=}CH{-}CH_2\cdot}$$

$$(3)\quad \mathrm{RO{-}CH_2{-}CH{=}CH{-}CH_2\cdot + CH_2{=}CH{-}CH{=}CH_2} \longrightarrow \mathrm{RO{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2\cdot}$$

then (3), (3), (3), etc.

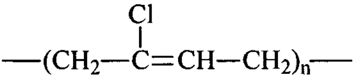
Vulcanization:

$$\mathrm{{-}(CH_2{-}CH{=}CH{-}CH_2)_n{-}} \xrightarrow[\Delta]{\mathrm{S}} \begin{array}{c}\mathrm{{-}(CH_2{-}CH{=}CH{-}CH)_n{-}} \\ \mathrm{|} \\ \mathrm{S} \\ \mathrm{|} \\ \mathrm{S} \\ \mathrm{|} \\ \mathrm{{-}(CH_2{-}CH{=}CH{-}CH)_n{-}}\end{array}$$

Figure 14.3 Free radical polymerization of 1,3-butadiene.

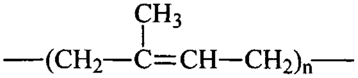
2.2 Free Radical Polymerization of Dienes

Conjugated dienes such as 1,3-butadiene very readily polymerize free radically. The important thing to remember here is that there are double bonds still present in the polymer. This is especially important in the case of elastomers (synthetic rubbers) because some cross-linking with disulfide bridges (vulcanization) can occur in the finished polymer at the allylic sites still present to provide elastic properties to the overall polymers. Vulcanization will be discussed in detail in Chapter 18, Section 3. The mechanism shown in Fig. 14.3 demonstrates only the 1,4-addition of butadiene for simplicity. 1,2-Addition also occurs, and the double bonds may be *cis* or *trans* in their stereochemistry. Only with the metal complex catalysts will the stereochemistry be regular. Other examples of common polymerized dienes are polychloroprene and polyisoprene.



$$—(CH_2—\overset{Cl}{C}=CH—CH_2)_n—$$

polychloroprene
(Neoprene®, Duprene®)

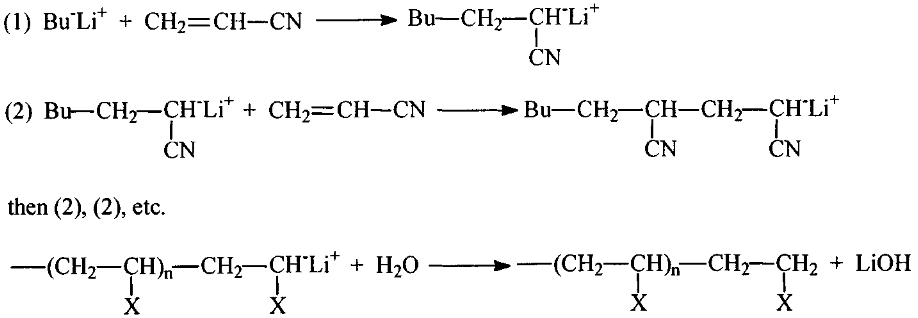


$$—(CH_2—\overset{CH_3}{C}=CH—CH_2)_n—$$

polyisoprene

2.3 Ionic Initiation

Although free radical initiation is by far the most common type of catalysis, accounting for about half of all polymerizations, other types of initiation are commonly employed, since some monomers cannot be polymerized well free radically. For instance, propylene cannot be free radically polymerized to a high molecular weight because of its reactive allylic hydrogens, which easily undergo chain transfer. As a general rule olefins containing an electron-withdrawing group can, in addition to free radical polymerization, use anionic initiation. Examples of anionic initiators commonly employed are *n*-butyllithium, sodium amide, and sodium or potassium metal in liquid ammonia or naphthalene. The mechanism for polymerization of acrylonitrile using *n*-butyllithium is given in Fig. 14.4. We can see that the electron-withdrawing cyano group by its inductive effect is able to stabilize the intermediate negative charges on the neighboring carbon for each propagation step and aid the polymerization process.



$$(1)\ Bu^-Li^+ + CH_2=CH—CN \longrightarrow Bu—CH_2—\underset{CN}{CH^-}Li^+$$

$$(2)\ Bu—CH_2—\underset{CN}{CH^-}Li^+ + CH_2=CH—CN \longrightarrow Bu—CH_2—\underset{CN}{CH}—CH_2—\underset{CN}{CH^-}Li^+$$

then (2), (2), etc.

$$—(CH_2—\underset{X}{CH})_n—CH_2—\underset{X}{CH^-}Li^+ + H_2O \longrightarrow —(CH_2—\underset{X}{CH})_n—CH_2—\underset{X}{CH_2} + LiOH$$

Figure 14.4 Anionic polymerization of acrylonitrile.

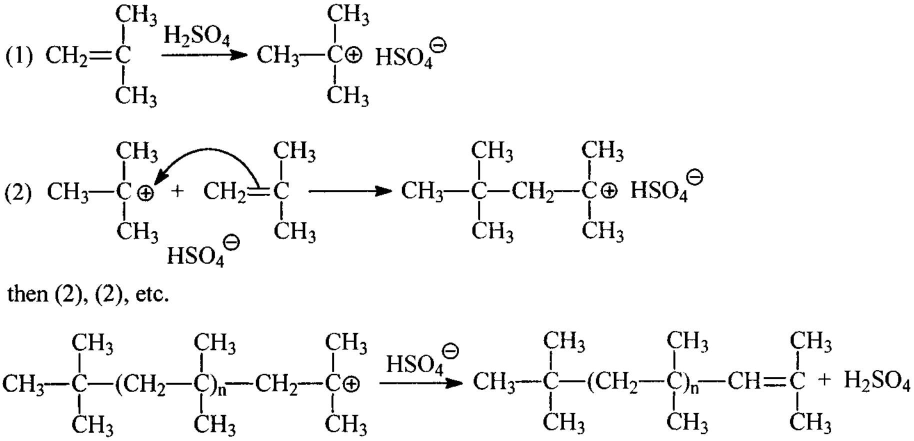
Although this mechanism is an oversimplification, it does give the basic idea. Chain termination is more complicated than in free radical polymerization. Coupling and disproportionation are not possible since two negative ions cannot easily come together. Termination may result from a proton transfer from a solvent or weak acid, such as water, sometimes present in just trace amounts.

Actually it is well known that ionic polymerization need not terminate. They have been termed "living" polymers. If further monomer is added, weeks or months later there will be a further molecular weight increase as the polymer chains grow longer. As long as the counterion is present (lithium in the preceding case), the anionic end group is perfectly stable.

Ionic polymerization may also occur with cationic initiations such as protonic acids like HF and H_2SO_4 or Lewis acids like BF_3, $AlCl_3$, and $SnCl_4$. The polymerization of isobutylene is a common example, shown in Fig. 14.5. Note that the two inductively donating methyl groups stabilize the carbocation intermediate. Chain termination, if it does occur, usually proceeds by loss of a proton to form a terminal double bond. This regenerates the catalyst.

2.4 Metal Complex Initiation (Ziegler-Natta Catalysis)

In the early 1950s Karl Ziegler in Germany and Giulio Natta in Italy found catalysts that polymerized olefins and dienes with stereoregularity and with mild polymerization conditions. For this revolutionary discovery they both won the Nobel Prize. Let us take the example of propylene, which we



$$(1)\ CH_2{=}\overset{CH_3}{\underset{CH_3}{C}} \xrightarrow{H_2SO_4} CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{\oplus}\ HSO_4^{\ominus}$$

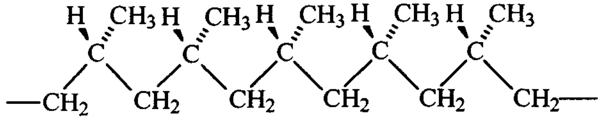
$$(2)\ CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{\oplus} + CH_2{=}\overset{CH_3}{\underset{CH_3}{C}} \ \ HSO_4^{\ominus} \longrightarrow CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{\oplus}\ HSO_4^{\ominus}$$

$$CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}(CH_2{-}\overset{CH_3}{\underset{CH_3}{C}})_n{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{\oplus} \xrightarrow{HSO_4^{\ominus}} CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}(CH_2{-}\overset{CH_3}{\underset{CH_3}{C}})_n{-}CH{=}\overset{CH_3}{\underset{CH_3}{C}} + H_2SO_4$$

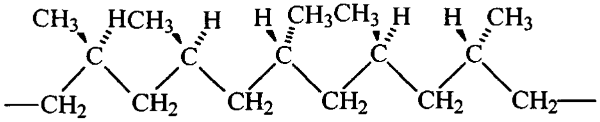
Figure 14.5 Cationic polymerization of isobutylene.

have already said is not easily polymerized free radically. Not only was high molecular weight polypropylene obtained, but it was isotactic, with the methyls arranged stereoregularly. This is to be contrasted to atactic (random) or syndiotactic (alternating) structures.

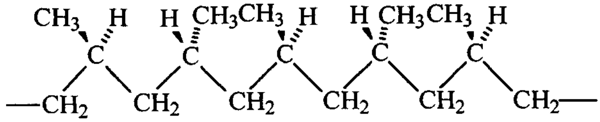
isotactic:



atactic:



syndiotactic:



Ziegler-Natta catalysts are primarily complexes of a transition metal halide and an organometallic compound whose structure is not completely understood for all cases. Let us use as an example $TiCl_4$ and R_3Al. The mechanism of the polymerization catalysis is somewhat understood. This is shown in Fig. 14.6. The titanium salt and the organometallic compound react to give a pentacoordinated titanium complex with a sixth empty site of

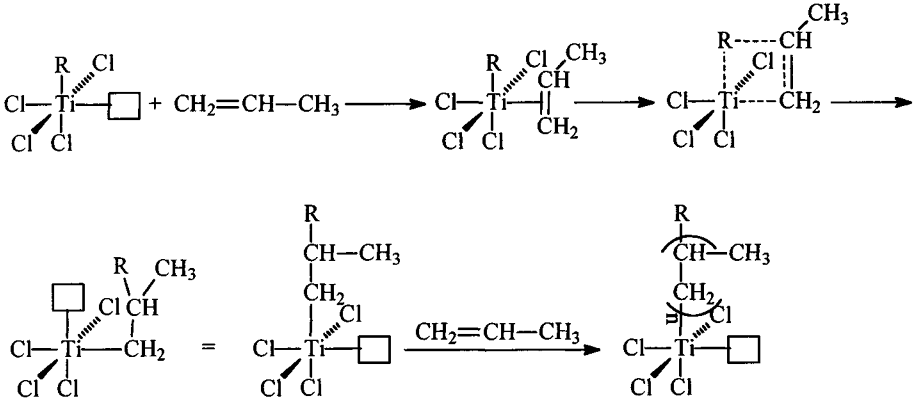


Figure 14.6 Ziegler-Natta catalysis in the polymerization of propylene.

the octahedral configuration. The monomer alkene is then complexed with the titanium and finally inserts between the titanium and alkyl group, leaving a new empty site for repetition of the process.

The versatility of Ziegler-Natta catalysis is shown in the polymerization of butadiene. Polybutadiene may have either a 1,2 or 1,4 configuration. The 1,4 polymer has a double bond as part of the main chain and this can be atactic, isotactic, or syndiotactic. Thus many different polybutadienes can be made and all of them have been made with the aid of Ziegler-Natta catalysts.

2.5 Metal Oxide Initiation

Researchers for Standard Oil of Indiana have developed a molybdenum oxide catalyst and for Phillips Petroleum a chromic oxide catalyst for the polymerization of polyethylene with very few branches due to cyclic hydrogen atom transfer (see this Chapter, Section 2.1). This is a much stiffer polymer and has properties substantially different from polyethylene with branches. Completely linear polyethylene formed from this type of catalysis is called high-density polyethylene (HDPE). More branched polyethylene has a much lower density because the chains cannot come as close together or be packed as tightly. An advantage over Ziegler-Natta is that this catalyst is not flammable. The main propagation step in this polymerization is a chromium-ethylene complex formation, followed by insertion of the two CH_2 units into the existing chromium-carbon bond (Fig. 14.7). Chromium d

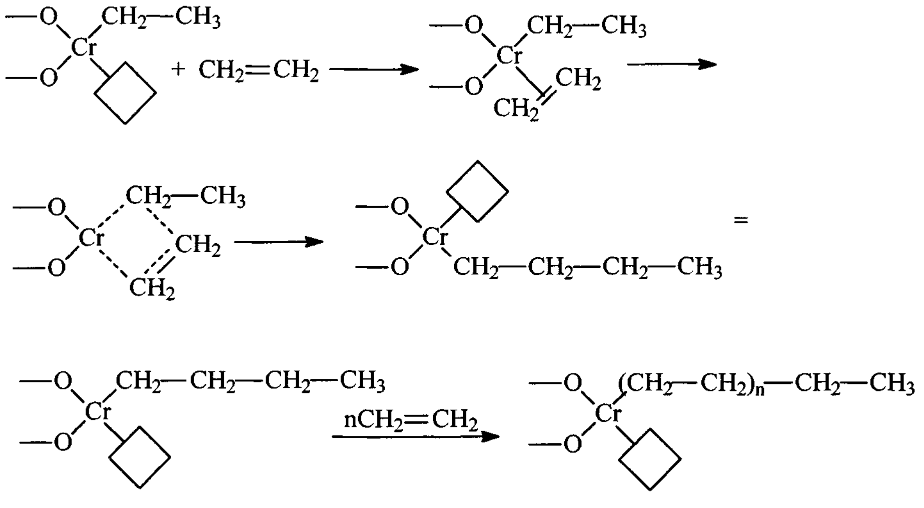


Figure 14.7 Metal oxide polymerization.

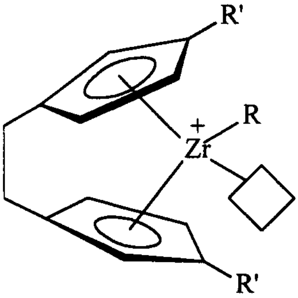
orbitals are involved in the process. It is also known that chromium is attached to a silica surface through Cr—O—Si bonds.

Sometimes a lower density polyethylene is made with both this type of catalysis or Ziegler-Natta. Branching is controlled by the addition of small amounts of 1-alkenes added to the ethylene. 1-Hexene would give a C_4 branch, 1-octene a C_6 branch, etc. If enough 1-alkene is used the polymer is called linear low-density polyethylene (LLDPE). It is made by a high-density polyethylene process but branching gives a lower density.

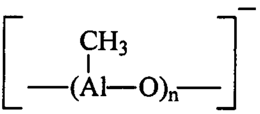
2.6 Metallocene Initiation

Metallocenes are the latest development in polymer catalysts, becoming important as recently as the 1990s. While Ziegler-Natta catalysts are heterogeneous and have many non-identical active sites, metallocenes are homogeneous and have a single type of active site for catalytic functionality. Polymers made from them have very narrow molecular weight distribution, low crystallinity, greater clarity, lower melting temperatures, better resistance to extraction, and lower taste and color. Very clear, tough films for packaging would be one example of an application.

Metallocenes have a transition metal sandwiched between two cyclopentadienyl rings. The cyclopentadienyl rings may not necessarily be parallel because of bridging. They may be further substituted to restrict access to the metal. The catalyst structure can be changed to make different polymeric properties. A typical example would be the zirconium metallocene shown below.



Metallocenes are of low activity unless they are used with a non-coordinating anion such as a methylalumoxane or borate. This non-coordinating anion can be anchored to a silica surface.



$$\left[-(\overset{\displaystyle CH_3}{\overset{|}{Al}}-O)_n- \right]^-$$

$[B(C_6F_5)_4]^-$

n = 4-20

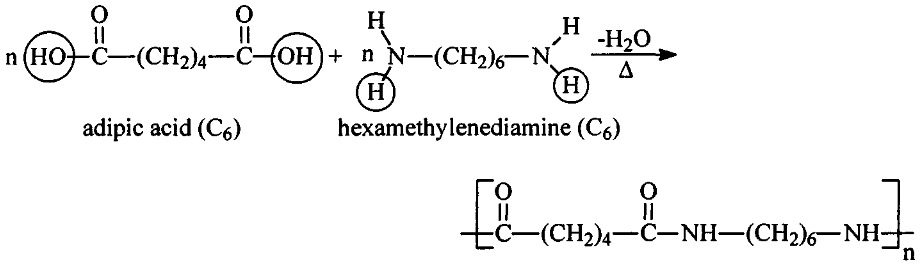
Unfortunately these are expensive catalysts and they have not yet made a serious dent in the large-scale polymer market. However, specialty applications in food packaging, personal care, and medicine are being utilized.

3. STEP GROWTH POLYMERIZATION

At the beginning of this chapter we described step growth polymerization chiefly to contrast it with chain polymerization. We now consider this subject in more detail and discuss various types of step growth polymers.

3.1 Polyamides (Nylons)

There are many naturally occurring polyamides (proteins). Synthetic work began in 1929-1930 by Carothers who worked at Du Pont. They were first interested in finding a cheap replacement for silk in women's stockings. Silk is a naturally occurring polyamide made up of a mixture of amino acid monomer units, especially glycine (44%) and alanine (40%). Wool is a protein, keratin, which contains 18 different amino acids, the highest percentage being glutamic acid (14%). Wool is also cross-linked with sulfur bridges. The first successful high molecular weight synthetic polyamide was made in 1935. Commercial production by Du Pont began in 1940. This polymer was poly(hexamethyleneadipamide), now commonly referred to as nylon 6,6.



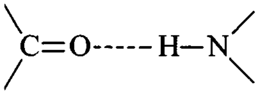
$$n\,HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + n\,\overset{H}{\underset{H}{N}}-(CH_2)_6-\overset{H}{\underset{H}{N}} \xrightarrow[\Delta]{-H_2O} \left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH \right]_n$$

adipic acid (C_6)

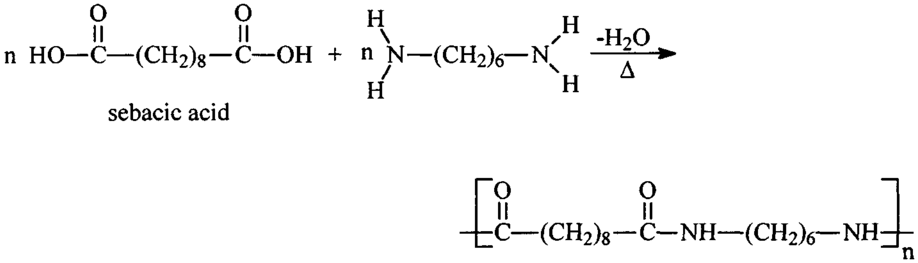
hexamethylenediamine (C_6)

nylon 6,6
molecular weight = 10,000-25,000
n = 40-110

This is an example of a common way of making nylons: reaction of a dicarboxylic acid and a diamine. The first number of the nylon nomenclature refers to the number of carbon atoms in the amine, the second to the number of carbons in the acid. Nylon 6,6 was soon found to have higher strength than any natural fiber. It has good chemical stability and a high melting point (265°C) due to hydrogen bonding of the carbonyls of one chain with the N—H groups of another.



The tensile strength (how much pressure can be applied on the ends of a fiber before it breaks) of polymers is very dependent on the molecular weight and, although nylon 6,6 was made ten years earlier, the technical production problem of obtaining good molecular weight had to be overcome before it was used as a substitute for silk. Another example of a common polyamide is nylon 6,10, used as bristles in brushes.

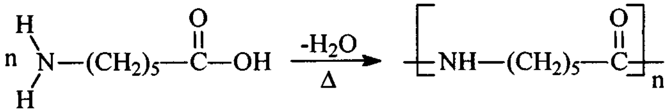


$$n\ HO-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH + n\ \underset{H}{\overset{H}{N}}-(CH_2)_6-\underset{H}{\overset{H}{N}} \xrightarrow[\Delta]{-H_2O} \left[\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\right]_n$$

sebacic acid

nylon 6,10

A second major method of producing polyamides is by using an amino acid as a monomer (amine and acid group in the same molecule) or by a ring opening of cyclic amide (lactam).

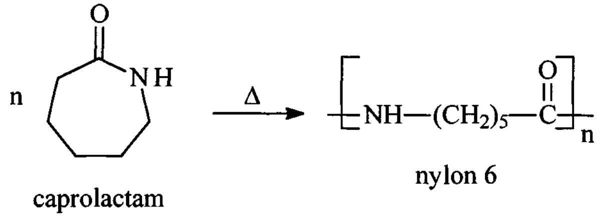


$$n\ \underset{H}{\overset{H}{N}}-(CH_2)_5-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{-H_2O} \left[NH-(CH_2)_5-\overset{O}{\overset{\|}{C}}\right]_n$$

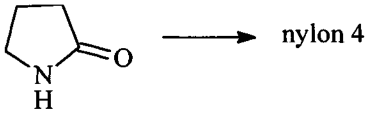
6-aminohexanoic acid

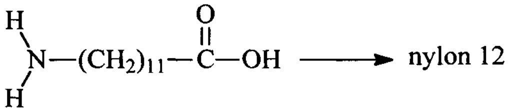
nylon 6

or:



Here only one number needs to be used in naming the nylon, designating the number of carbons in the starting amino acid or lactam. Note that the structure of nylon 6 is different from nylon 6,6. In nylon 6 all of the amine groups are "facing the same way." However, both polymers have relatively similar physical properties. Nylon 6 is not quite so strong or as high melting (mp 215°C) as nylon 6,6. But it is less expensive. It has found use in tire cords, carpet and brush fibers, and various molded articles. Other examples of single number nylons are nylon 4 and nylon 12.



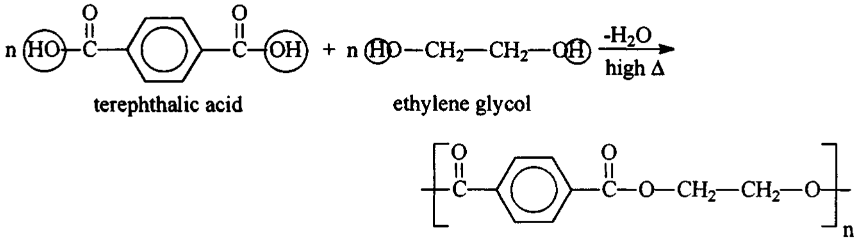


$$H_2N-(CH_2)_{11}-\overset{O}{\overset{\|}{C}}-OH \longrightarrow \text{nylon 12}$$

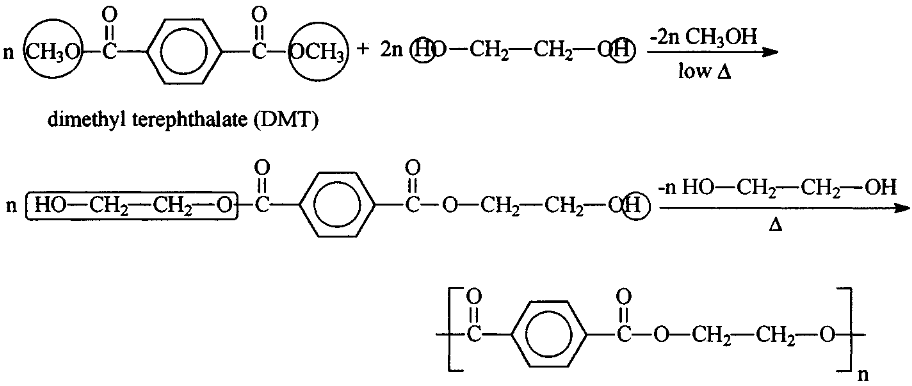
It is interesting to note that the strength and melting point of polyamides is decreased as the number of carbons in the monomer is increased. This has to do with the number of amide linkages (and hydrogen bonds) per unit of weight in the polymer. The fewer the hydrogen bonds there are between chains, the freer the molecules are to move.

3.2 Polyesters

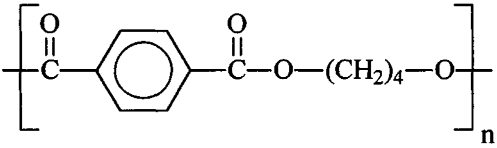
Polyesters are made in one of two ways: by either direct reaction of a diacid and a diol or ester interchange of a diester and a diol. By far the most commercially useful polyester is poly(ethylene terephthalate) (PET). Both methods are illustrated here.



or:

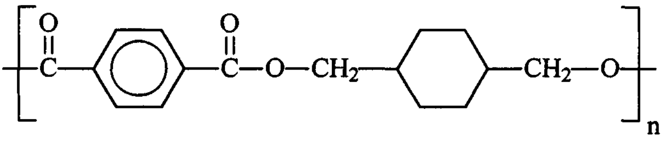


Poly(ethylene terephthalate) is known commonly by the trademarks Dacron®, Terylene®, and Fortrel® fibers and Mylar® film. The polymer melts at 270°C and has very high strength and elasticity. It is three times as strong as cellulose. It is also particularly resistant to hydrolysis (washing!) and resists creasing. Hence it has been used in clothing in all kinds of blends with cotton, wool, and other fibers. Its excellent clarity has made it useful in photographic film, overhead transparencies, and soft drink bottles. It is recyclable. Most useful polyesters have need for the strong, rigid aromatic ring in their structure since they lack the hydrogen bonding prevalent in polyamides. Other examples of polyesters are given here.



poly(tetramethylene terephthalate)

C_4 chain weaker but more flexible than C_2 link



Kodel® fiber, Kodak® film

Although we will not be discussing the mechanism of each type of step growth polymer because these reactions are very similar to the corresponding monomer chemistry, we should be aware of this analogy. For instance, an acid reacts with an alcohol under acid-catalyzed conditions by a certain well-studied and proven mechanism. This same mechanism is followed each time an ester linkage of a polyester is formed. One such transformation is outlined in Fig. 14.8. The equilibrium is shifted in the direction of the product by distillation of the water from the reaction mixture (and condensing it in a separate container—hence the name condensation polymers for this type).

3.3 Polycarbonates

The chemistry of polycarbonates is similar to the chemical behavior of polyesters. We can think of a carbonate as being a diester of carbonic acid, H_2CO_3, which is unstable itself. Polycarbonate is a strong, clear plastic used in automobiles (25%), glazing and sheet (20%), optical media (15%), appliances (8%), computers (7%), medical industry (7%), and recreation and

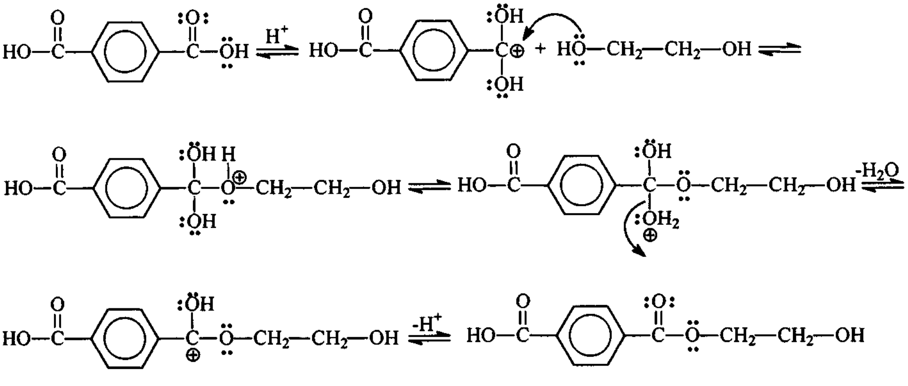
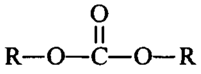


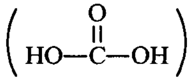
Figure 14.8 Mechanism of esterification.

safety (7%). One billion lb are made per year in the U.S. It is increasing at a rate of 6-8% per year because of its use in CDs and DVDs.



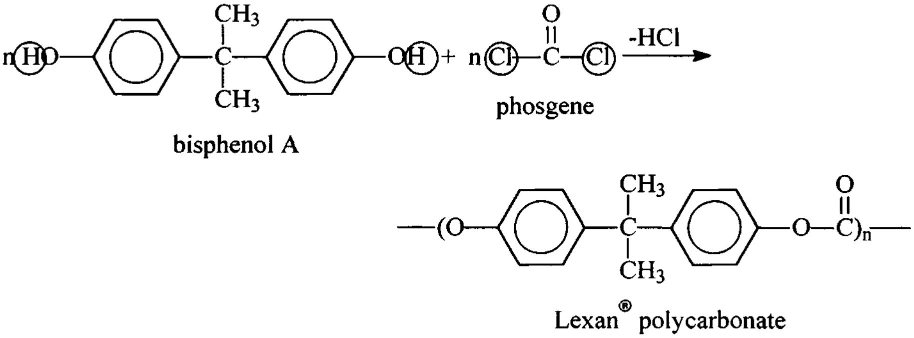
$$R-O-\overset{O}{\overset{\|}{C}}-O-R$$

a dialkyl carbonate



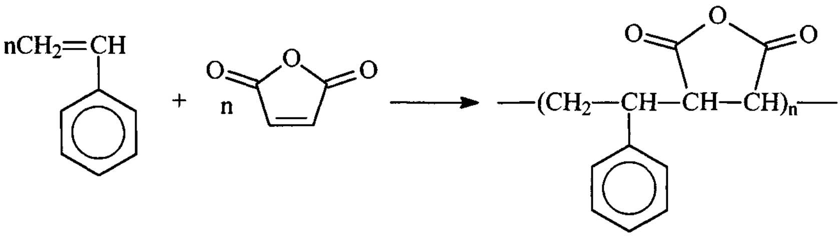
$$\left(HO-\overset{O}{\overset{\|}{C}}-OH\right)$$

carbonic acid

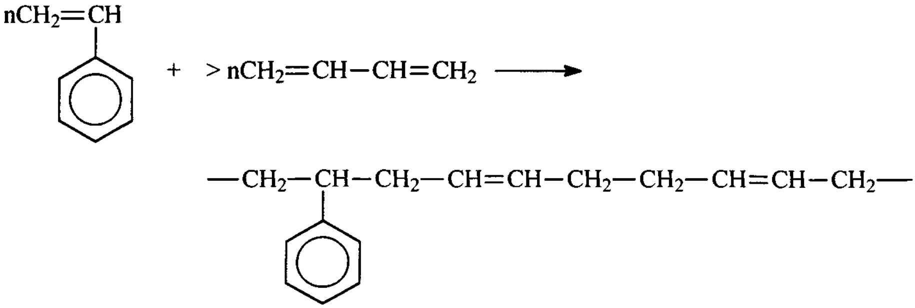


4. COPOLYMERIZATION

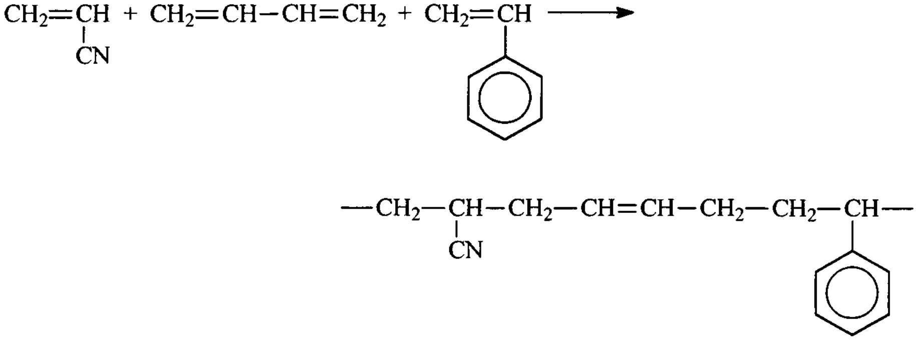
Copolymers are polymers made from two or more monomers. In *regular (or alternating) polymers* the monomer units alternate. Many step growth polymers are regular. An example of a regular chain growth copolymer is one based on maleic anhydride and styrene. The reaction rate between these two monomers is greater than the reaction of either of them with themselves. This is what causes the regularity.



To form a *random polymer* the two monomers must react with themselves at a rate comparable to that at which they react with each other. In random polymers they need not be present in equal amounts either. The most important synthetic elastomer, styrene-butadiene rubber (SBR), is a copolymer of approximately 6 mol of butadiene to 1 mol of styrene. The properties of the final polymer are changed considerably by simply changing the ratio of starting monomers.



ABS resin (acrylonitrile-butadiene-styrene) is an example of a random copolymer with three different monomer units, not necessarily present in the same amount.



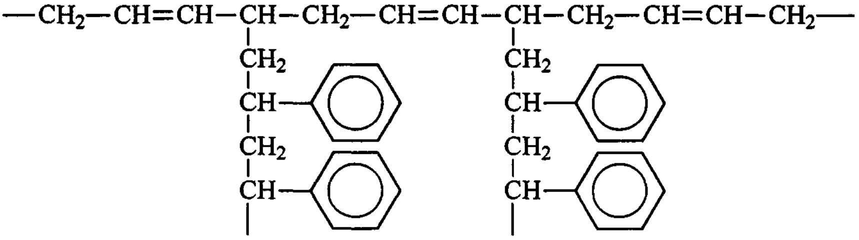
Another type of copolymer is a *block copolymer*. Here a low molecular weight polymer may be extended by reaction with a new monomer. Recall that we talked about "living" polymers in this Chapter, Section 2.3. If, for example, we polymerized styrene alone first, then added some butadiene and polymerized it further, we would have a number of styrene units bundled together and a number of butadienes also together.

—S—S—S—S—S—B—B—B—S—S—S—S—S—B—B—

This block copolymer has substantially different physical properties as compared to a random styrene-butadiene copolymer.

Lastly, there are *graft copolymers* that result when a polymer chain of one monomer is grafted on to an existing polymer backbone by creation of a free radical site along the backbone that initiates growth of a polymer chain.

The concept is similar to the grafting of plants in botany. To form a styrene-butadiene graft polymer, already polymerized butadiene is dissolved in monomeric styrene and an initiator is added. Because polybutadiene readily undergoes chain transfer at the allylic sites, polystyrene chains grow on the polybutadiene backbone. This forms high impact polystyrene, a low cost plastic that is otherwise too brittle without the grafting.



5. POLYMERIZATION PROCEDURES

Polymers may be made by four different experimental techniques: bulk, solution, suspension, and emulsion processes. They are somewhat self-explanatory. In *bulk polymerization* only the monomers and a small amount of catalyst is present. No separation processes are necessary and the only impurity in the final product is monomer. But heat transfer is a problem as the polymer becomes viscous. In *solution polymerization* the solvent dissipates the heat better, but it must be removed later and care must be used in choosing the proper solvent so it does not act as a chain transfer agent. In *suspension polymerization* the monomer and catalyst are suspended as droplets in a continuous phase such as water by continuous agitation. Finally, *emulsion polymerization* uses an emulsifying agent such as soap, which forms micelles where the polymerization takes place.

Suggested Readings

Carraher, *Seymour/Carraher's Polymer Chemistry: An Introduction*, pp. 230-357.

Wittcoff and Reuben, *Industrial Organic Chemicals*, pp. 404-444.

Chapter 15

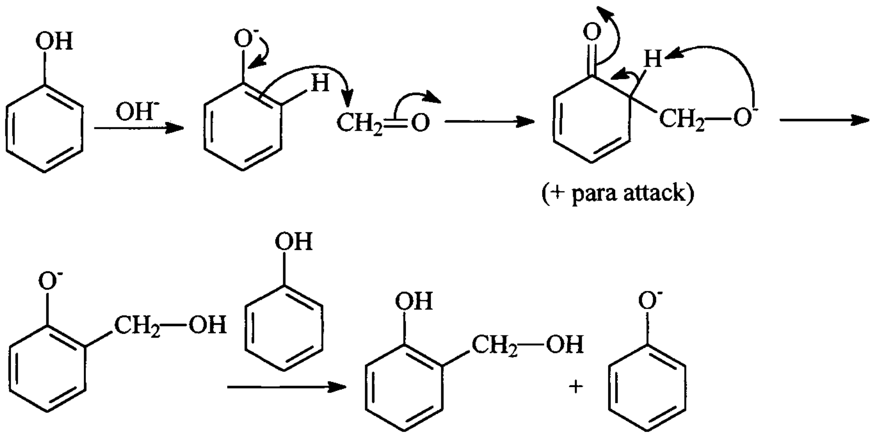
Basic Polymer Chemistry: Thermosets

In the previous chapter we talked about linear polymers and have mentioned the concept of cross-linking only in passing. Linear polymers are usually *thermoplastic*: they soften or melt when heated and will dissolve in suitable solvents. They can be remelted and shaped into their finished product with no further chemical reactions. *Thermoset resins*, those having elaborately cross-linked three-dimensional structures, set or harden by undergoing a chemical reaction during the manufacture of finished products. They decompose on heating and are infusible and insoluble. Their chemistry and physical properties are quite different from thermoplastic polymers. The important ones are now discussed.

1. PHENOL-FORMALDEHYDE POLYMERS (PHENOLIC RESINS)

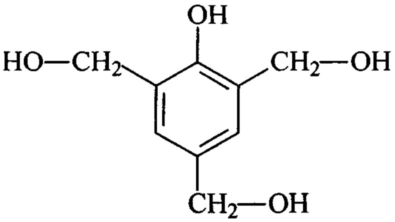
1.1 One-Stage Resins

These copolymers of phenol and formaldehyde were the first fully synthetic polymers made. They were discovered in 1910 by Leo Baekeland and given the tradename Bakelite.® They may be prepared in two ways, both involving step growth polymerization. A "one-stage" resin may be obtained using an alkaline catalyst and excess formaldehyde to form linear, low molecular weight resol resins. Slight acidification and further heating causes the curing process to give a highly cross-linked thermoset. This complex reaction is summarized here in steps. First we see the alkaline catalyst with phenol and formaldehyde reacting to form methylolphenols.



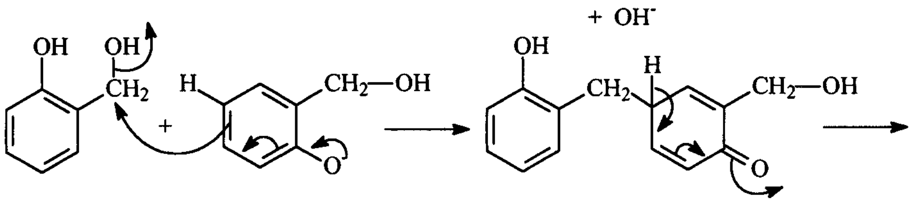
o-methylolphenol (+ *p*)

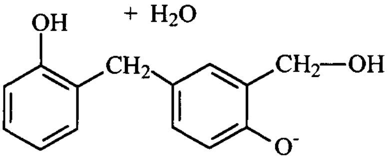
The *o*- and *p*-methylolphenols are more reactive toward formaldehyde than the original phenol and rapidly undergo further reaction to give di- and trimethylol derivatives.



trimethylolphenol

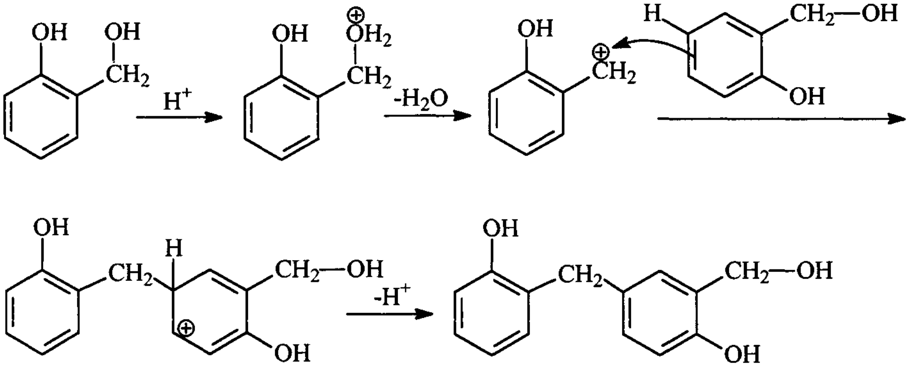
The methylolphenols will react to form di- and trinuclear phenols at still free ortho and para positions.



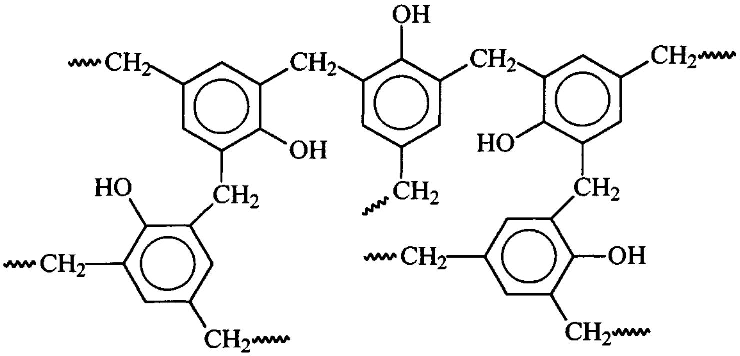


resol

Although these resols can be cross-linked under basic conditions, acidification and further heating is preferred. The mechanism of polymerization under acidic conditions involves carbocation chemistry.



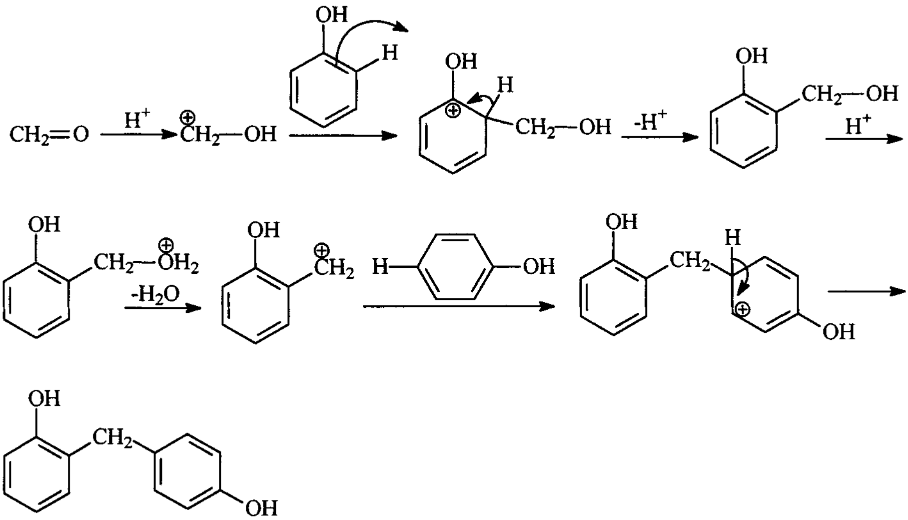
The final structure of the product is very highly branched. Most linkages between aromatic rings are —CH_2— groups, though some —CH_2—O—CH_2— linkages are present.



a phenolic or Bakelite® resin

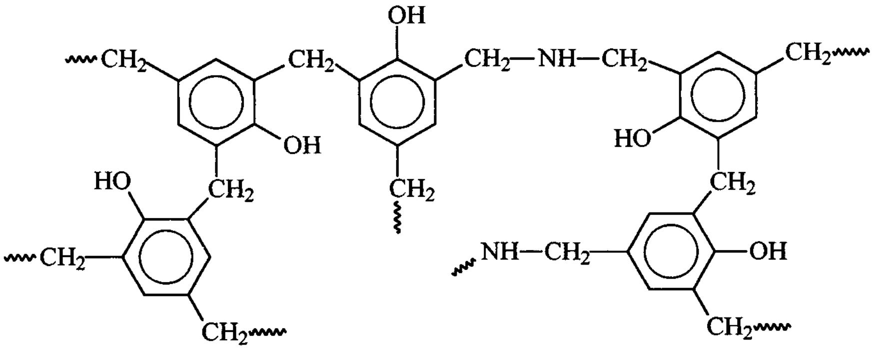
1.2 Two-Stage Resins

The second method, called a "two-stage" process, uses an acid catalyst and excess phenol to give a linear polymer that may be stored or sold. These are called novolacs and have no free methylol groups for cross-linking.



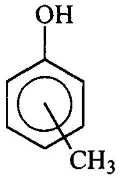
novolac

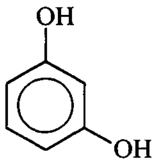
Thus in a separate second part of this "two-stage" process a cross-linking agent is added and further reaction occurs. Although formaldehyde may be added, quite often hexamethylenetetramine is used, which decomposes to formaldehyde and ammonia. Occasional nitrogen bridges occur in the final structure of some phenolics made by this method.

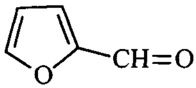


a phenolic

Other modifications in making phenolics are the incorporation of cresols or resorcinol as the phenol and acetaldehyde or furfural as the aldehyde.

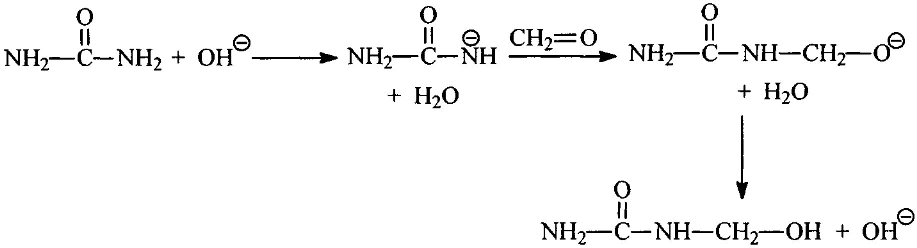

cresols


resorcinol


furfural

2. UREA-FORMALDEHYDE POLYMERS (UREA RESINS)

Urea will give cross-linked resins with formaldehyde. Methylolureas are formed first under alkaline conditions.

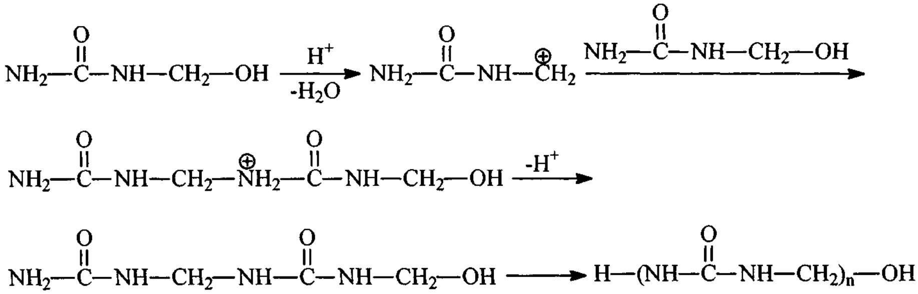


$$\mathrm{NH_2-\overset{O}{\overset{\|}{C}}-NH_2 + OH^{\ominus} \longrightarrow \underset{+\ H_2O}{NH_2-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{N}H} \xrightarrow{CH_2=O} \underset{+\ H_2O}{NH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-O^{\ominus}}}$$

$$\downarrow$$

$$\mathrm{NH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-OH + OH^{\ominus}}$$

Continued reaction under acidic conditions gives a fairly linear, low molecular weight intermediate polymer.

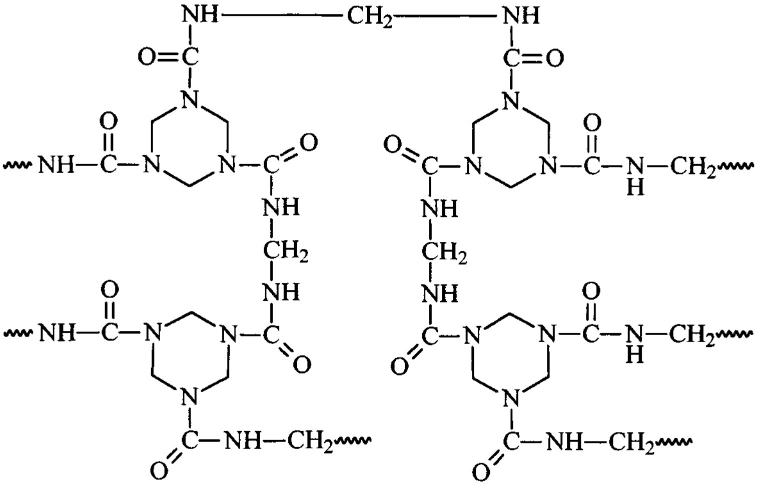


$$\mathrm{NH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-OH \xrightarrow[-H_2O]{H^+} NH_2-\overset{O}{\overset{\|}{C}}-NH-\overset{\oplus}{C}H_2 \xrightarrow{NH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-OH}}$$

$$\mathrm{NH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{\oplus}{N}H_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-OH \xrightarrow{-H^+}}$$

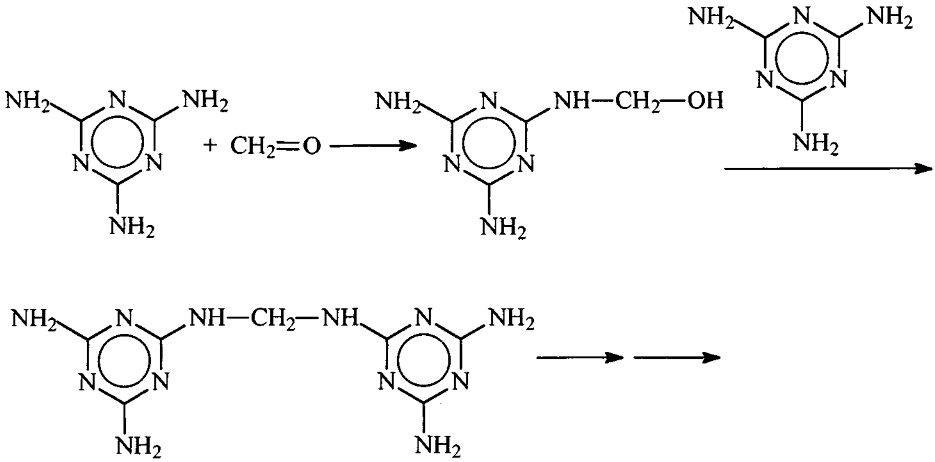
$$\mathrm{NH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-NH-\overset{O}{\overset{\|}{C}}-NH-CH_2-OH \longrightarrow H-(NH-\overset{O}{\overset{\|}{C}}-NH-CH_2)_n-OH}$$

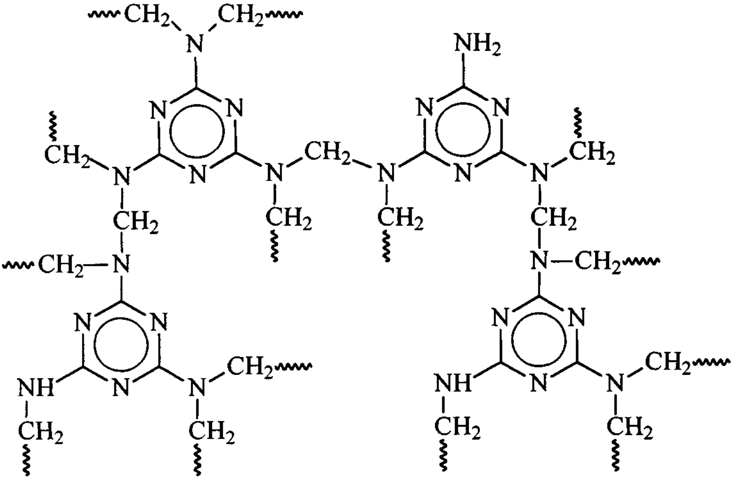
Heating for an extended period of time under acidic conditions will give a complex thermoset polymer of poorly defined structure including ring formation, of which the following may be typical.



3. MELAMINE-FORMALDEHYDE POLYMERS (MELAMINE RESINS)

Melamine, having three amino groups and six labile hydrogens, will form thermoset resins with formaldehyde. The chemistry is similar to that for the urea resins.

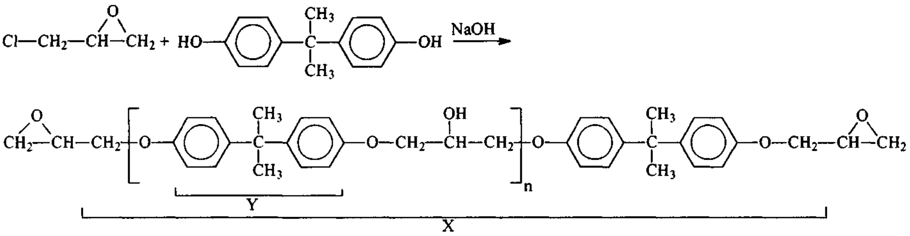




a melamine or Formica® resin

4. EPOXY RESINS

This type of thermoset polymer is typically made first by reaction of the sodium salt of bisphenol A and excess epichlorohydrin, which forms a low molecular weight polymer with terminal epoxy groups; n is between 1 and 4.



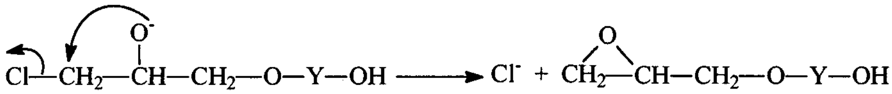
This reaction is best summarized in steps:

(1) Formation of the sodium salt of bisphenol A

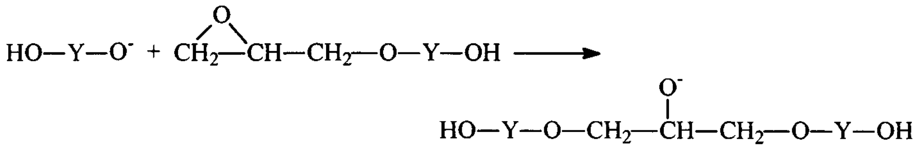
$$\mathrm{HO{-}Y{-}OH} + \mathrm{OH^-} \longrightarrow \mathrm{^-O{-}Y{-}OH} + \mathrm{H_2O}$$

(2) Reaction of the epoxy group of epichlorohydrin with the phenoxide anion

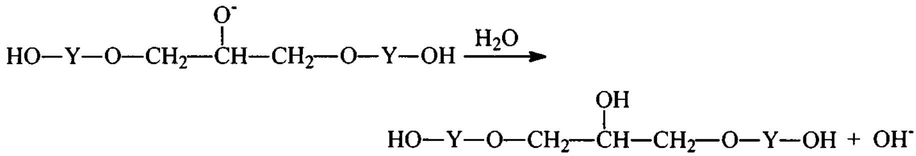
(3) Elimination of chloride ion



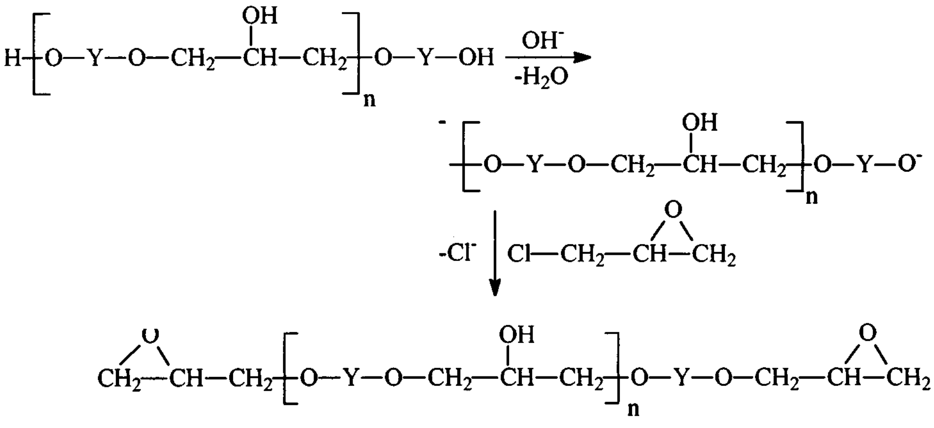
(4) Reaction of the new epoxy group with the phenoxide ion



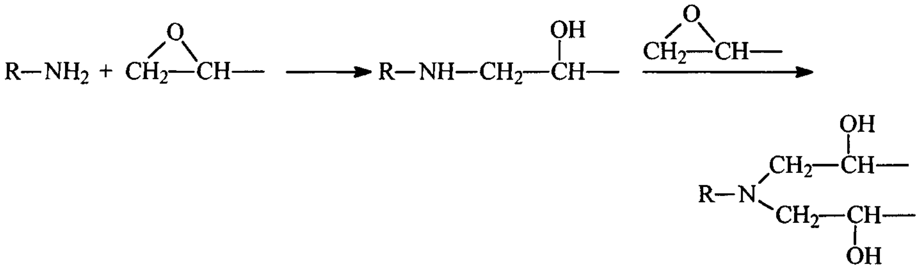
(5) Formation of a hydroxy group by protonation



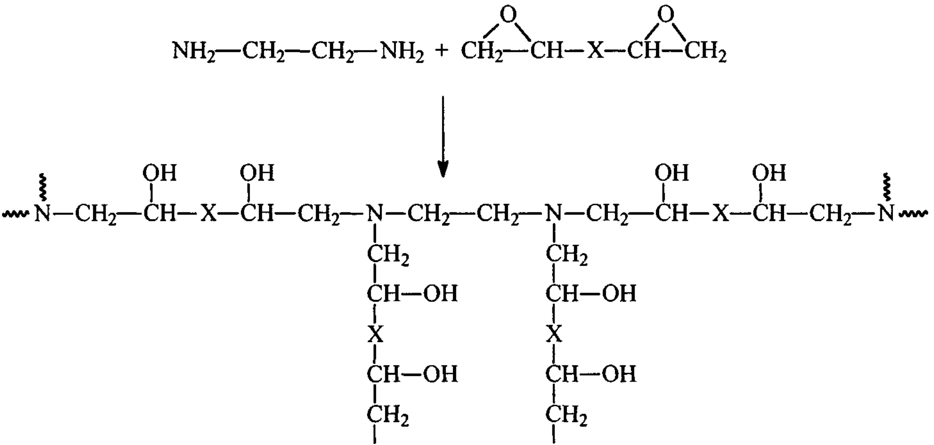
(6) Reaction with the excess epichlorohydrin causing the low molecular weight polymer to have terminal epoxy groups



These low molecular weight compounds with epoxy end groups are cross-linked by adding a curing agent such as ethylenediamine. Primary amines react with epoxides to form tertiary amines and branches.

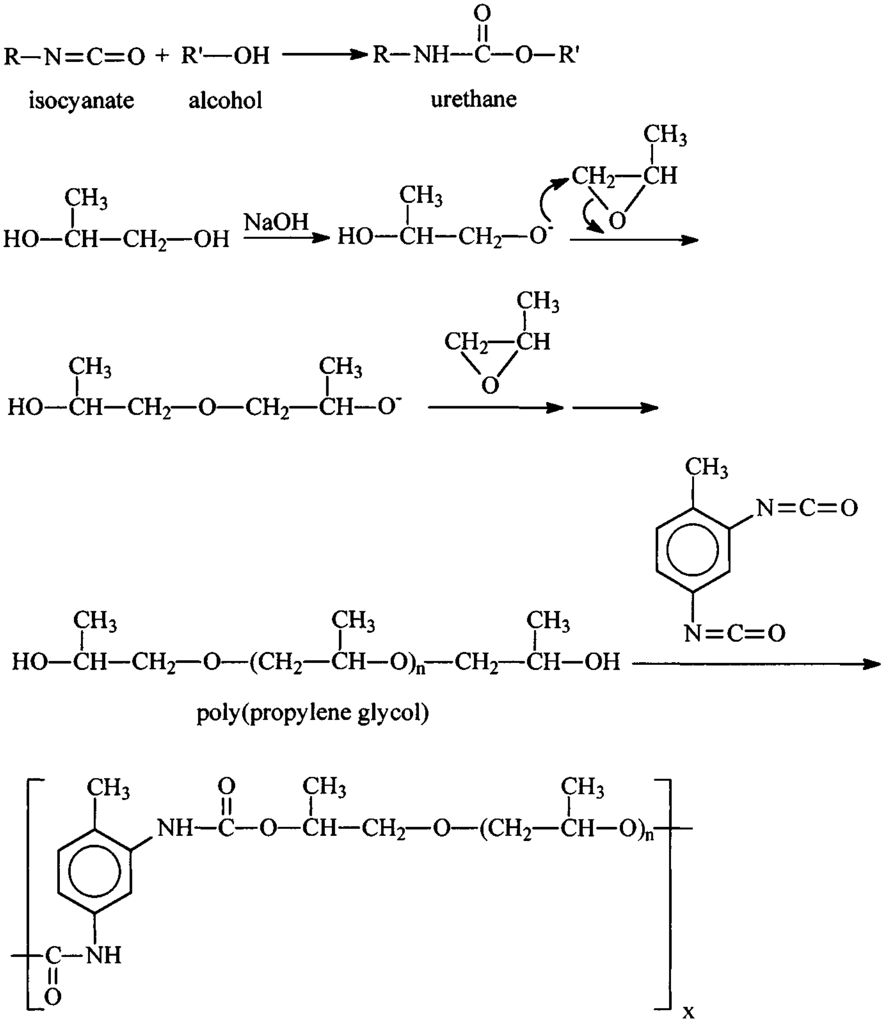


Thus a cross-linked polymeric structure is the final result when a primary diamine and a diepoxide react and all four N—H bonds on the two amine groups are broken.



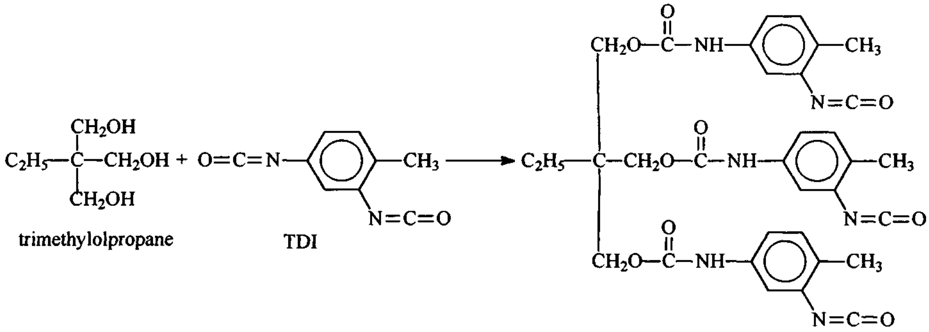
5. POLYURETHANE FOAMS

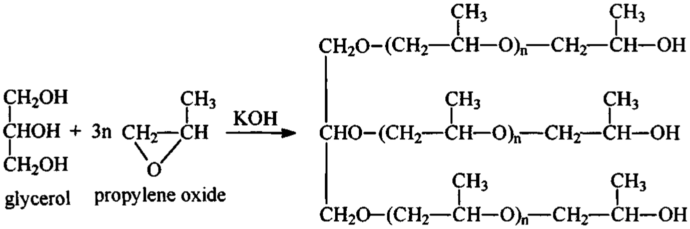
Most useful polyurethanes are cross-linked. Those commonly used in foams start with a diisocyanate like toluene diisocyanate (TDI) and a low molecular weight polyether such as poly(propylene glycol). Recall that the basic reaction of an isocyanate plus an alcohol gives the urethane functionality.



a linear polyurethane

One way of obtaining the more useful cross-linked polyurethanes is by using a trifunctional reagent. Thus either the TDI can react with a triol or the propylene oxide can be polymerized in the presence of a triol. Then the isocyanate-alcohol reaction would of course give a cross-linked urethane.





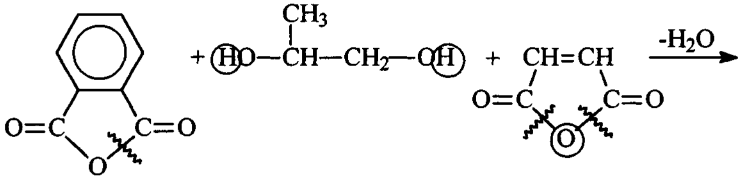
Remember that difunctional molecules give a linear polymer. Trifunctional molecules yield a cross-linked polymer.

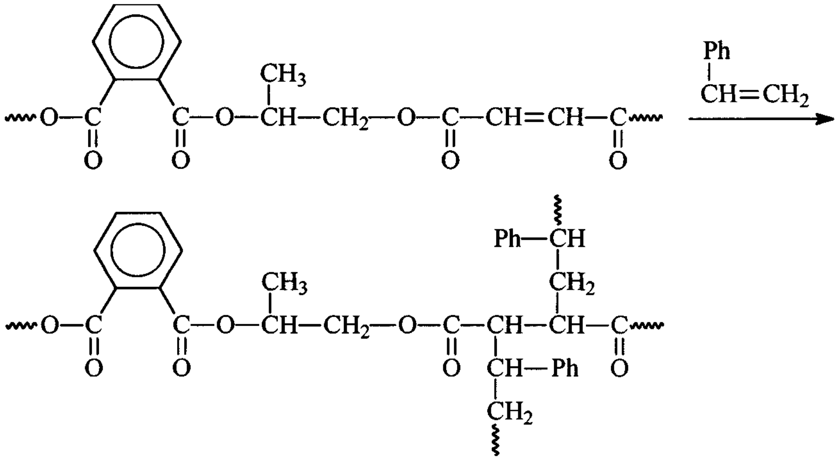
In the urethane process a small amount of water is added to convert some isocyanate functionalities into CO_2 gas and amines. The degree of foaming can be controlled by the amount of water added.

$$R{-}N{=}C{=}O + H_2O \longrightarrow R{-}NH_2 + CO_2\uparrow$$

6. UNSATURATED POLYESTERS

An unsaturated polyester resin consists of a linear polyester whose chain contains double bonds and an unsaturated monomer such as styrene that copolymerizes with the polyester to provide a cross-linked product. The most common unsaturated polyester is made by step growth polymerization of propylene glycol with phthalic and maleic anhydrides. Subsequent treatment with styrene and a peroxide catalyst leads to a solid, infusible thermoset.

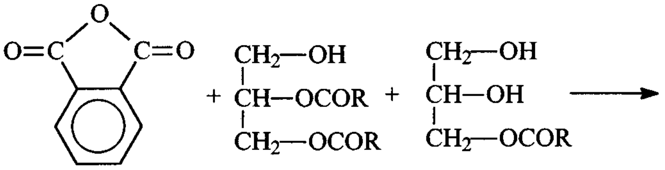


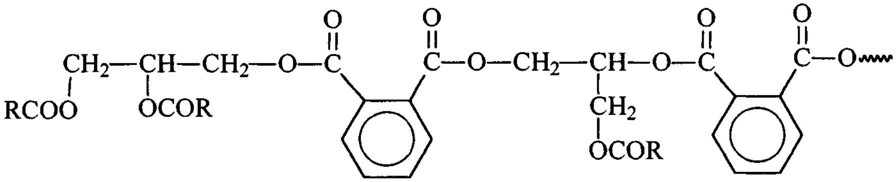


Unsaturated polyesters are relatively brittle and about 70% are used with fillers, of which glass fiber is easily the most popular. Glass fiber-reinforced polyester for small boat hulls consumes one quarter of unsaturated polyesters. Automobiles, furniture, and construction also make use of this thermoset resin.

7. ALKYD RESINS

This is a very broad class of compounds commonly used in coatings. Over 400-500 different alkyd resins are commercially available. They are polyesters containing unsaturation that can be cross-linked in the presence of an initiator known traditionally as a "drier." A common example is the alkyd formed from phthalic anhydride and a glyceride of linolenic acid obtained from various plants. Cross-linking of the multiple bonds in the long unsaturated chain R produces the thermoset polymer by linking R groups of separate molecules with each other.

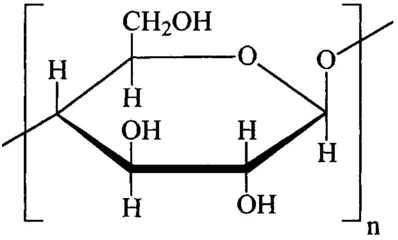




$R = CH_3{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7{-}$

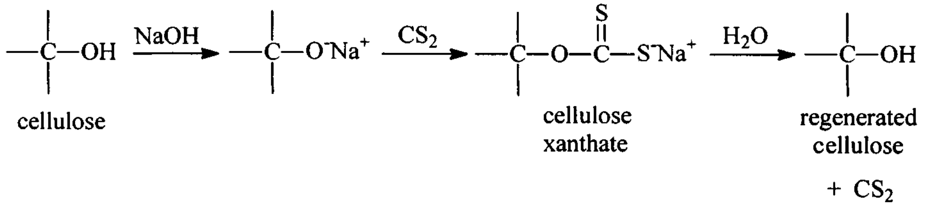
8. NATURAL POLYMERS

Mention has already been made of two polymers that can be obtained naturally from living animals: silk (from the silkworm) and wool (from sheep). They are proteins made of various amino acids; both are used in textiles. Other biologically derived polymers are also familiar such as wood, starch, and some sugars. We will not cover these in detail here. However, certain cellulosics we will discuss briefly since they are compared to synthetic fibers later. Cellulose is the primary substance of which the walls of vegetable cells are constructed and is largely composed of glucose residues. It may be obtained from wood or derived in very high purity from cotton fibers, which are about 92% pure cellulose.

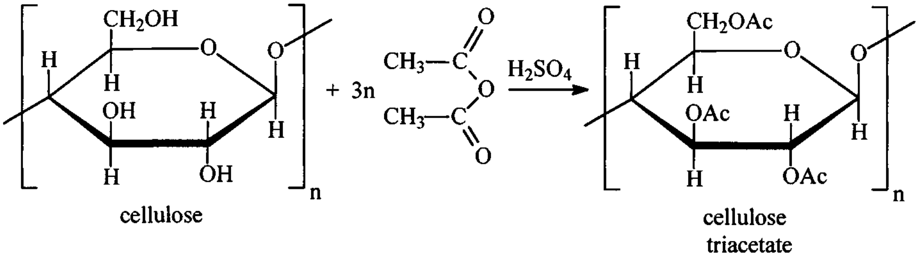


cellulose

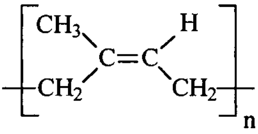
The important fiber rayon is simply "regenerated" cellulose from wood pulp that is in a form more easily spun into fibers. Cellophane film is regenerated cellulose made into film. One method of regeneration is formation of xanthate groups from selected hydroxy groups of cellulose, followed by hydrolysis back to hydroxy groups.



Cellulose acetate and triacetate may be used as plastics or spun into fibers for textiles. They are made by the reaction of cellulose with acetic anhydride.



Finally, one last type of natural polymer is natural rubber, obtained from the rubber tree and having the all *cis*-1,4-polyisoprene structure. This structure has been duplicated in the laboratory and is called "synthetic rubber," made with the use of Ziegler-Natta catalysis.



natural rubber

The biosynthesis of synthetic natural rubber has been completely determined and appears in Fig. 15.1. Many plants and animals use this same biosynthetic pathway to make hundreds of terpenes and steroids from their common isoprenoid building blocks.

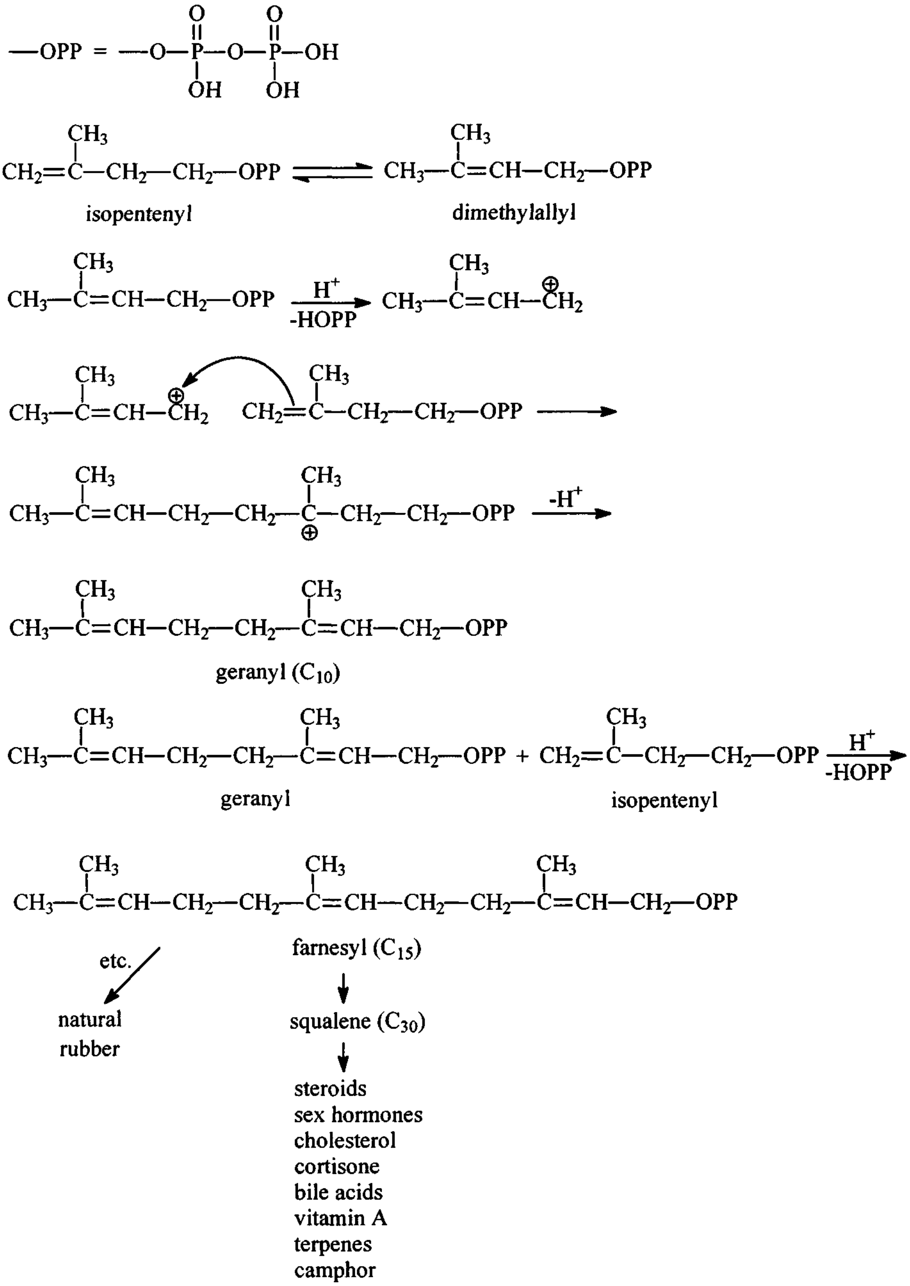


Figure 15.1 Biosynthesis of natural rubber.

9. POLYMER PROPERTIES

9.1 Molecular Weight

The detailed treatment of the molecular weight analysis of polymers is left to other texts. We should be aware that there are two types of molecular weights, *number average* and *weight average.*

$$M_n = \frac{\Sigma N_l M_l}{\Sigma N}$$

M_n = number average molecular weight
N_l = number of molecules with a molecular weight of M_l
N = total number of molecules

$$M_w = \frac{\Sigma w_l M_l}{\Sigma w_l} = \frac{\Sigma N_l M_l^2}{\Sigma N_l M_l}$$

M_w = weight average molecular weight
w_l = weight of molecules with a molecular weight of M_l

Because the weight average is biased toward molecules with higher molecular weight, it is larger than the number average. Boiling point elevation, freezing point depression, osmotic pressure, and end group analysis give the number average molecular weight. Light scattering and sedimentation give the weight average. Viscosity measurements give a value somewhere between the two. Molecular weight and mechanical strength are related since strength increases rapidly as the degree of polymerization (or the number of repeating units, n) increases from 50 to 500. Further increases in molecular weight have a smaller effect.

9.2 Crystallinity

This is a key factor in governing polymer properties. If the polymer molecules can align themselves with a high lateral order and the chains lie side by side, we say that the polymer is highly crystalline. Bulky groups or branching prevent the polymer from being highly crystalline. Another thing affecting crystallinity is the magnitude of attractive forces between neighboring polymer molecules. Strong intermolecular forces, such as hydrogen bonding in the nylons, promote greater crystallinity. Isotactic polymers are always more crystalline than atactic polymers because of the regularity of any large groups. Ziegler-Natta catalysts promote isotactic, crystalline polymerizations.

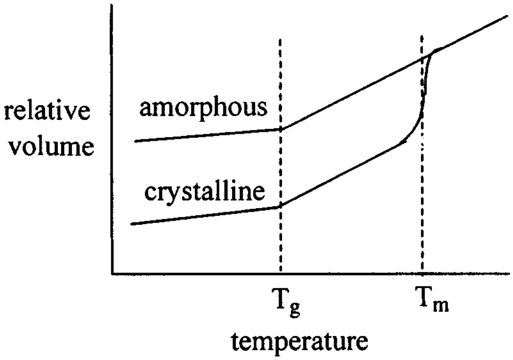
Crystalline polymers tend to have greater mechanical strength, higher melting points, and higher densities than amorphous polymers. On the other hand, they are usually much less transparent (more opaque) because light is reflected or scattered at the boundary between the crystalline and amorphous portions of the polymeric structure. Amorphous polymers are transparent and glasslike.

Examples of crystalline polymers are nylons, cellulose, linear polyesters, and high-density polyethylene. Amorphous polymers are exemplified by poly(methyl methacrylate), polycarbonates, and low-density polyethylene. The student should think about why these structures promote more or less crystallinity in these examples.

The crystallinity of a specific polymer may be altered by orientation or stretching the polymer mechanically in a certain direction. On stretching, the molecules align themselves and become more crystalline. Did you ever notice that a rubber band becomes more opaque on stretching? However, if a crystalline polymer is biaxially oriented, as with a drawn nylon sheet, then the whole sheet is in effect a single crystal and is very transparent! The stretching or drawing of fibers causes greater crystallinity and gives the longitudinal strength required in fibers.

9.3 Temperature Dependency of Polymers

Polymers usually do not have a single, sharp melting point like a pure chemical might. Then too each polymer is a little different in its reaction to temperature changes, and the same polymer but with different molecular weights will have different observable changes when heated or cooled. The glass transition temperature, T_g, and the crystalline melting point, T_m, are most often used to describe the rather nebulous changes of a polymer with temperature, shown here with a graph of volume versus temperature.



An amorphous material such a polystyrene does not solidify sharply. It goes from a viscous liquid to a rubbery solid, then to a leathery solid. Finally, it becomes a glassy solid. This last change is a sharper one and the temperature at which it occurs is called the *glass transition temperature*, T_g. Or upon heating a polymer, it is the temperature at which the polymer loses its hardness or brittleness and becomes more flexible and takes on rubbery or leathery properties. At this transition temperature noticeable changes in the specific volume, thermal conductivity, refractive index, stiffness, heat content, and dielectric loss are apparent.

More crystalline polymers have a glass transition temperature because all polymers have amorphous regions between the crystalline regions. Crystalline polymers also have a *crystalline melting point*, T_m. It is the temperature at which a molten polymer changes from a viscous liquid to a microcrystalline solid. It is accompanied by more sudden changes in density, refractive index, heat capacity, transparency, and similar properties, but it is still not so sharp as a nonpolymeric melting point. Usually T_g is about one half to two thirds of T_m for most polymers if expressed in degrees Kelvin.

Table 15.1 gives the appropriate T_g's for a few selected polymers. Note

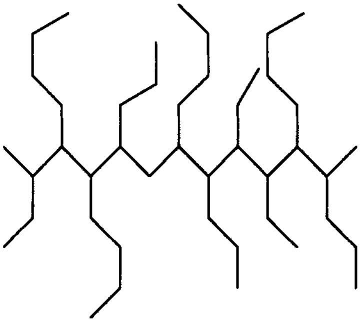
Table 15.1 Approximate Glass Transition Temperatures (T_g) for Selected Polymers

Polymer	T_g (°K)
Cellulose acetate butyrate	323
Cellulose triacetate	430
Polyethylene (LDPE)	148
Polypropylene (atactic)	253
Polypropylene (isotactic)	373
Poly(ethyl acrylate)	249
Poly(methyl acrylate)	279
Poly(butyl methacrylate) (atactic)	339
Poly(methyl methacrylate) (atactic)	378
Polyacrylonitrile	378
Poly(vinyl acetate)	301
Poly(vinyl alcohol)	358
Poly(vinyl chloride)	354
cis-Poly-1,3-butadiene	165
trans-Poly-1,3-butadiene	255
Poly(hexamethylene adipamide) (nylon 6,6)	330
Poly(ethylene adipate)	223
Poly(ethylene terephthalate)	342
Poly(dimethyl siloxane) (silicone)	150
Polystyrene	373

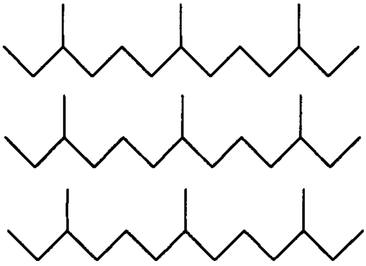
Source: Seymour/Carraher

that the T_g values are low for elastomers and flexible polymers (low-density polyethylene, *cis*-poly-1,3-butadiene, silicone) and relatively high for hard amorphous plastics [polypropylene-isotactic; polyacrylonitrile; poly(vinyl alcohol); nylon 6,6; poly(ethylene terephthalate); polystyrene]. Notice also that T_g varies with even slight changes in structure. For instance, T_g decreases as the size of the ester groups increases in polyacrylates and polymethacrylates. T_g increases when aromatics are added [poly(ethylene adipate) vs. poly(ethylene terephthalate)].

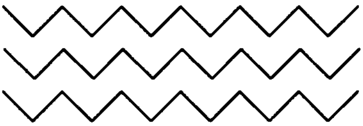
Even a single polymer can vary significantly in its amorphous or crystalline nature depending on how it was made and the degree of branching. Low-density polyethylene (LDPE) is amorphous because the many branches prevent crystallinity. Linear low-density polyethylene (LLDPE) has a few branches and is semi-crystalline. High-density polyethylene (HDPE) has no significant amount of branching and is highly crystalline.



LDPE

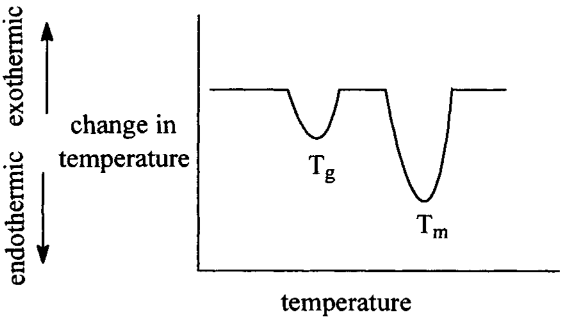


LLDPE



HDPE

Many different test methods can be used to study polymers and their physical changes with temperature. These studies are called thermal analysis. Two important types of thermal analysis are called *differential scanning calorimetry (DSC)* and *differential thermal analysis (DTA)*. DSC is a technique in which heat flow away from a polymer is measured as a function of temperature or time. In DTA the temperature difference between a reference and a sample is measured as a function of temperature or time. A typical DTA curve easily shows both T_g and T_m.



9.4 Tensile Properties

Many of the quoted physical properties of a polymer are derived from a stress-strain experiment. The polymer is cut into an appropriate shape. For instance, plastics are cut into the shape shown here (sometimes called a dogbone). They are placed in two jaws of a special instrument (Fig. 15.2).

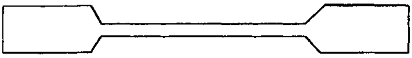


Figure 15.2 Tensile testing instrumentation. Polymer samples are stretched under controlled conditions and the tensile properties are evaluated. (Courtesy of Du Pont)

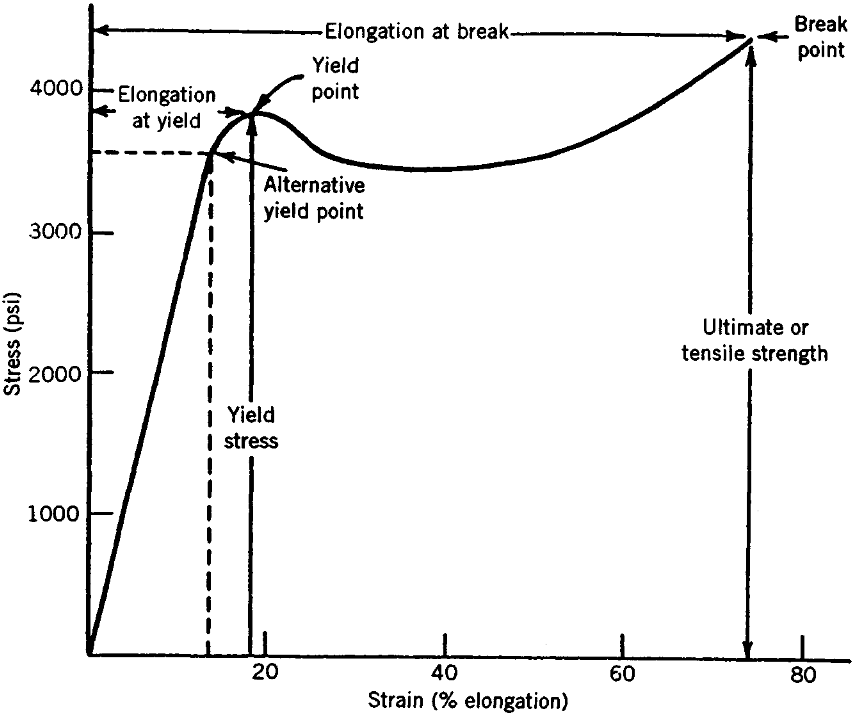
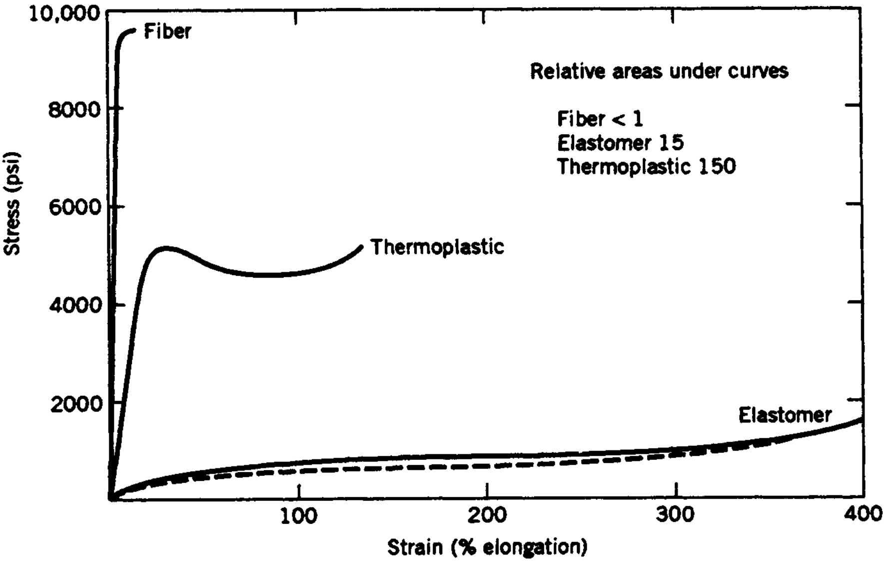


Figure 15.3 Common stress-strain curve for a thermoplastic. (*Source:* Wittcoff and Reuben, *Industrial Organic Chemicals*, John Wiley & Sons, 1996. Reprinted by permission of John Wiley & Sons, Inc.)

The ends are pulled apart at a certain speed and the distance pulled is plotted versus pounds per square inch of tension placed on the sample. A typical stress-strain curve for a thermoplastic is given in Fig. 15.3.

In the initial stages of the extension the graph is sometimes linear and obeys Hooke's law. The slope of this section is called Young's modulus. This portion of the curve is reversible. Because many polymers do not obey Hooke's law the modulus is frequently expressed as pounds per square inch at a certain elongation or extensibility. The 2% modulus is a common quotation. Some elastomers are better described as a 100% modulus. The stiffer the polymer is that is tested, the higher will be the modulus value that is recorded.

After the initial stress a yield point is reached, beyond which permanent deformation and nonreversible extension occur. Then the stress and elongation gradually increase until the plastic is broken. The stress at this point is called the ultimate tensile strength (or tensile strength) and the strain



	Elastomers	Plastics	Fibers
Modulus (psi)	15-150	1,500-200,000	150,000-1,500,000
Percent Elongation	100-1000	20-100	<10
Crystallinity	Low	Moderate	High
Example	Natural rubber	Polyethylene	Nylon

Figure 15.4 Stress-strain diagrams for typical polymers. (*Source:* Wittcoff and Reuben, *Industrial Organic Chemicals*, John Wiley & Sons, 1996. Reprinted by permission of John Wiley & Sons, Inc.)

is the percent elongation (at break) where 100% would mean it could be stretched to twice its original length before breaking.

Figure 15.4 gives the stress-strain diagrams for a typical fiber, plastic, and elastomer and the average properties for each. The approximate relative area under the curve is fiber, 1; elastomers, 15; thermoplastics, 150. Coatings and adhesives, the two other types of end-uses for polymers, will vary considerably in their tensile properties, but many have moduli generally between elastomers and plastics. They must have some elongation and are usually of low crystallinity.

9.5 Other Properties

There are many other properties of polymers that can become very important depending on the type of processing and final use. Rheological or

Table 15.2 Estimated Use Percentage for Polymers

Plastics	71%
Fibers	11
Elastomers	7
Coatings	6
Adhesives	5

melt properties are especially critical as a polymer is processed into a certain shape and type of material (plastic, fiber, etc.). Viscosity and melt strength are important here. Optical clarity, refractivity, and water vapor and gas permeability are important in packaging. Abrasion and wear resistance for clothing, weatherability and UV stability for outdoor use, hardness, electrical properties, chemical resistance, flammability, toxicity, and blendability are all properties that can be specifically tested using a detailed method published by the American Society for Testing and Materials (ASTM).

With this brief introduction into polymer chemistry, let us now turn our attention to specific studies of the five major applications of polymers: plastics, fibers, elastomers, coatings, and adhesives, with the approximate use percentages as shown in Table 15.2.

Suggested Readings

Carraher, *Seymour/Carraher's Polymer Chemistry: An Introduction*, pp. 19-164.

Wittcoff and Reuben, *Industrial Organic Chemicals*, pp. 445-467.

Chapter 16

Plastics

1. INTRODUCTION AND ECONOMIC FACTORS

Having studied some of the basic chemistry and properties of polymers, we now consider in detail the major applications of these fascinating molecules. By far the most important use of polymers is in the plastics industry.

Plastics Material and Resin Manufacturing (NAICS 325211) makes up 11% of shipments for Chemical Manufacturing (NAICS 325), the highest percentage of any polymer application. Fig. 16.1 shows the growth of shipments in plastics compared to cellulosic and non-cellulosic fibers and synthetic rubber, other major uses for polymers. Note the very steep incline for plastics, now at $45 billion in shipments. NAICS 325211 includes mainly basic polymer resins and forms, including molded and extruded material. Plastics and Rubber Products Manufacturing (NAICS 326), a NAICS division separate from Chemical Manufacturing, is part of our larger chemical process industries definition of “the chemical industry,” as explained in Chapter 1. This class deals with finished consumer products bought retail which contain rubber or plastic material.

Table 16.1 shows the breakdown in value of shipments in Plastics and Rubber Products and its subdivisions. It is divided into 78.5% Plastics Products and 21.5% Rubber Products. Plastics products are then subdivided into products such as film, sheet, bags, pipe, laminate, foam, bottles, and miscellaneous. While film, sheet, and bags are the largest subdivision of plastics, the large miscellaneous “other” category demonstrates the breadth and scope of plastics. It cannot be denied that our modern standard of living

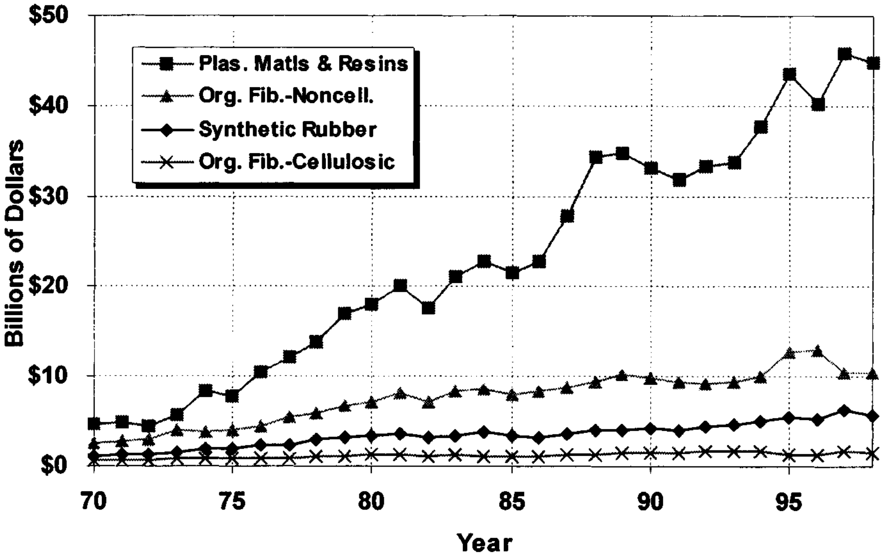


Figure 16.1 U.S. shipments of plastics, fibers, and synthetic rubber. (*Source*: *Annual Survey of Manufactures*)

Table 16.1 U.S. Shipments of Plastics and Rubber Products Manufacturing

Industry Group	NAICS	Shipments ($billion)	%
Unsupported Plastic Film, Sheet, & Bags	32611	24.5	
Plastic Pipe, Pipe Fittings, & Unsupported Profile Shapes	32612	9.3	
Laminated Plastic Plate, Sheet, & Shape	32613	2.9	
Polystyrene Foam Products	32614	5.5	
Urethane & Other Foam Products	32615	6.7	
Plastic Bottles	32616	7.0	
Other Plastics Products	32619	72.8	
Plastics Products	**3261**	**128.7**	**78.5**
Rubber Products	**3262**	**35.3**	**21.5**
Plastics & Rubber Products	**326**	**164.0**	**100.0**

Source: *Annual Survey of Manufactures*

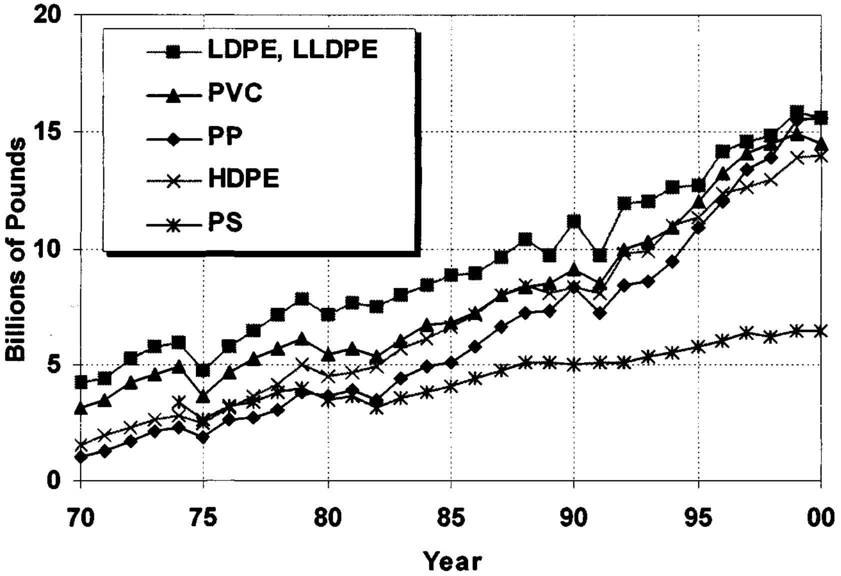


Figure 16.2 U.S. production of polymers. (*Source*: *Chemical and Engineering News*)

would be changed drastically without the plastics industry. Although many criticisms of "cheap" plastic materials are sometimes justified, no one would willingly return to the preplastic age, and especially have to pay for the difference. Indeed, many consumer products would not be possible without the availability of plastic materials. It is a high-growth industry.

If we look at pounds instead of dollars, we see the more gradual increases of the last twenty years in U.S. production (Fig. 16.2) for the five major polymers. Be sure to know the important standard abbreviations for the major plastics: high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), polypropylene (PP), poly(vinyl chloride) (PVC), polystyrene (PS), and poly(ethylene terephthalate) (PET). LDPE, LLDPE, and PP have been tops for many years and will probably continue to be the leaders for some time to come. The LDPE numbers include both LDPE and LLDPE since their properties and uses are similar. However, since 1989 separate data for LLDPE is available. Production data for the three separate polyethylenes is given in Fig. 16.3. Notice the very rapid increase in LLDPE while production of LDPE remained nearly flat. The average annual % change in LLDPE in the last decade is 7%, while it is only 5% for HDPE and 0.5% for LDPE. PP is also fast growing at 7% per year. Poly(ethylene terephthalate)

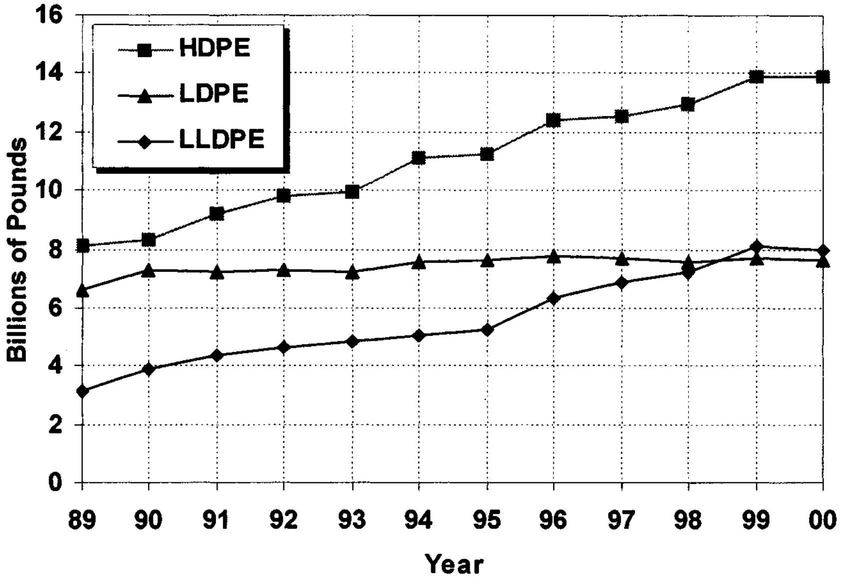


Figure 16.3 U.S. production of polyethylenes. (*Source*: *Chemical and Engineering News*)

(PET) is not in the figures but is rapidly increasing in plastics use as a clear bottle, especially for soft drinks. It is the major synthetic fiber and will be discussed more in Chapter 17. As a plastic its production is now up to over 4 billion lb per year.

Price trends in polymers (Fig. 16.4) are more up and down depending on the economy for a given year. All of these major use polymers in the plastics industry are 30-50 ¢/lb to be competitive. LLDPE can be made more economically than LDPE. It is usually about 4 ¢/lb lower in price.

Table 16.2 shows the amount of plastics produced in the U.S. per person for selected years. The very large growth rate is apparent until 1980. It is amazing that each of us uses 200 lb per year.

What was the first synthetic plastic? Although some nineteenth-century experiments should be mentioned, such as the 1869 molding process for cellulose nitrate discovered by John and Isaiah Hyatt, probably the first major breakthrough came in 1910 with Leo Baekeland's discovery of phenol formaldehyde resins (Bakelite®). These are still the leading thermoset plastics made today. The pioneering work of Wallace Carothers at Du Pont in 1929 produced the nylons now used primarily as fibers but known as the beginning of thermoplastic resin technology.

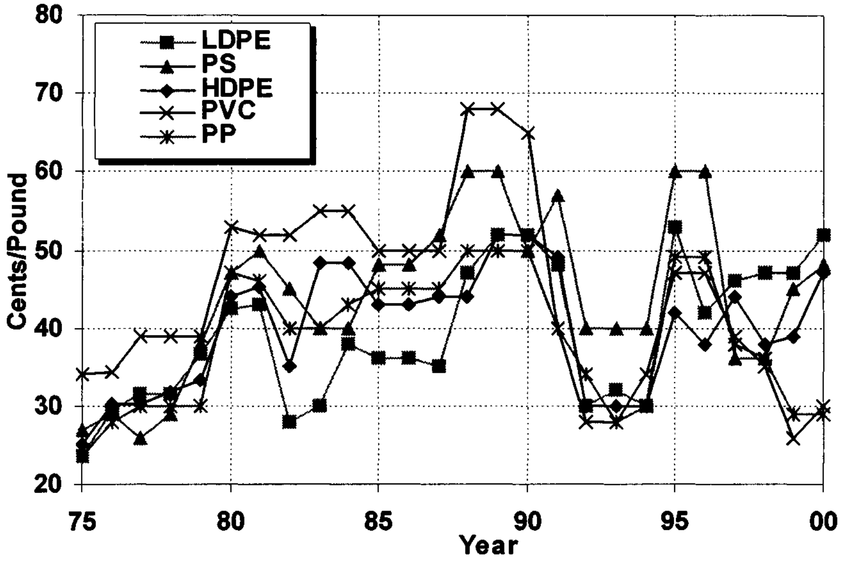


Figure 16.4 U.S. prices of polymers. (*Source*: *Chemical Marketing Reporter*)

2. GENERAL USES OF PLASTICS

Although we will be discussing plastics according to their various types and what applications each type might fill, it is good to know something

Table 16.2 Per Capita Use of Plastics in the U.S.

Year	Lb of Plastics/Person
1930	0.25
1940	1.5
1950	12
1960	31
1970	90
1980	209
1990	210

Table 16.3 Uses of Thermoplastics

Packaging	32%
Building & construction	14
Consumer products	13
Electrical equipment	6
Furniture	5
Transportation equipment	4
Miscellaneous	26

Source: Chemical and Engineering News

Table 16.4 Uses of Thermosets

Building & construction	69%
Transportation	8
Adhesives, coatings	4
Consumer products	4
Electrical equipment	4
Miscellaneous	11

Source: Chemical and Engineering News

general about uses of plastics. Table 16.3 divides the uses of thermoplastics into some general areas. Table 16.4 shows some general uses of thermosets. Packaging, the largest use for thermoplastics, includes containers and lids, probably one half of this use, and packaging film, another one third. Liners, gaskets, and adhesives for packaging make up the rest. Building and construction, largest use area for the thermosets and second largest for thermoplastics, includes various types of pipes, fittings, and conduit. Plywood adhesives are also big.

3. DEFINITIONS AND CLASSES OF PLASTICS

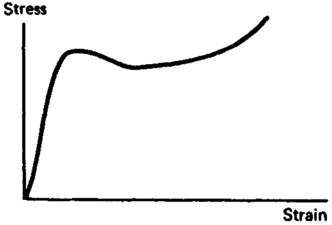
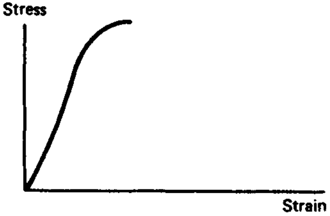
Your own intuition and experience should give you a good idea of what a plastic is. It is more difficult to define precisely because there are so many types, they have such a wide variety of properties, and their methods of fabrication are so diverse. Not all polymers are good plastics, although many polymers serve important plastic applications. Probably the best, simplest, and all inclusive definition is that *plastics are polymers that have been converted into shapes by processes involving a flow of the liquid phase before solidification*. In short, a polymer must be easily shaped if it is to serve in any important plastic application.

The best type of chemical classification of plastics is that same division that we use for all polymers: they are thermoplastic (linear) and thermoset (cross-linked). Unfortunately, there is an overlap in the all-important mechanical properties when you use this chemical division. In 1944 Carswell and Nason categorized plastics by the shape of their stress-strain curves, one of the important properties of any plastic. These curves are pictured in Fig. 16.5. The five major types are: (1) hard-tough, (2) hard-strong, (3) hard-brittle, (4) soft-weak and (5) soft-tough. General characteristics of these classes and some representative plastics for each type are given. The words hard, soft, tough, strong, brittle, and weak are not chosen lightly. A hard plastic is one that has a high tensile strength and modulus; a soft plastic has a relatively low strength and modulus. Tough refers to a high elongation; brittle refers to a very low elongation. Strong and weak are applied to plastics of moderate elongations and depend on their overall tensile strength as well.

Fig. 16.6 is a graph of the range of tensile properties for each specific plastic, plotting tensile strength versus elongation. Note that the hard-tough plastics such as the nylons are in the upper right (high tensile strength, high elongation), the hard-brittle plastics such as the thermosets and polystyrene are in the upper left (high tensile strength, low elongation), and the soft-tough plastics such as low-density polyethylene are in the lower right (low tensile strength, high elongation). There are no common uses for soft-weak plastics. Specific examples and details for each of these important categories of plastics will be given in Section 6.

4. FABRICATION OF PLASTICS

An important step in the manufacture of any plastic product is the fabrication or the shaping of the article. Most polymers used as plastics when manufactured are prepared in pellet form as they are expelled from the reactor. These are small pieces of material a couple of millimeters in size. This resin can then be heated and shaped by one of several methods. Thermoset materials are usually compression molded, cast, or laminated. Thermoplastic resins can be injection molded, extruded, or blow molded most commonly, with vacuum forming and calendering also used but to a lesser extent.

Class of Plastic		Modulus	Yield Stress	Ultimate Tensile Strength	Elongation at Break	Examples
Hard and tough		High	High	High	High	ABS High density polyethylene Cellulosics Polyamides Polypropylene Fluoroplastics Engineering plastics Polyacetal, polycarbonate Polyimide, polyphenylene sulfide, polyphenylene oxide Polysulfone Poly(vinylidene chloride)
Hard and strong		High	High	High	Moderate	Rigid PVC Impact polystyrene Styrene–acrylonitrile

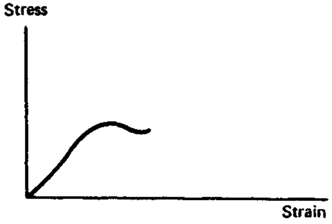
Hard and brittle		High	No well-defined yield point	High	Low	P/F, U/F and M/F resins Polystyrene Polymethyl methacrylate Unsaturated polyester resins Epoxy resins
Soft and weak		Low	Low	Low	Moderate	Polyethylene waxes
Soft and tough		Low	Low yield point	Low	High	Low density polyethylene Plasticized PVC Ionomer

Figure 16.5 Classes of plastics by shape of stress-strain curve. (*Source*: Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, John Wiley & Sons, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

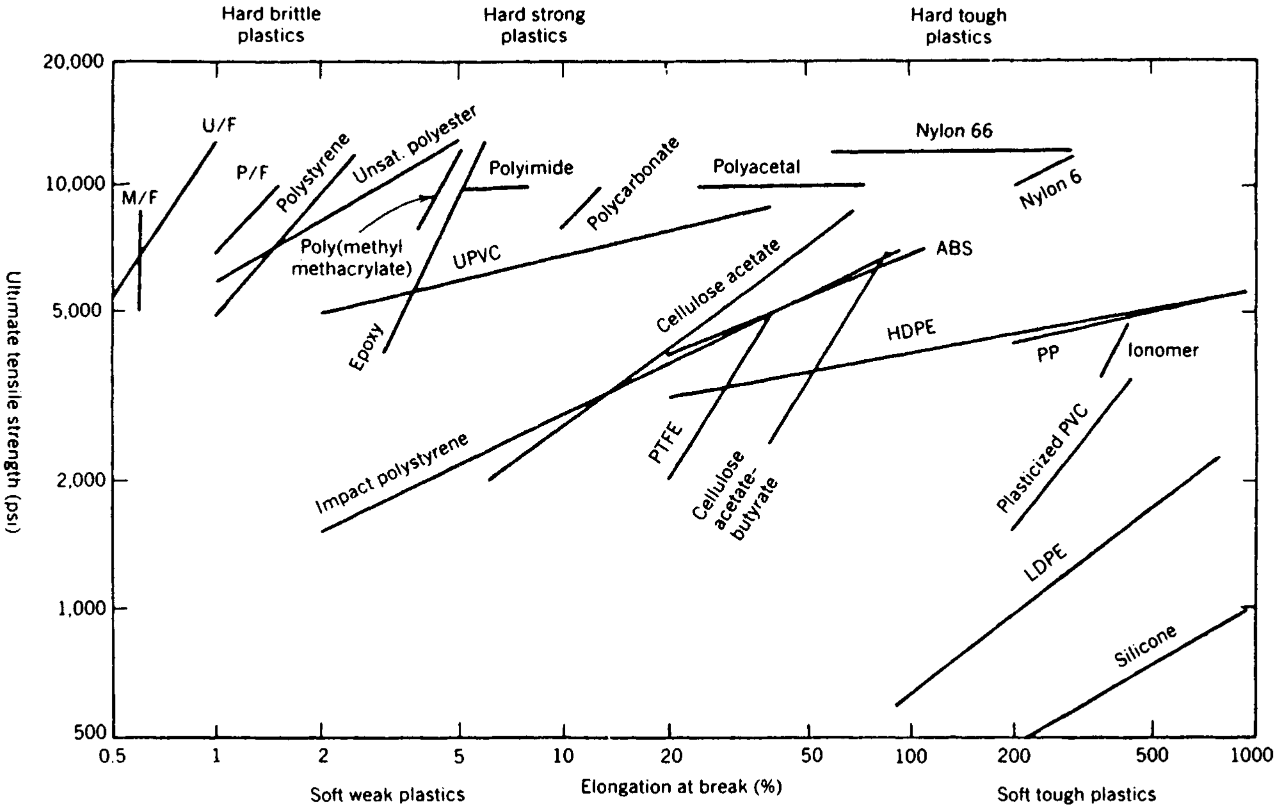


Figure 16.6 Range of tensile properties for various plastics. (*Source*: Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, John Wiley & Sons, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

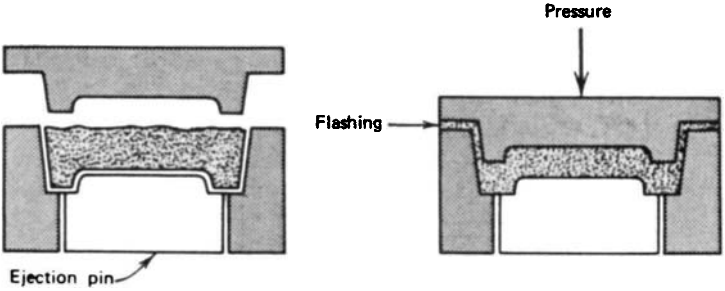


Figure 16.7 Compression molding. (*Source*: Wittcoff and Reuben II and Reuben and Burstall 1974, Reprinted by permission of Pearson Education Limited.)

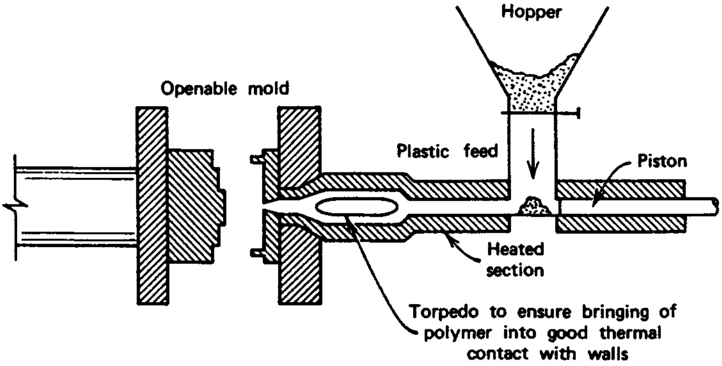


Figure 16.8 Injection molding. (*Source*: Wittcoff and Reuben II and Reuben and Burstall 1974, Reprinted by permission of Pearson Education Limited.)

Compression molding (Fig. 16.7) is practically the oldest method of fabricating polymers and is still widely used. The polymer is placed in one half of a mold and the second half compresses it to a pressure of about 1 ton/in^2. The powder is simultaneously heated, which causes the resin to cross-link.

In injection molding (Fig. 16.8) the polymer is softened in a heated volume and then forced under high 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.

Extrusion (Fig. 16.9) is a method of producing lengths of plastic material of uniform cross section. The extruder is similar to a domestic mincing machine with the added facility that it can be heated and cooled. The pellets enter the screw section via the hopper, are melted, and then pass through the

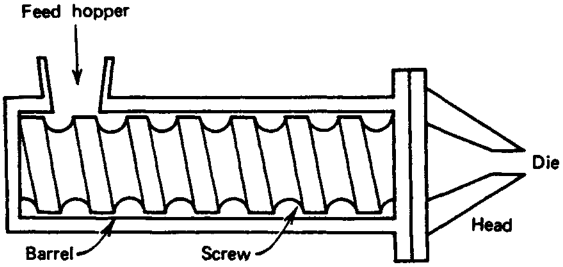


Figure 16.9 Extrusion. (*Source*: Wittcoff and Reuben II and Reuben and Burstall 1974, Reprinted by permission of Pearson Education Limited.)

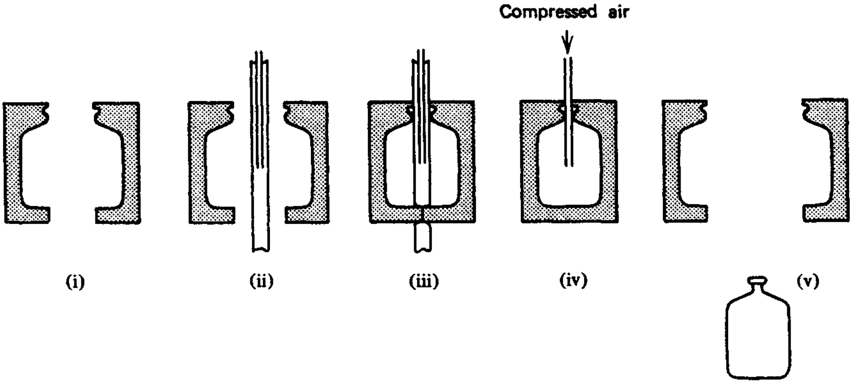


Figure 16.10 Blow extrusion. (*Source*: Wittcoff and Reuben II and Reuben and Burstall 1974, Reprinted by permission of Pearson Education Limited.)

breaker plate into the die. The plastic material 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 is also used to make pellets. A long rod is extruded and then a cutting wheel makes small pieces from the long rod. This is often used to expel the polymer from the reactor and make pellets from it for storage or shipping.

Blow extrusion, in which the initial lump of polymer is formed by an extrusion process, is the most common form of blow molding and is shown diagrammatically in Fig. 16.10. A short length of plastic tubing is extruded through a crossed die and the end is scaled by the closing of the mold.

Figure 16.11 Research injection molding equipment. (Courtesy of Du Pont)

Compressed air is passed into the tube and the "bubble" is blown out to fill the mold.

Fig. 16.11-16.14 show the types of equipment used in some of these processes.

5. RECYCLING OF PLASTICS

Since about 1990 plastics recycling has been a growing and developing business. It is here to stay in one form or another. Collection and separation are the main problems. PET and HDPE by far are the main plastics that are most easily recycled. These two polymers are used as containers and easily reprocessed. Plastic films (especially LDPE) have a potential for recycling increases, but this form of plastic material is not as easily collected and stored.

Figure 16.12 Polymer ribbon in a molten state at high temperatures ready to enter an extruder. (Courtesy of BP Chemicals, Alvin, Texas)

Melt recycling works well only when the processes can acquire large quantities of clear, single polymer material such as PET soda bottles and HDPE milk jugs. For mixed streams separation of different types of polymers is a major cost component. Density differences, magnetic characteristics, color, X-ray, single wavelength infrared, and full-spectrum infrared are some sorting and detection methods.

X-rays can easily determine the presence of PVC via the chlorine atom. Single wavelength infrared is used to separate clear (PET and PVC), translucent (HDPE and PP), and opaque (all pigmented materials and colored HDPE) streams. Full-spectrum infrared can detect differences in

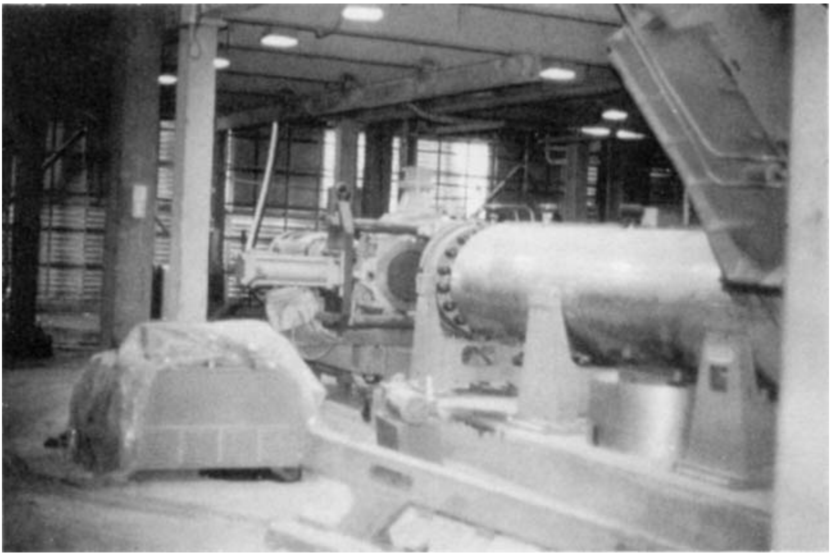


Figure 16.13 Extruding equipment. The extruder is opened in the middle of this picture to show the die for making over 1000 simultaneous strands. (Courtesy of BP Chemicals, Alvin, Texas)

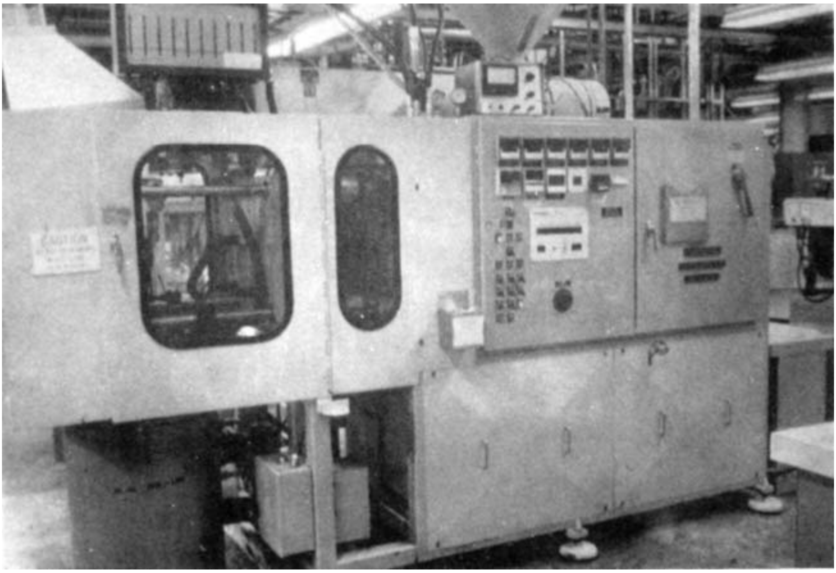


Figure 16.14 Research size blow molding equipment. (Courtesy of Du Pont)

each of the plastics because of the unique fingerprint in the infrared spectrum for each plastic. This latter system is 98-100% accurate, except for separating LDPE from HDPE where it is 90% successful. Markers have been considered as a way to code each plastic product with an easily identifiable sign. Unique molecular markers on the polymer molecules during production have also been given some thought. Many plastic products now have the standard visual marker, abbreviation, and number shown on the surface: PETE (PET), 1; HDPE, 2; V (PVC), 3; LDPE, 4; PP, 5; PS, 6; and other, 7.

Total recycled thermoplastic resin production almost tripled between 1990 and 1995 and is well over 1 billion lb per year. The percentage breakdown of the amount for recycling is the following: HDPE (especially bottles), 35%; PET (soft drink bottles), 34%; PP (auto battery cases), 14%; LDPE (film), 9%; PS (packaging), 3%; PVC, 0.5%; other, 4%.

6. IMPORTANT PLASTICS

The diversity in properties and uses of plastics is greater than any other area of polymer chemistry. It is best simply to select a few of the most important plastics and become acquainted with them individually. In the following sections there is important information on certain polymers having wide applications as plastics. We will use our general categories of hard-tough, hard-strong, hard-brittle, and soft-tough to determine their order of treatment and also to emphasize which plastics compete with each other. Although some plastics are similar to others they all have their own set of advantages and disadvantages for a given application. Indeed, it is the job of the plastics companies to fit the best polymer to a particular use. The chemistry of manufacture of these polymers is given in Chapters 14 and 15. Production figures are given in Chapter 1 and in this chapter.

6.1 Hard-Tough

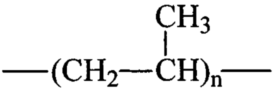
6.1.1 High-Density Polyethylene, HDPE

$$—(CH_2—CH_2)_n—$$

1. Manufacture
   Introduced in the 1950s
   Moderate to low pressures
   Metal oxide catalysis (usually)

2. Properties
   No branches, 90% crystalline, $T_m = 135\,°C$, $T_g = -70$ to $-20\,°C$
   More opaque than LDPE
   Stiffer, harder, higher tensile strength than LDPE
   Specific gravity = 0.96
3. Uses
   Blow molding (containers and lids, especially food bottles, auto gas tanks, motor oil bottles), 35%; injection molding (pails, refrigerator food containers, toys, mixing bowls), 22%; film, 17%; pipe and conduit, 14%; sheet, 6%; wire and cable, 1%; miscellaneous, 5%
4. Economics
   2004 demand expected to be 17 billion lb
   Growth from 1990-2000 of 5.3%/yr

6.1.2 Polypropylene, PP



$$—(CH_2—\overset{\overset{\displaystyle CH_3}{|}}{C}H)_n—$$

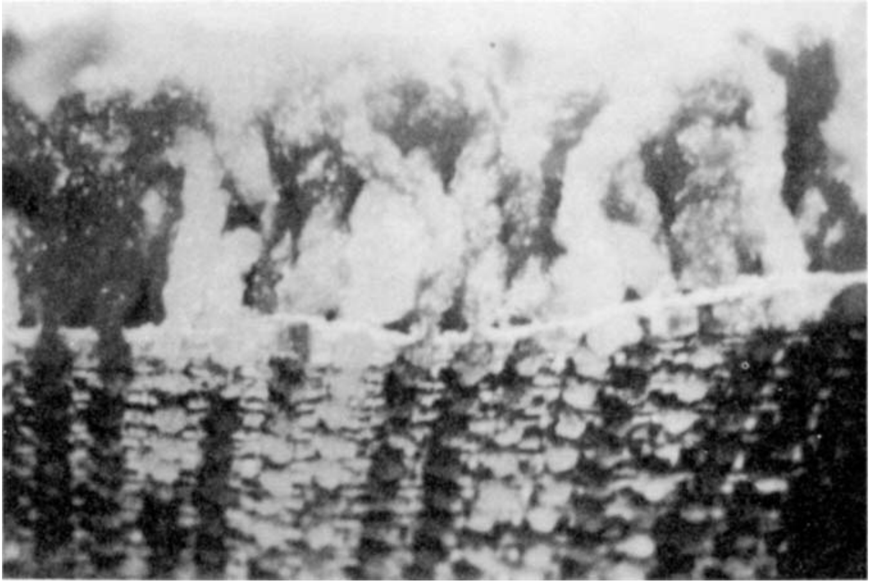
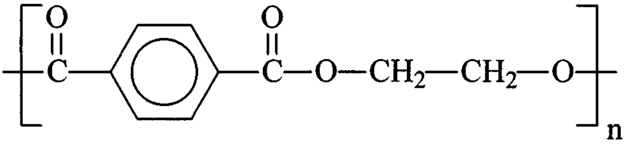


Figure 16.15 Polypropylene carpet backing is one important application of this versatile plastic. (Courtesy of BP Chemicals, Alvin, Texas)

1. Manufacture
   Ziegler-Natta or metal oxide catalysis
2. Properties
   T_m = 170°C, higher than HDPE, can be sterilized at 140°C for hospital applications
   T_g = -10°C, more brittle at low temperatures than HDPE
   Stiffer, harder, higher tensile strength than HDPE
   More degraded than HDPE by heat, light, and oxygen because of tertiary hydrogens. Antioxidants and UV stabilizers can be added.
   Shiny surfaces
   Resists marring
3. Uses
   Injection molding (containers, lids, bottles, toys, plastic chairs, luggage, steering wheels, battery cases, fan shrouds, air cleaner ducts), 31%; fibers and filament (carpet backing, indoor-outdoor carpeting, rope), 30%; resellers, distributors, and compounders, 23%; film and sheet, 11%; blow molding, 2%; miscellaneous, 3%
4. Economics
   Growth from 1990-2000 of 6.5%/yr

6.1.3 Poly(ethylene terephthalate), PET

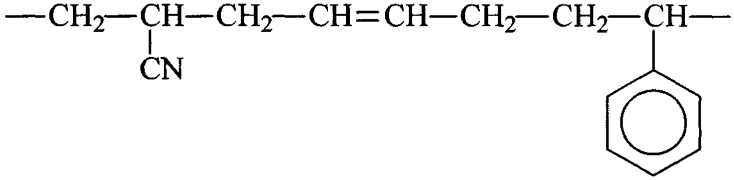


1. Manufacture
   Made from ethylene glycol and either dimethyl terephthalate or terephthalic acid at 200-300°C *in vacuo*
2. Properties
   T_g = 80°C, T_m = 250-265°C
3. Uses
   Bottles for carbonated soft drinks, 60%; custom containers for products other than carbonated soft drinks, 30%; amorphous (packaging) and crystallized (microwave and oven trays for frozen foods), 10%
4. Economics
   Growth from 1989-1998 of 10-15%/yr

Continued strength in the soft drink market and development of PET containers for bottled water give an anticipated growth rate of 10-15%/yr.

New developments for PET beer containers are overcoming problems with O_2 and CO_2 permeability.

6.1.4 Acrylonitrile-Butadiene-Styrene Terpolymer, ABS



1. Manufacture

   Graft polymerization of acrylonitrile and styrene on a preformed polybutadiene elastomer
2. Properties

   Specific gravity = 1.06

   Opaque

   Higher tensile strength, lower elongation than HDPE or PP
3. Uses

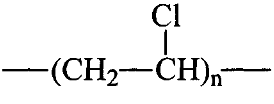
   Transportation, 27%; appliances, 23%; pipe, conduit, and pipe fittings, 13%; electrical, electronic components, 11%; miscellaneous, 26%

   Examples of ABS products: radio housings, telephones, pocket calculators, lawn mower housing, luggage
4. Economics

   U.S. production of ABS resins is 1.4 billion lb/yr

6.2 Hard-Strong

6.2.1 Poly(vinyl chloride), PVC



$$-(CH_2-\overset{\overset{\displaystyle Cl}{|}}{C}H)_n-$$

1. Manufacture

   Discovered in 1915 by Fritz Klatte

Developed in 1926-28 by B. F. Goodrich, Union Carbide, and Du Pont

Peroxide free radical initiation

Suspension (mostly), emulsion, or bulk procedure

2. Properties

$T_m = 140°C$

T_g = 70-85°C, higher than polyolefins because polar C—Cl bond gives dipole-dipole intermolecular attractions

Low crystallinity

Good impact strength

Good chemical resistance

Resistant to insects and fungi

Non-flammable

Easily degraded by heat and light via weak C—Cl bond

Brittle at low temperatures

Becomes a soft-tough polymer and very flexible with 1-2% plasticizer such as dioctyl phthalate, then competing with LDPE

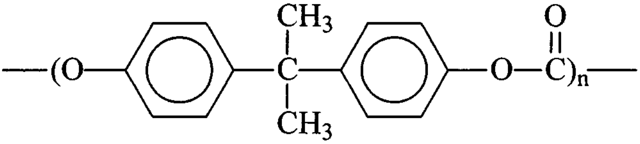
3. Uses

Construction, 76% (including pipe and tubing, roofing, siding, windows and doors, flooring and pipe fittings); consumer goods, 6%; electrical fittings and wire and cable coatings, 4%; transportation, 2%; home furnishings, 2%; miscellaneous, 4%

4. Economics

Growth has been good at 6.4% per year in the last few years, but should be slower in the next few years unless the construction industry improves.

6.2.2 Polycarbonate



1. Manufacture

From a bisphenol A and phosgene slurry with a phase transfer catalyst

2. Properties

A very clear, transparent, strong plastic

Good mechanical properties

High impact strength

Good thermal and oxidative stability

Low moisture absorption

3. Uses

   Automotive (instrument panels and lighting systems), 25%; glazing and sheet (windows), 20%; optical media (eyeglasses), 15%; appliances, 8%; computer and business machines (CD and DVD disks), 7%; medical, 7%; recreation and safety, 7%; miscellaneous, 11%
4. Economics

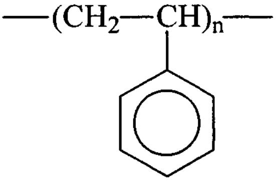
   Overall U.S. demand over 1 billion lb/yr

   Growth good at 7.5%/yr

   Projections to continue at 6-8%/yr because of automotive and computer applications

6.3 Hard-Brittle

6.3.1 Polystyrene, PS



1. Manufacture

   Peroxide initiation

   Suspension or bulk
2. Properties

   $T_m = 227\,^\circ C$, $T_g = 94\,^\circ C$, wide spread good for processing

   Amorphous and transparent—bulky phenyls inhibit crystallization

   Easily dyed

   Very flammable—can add flame retardants

   Not chemically resistant

   Weathers poorly

   Yellows in light—can add UV absorbers
3. Uses

   Packaging and one-time use, 48%; electrical and electronics, 17%; construction, building products, and furniture, 13%; consumer products, including toys, 9%; medical products, 7%; miscellaneous, 6%
4. Economics

   Growth from 1990-2000 only 2.5%/yr

Should be about the same in the near future

Polystyrene's chief weakness is its image. There is a continuing effort to replace it with paper products. The prior use of CFCs as blowing agents in its foam products has contributed to this negative image.

6.3.2 Phenol-Formaldehyde, Phenolics, P/F

1. Manufacture

   One-stage cured by heat

   Two-stage cured by heat and hexamethylenetetramine
2. Properties

   Heat resistance

   Water and chemical resistance

   Dark color
3. Uses

   Plywood adhesive, 48%; fibrous and granulated wood adhesive, 16%; insulation adhesive, 13%; laminate adhesive, 6%; molding compounds, 5%; foundry adhesive, 3%; miscellaneous, 9%

6.3.3 Urea-Formaldehyde, U/F

1. Manufacture

   Methylolurea formation under alkaline conditions, followed by heating under acidic conditions
2. Properties

   White translucent (nearly transparent)

   Can be pigmented to a wide variety of colors

   Light stable

   Less heat and water resistant than phenolics

   Good electrical properties
3. Uses

   Particleboard, 62%; medium density fiberboard, 19%; hardwood plywood, 5%; glass fiber roofing mats, 4%; molding compounds, 3%; miscellaneous, 7%

6.3.4 Melamine-Formaldehyde, M/F

1. Manufacture

   Melamine and formaldehyde, similar to urea-formaldehyde polymerization
2. Properties

Figure 16.16 Polymers are often pelletized during the extrusion process, a convenient state in which to store and ship plastics before final fabrication. (Courtesy of BP Chemicals, Alvin, Texas)

Combines good properties of P/F and U/F resins
Water and heat resistant
Pastel colors
More expensive than P/F or U/F resins

3. Uses
   Surface coatings, 39%; laminates, 33%; molding compounds (especially dinnerware), 8%; paper coating, 7%; miscellaneous, 13%

6.3.5 Unsaturated Polyesters

1. Manufacture
   Maleic and phthalic anhydrides with propylene glycol
   Cross-linked with free radical initiator and styrene
2. Properties
   Variation of monomer percentage gives wide range of properties

3. Uses

Construction, 36%; marine (especially boat hulls), 17%; synthetic marble, 13%; transportation (especially automobile bodies), 10%; miscellaneous, 24%

Examples of products: fireplaces, vanities, plaques, shower stalls, playground equipment, bowling balls, sewer pipe, pistol grips, corrosion resistant tanks

6.3.6 Epoxies

1. Manufacture

Epichlorohydrin, bisphenol A, and ethylenediamine

2. Properties

Fast-setting, strong adhesives

3. Uses

Protective coatings, 53%; electrical/electronic laminates, 11%; bonding and adhesives, 10%; flooring, paving, construction, 8%; composites, 6%; miscellaneous, 12%

6.4 Soft-Tough

6.4.1 Low-Density Polyethylene, LDPE

$$—(CH_2—CH_2)_n—$$

1. Manufacture

Free radical initiators

High pressure and temperature required, 15,000-40,000 psi and 300-500°C

Discovered by ICI in the U.K. in 1933, commercialized in 1938

2. Properties

Much C_4 branching, only 50-60% crystalline, 30 branches per 100 carbons

$T_m = 115°C$, lower than HDPE and LLDPE

Specific gravity = 0.91-0.94, lower than HDPE

Easily processed

Flexible without plasticizers

Resists moisture and chemicals—but porous to oxygen

Easier processed than LLDPE and has good strength and clarity

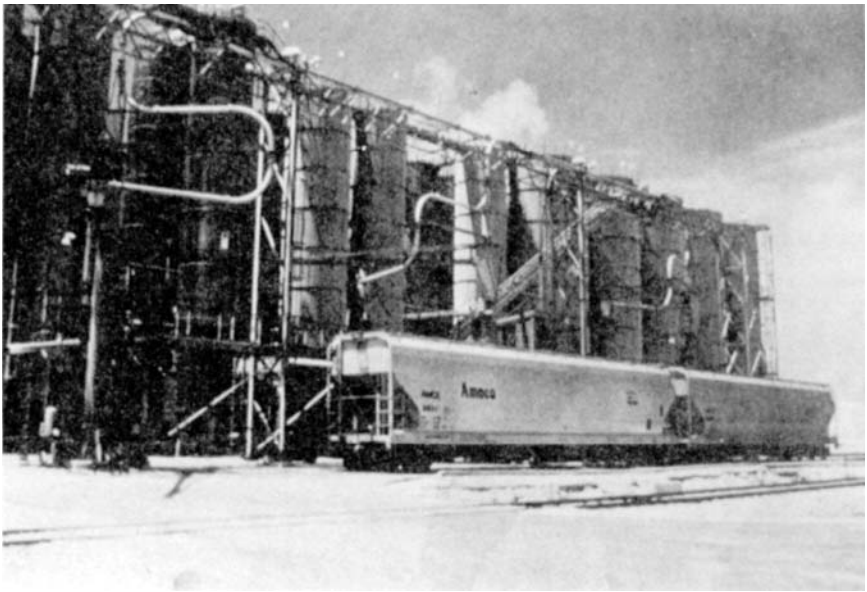


Figure 16.17 Polymer storage in pellet form can be done in large silos, each of which can hold 185,000 lb (7-10 hr of production). The silos can be mixed to ensure uniformity before the pellets are added to a tank car holding nearly the same amount as one silo. (Courtesy of BP Chemicals, Alvin, Texas)

3. Uses
   Film (packaging, trash bags, household wrap, drapes, tablecloths), 59%; extrusion coating, 17%; injection molding (squeeze bottles, toys, kitchen utilityware), 6%; wire and cable, 4%; adhesives and sealants, 4%; miscellaneous, 10%
4. Economics
   Growth of 1%/yr may even be lower in the years to come because of LLDPE

6.4.2 Linear Low-Density Polyethylene, LLDPE

$$—(CH_2—CH_2)_n—$$

1. Manufacture
   Introduced in the late 1970s
   Copolymer of ethylene and small amounts of 1-alkenes for limited branching

Made in a low pressure, low temperature process, 300-600 psi and 100-200°C

Can be made with equipment used for HDPE

2. Properties

   Can be varied by changing the percentage of comonomer

   Higher melting, better tensile strength, but lower clarity than LDPE
3. Uses

   Film, 72%; injection molding, 9%; rotomolding, 6%; wire and cable, 3%; miscellaneous, 10%
4. Economics

   Growth from 1990-2000 of 7.4%/yr

   Will be 5%/yr in the future

Suggested Readings

Chemical Economics Handbook, various articles.

Chemical Profiles in *Chemical Marketing Reporter*, 1-11-99, 6-14-99, 4-10-00, 4-17-00, 3-12-01, 3-26-01, 4-2-01, and 4-9-01.

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 623-707.

Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, pp. 39-103.

Chapter 17

Fibers

1. HISTORY, ECONOMICS, AND TYPES OF FIBERS

Fibers have been used for thousands of years to make various textiles. For centuries certain natural products have been known to make excellent fibers. Probably the first synthetic fiber experiment came with the work of Christian Schönbein, who made cellulose trinitrate in 1846. After breaking a flask of nitric and sulfuric acids, he wiped up the mess with a cotton apron and hung it in front of the stove to dry. Cellulose trinitrate was developed by Hilaire de Chardonnet as a substitute for silk in 1891, but it was very flammable and was soon nicknamed "mother-in-law silk," being an appropriate gift for only disliked persons. When rayon came along in 1892, "Chardonnet silk" was soon forgotten. Then the entirely synthetic fibers came, with the pioneering work of W. Carothers at Du Pont synthesizing the nylons in 1929-30. Commercialization occurred in 1938. Polyesters were made by Whinfield and Dixon in the U.K. in 1941. They were commercialized in 1950.

It is important to understand the different types of fibers. Classes are best differentiated based on both the origin of the fiber and its structure. The structure and chemistry of many of these polymers was discussed earlier in Chapter 14. Table 17.1 contains a list of the three important types of fibers—natural, cellulosic, and noncellulosic—as well as a list of specific polymers as examples of each type. The ones marked with an asterisk are the most important.

Table 17.1 Types of fibers

Natural

1. From plant sources—all are cellulose polymers
   - a. *Cotton (from the cotton plant)
   - b. Flax (from blueflowers)—used to make linen
   - c. Jute (from an East Indian plant)—used for burlap and twine
2. From animal sources—all are proteins
   - a. Silk (from the silkworm)—mostly glycine and alanine
   - b. *Wool (from sheep)—complex mixture of amino acids
   - c. Mohair (from the Angora goat)
3. From inorganic sources
   - a. Asbestos—mostly calcium and magnesium silicates
   - b. Glass—silicon dioxide

Cellulosic

These fibers are also called semisynthetic since the natural cellulose is modified in some way chemically.

1. *Rayon (regenerated cellulose)
2. *Cellulose acetate
3. Cellulose triacetate

Noncellulosic

These are entirely synthetic, made from polymerization of small molecules.

1. *Nylons 6 and 6,6
2. *Polyester—poly(ethylene terephthalate) mostly
3. *Polyolefins—polypropylene mostly
4. Acrylic—polyacrylonitrile
5. Polyurethane

Referring back to Fig. 16.1, we see that the value of U.S. shipments for cellulosic and noncellulosic fibers, though quite small compared to plastics, is still a big industry. While Plastics Materials and Resins (NAICS 325211) in 1998 was $44.9 billion, Noncellulosic Fibers (NAICS 325222) was $10.5 billion and Cellulosic Fibers (NAICS 325221) was $1.5 billion. These two fibers together have a $12.0 billion value, which is 3% of Chemical Manufacturing. We must also remember that many of these fibers are sold outside the chemical industry, such as in Textile Mill Products, Apparel, and Furniture, all large segments of the economy. The importance of fibers is obvious. In 1920 U.S. per capita use was 30 lb/yr, whereas in 1990 it was 66 lb/yr. From 1920 to 1970 the most important fiber by far was cotton.

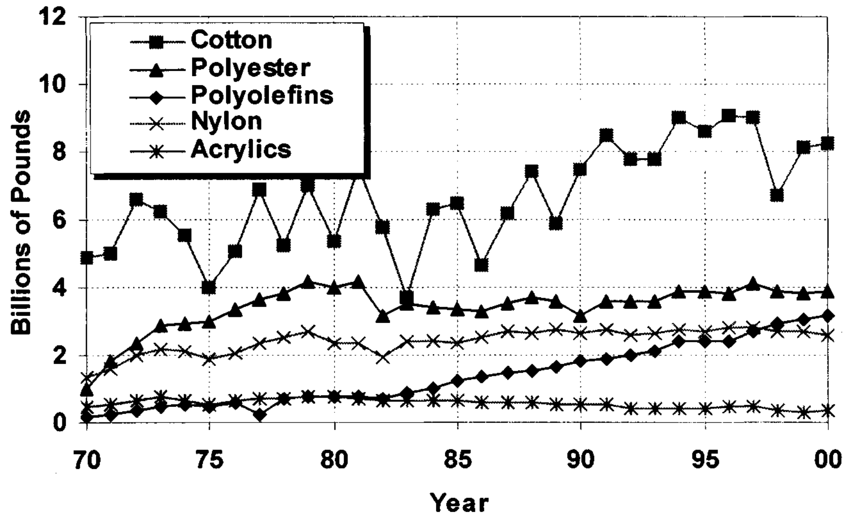


Figure 17.1 U.S. production of fibers. (*Source: Chemical and Engineering News, Chemical and Economics Handbook*, and the U.S. Department of Agriculture/Foreign Agriculture Service)

However, synthetic fibers (cellulosic and noncellulosic) increased much more rapidly in importance, with cellulosics booming between World Wars I and II and noncellulosics dominating after World War II, while all that time cotton showed only a steady pace in comparison. The more recent competition between the various fibers in the United States is given in Fig. 17.1. Nylon was originally the most important synthetic (1950-1971) but polyester now leads the market (1971-present). For a few years (1970-1980) acrylics were third in production, but since 1980 polyolefins have been rapidly increasing. Polyolefins are now second only to polyester in synthetic fiber production. Cotton, being an agricultural crop, certainly demonstrates its variable production with factors such as weather and the economy. It is an up-and-down industry much more so than the synthetics.

The student should also review Chapter 1, Table 1.16, where the top polymer production is given numerically. Overall a 1.8% per year growth was recorded for 1990-2000 in synthetic fibers. A net decrease in the cellulosics of 3.6% per year shows their diminishing importance. Acrylics also decreased 3.9% annually in this period. The rising star is polyolefins, which increased 5.8% per year in the past decade.

U.S. price trends show that cotton and polyester are the most popular for good reason: they are the cheapest. Nylon and acrylic have had price increases over the last few years, part of which may be due to improvements and safeguards needed to manufacture their precursors acrylonitrile, butadiene, and benzene, which are on carcinogen lists.

2. PROPERTIES OF FIBERS

It is important to understand some common terms used in this industry before studying fiber properties or individual fibers. The term *fiber* refers to a one-dimensional structure, something that is very long and thin, with a length at least 100 x its diameter. Fibers can be either staple fibers or monofilaments. *Staple fibers* are bundles of parallel short fibers. *Monofilaments* are extruded long lengths of synthetic fibers. Monofilaments can be used as single, large diameter fibers (such as in fishing line) or can be bundled and twisted and used in applications similar to staple fibers.

Fabrics are two-dimensional materials made from fibers. Their primary purpose is to cover things and they are commonly used in clothes, carpets, curtains, and upholstery. The motive for covering may be aesthetic, thermal, or acoustic. Fabrics are made out of *yarns* or twisted bundles of fibers. The *spinning of yarns* can occur in two ways: staple fibers can be twisted into a thread ("spun yarn") or monofilaments can be twisted into a similar usable thread ("filament yarn" or "continuous filament yarn"). All these definitions are important in order to understand the conversation of the fiber industry.

The tensile properties of fibers are not usually expressed in terms of tensile strength (lb/in^2 or kg/cm^2). The strength of a fiber is more often denoted by tenacity. *Tenacity* (or breaking tenacity) is the breaking strength of a fiber or yarn in force per unit denier (lb/denier or g/denier). A *denier* is the weight in grams of 9,000 m of fiber at 70°F and 65% relative humidity. A denier defines the linear density of a fiber since it depends on the density and the diameter of a fiber. To give you an idea of common values of deniers for fibers, most commercially useful fibers are 1-15 denier, yarns are 15-1600 denier, and monofilament (when used singly) can be anywhere from 15 denier on up. Table 17.2 lists common values of tenacity for various fibers and compares these values to tensile strength. Tenacities can be converted into tensile strength in pounds per inch square by the following formula:

$$\text{tensile strength (lb/in}^2\text{)} = \text{tenacity (g/denier)} \times \text{density (g/cm}^2\text{)} \times 12{,}791$$

Note that tenacity values for most fibers range from 1-8 g/denier.

Table 17.2 Physical Properties of Typical Fibers

Polymer	Tenacity (g/denier)	Tensile Strength (kg/cm^2)	Elongation (%)
Cellulose			
Cotton	2.1-6.3	3000-9000	3-10
Rayon	1.5-2.4	2000-3000	15-30
High-tenacity rayon	3.0-5.0	5000-6000	9-20
Cellulose diacetate	1.1-1.4	1000-1500	25-45
Cellulose triacetate	1.2-1.4	1000-1500	25-40
Proteins			
Silk	2.8-5.2	3000-6000	13-31
Wool	1.0-1.7	1000-2000	20-50
Nylon 6,6	4.5-6.0	4000-6000	26
Polyester	4.4-5.0	5000-6000	19-23
Polyacrylonitrile (acrylic)	2.3-2.6	2000-3000	20-28
Polyurethane (Spandex)	0.7	630	575
Polypropylene (polyolefin)	7.0	5600	25
Asbestos	1.3	2100	25
Glass	7.7	2100	3

Source: Seymour/Carraher

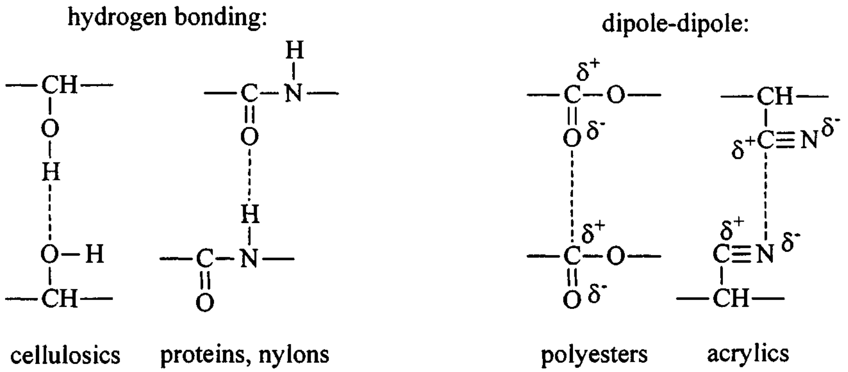
In general, you should recall that the tensile strength and modulus of fibers must be much higher than that for plastics and their elongation must be much lower. Synthetic fibers are usually stretched and oriented uniaxially to increase their degree of parallel chains and increase their strength and modulus.

What makes a polymer a good fiber? This is not an easy question to answer. If one fact can be singled out as being important, it would be that all fibrous polymers must have strong intermolecular forces of one type or another. Usually this means hydrogen bonding or dipole-dipole interactions, shown on the following page for various types of fibers.

Besides the high tenacity, a number of other properties are considered necessary for most fiber applications. Although no one polymer is superior in all of these categories, the list in Table 17.3 represents ideals for polymers being screened as fibers.

Table 17.3 Ideal Properties of Polymers for Fiber Applications

1. High tensile strength, tenacity, and modulus
2. Low elongation
3. Proper T_g and T_m. A low T_g aids in easy orientation of the fiber. The T_m should be above 200°C to accept ironing (as a textile) but below 300°C to be spinnable.
4. Stable to chemicals, sunlight, and heat
5. Nonflammable
6. Dyeable
7. Resilient (elastic) with a high flex life (flexible lifetime)
8. No static electrical build-up
9. Hydrophilic (adsorbs water and sweat easily)
10. Warm or cool to the touch as desired
11. Good "drape" (flexible on the body) and "hand" (feel on the body)
12. No shrinking or creasing except where intentional
13. Resistance to wear after repeated washing and ironing

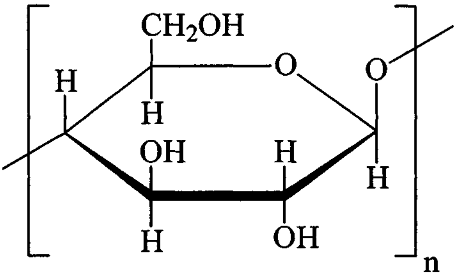


3. IMPORTANT FIBERS

A study of the fiber industry is not complete without some knowledge of the characteristics of individual fibers. Since each is so different it is difficult to generalize or compare directly. This section presents a summary of each important fiber, including pertinent information on their manufacture, properties, uses, and current economics in a brief, informal and concise manner.

3.1 Natural

3.1.1 Cotton



(a pure form of cellulose)

1. Fewer processing steps, cheaper than wool
2. Good hand
3. Wears hard and long
4. Easily dyed via free hydroxy groups
5. Absorbs water but dries easily. If preshrunk, it is stable to washing and ironing more than other fibers.
6. Hydrophilic—cool and comfortable. Comfort never matched by synthetics. Used especially in towels and drying cloths.
7. Disadvantages: creases easily, requiring frequent ironing; agricultural variables in growing the plant; brown lung disease in workers in mills; waste about 10% in harvest; variable strength; unpredictable price

3.1.2 Wool

(protein, mostly keratin, a complex mixture of amino acids)

1. Processing requires 20 stages, therefore very expensive
2. Good resilience (elasticity) because orientation changes α-keratin (helical protein) into β-keratin (zigzag). Example: woolen carpet recovers even after years of heavy furniture.
3. Good warmth due to natural crimp (many folds and waves) which retains air, therefore a good insulator
4. Hydrophilic—absorbs perspiration away from body and is comfortable, not sweaty
5. Dyed easily since it has acidic and basic groups in the amino acid
6. Disadvantages: expensive; retains water by hydrogen bonding with washing, causing shrinkage; many people allergic to protein

3.2 Cellulosic

3.2.1 Rayon

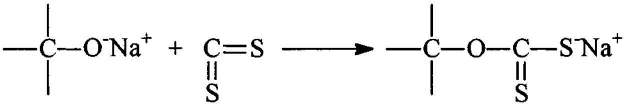
(regenerated cellulose from wood pulp, especially higher molecular weight "alpha" fraction not soluble in 18% caustic)

1. Manufacture
   a. Steeping 1 hr in 18% caustic gives "soda" cellulose,

$$(C_6H_{10}O_5)_n + NaOH \longrightarrow [(C_6H_{10}O_5)_2 \cdot NaOH]_n$$

where some C—OH are converted into C—O$^-$Na$^+$

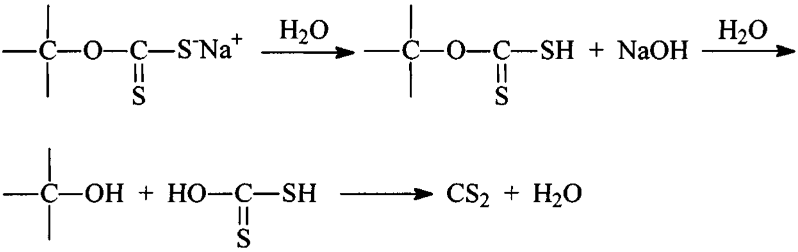
   b. Reaction with CS_2,



$$-\overset{|}{\underset{|}{C}}-O^-Na^+ + \underset{\underset{S}{\|}}{C}=S \longrightarrow -\overset{|}{\underset{|}{C}}-O-\underset{\underset{S}{\|}}{C}-S^-Na^+$$

about 1 xanthate for each two glucose units, soluble in 6% NaOH for spinning, called "viscose rayon"

   c. Ripening—slow hydrolysis

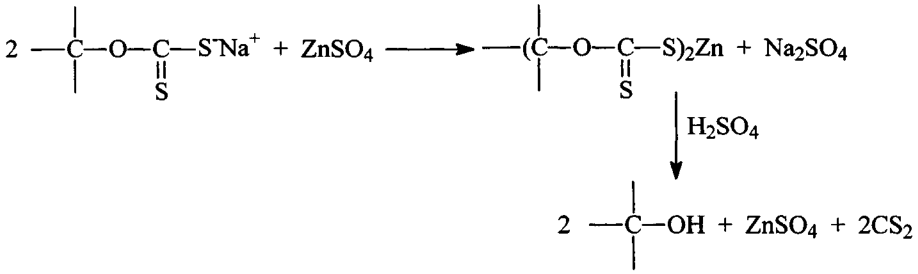


$$-\overset{|}{\underset{|}{C}}-O-\underset{\underset{S}{\|}}{C}-S^-Na^+ \xrightarrow{H_2O} -\overset{|}{\underset{|}{C}}-O-\underset{\underset{S}{\|}}{C}-SH + NaOH \xrightarrow{H_2O}$$

$$-\overset{|}{\underset{|}{C}}-OH + HO-\underset{\underset{S}{\|}}{C}-SH \longrightarrow CS_2 + H_2O$$

"viscose"—different molecular weight than starting cellulose, has some xanthate groups

   d. Spinning—$ZnSO_4$, H_2SO_4 bath.
   H_2SO_4 neutralizes NaOH of viscose solution. $ZnSO_4$ gives intermediate which decomposes more slowly.



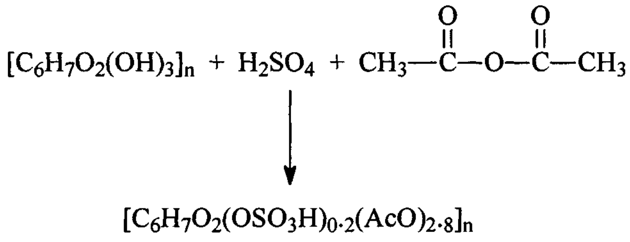
$$2\ -\overset{|}{\underset{|}{C}}-O-\underset{\underset{S}{\|}}{C}-S^-Na^+ + ZnSO_4 \longrightarrow -(\overset{|}{\underset{|}{C}}-O-\underset{\underset{S}{\|}}{C}-S)_2Zn + Na_2SO_4$$

$$\xrightarrow{H_2SO_4} 2\ -\overset{|}{\underset{|}{C}}-OH + ZnSO_4 + 2CS_2$$

2. Properties
   Dyeable (free hydroxy groups), hydrophilic (comfortable), stable, low price, poor wash and wear characteristics
3. Uses
   Apparel, 31%; home furnishings (curtains, draperies, upholstery, mattress ticking), 24%; nonwovens (medical and surgical, wipes and towels, fabric softeners), 33%; miscellaneous, 12%.
4. Economics
   Peak production in 1950s, 1960s. Declined by 5.6%/yr in 1970-1980, 4.9%/yr in 1980-1990, and 3.6%/yr in 1990-2000.

3.2.2 Acetate

1. Manufacture
   a. Esterification



$$[C_6H_7O_2(OH)_3]_n + H_2SO_4 + CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow [C_6H_7O_2(OSO_3H)_{0.2}(AcO)_{2.8}]_n$$

   b. "Ripening" with $Mg(OAc)_2$, H_2O

$$\text{cellulose sulfoacetate} \xrightarrow[H_2O]{Mg(OAc)_2} [C_6H_7O_2(OH)_{0.65}(AcO)_{2.35}]_n + MgSO_4$$

Usually the primary carbon has the OH, secondary carbons the OAc. Cellulose triacetate has three OAc groups.

2. Properties

   Lower tenacity than any other fiber because the bulky OAc group keeps molecules far apart

   Free OH more easily dyed and more hydrophilic than triacetate

   Random acetate groups make it less crystalline than triacetate. So triacetate is better for ironing. But triacetate gives stiffer fabrics with inferior drape and hand.

   Both are softer than rayon but not so strong, have poor crease resistance, and are not colorfast.

3. Uses

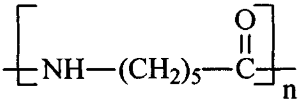
   Cigarette filters, 61%; yarn (especially for apparel, curtains, draperies, bedspreads, quilt covers), 39%.

4. Economics

   Down 4.5%/yr from 1970-1980, 4.2%/yr from 1980-90, and 3.6%/yr from 1990-2000

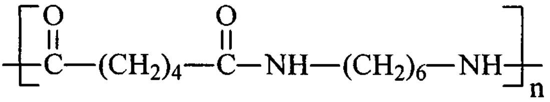
3.3 Noncellulosic

3.3.1 Nylon 6 and 6,6



$$\left[NH-(CH_2)_5-\overset{O}{\overset{\|}{C}} \right]_n$$

nylon 6



$$\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH \right]_n$$

nylon 6,6

1. Manufacture

   Nylon 6,6 developed by W. H. Carothers of Du Pont in 1930s. Adipic acid, HMDA, 280-300°C, 2-3 hr, vacuum. Trace of acetic acid terminates chains with acid groups and controls molecular weight.

   Nylon 6 developed by Paul Schlak in Germany in 1940. Caprolactam plus heat plus water as a catalyst.

   Fibers are melt spun (no solvent) while still above T_m (= 265-270°C for nylon 6,6 and 215-220°C for nylon 6). Extruded through a spinerette.

   Fibers oriented by stretching to 4 x original length by cold drawing (two pulleys at different speeds) or by spin drawing as it is being cooled

2. Properties

   Strongest and hardest wearing of all fibers

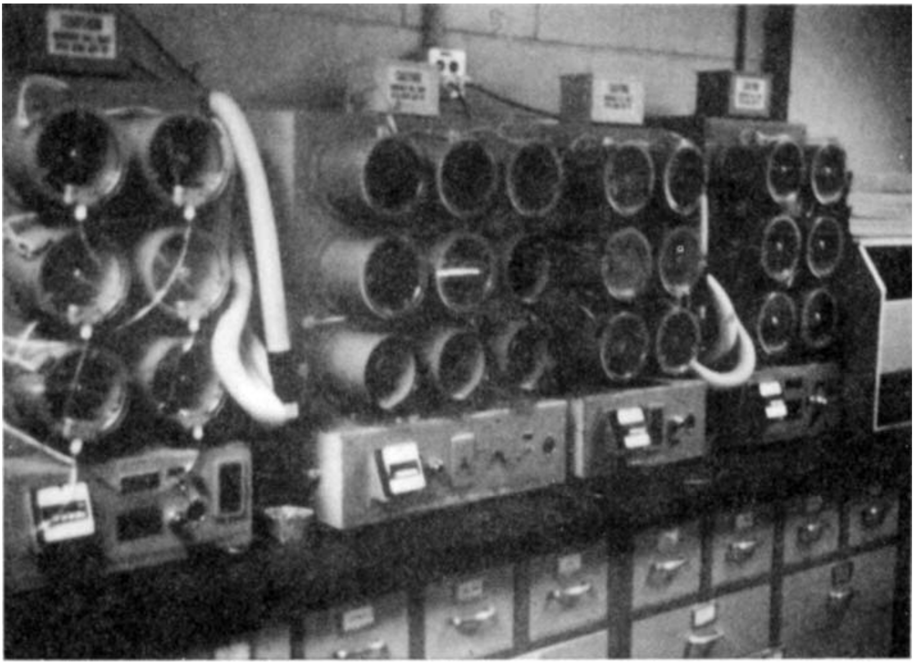


Figure 17.2 Pilling chambers to test, by rapid rotation, the tendency of a fabric to form pills as in repeated washings and use. (Courtesy of Du Pont)

Heat stable

Dyeable

Disadvantages: hydrophobic ("cold and clammy"), degraded by UV, yellows with age, poor hand, tends to "pill" (gentle rubbing forms small nodules or pills, where surface fibers are raised, see Fig. 17.2)

3. Uses

Carpets and rugs, 74%; industrial and other (tire cord and fabric, rope and cord, belting and hose, sewing thread), 16%; apparel (especially hosiery, anklets, and socks), 10%

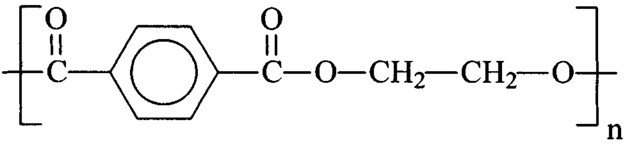
4. Economics

Production increased 5.7%/yr from 1970-1980, only 1.2%/yr from 1980-1990, and decreased 0.2%/yr from 1990-2000.

The carpet and rug market has increased dramatically in recent years.

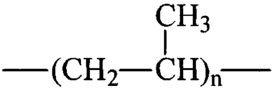
Nylon 6,6 is two thirds of the U.S. market, nylon 6 one third.

3.3.2 Polyester, Poly(ethylene terephthalate), PET



1. Manufacture
   - Developed by Whinfield and Dixon in the U.K. Originally made by transesterification of DMT and ethylene glycol in a 1:2.4 ratio, distillation of the methanol, then polymerization at 200-290°C *in vacuo* with SbO_3 as catalyst.
   - In early 1960s pure TA began to be used with excess ethylene glycol at 250°C, 60 psi to form an oligomer with $n = 1\text{-}6$, followed by polymerization as in the DMT method. Now both methods are used.
   - Melt spin like nylon, $T_m = 250\text{-}265\,°C$
   - Orientation above T_g of 80°C to 300-400%
2. Properties
   - Stable in repeated laundering
   - Complete wrinkle resistance
   - Blends compatibly with other fibers, especially cotton
   - Can vary from low tenacity, high elongation to high tenacity, low elongation by orientation
   - Disadvantages: stiff fibers (aromatic rings), poor drape except with cotton blends, hydrophobic, pilling, static charge buildup, absorbs oils and greases easily (stains)
3. Uses
   - Clothing (suits, pants, shirts, and dresses either nonblended or blended with other fibers such as cotton), 50%; home furnishings (carpets, pillows, bedspreads, hose, sewing thread, draperies, sheets, pillowcases), 20%; industrial (tire cords), 30%
4. Economics
   - Production increased 10.5%/yr from 1970-1980, decreased 2.2%/yr from 1980-1990, and increased 1.9%/yr from 1990-2000.

3.3.3 Polyolefin



$$-(CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H)_n-$$

Figure 17.3 Spinning of fibers for use in carpets. (Courtesy of Du Pont)

1. Manufacture
   - Mostly isotactic polypropylene homopolymer, but some copolymer with polyethylene, and some HDPE
   - A high molecular weight is needed, 170,000-300,000, for good mechanical strength because of weak intermolecular forces, only van der Waals.
   - Fiber produced by melt spinning
2. Properties
   - Low density (0.91), the lowest of all commercial fibers, meaning lightness and high cover
   - Outstanding chemical resistance, serving industrial filtration
   - High abrasion resistance for floor covering, upholstery, and hosiery
   - Insensitive to water, giving dimensional stability and fabric dryness in contact with the skin
   - Resistance to mildew, microorganisms, and insects
   - Good insulator and electrical properties
   - Lowest thermal conductivity of commercial fibers, giving high thermal insulation in textiles
   - No skin irritation or sensitization, non-toxic

Disadvantages: not easily dyeable, low resistance to oxidation—but additives help, easily soiled, poor for ironing, poor for dry cleaning

3. Uses

   Industrial, including rope, twine, conveyor belts, carpet backing, tarpaulin, awnings, cable, bristles; home textile applications, including floor covering, upholstery fabric, wall covering, blankets; apparel, especially sportswear and hosiery

4. Economics

   Growth rate large, 11%/yr from 1970-1980, 9%/yr from 1980-1990, and 5.8%/yr from 1990-2000

   Surpassed acrylics in 1980, nylon in 1998, and is catching up to polyester

Suggested Readings

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 735-799.

Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, pp. 104-125.

Chapter 18

Elastomers

1. HISTORY AND ECONOMICS

Although naturally occurring rubber from the tropical tree has been known for ages, the Spanish navigator and historian Gonzalo Valdez (1478-1557) was the first to describe the rubber balls used by Indians. Natural rubber was brought back to Europe from the Amazon in 1735 by Charles Condamine, a French mathematical geographer, but it remained only a curiosity. Michael Faraday made a rubber hose from it in 1824. But it was not until Charles Goodyear discovered vulcanization in 1839 that natural rubber got its first wave of interest. As the story goes, Charles became so involved with his job that he set up a laboratory at home to study the chemistry of rubber. Because his wife hated the odor of his experiments, he could only continue his work at home when she was not around. While studying the effect of sulfur and other additives on the properties of rubber he was interrupted unexpectedly by his wife one day when she returned home early from shopping. He quickly shoved his latest mixture into the oven to hide it. As fate had it, the oven was lit, the rubber was vulcanized, and the modern era of elastomer research was born. His first patent covering this process was issued in 1844.

Today both natural rubber, an agricultural crop, and synthetic elastomers are multi-billion dollar businesses. Looking back at Fig. 16.1, we see that Synthetic Rubber (NAICS 325212) totals $5.7 billion. It is a large area of polymer use and is 1% of Chemical Manufacturing. But in the related industry covering final end products called Plastics and Rubber Products

Table 18.1 U.S. Production of Synthetic Elastomers, Consumption of Natural Rubber

Natural rubber	29%
SBR	25
Polybutadiene	17
Ethylene-propylene	10
Nitrile	3
Polychloroprene	2
Miscellaneous	14

Source: Chemical and Engineering News, and *Chemical Economics Handbook*

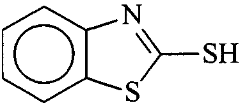
Manufacturing (NAICS 326), Rubber Products (NAICS 3262) totals $35.3 billion, of which Tires (NAICS 32621) makes up $15.4 billion, showing the dominance of the automobile tire market in this sector of the chemical industry. The top polymer production summary in Table 1.16 gives a numerical list of important synthetic elastomers. Styrene-butadiene rubber (SBR) dominates the list at 1.93 billion lb for U.S. production. All other synthetic elastomers are much smaller. While elastomers had a slight increase in production from 1980-1990, only 0.5% annually, SBR was down 2.3% per year. From 1990-2000 it was up 1.0% per year. The fastest growing elastomer is ethylene-propylene, up 5.2% annually for 1990-2000. Table 18.1 gives a breakdown in percent production of synthetic elastomers and consumption of natural rubber in the U.S.

2. NATURAL RUBBER

Natural rubber can be found as a colloidal emulsion in a white, milky fluid called latex and is widely distributed in the plant kingdom. The Indians called it “wood tears.” It was not until 1770 that Joseph Priestly suggested the word *rubber* for the substance, since by rubbing on paper it could be used to erase pencil marks, instead of the previously used bread crumbs. At one time 98% of the world’s natural rubber came from a tree, *Hevea brasiliensis*, native to the Amazon Basin of Brazil which grows to the height of 120 ft. Today most natural rubber is produced on plantations in Malaysia, Indonesia, Singapore, Thailand, and Sri Lanka. Other rubber-bearing plants can be cultivated, especially from a guayule shrub, which is now more important than the tree.

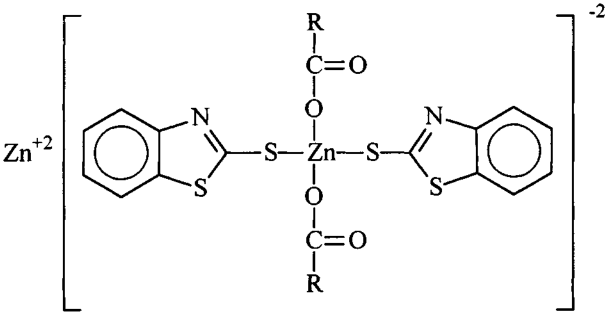
3. VULCANIZATION

The process that makes the chemistry, properties, and applications of elastomers so different from other polymers is cross-linking with sulfur, commonly called vulcanization. The modern method of cross-linking elastomers involves using a mixture of sulfur and some vulcanization accelerator. Those derived from benzothiazole account for a large part of the market today. Temperatures of 100-160 °C are typical.

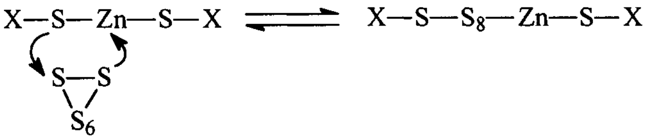


2-mercaptobenzothiazole

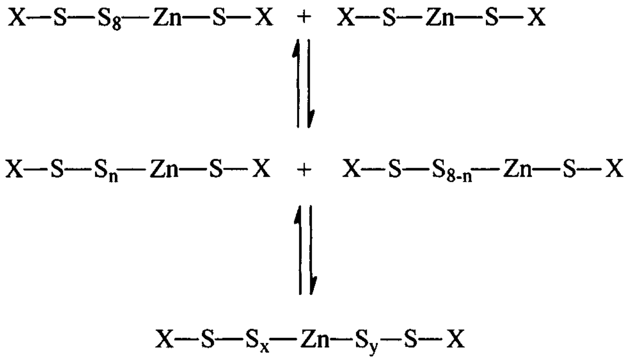
Zinc oxide and certain fatty acids (R—COOH) are also added. Although this mechanism is by no means completely understood, it is proposed that the benzothiazole and zinc oxide give a zinc mercaptide, and this forms a soluble complex with the fatty acid.



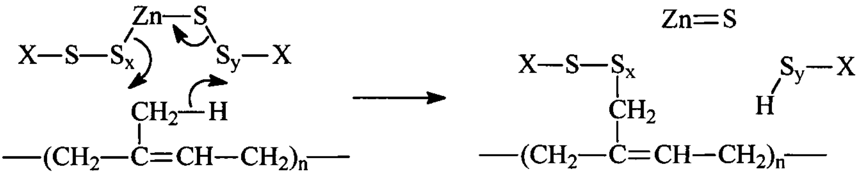
Reaction of this with S_8 molecules gives a persulfidic complex (X = benzothiazole).



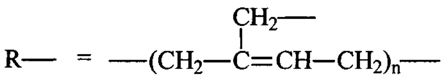
Interchange with the original complex leads to the formation of a mixture of polysulfidic complexes, which are considered to be the active sulfurating species.



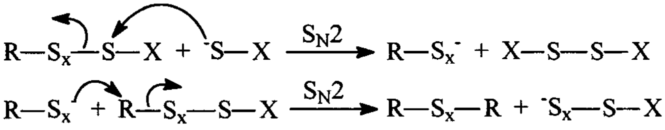
These complexes then react with the allyl carbons of rubber, the most reactive sites in the polymer.



The cross-linking occurs by reactions of the following type, where



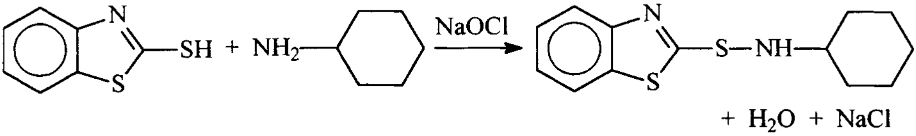
$$\text{R—} = \text{—(CH}_2\text{—}\overset{\text{CH}_2\text{—}}{\text{C}}\text{=CH—CH}_2\text{)}_n\text{—}$$



Usually a mono- or disulfide cross-link occurs but larger numbers of sulfur atoms are possible. If the total percentage of sulfur in the material is <5%, it is usually very elastic. If >5% of sulfur is added, it produces a very hard, dark, nonelastic material called ebonite, sometimes used for things like combs and buttons.

4. ACCELERATORS

In 1906 Oenslager and Marks at Diamond Rubber Co. (later B. F. Goodrich Co.) began working on accelerators for cross-linking with sulfur. These substances not only increase the rate of vulcanization but create a final product that is more stable and less susceptible to aging. Benzothiazoles now own 22% of the accelerator market, which is about 100 million lb/yr. Other types of accelerators are sulfenamides (50%), dithiocarbamates (5%), thiurams (4%), and others (19%). The reason for the differences is that some cause very fast vulcanization rates like sulfenamides, and some slower like benzothiazoles. Sulfenamides such as N-cyclohexyl-2-benzothiazolsulfenamide can be made from benzothiazoles by reaction of an amine and an oxidizing agent such as NaOCl, HNO_2, or H_2O_2.



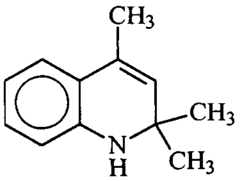
5. REINFORCING AGENTS

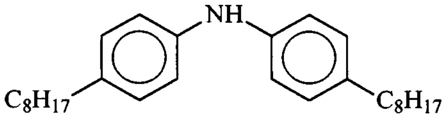
Even with vulcanization, however, many elastomers lack the balance of properties required for good wear. Reinforcing agents have been studied to strengthen the rubber mechanically. In 1912 the Diamond Rubber Co. found that addition of carbon to rubber tires caused them to last ten times longer than without this reinforcing agent. Rubber became the substance of choice for automobile tires and conveyor belts. Glass, nylon, polyester, and steel now aid carbon in reinforcement for many applications. Up to 20% of these reinforcing agents can increase the tensile strength of the rubber by 40%.

6. ANTIDEGRADANTS

Most polymers are attacked by oxygen, ozone, and ultraviolet light. Rubber is one such polymer that is rapidly degraded in molecular weight and mechanical strength. Over 100 chemicals, collectively called age resistors or age antidegradants, are added to elastomers to keep them from becoming brittle, turning sticky, developing cracks, etc.

Most oxidation inhibitors today are either amines, phenols, or phosphites. Phenols were suggested as early as 1870 to combat aging. Amines are now used more than phenols in elastomers. Combinations are often used for heat, oxygen, ozone, UV, and moisture resistance. Two examples of amine age resistors are given here. The market is about 150 million lb/yr, of which amines are about 60%. The market breakdown for antidegradants is phenylenediamines (50%), phenolics (13%), phosphites (13%), quinolines (10%), diphenylamines (6%), and others (8%).



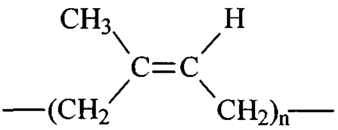


Other kinds of rubber chemicals are blowing agents, peptizers, and retarders. The total market for all chemical additives for rubber is over 250 million lb/yr.

7. DEVELOPMENT OF SYNTHETIC RUBBER

Until the 1930s natural rubber from *Hevea brasiliensis* was the only available elastomer. The United States had to, and still does, import every pound. Although research on synthetic substitutes began before 1940 in this country, World War II influenced speedy development of substitutes when our supply of natural rubber from the Far East was cut off. Gasoline had to be rationed not because of its shortage, but because of the automobile tire shortage.

In 1910 scientists concluded that natural rubber was *cis*-1,4-polyisoprene.



In 1931 Du Pont introduced the first synthetic elastomer, polychloroprene (Neoprene®, Duprene®), and Thiokol Corporation introduced a polysulfide rubber called Thiokol®. Polychloroprene, although very expensive compared to polyisoprene, has superior age resistance and chemical inertness. It is also nonflammable.

The Government Rubber Reserve Company in the 1940s pioneered the development of styrene-butadiene copolymers, by far the largest volume of synthetic rubber used today. Now usually known as SBR, it has also been called Buna-S, *Bu*tadiene with a sodium (*Na*) catalyst and copolymerized with *s*tyrene, or GR-S, *G*overnment *R*ubber *S*tyrene. Although it took many years to develop, it is now the rubber of choice for most applications today, especially automobile tires.

Polyisobutylene, commonly called butyl, was first developed in 1937 by Esso Research and Engineering Co. Its main repeating unit is isobutylene but it contains some isoprene for cross-linking. Originally butyl was used for automobile tire inner tubes, where it was replaced in 1955 by tubeless tires. However, most inner tubes still employed today are butyl rubber. In addition to being used for engine mounts and suspension bumpers, it has found large volume uses as liners in reservoirs and in irrigation projects.

Hypalon® chlorosulfonated polyethylene was introduced by Du Pont in 1952. Although not a high volume rubber it has found use in coatings and hoses.

8. CATALYSTS AND MECHANISMS

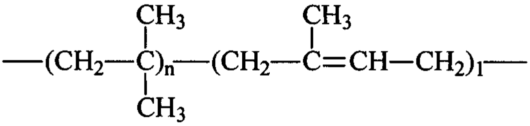
The mid-1950s saw the first commercial production by Goodrich, Firestone, and Goodyear of polymers with stereochemistry which is consistent or regular. In the early 1950s Karl Ziegler in Germany and Giulio Natta in Italy found catalysts that polymerized olefins with regular configurations. The Ziegler-Natta catalysts were primarily a combination of a transition metal salt ($TiCl_3$ or $TiCl_4$) and an organometallic compound (Et_3Al). By proper manipulation of the ratio of these two substances either *cis*-1,4- or *trans*-1,4-polyisoprene from isoprene can now be prepared. The mechanism of Ziegler-Natta polymerization was given for polypropylene in Chapter 14, Section 2.4. Review this and work through the mechanism with an elastomer monomer such as butadiene.

Many of the synthetic elastomers now made are still polymerized by a free radical mechanism. Polychloroprene, polybutadiene, polyisoprene, and styrene-butadiene copolymer are made this way. Initiation by peroxides is common. Many propagation steps create high molecular weight products. Review the mechanism of free radical polymerization of dienes given in Chapter 14, Section 2.2.

Butyl rubber, polyisobutylene, is an example of cationic polymerization with an acid. Review Chapter 14, Section 2.3. A small amount of isoprene is added to enable cross-linking during vulcanization through the allylic sites.

$$R^{\oplus} + CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 \longrightarrow R{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2^{\oplus}$$

The more complex structure of this polymer must therefore be



$$—(CH_2—\overset{CH_3}{\underset{CH_3}{C}})_n—(CH_2—\overset{CH_3}{C}=CH—CH_2)_1—$$

9. SBR VS. NATURAL RUBBER

By far the largest selling elastomers are SBR and natural rubber. SBR at 1.93 billion lb/yr accounts for about 35% of the U.S. synthetic rubber market and 25% of the total rubber market. The U.S. imports about 2.2 billion lb of natural rubber per year. A distant third is polybutadiene at 1.33 billion lb. In 1940 natural rubber had 99.6% of the U.S. market. Today it has only 29%. In 1950 synthetic elastomer consumption passed natural rubber use in the U.S. Since then it has been a battle between the leading synthetic, SBR, and the natural product. It is apparent that these two polymers are very important. Table 18.2 summarizes and compares them by their properties.

Table 18.2 SBR and Natural Rubber

Property	Natural	SBR
Tensile, strength, psi	4,500	3,800
Percent elongation	600	550
300-400% modulus, psi	2,500	2,500
Temperature range for use, °C	-60 to 100	-55 to 100
Degree of elasticity	Excellent	Good
Tear resistance	Good	Moderate
Abrasion resistance	Moderate	Good
Age resistance	Poor	Moderate
Solvent resistance	Poor	Poor
Gas impermeability	Good	Moderate
Uniformity	Variable	Constant
Versatility	Lower	Higher
Processibility	Easier	Harder
Tolerance for oil and carbon additives	Lower	Higher
Price stability	Bad	Good
Percent of U.S. market	29	25

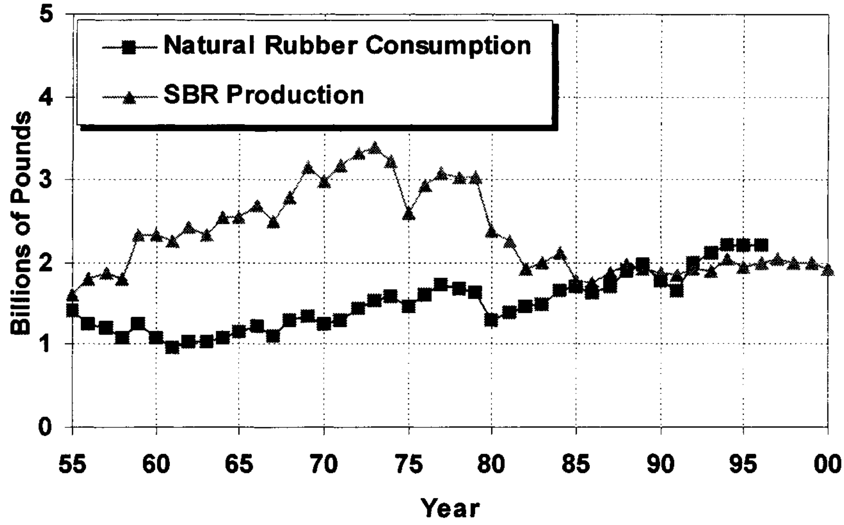


Figure 18.1 U.S. consumption of natural rubber vs. SBR production. (*Source: Chemical and Engineering News* and *Chemical Economic Handbook*)

The balance between natural rubber and SBR is a delicate one. Natural rubber has made a comeback and reversed its downward trend. Developments of rubber farming have raised the yield from 500 lb/acre/yr to 2,000-3,000. Petrochemical shortages and price increases have hurt SBR. Finally, the trend toward radial-ply tires, which contain a higher proportion of natural rubber, favors this comeback. Fig 18.1 shows the U.S. natural rubber consumption trends vs. U.S. SBR production, where this "bounceback" of the natural rubber market is very evident from 1980 to the present. The competitive price structure for these two elastomers through the years has been very evident, and their prices are never too far apart.

10. TIRES

No discussion of elastomers is complete without a mention of tire technology. About 70% of all synthetic elastomers in the U.S. are used in tires. About 264 million tires are produced in the U.S. annually, 217 million for cars and the rest for trucks and busses. A typical tire is made up of four parts: (1) the tread, which grips the road; (2) the sidewall, which protects the

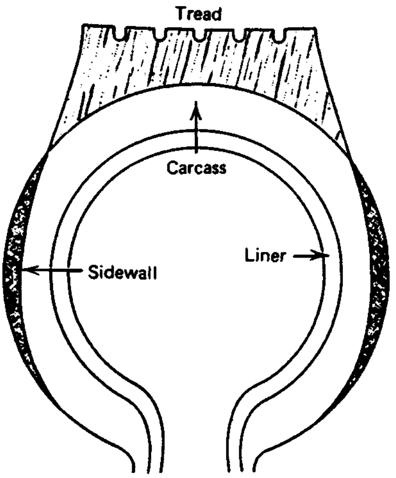


Figure 18.2 Parts of a typical tire. (*Source:* Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, John Wiley & Sons, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

sides of the tire; (3) the liner, which prevents air loss; and (4) the carcass, which holds the layers together (Fig. 18.2).

The tire is about 50% rubber by weight. Carbon black (as a reinforcing agent), extender oil, and the tire cord in the carcass make up the rest. The cord was rayon for many years. Glass fiber has also been popular. But now nylon, polyester, and steel are the major cord components. Steel became most popular in radial tires of the 1980s and is growing in importance as the primary reinforcing agent. About 75% of car radial tires and 92% of truck radials are steel belted.

The tread must have the best possible "grip" to the road. Grip is inversely related to elasticity, and natural rubber has good elasticity but poor grip, so no natural rubber is used in automobile tire treads. Treads are blended of SBR and polybutadiene in an approximate ratio of 3:1. Truck tire treads do have natural rubber, between 65-100%, to avoid heat buildup and because grip is not so necessary in heavy trucks. Aircraft tires consist of 100% natural rubber.

The carcass requires better flexing properties than the tread and is a blend of natural rubber and SBR, but at least 60% of natural rubber. The sidewalls have a lower percentage of natural rubber, from 0-50%. The liner is made of butyl rubber because of its extreme impermeability to air.

The most important single trend in the U.S. tire market is the switch from cross-ply and belted bias-ply to radial-ply tires. Radials held only 8% of the

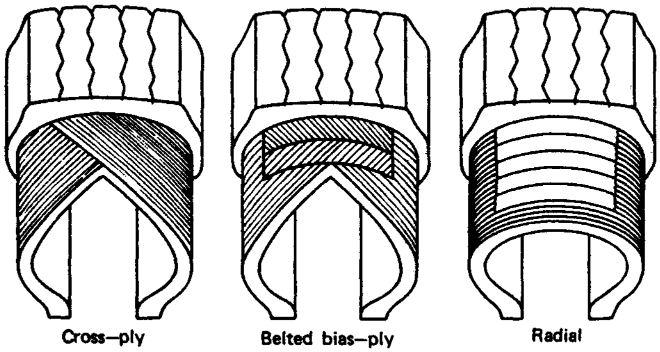


Figure 18.3 Types of plies in tires. (*Source:* Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, John Wiley & Sons, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

U.S. car tire market in 1972, but by 1977 it had grown to 50% and it is now 89%. The difference in the three is shown in Fig. 18.3.

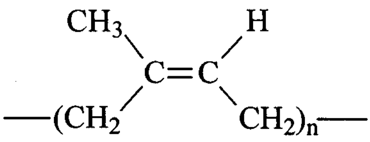
A tire carcass contains plies of rubberized fabric. In the cross-ply the cords cross the tire at an angle. In the belted bias-ply the cords cross at an angle and an additional belt of fabric is placed between the plies and the tread. In the radial-ply the cords run straight across the tire and an extra belt of fabric is included. Radial tires have better tread wear average (66,000 miles radial, 40,000 miles bias-ply) and better road-holding ability. However, they are more easily damaged on the sidewall and they give a less comfortable ride. They also require a higher proportion (80% vs. 50%) of the more expensive natural rubber. It seems likely that the popularity of radial-ply tires will continue, and natural rubber consumption may continue its comeback.

Today the elastomer can be reclaimed from discarded tires. Over 2 billion are available for recycling. Most reclaiming of the elastomer is done by an alkali process with 5-8% caustic soda and heating. Reclaiming is not profitable unless it costs no more than half as much as pure elastomer, since reclaimed material contains only 50% elastomer hydrocarbon. Approximately 0.66 billion lb of elastomer is reclaimed each year in the U.S., only about 10% of the total elastomers used. Efforts are also being made to burn discarded tires for fuel to generate electricity, since each tire contains energy equivalent to 2.5 gallons of oil as fuel, enough to heat an average house for a day.

11. IMPORTANT ELASTOMERS

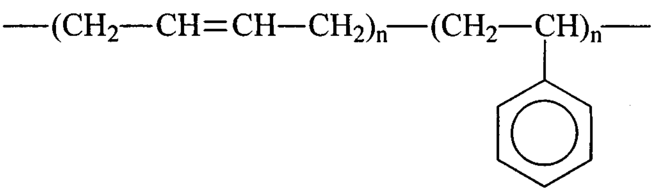
We will finish this chapter with the following sections that give many of the details for elastomers including chemical structure, manufacturing process, some properties, and main uses. Some familiarity with these elastomers is essential.

11.1 Natural Rubber, NR, *cis*-1,4-Polyisoprene



1. Manufacture
   Biological polymerization in rubber tree
   See Fig. 15.1 for biosynthesis
   98% *cis* configuration, MW = 350,000-500,000
2. Properties, see table 18.2
3. Uses
   76% in tires, other miscellaneous uses
4. Economics
   Radial tires, favoring natural rubber, gave good growth since 1980.
   Will slow now that radial tires no longer increasing
   No production in U.S.
   U.S. consumption from imports at 2.2 billion lb/yr

11.2 Styrene-Butadiene Rubber, SBR, Buna-S, GR-S

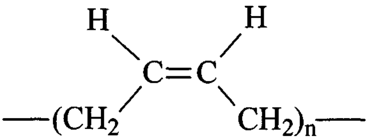


1. Manufacture
   Introduced in 1933
   Emulsion and solution polymerization
   Free radical catalyst at low temperatures
   75% Butadiene by weight, 85% butadiene molar

1,2- and 1,4-Butadiene units mixed

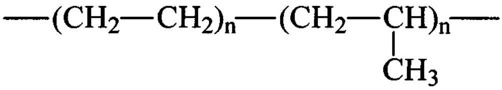
2. Properties, see Table 18.2
3. Uses
   Tires and tire products, including tread rubber, 77%; mechanical goods, 15%; automotive, 5%; miscellaneous, 3%
4. Economics
   2000 Production at 1.93 billion lb
   SBR suffering since 1980
   Change to radial tires, favoring natural rubber, now complete
   Replacement automotive parts a growing use
   1990-2000 Annual change of 1.0%

11.3 Polybutadiene, BR



1. Manufacture
   Introduced in 1955
   Solution and emulsion polymerization
   Ziegler-Natta catalysis
   Mostly *cis* configuration
2. Properties
   Excellent abrasion resistance
   Low temperature flexibility
   Poor traction
3. Uses
   Tires and treads for automobiles, trucks, and buses, 72%; high-impact resin modification, 25%; industrial products (conveyor belts, hoses, seals, and gaskets) and other applications, 3%
4. Economics
   2000 Production at 1.33 billion lb
   Tire use expanding
   Impact modifier for styrene growing

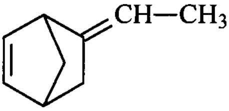
11.4 Ethylene-Propylene, EPDM, EPM, EP



$$-(CH_2-CH_2)_n-(CH_2-\underset{CH_3}{\underset{|}{CH}})_n-$$

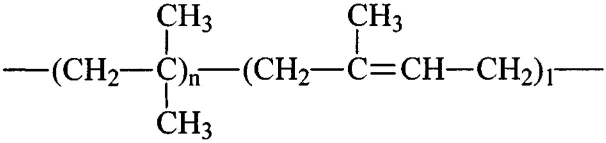
1. Manufacture
   Introduced in 1963
   Ziegler-Natta catalysis
   EP is abbreviation, EPM means ethylene and propylene only, EPDM means ethylene, propylene, and dimer
   Most, about 85%, of EP is EPDM
   55% Ethylene, 40% propylene, 5% dimer for cross-linking

dimer =



2. Properties
   Low-temperature flexibility
   Good age, heat, and abrasion resistance
3. Uses
   Automotive, 44%; roofing membrane, 18%; oil additive, 10%; wire and cable, 8%; miscellaneous, 20%
4. Economics
   2000 Production 0.76 billion lb
   1990-2000 Increase 5.2%/yr
   Fastest growing elastomer
   Growing markets in automotive, building materials, and petroleum additives

11.5 Butyl Rubber, Polyisobutylene



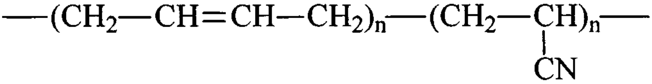
$$-(CH_2-\overset{CH_3}{\underset{CH_3}{C}})_n-(CH_2-\overset{CH_3}{C}=CH-CH_2)_1-$$

1. Manufacture
   Introduced in 1937
   Low-temperature solution polymerization

Cationic initiation
0.6-3.5% Isoprene added for cross-linking

2. Properties
   Low permeability to air and water
   Weather resistance
   Noise and vibration resistance
3. Uses
   Tires, tubes, and other pneumatic products, 83%; automotive mechanical goods, 6%; adhesives, caulks, and sealants, 6%; pharmaceutical uses, 4%; miscellaneous, 1%

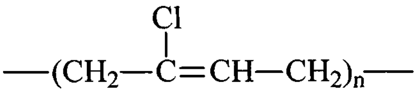
11.6 Nitrile Rubber, Poly(butadiene-acrylonitrile), NBR



$$—(CH_2—CH{=}CH—CH_2)_n—(CH_2—\underset{\displaystyle CN}{\underset{|}{C}}H)_n—$$

1. Manufacture
   Introduced in 1937
   Emulsion polymerization
   Free radical catalyst
   10-40% Acrylonitrile
2. Properties
   Solvent, fat, and oil resistance
   Wide temperature performance
   Low coefficient of friction
3. Uses
   Hose, belting, and cable, 28%; O-rings and seals, 20%; latex, 15%; molded and extruded products, 15%; adhesives and sealants, 10%; sponge, 5%; footwear, 2%; miscellaneous, 5%

11.7 Polychloroprene, CR



$$—(CH_2—\overset{\displaystyle Cl}{\overset{|}{C}}{=}CH—CH_2)_n—$$

1. Manufacture
   Introduced in 1931
   Emulsion polymerization
   Free radical catalysis
   Mostly *trans* configuration
2. Properties

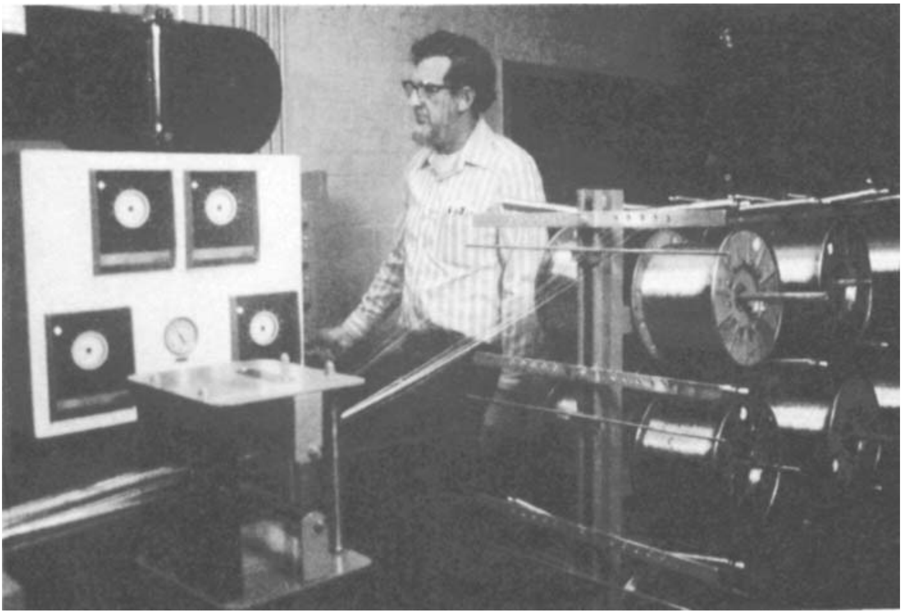


Figure 18.4 Research size equipment for ply building in tires to test the usefulness of various fibers as the plies in tires. (Courtesy of Du Pont)

Flame, solvent, age, and heat resistance

3. Uses

Mechanical rubber goods, 30%; automotive, 30%; adhesives, 20%; construction, 5%; coated fabrics, 5%; miscellaneous, including wire and cable, 10%

Suggested Readings

Chemical Profiles in *Chemical Marketing Reporter*, 10-28-96, 11-8-99, 2-28-00, 3-20-00, 3-27-00, and 4-3-00.
Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 598-622.
Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, pp. 126-142.

Chapter 19

Coatings and Adhesives

1. INTRODUCTION TO COATINGS

Having treated three major end uses of polymers in the last three chapters, we now present the last two general areas of polymer use, coatings and adhesives. These are quite large areas of the chemical industry. The size of the coatings industry is best estimated by NAICS 325510, Paints and Coatings, which had 1998 U.S. shipments of $18.7 billion. The increase in this segment is graphed in Fig. 19.1 along with the three main subdivisions of the industry, Architectural Coatings (NAICS 3255101), Product Finishes for Original Equipment Manufacturers (OEM) (NAICS 3255104), and Special Purpose Coatings (NAICS 3255107). It is 4% of Chemical Manufacturing, which is higher than that of fibers.

Coatings are sold in terms of volume rather than weight because they are usually solids dissolved in solvents. Approximately 1.5 billion gal/year are sold in the U.S. with 45% of this going to architectural coatings, 30% to product coatings, and 25% to special-purpose coatings. Table 19.1 gives a listing of the types of uses falling into these categories. Architectural coatings are used on houses and buildings and are applied by the personal consumer or by a professional painter. Product coatings are used by the manufacturer for many types of products. The automobile industry is the largest single user, applying around 10% of all coatings. Special-purpose coatings usually are specifically designed for one of the purposes listed in the table.

Coating is a general term for a thin film covering something. It may be decorative, protective, or functional. Adhesives have a separate use because

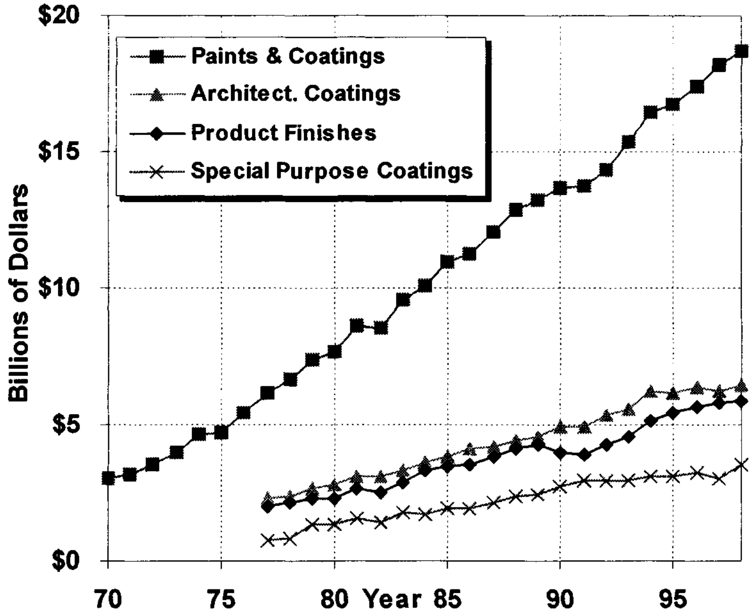


Figure 19.1 U.S. shipments of paints and coatings and its subdivisions. (*Source: Annual Survey of Manufactures*)

they are applied between two things. Adhesives will be discussed later in this chapter.

Coatings must have both adhesion and cohesion. *Adhesion* is the attraction of the coating to the substrate. It is the "outward force" of a coating. For good adhesion the coating must have weaker, stickier mechanical properties; it must be soluble, soft, and permeable to gases. *Cohesion* is the attraction of the coating to itself, the "inward force" of the coating. Good cohesion requires stronger mechanical properties; the coating must be only sparingly soluble, hard, and nonpermeable to gases. As you can see adhesion and cohesion are diametrically opposed. Coatings are a happy medium. They must have balanced properties.

2. TYPES OF COATINGS

There are hundreds of different types of coatings, many being complex formulations with numerous components. Indeed, to be successful a coatings chemist and company must be able to change a formulation to fit

Table 19.1 Three Major End-Use Groups of Coatings

Architectural Coatings	**Product Coatings-OEM**
Exterior house paints	Wood furniture and fixtures
Interior house paints	Automotive metal containers
Undercoats, primers, and sealers	Machinery and equipment
Varnishes	Factory-finished wood
Stains	Metal furniture and fixtures
	Sheet, strip, and coil
Special-Purpose Coatings	Transportation (nonautomotive)
Automotive and machinery refinishing	Appliances
High-performance	Electrical insulation
Traffic paint	Marine
Roof	Film, paper, and foil
Bridge	Pipe
Aerosol	Toys and sporting goods
Swimming pool	Misc. consumer and industrial products
Arts and crafts	
Metallic	
Multicolored	

Source: Chemical and Engineering News and SRI International

the needs of a given specific coating application, problem, and use. Close cooperation and communication between supplier and user is necessary. But in general there are four broad classes of coatings: paints, varnishes, lacquers, and shellac. A definition of each class follows.

Paint: A coating with a colored pigment included. It is always opaque.

Varnish (Enamel): A clear, transparent coating that dries by evaporation of solvent and oxidation or polymerization of a resin. It has no pigment.

Lacquer: A rapid-drying coating by evaporation of solvent only. It will redissolve in the solvent, and it may be lightly pigmented.

Shellac: A natural product from insect secretions. It is a hard tough coating like a varnish, which contains mostly aliphatic polyhydroxy acids about C_{60}.

3. BASIC COMPOSITION OF COATINGS

Although coatings are complex formulations, they can be divided into four main types of materials: a pigment, a binder, a thinner, and additives.

Pigment: An opaque coloring; some dyes are used (transparent coloring) but they are not so common in the coatings industry.

Binder: A polymer resin or resin-forming material.

Thinner: A volatile solvent that deposits the film on evaporation.

Additives: Defoamers, thickeners, coalescing agents, flowing agents, driers, biocides, etc.

The binder plus the thinner is often called the *vehicle* for the coating.

4. PIGMENTS

There are many reasons why pigments are added to coatings to make paints. The pigment imparts opaqueness and color to the coating. It can adjust the gloss or shininess of the coating, improve the anticorrosive properties of the coating, and help to reinforce the binder.

Pigments must have certain key properties. They are rated in *hiding power*, the ability to obscure an underlying color. Hiding power is proportional to the difference between the index of refraction of the pigment and the vehicle. It is expressed in square meters of surface that can be covered per kilogram of paint. Dark pigments are usually higher in hiding power than are light ones. Smaller particle size is better than larger size pigment particles.

Pigments also have a *tinting strength*, the relative capacity of a pigment to impart color to a white base. In addition to these properties, pigments must be inert, insoluble in the vehicle but easily dispersed, unaffected by temperature changes, and nontoxic. We will briefly discuss two important inorganic and organic pigments as examples. The inorganic pigments are known for their superior hiding power, the organic pigments for their tinting strength. Dyes and pigments are a vast industry in themselves. We will cover just a couple of examples.

Table 19.2 Hiding Power and Tinting Strength of Pigments

Pigment	Hiding Power (m^2/kg)	Index of Refraction	Tinting Strength
Rutile	30.1	2.76	1800
Anatase	23.6	2.55	1250
Lithopone ($BaSO_4 \bullet ZnS$)	5.5	2.37	280
Zinc oxide (ZnO)	4.1	2.02	210

4.1 Inorganic Pigments

4.1.1 Titanium Dioxide

This is by far the most important white pigment. It has dominated the market since 1939 and is in the top 50 chemicals. About 2.8 billion lb were sold in 2001, and total commercial value was $2.9 billion. Two types of titanium dioxide are made, anatase and rutile. Anatase is made by taking ilmenite ore ($FeO \bullet TiO_2$) and treating it with sulfuric acid to purify and isolate TiO_2. Rutile is made by taking rutile ore (mostly TiO_2), chlorinating and distilling $TiCl_4$, and oxygenating back to pure TiO_2. See Chapter 6, Section 6. The hiding power and index of refraction of the two types of titanium dioxide, along with two other common inorganic pigments, is given in Table 19.2. Note the superiority of rutile and anatase in hiding power. Most vehicles have an index of refraction about 1.5. Although the hiding power increases as the difference in index of refraction between pigment and vehicle increases, it jumps very high for titanium dioxide. Rutile is slightly more expensive than anatase. They are about $1.03/lb.

4.1.2 Carbon Black

This most widely used black pigment is also in the top 50 chemicals. About 4.0 billion lb of carbon black were made in 2001. Commercial value was $1.4 billion at 35¢/lb, but 93% of this is used for reinforcement of elastomers. Only 7% is used in paints and inks. Carbon black is made by the partial oxidation of residual hydrocarbons from crude oil. See Chapter 6, Section 7.2. The hydrocarbons are usually the heavy by-product residues from petroleum cracking, ideally high in aromatic content and low in sulfur and ash, bp around 260 °C.

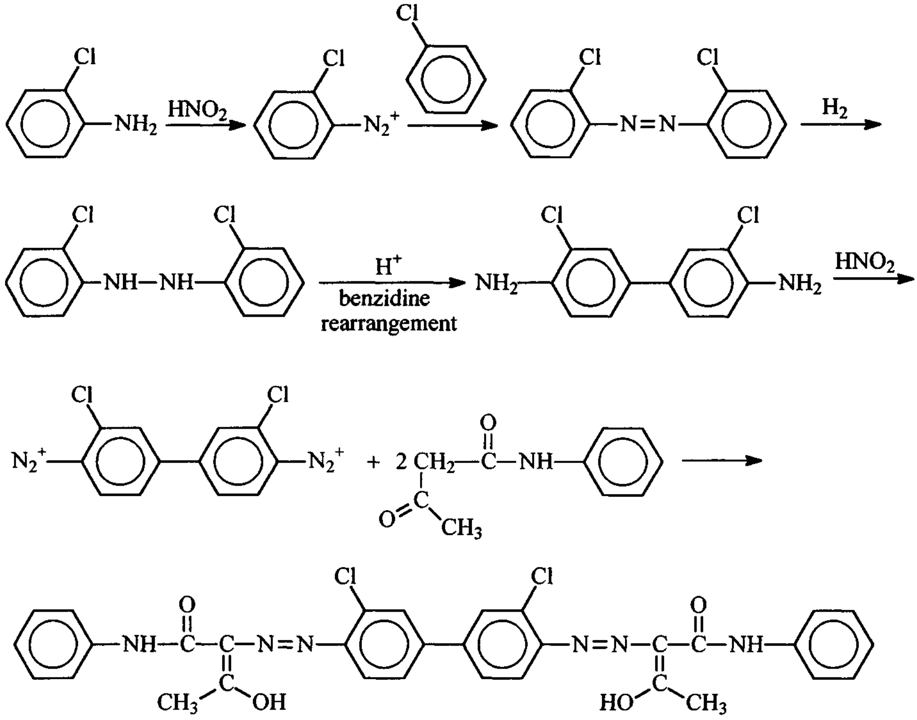


Figure 19.2 Synthesis of benzidine yellow.

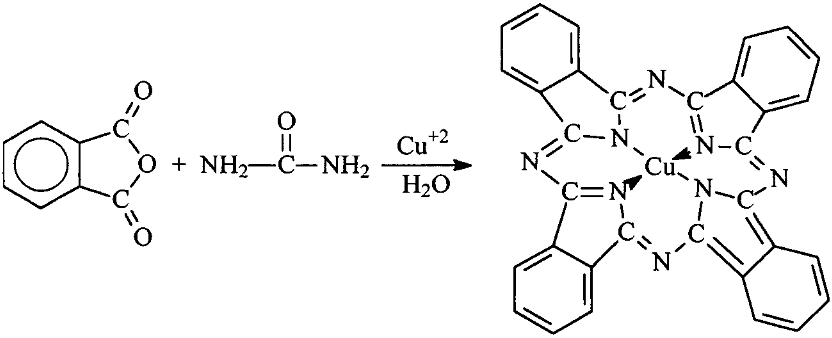
4.2 Organic Pigments

Of all synthetic organic pigments, the azo compounds are by far the most important, making up 48% of the total. Some 66 million lb are made each year in the U.S. Second in importance are the phthalocyanines, produced at the 33 million lb level. By color, red, blue, and yellow pigments are all equally important.

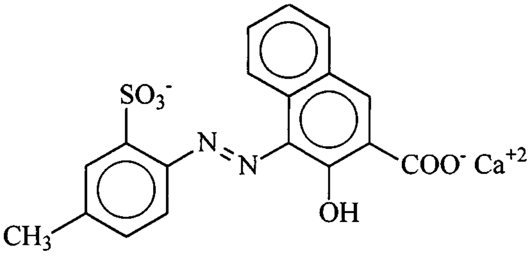
Individually, diarylide yellow AAA, also known as benzidine yellow or Pigment Yellow 12 (PY 12), is made in the greatest amount at 30 million lb, followed by phthalocyanine blue or Pigment Blue 15:3 (PB 15:3) at 28 million lb and Lithol® rubine calcium salt or Pigment Red 57:1 (PR 57:1) at 26 million lb.

Benzidine yellow is an example of a large class of organic pigments that contain an azo linkage, -N=N-. Its synthesis relies very heavily on diazonium salt coupling reactions and the benzidine rearrangement. Although benzidine is banned in the U.S. because of suspected carcinogenicity, 3,3′-dichlorobenzidine is only a "controlled substance" and its manufacture is at present permitted under rigorous safeguards. The synthesis is outlined in Fig. 19.2.

In contrast to the azo dyes the synthesis of phthalocyanine blue is easy. It is made in one step from readily available compounds phthalic anhydride, urea, and a copper salt.



Lithol® rubine is a second example of an azo dye and is important in printing inks. It is a brilliant color and has high tinting strength, good lightfastness, and solvent resistance.

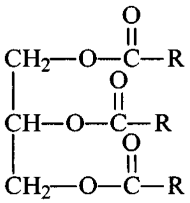


5. BINDERS

Perhaps the most important part of a coating is the binder or resin. Binders can be in the form of solutions, where the resin is dissolved in a solvent, or a dispersion, where the resin is suspended in water or an organic liquid with a particle size of 10 microns or less. We will subdivide our discussion of binders into four primary types and summarize their important properties and uses.

5.1 Natural Oils

The oldest type of coating is that which has a binder made from natural oil, especially linseed oil. Linseed oil is the triglyceride of linolenic acid, a natural fatty acid. The double bonds polymerize and cross-link when exposed to atmospheric oxygen catalyzed by lead, cobalt and manganese salts of fatty acids. The binders are good for coating "receptive" (porous) surfaces such as wood, paper, and cellulose but not metal, glass, or plastic. They must be highly pigmented for good protection from ultraviolet aging. Linseed oil-based coatings make very flexible films, especially good for easily swelled wood substrates. They are porous films that allow moisture to escape. They are easily applied with a brush because of their low molecular weight but are not very resistant to abrasion or chemicals. These coatings have been partially replaced by alkyd resins for exterior paints and by waterborne emulsions for interior use.



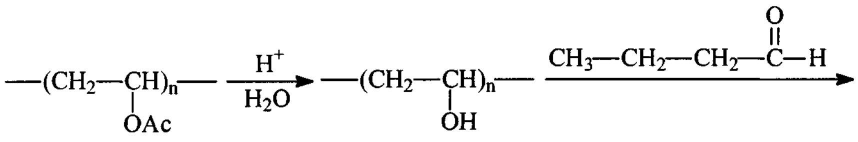
$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-R \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-R \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-R \end{array}$$

$R = CH_3-CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH-C_7H_{14}-$

linseed oil

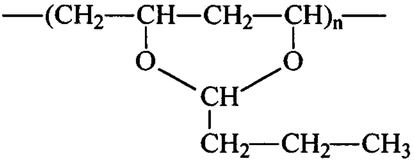
5.2 Vinyls

Vinyl coatings are used primarily on metal surfaces. They provide excellent protection by their strong cohesive forces, although their adhesion to the metal is not good. Used with a phosphoric acid-containing primer to etch the metal surface, this adhesion is markedly improved. The primer also contains poly(vinyl butyral) and is approximately 0.2-0.3 mil thick (1 mil = 1/1000th inch). Poly(vinyl butyral) is made from polymerized vinyl acetate by hydrolysis and reaction with butyraldehyde.



$$-(CH_2-\underset{\underset{OAc}{|}}{CH})_n- \xrightarrow[H_2O]{H^+} -(CH_2-\underset{\underset{OH}{|}}{CH})_n- \xrightarrow{CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H}$$

poly(vinyl acetate) poly(vinyl alcohol)



poly(vinyl butyral)

After this primer is applied vinyl chloride-vinyl acetate copolymer is added in a series of thin films. The total thickness is usually 5 mils. Pigments like iron oxide, lead, or zinc chromate prevent corrosion of the metal substrate in acid environments and may also be included in the coating. The final coated metal has good resistance to water and many chemicals with about a ten-year lifetime.

5.3 Alkyd Resins

The structural chemistry of alkyds has already been covered in Chapter 15, Section 7. Although there are over 400-500 varieties of such resins, they are all polyesters with carbon-carbon double bonds that can be cross-linked. They are very versatile in coatings, and their diverse properties can be matched for particular uses. They are the most widely used resins for protective coatings. Their best points can be summarized as follows: (1) easy to apply; (2) can have flat, semigloss, or high-gloss finish; (3) useful for most surfaces except concrete or plaster (alkaline); (4) good color retention; and (5) odorless (some of them).

There are important modifications of alkyds that help in specific applications. Phenolics can be added to improve film hardness and water resistance, but these confer increased yellowing tendencies on the final coating. Silicones impart heat resistance and exterior durability. Styrene increases the drying speed. Methyl methacrylate when added gives faster drying properties and improves the color and durability of the coating.

5.4 Latex or Emulsion (Water Dispersion)

About 90% of all interior wall paint is now water dispersed. These coatings have become very popular because of easy cleanup, nonflammability, and minimization of air pollution. There are three principal types.

1. Styrene-butadiene binders started the “water revolution” in coatings after World War II. Most formulations use about a 2:1 ratio of

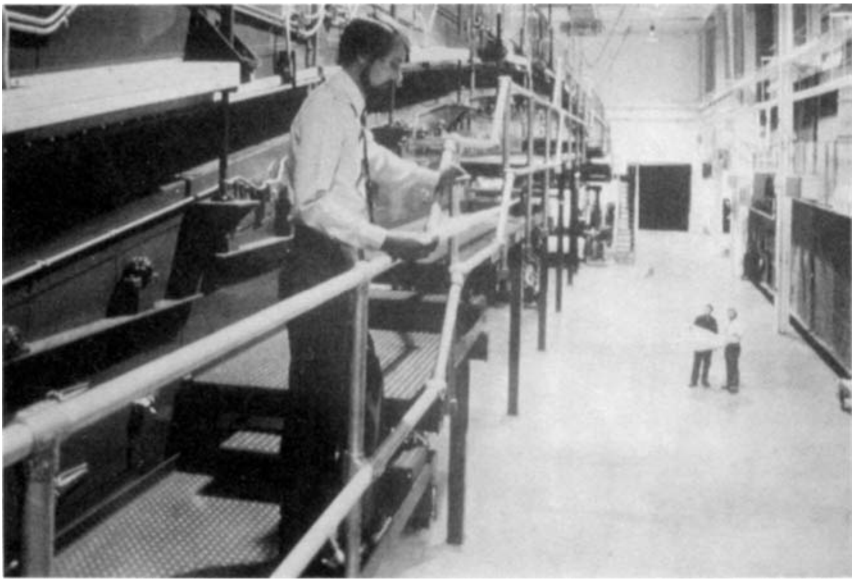


Figure 19.3 Full-scale coating line for industrial application. This line processes water-based coatings. (Courtesy of Brady Corporation, Milwaukee, WI)

styrene to butadiene (just the reverse of SBR elastomer). The coatings are low cost and provide excellent alkali resistance.

2. Poly(vinyl acetate) dispersions are more sensitive to hydrolysis but have good color retention and resistance to grease and oil.
3. *Acrylics* is a general term referring especially to polymers of methyl methacrylate and acrylic acid esters as binders. They are tough, flexible films with excellent durability and color retention, along with alkali, water, grease, and oil resistance. But they are more expensive. The acrylics became popular when Du Pont found that a molecular weight of 100,000 gives the desired properties. Today most automobiles are finished with acrylics.

6. SOLVENTS

Although we usually think of solvents as being just something to dissolve a solute, the chemistry and formulation technology of these materials in the coatings industry is very complex and critical to the success of the finished product. There is a large market for solvents, too, since 20% of all industrial solvents are used in coatings. Aliphatic hydrocarbons are good solvents because they are inexpensive and lack environmental effects, but they are not so good at dissolving most binders. Alcohols are generally well-liked and accepted in the industry. Although ketones, esters, or aromatic hydrocarbons dissolve well, they cause much more profound pollution problems in the form of smog. Their emissions are restrictive. Water, of course, is ideal for those binders that form good dispersions. Finally, chlorinated solvents are nonflammable but have for the most part found limited applications lately due to their high toxicity.

Today in the coatings industry there is a big drive to replace solvents that cause air pollution problems. This has led to a nationwide program to limit volatile organic compounds (VOCs). These are calculated as pounds of solvents per gallons of coating. Prior to 1970 the VOC content of most paints was above 5 lb/gal. Major industrial paints are now limited to 3.5 lb/gal of VOCs, and this limit will be lower in the future. Although the U.S. Environmental Protection Agency (EPA) has set minimum standards, states may adopt their own stricter standards, thus causing wide variation throughout the country.

7. INTRODUCTION TO ADHESIVES

An adhesive or bonding agent is any substance that produces a bond between two or more similar or dissimilar substrates. In other words, it holds two things together. The term *adhesive* has become generic and includes more popular terms such as cement, glue, and paste. *Sealants* or caulks, having a different type of use, fill gaps or joints between two surfaces. They must remain flexible and also prevent the passage of liquid or gas between surfaces. Some products serve both adhesive and sealant purposes. The adhesives and sealants business is particularly difficult to define since many substances with adhesive and sealant properties are used in borderline applications where bonding and sealing are secondary to such primary functions as coating.

The importance of adhesives lies in the fact that they allow for a combination of the properties of dissimilar materials. For example, a laminate of polyethylene, with its heat sealability and water resistance, is ideally combined with cellophane, a grease resistant material that accepts ink printing, for packaging applications.

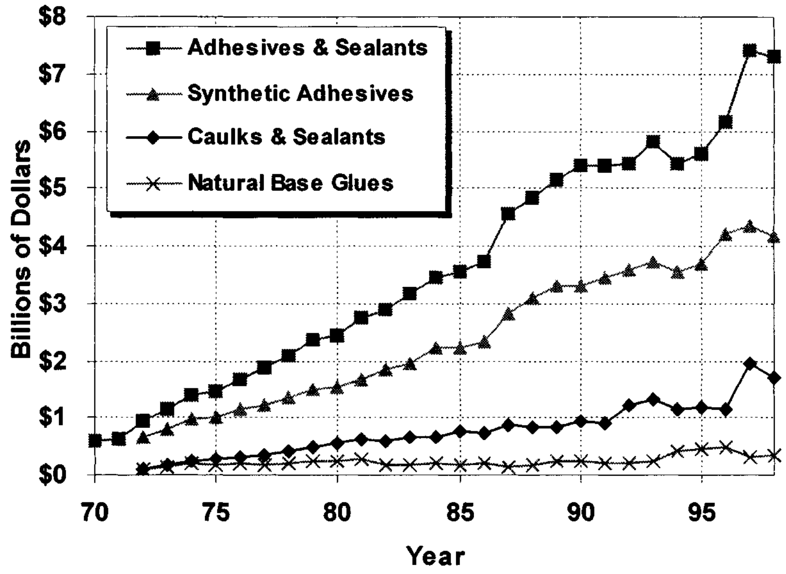


Figure 19.4 U.S. shipments of adhesives and sealants. (*Source: Annual Survey of Manufactures*)

8. MARKET FOR ADHESIVES

Fig. 19.4 gives the trend in U.S. shipments of Adhesives and Sealants (NAICS 325520) and its major subdivisions of Natural Base Glues and Adhesives (NAICS 3255201), Synthetic Resin and Rubber Adhesives (NAICS 3255204), and Caulking Compounds and Sealants (NAICS 3255207 plus 325520A). Adhesives and sealants are a fast growing business. U.S. shipments for 1998 totalled $7.3 billion, which is 2% of Chemical Manufacturing. Through the 1970s and '80s the average annual growth was 15%.

The U.S. market is probably near 12 billion lb of adhesives. The business is very diffuse and is one of the few areas of the chemical industry where a small company can thrive. Over 500 U.S. companies manufacture adhesives and sealants. Industrial use is high (60%), but consumers (20%) and craftspersons (20%) also use them.

9. THE ADHESION PROCESS

There is still much art as well as science in the adhesion field, but a few generalizations can be made. Adhesion occurs by forming electrovalent or covalent bonds or by the use of weaker secondary attractions such as hydrogen bonding, London, dispersion, induced dipole, or van der Waals forces. Molecular "nearness" and good "wetting" properties are important. The adhesive must be flexible for good nearness. The substrate (to which the bond is made) must have a clean surface. A thin layer of adhesive is better than a thick layer. The thinner the layer is, the greater will be the adhesive force and the less will be the cohesive force. Putting on an adhesive in a series of these layers is ideal.

Finally, the solubility parameter of the adhesive and the substrate must be close. Without getting too technical, the solubility parameter is a rough estimate of polarity. The old saying "like dissolves like" can be extended to "like bonds like." More accurately, the solubility parameter is the calculated potential energy of 1 cm^3 of material for common solvents. Polymers are assigned solubility parameters of solvents in which they are soluble. Table 19.3 lists solubility parameters for various solvents and polymers. As an example of how to use this table, butadiene-acrylonitrile rubber with $\delta = 9.5$ bonds natural rubber ($\delta = 7.9\text{-}8.3$) to phenolic plastics ($\delta = 11.5$). Note that its solubility parameter is between that of the two substrates.

10. FORMS OF ADHESIVES

Adhesives are available in various physical states and are applied by many different techniques: water dispersions (59%), solvent borne (9%), reactive (10%), hot melt (20%), and miscellaneous (2%). Because they are less polluting water dispersions are rapidly increasing in their percentage in the last ten years, from 43% to 59%. Water dispersions deposit a film of adhesive after the water evaporates. Organic soluble adhesives form films when the organic solvent evaporates. Some adhesives are two-component solventless systems that react and form a strong cross-linked thermoset upon mixing. Examples would be epoxy resins (epoxy plus amine) and unsaturated polyesters (polyester plus styrene). Hot melts are thermoplastic resins that can be melted to a freely flowing material, be applied to the substrate, and form a good bond upon cooling. The advantage of hot melts is that they can be applied in an automated high-speed process. We are all familiar with common pressure-sensitive adhesives (PSAs), such as Scotch® tape, which have a permanently sticky adhesive on the tape that is applied to a second substrate with minimum pressure, good for temporary bonding

Table 19.3 Solubility Parameters

Solvent	δ	Polymer	δ
n-Hexane	7.3	Poly(tetrafluoroethylene)	6.2
Cyclohexane	8.2	Poly(chlorotrifluoroethylene)	7.2
1,1,1-Trichloroethane	8.3	Poly(dimethyl siloxane)	7.3-7.6
Carbon tetrachloride	8.6	Ethylene-propylene rubber	7.9
Toluene	8.9	Polyethylene	7.9-8.1
Ethyl acetate	9.1	Natural rubber	7.9-8.3
Trichloroethylene	9.2	Polystyrene	8.6-9.1
Methyl ethyl ketone	9.3	Poly(methyl methacrylate)	9.3
Methyl acetate	9.6	Butadiene-acrylonitrile rubber	9.5
Cyclohexanone	9.9	Poly(vinyl chloride)	9.5-9.7
Dioxane	10.0	Epoxy resin	9.7-10.9
Acetone	10.0	Polyurethane resin	10.0
Carbon disulfide	10.0	Ethyl cellulose	10.3
Nitrobenzene	10.0	Poly(vinyl chloride-acetate)	10.4
Dimethylformamide	12.1	Poly(ethylene terephthalate)	10.7
Nitromethane	12.6	Cellulose acetate	10.4-11.3
Ethanol	12.7	Cellulose nitrate	9.7-11.5
Dimethyl sulfoxide	13.4	Phenol-formaldehyde resin	11.5
Ethylene carbonate	14.5	Poly(vinylidene chloride)	12.2
Phenol	14.5	Nylon 6,6	13.6
Methanol	14.5		
Water	23.2		

Source: Wittcoff and Reuben II

uses. Finally, newer methods of bonding are being researched, such as those involving ultrasonic energy, magnetic fields, dielectric sealing, or ultraviolet light.

11. CHEMICAL TYPES OF ADHESIVES AND SAMPLE USES

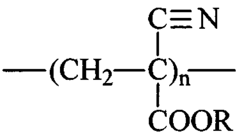
Adhesives are so numerous and versatile that it is difficult to generalize by chemical type. One breakdown of synthetic adhesives by polymer type gives phenolics (37%), urea and melamine (19%), vinyls (18%), synthetic elastomers (15%), acrylics (4%), polyurethanes (3%), and epoxies, polyesters, and others (4%). For purposes of organization we divide them into four general areas and list a few representative examples of these types and their uses. Review the structure and chemistry of these materials as discussed in Chapters 14 and 15.

11.1 Thermoplastic

1. Poly(vinyl acetate) emulsions are used in bookbinding, milk cartons, envelopes, and automobile upholstery.
2. Polyethylene and polypropylene are used as carpet backing and as hot melts in packaging.
3. Poly(vinyl chloride) is used as a plastisol (dispersion with plasticizers), solution, or water dispersion. It is a good cement for pipes and is used extensively as an adhesive in automobiles.
4. Poly(vinyl butyral) has clarity and a refractive index similar to glass. It has good flexibility and adhesion to glass, even at low temperatures. It is used as safety glass interlining.

11.2 Thermoset

1. Phenolics are used in bonding wood and plywood. They are also good adhesives for automobile brake linings. A phenolic plus poly(vinyl butyral) is used to bond copper to paper or glass fiber for printed circuits.
2. Urea-formaldehyde and melamine-formaldehyde adhesives are resins in particleboard.
3. Epoxy adhesives are common two-part consumer glues that bond concrete blocks together and keep glass reflectors on highways in place.
4. Unsaturated polyesters are auto body fillers. They are commonly used in place of solder for many applications.
5. Urethanes (alkyd resin plus diisocyanate) bind sand to form a temporary mold in many foundry operations.
6. Cyanoacrylate adhesives, the famous consumer Super glue®, is a monomer that polymerizes when it comes in contact with moisture, even with atmospheric moisture.



$$-(CH_2-\overset{\displaystyle C\equiv N}{\underset{\displaystyle COOR}{C}})_n-$$

11.3 Elastomeric

1. Both natural rubber and SBR are used in Scotch® tape, masking tape, and adhesive-backed floor tiles. They are used in automobiles to bond fabric, carpets, and tire cord.
2. Polychloroprene plus a phenolic is a "contact adhesive" to bond flooring to concrete or wood, to attach soles to footwear, and to bond vinyl seats and roofs to automobile bodies.

11.4 Natural Products

1. Starch glues are water dispersions for "library paste" and wallpaper paste. They coat paper for better receptivity of inks and keep the inks "held out" on the paper surface. They are also used in corrugated cardboard and paper laminating.
2. Protein glues are good for bonding rubber to steel, cork to plywood.
3. Asphalt makes a good adhesive for roofing of homes.

12. USE SUMMARY

The single largest industrial application for adhesives is now in packaging, accounting for 40% of total consumption. The construction industry accounts for 17% of the physical volume of adhesives, especially with increased numbers of prefinished products and factory-built homes and modular units. Nonrigid bonding (15%), rigid bonding (9%), pressure-sensitive tapes and labels (14%), and transportation and other uses (5%) make up the remaining market.

Suggested Readings

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 1050-1067 and 708-734.

Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, pp. 143-181.

Chapter 20

Pesticides

1. WHAT NEXT?

Thus far in our study of industrial chemistry we have covered in some detail the top 100 chemicals produced as well as the important polymers made by the chemical industry. We have especially studied their manufacture and end uses, but have also looked at some history, economics, and toxicological and environmental problems associated with some of these products. In terms of net worth of shipments coming from these sectors, this is over half of the chemical industry. What should we study next? Table 20.1 lists the U.S. shipments of the most important sectors of Chemical Manufacturing along with other sectors of the chemical process industries. If we add up the sectors already studied—Basic Chemicals; Resin, Synthetic Rubber, and Artificial and Synthetic Fibers and Filaments; and Paints, Coatings, and Adhesives—we have 47% of Chemical Manufacturing. We have also covered some of the chemistry associated with sectors outside Chemical Manufacturing, such as Petroleum and Coal Products and Plastics and Rubber Products, also big industries. We will now present in the following chapters some specific selected technologies that will allow us to learn about other important areas of the chemical industry. After we complete our study of additional sectors—Pesticides, Fertilizers, and Other Agricultural Chemicals; Pharmaceuticals and Medicine; and Soap, Cleaning Compounds, and Toilet Preparations—we will have increased our coverage of Chemical Manufacturing to 91%. We have also included a chapter on Paper Manufacturing, a fascinating industry with some interesting chemistry, and one that employs many chemists.

Table 20.1 Shipments of Selected Sectors of Chemical Manufacturing and Other Chemical Process Industries

NAICS Code	Sector	Shipments $Billion	%
3251	Basic Chemicals	110.015	25.9
3252	Resin, Synth. Rubber, & Artificial & Synth. Fibers	63.334	14.9
3255	Paints, Coatings, and Adhesives	27.161	6.4
3253	Pesticides, Fertilizers, Other Agricultural Chem.	24.343	5.7
3254	Pharmaceuticals & Medicine	102.995	24.2
3256	Soap, Cleaning Compounds, & Toilet Preparations	58.462	13.8
3259	Other Chemical Products	37.842	9.0
325	**Chemical Manufacturing**	**424.152**	**100.0**
322	Paper	156.251	
324	Petroleum and Coal Products	137.066	
326	Plastics and Rubber Products	164.041	

Source: Annual Survey of Manufactures

2. INTRODUCTION TO PESTICIDES

Although pesticides have been criticized for many years as having many side effects, it should be remembered that chemicals have been a prime factor in agriculture's ability to keep pace with the hunger problem in the world. Production of food crops would decrease by 30% without pesticides. Production of livestock would drop 25%. Food prices would increase by 50-75%. Because of pesticides, farmers can conserve wildland since they need only half the land they used previously for the same amount of crops. Also, pesticides have helped control many insect-borne diseases such as malaria, yellow fever, encephalitis, and typhus. It is estimated that DDT alone (a bad word nowadays) has saved 25,000,000 lives from sickness and famine and has increased the lifespan in India by 15 years. Malaria is still a problem in many of the world's countries, with a million per year dying of the disease. Because of DDT's introduction during the 1940s, World War II was the first war in which bullets killed more soldiers than insects. There is a definite need to weigh carefully the benefits of technology on the one hand and the risks in its application on the other.

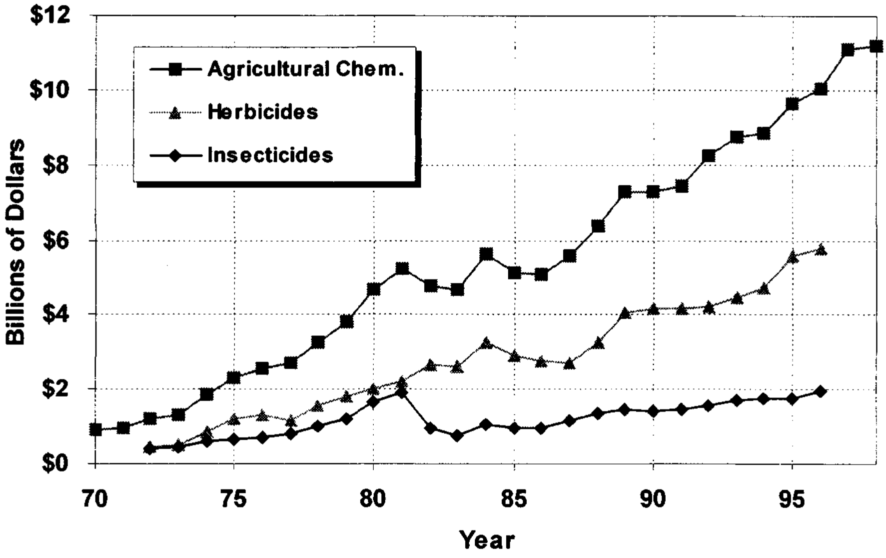


Figure 20.1 U.S. shipments of pesticides. (*Source: Annual Survey of Manufactures*)

Among the distinguishing characteristics of the pesticide industry are (1) the multiplicity of chemicals used, (2) a high price range, (3) a rapid obsolescence for the chemicals employed, and (4) a high degree of government regulation. The last point is particularly interesting. Today all pesticides used in the U.S. must receive registrations from the Environmental Protection Agency (EPA). These require complex and detailed toxicological and metabolic studies on both the active ingredient and impurities. The cost of development of a new herbicide is estimated at $50 million now as compared to $3 million in the 1950s. Over 22,000 compounds are screened for each new effective pesticide.

Fig. 20.1 gives the value of U.S. shipments of Pesticides and Other Agricultural Chemicals (NAICS 325320), the best government estimate of the size of the pesticide industry. Also given are the shipments for the two most important subsections, Herbicides and Insecticides, which as of 1996 are no longer determined separately. During the 1970s the pesticide industry had a dramatic rise from $1 billion to $5 billion. The decreasing use of insecticides slowed the growth in the 1980s, though some recent rebounding is apparent in the 1990s, and the industry is now at $11 billion.

Fig. 20.2 shows the U.S. production of various types of pesticides in billions of pounds. Over a billion lb of total pesticides are made each year. Throughout the 1940s, 1950s, and 1960s insecticides were the largest

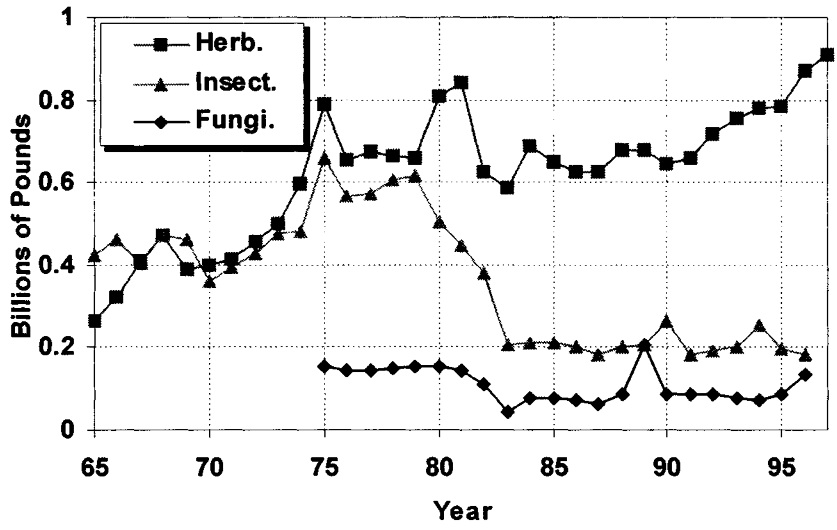


Figure 20.2 U.S. production of pesticides. (*Source: Chemical and Engineering News*, "Facts and Figures for the Chemical Industry," and *Chemical Economics Handbook*)

branch. Herbicides passed them up in 1970 and have increased since then while insecticides have decreased. Total production of insecticides today is half of what it was in 1965, while herbicide use has increased four-fold since 1965. Table 20.2 gives the present production percentages of types of pesticides, which are categorized by the type of pest that they attempt to control. Other kinds are germicides, rodenticides, and miticides. Agriculture uses about two thirds of all pesticides, with industrial, commercial, home and garden, and government use dividing the other third. Table 20.3 shows the percentage use of pesticides on various important agricultural crops.

Table 20.2 Types of Pesticides

Herbicides	65%
Insecticides	14
Fungicides	10
Fumigants/Nematocides	11

Source: Chemical Economics Handbook

Table 20.3 Uses of Pesticides on Crops

Corn	29%
Soybeans	19
Cotton	14
Deciduous Fruits/Nuts/Citrus	9
Other	29

Source: Chemical Economics Handbook

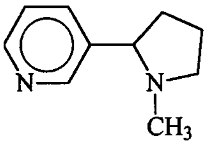
3. INSECTICIDES

3.1 History

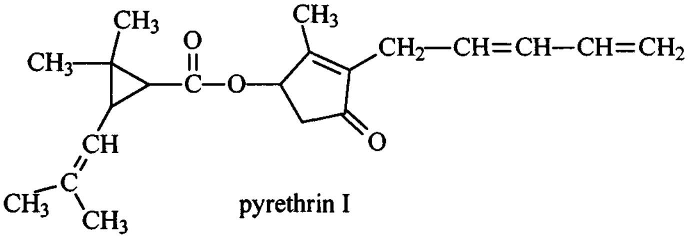
Besides causing sickness, death, famine, and suffering, insects alone cause a large financial loss. People have tried to control insects since antiquity. Most early insecticides (first-generation insecticides) were inorganic compounds of arsenic, lead, copper, and sulfur. Bordeaux mixture (copper sulfate/calcium hydroxide) is still used sparingly today. Millions of lb of lead and arsenic pesticides used in the first half of this century cause occasional problems as soil residues where concentrations are high, such as at mixing stations. Lead arsenate is still used against the potato beetle, since no residue stays in the potato itself.

$$Pb(NO_3)_2 + H_3AsO_4 \longrightarrow PbHAsO_4 + 2HNO_3$$

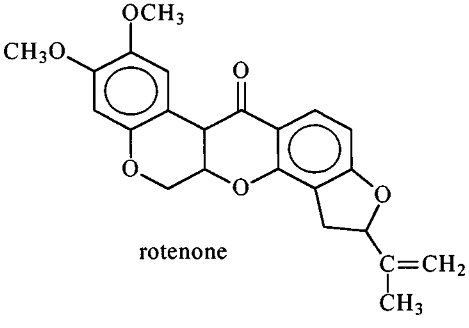
Early insecticides also included organic natural products such as nicotine, rotenone, and pyrethrin. Rotenone is used today as a method of killing rough fish when a lake has been taken over completely by them. A couple of weeks after treatment the lake is then planted with fresh game fish. The



nicotine



pyrethrin I



pyrethrins, originally obtained from Asian or Kenyan flowers, can now also be synthesized laboriously. Nicotine is no longer used as an insecticide because it is not safe for humans (smokers note).

As late as 1945 inorganic chemicals accounted for almost 75% of all pesticide sales, with oil sprays and natural products being most of the remainder. None of these first-generation insecticides are used much now. During the 1950s the second generation of insecticides made an explosive growth with the development of DDT and other chlorinated hydrocarbons. Second-generation insecticides are of three major types: chlorinated hydrocarbons, organophosphorus compounds, and carbamates. Synthetic pyrethroids are a recent fourth type. Fig. 20.3 pictures the trend in

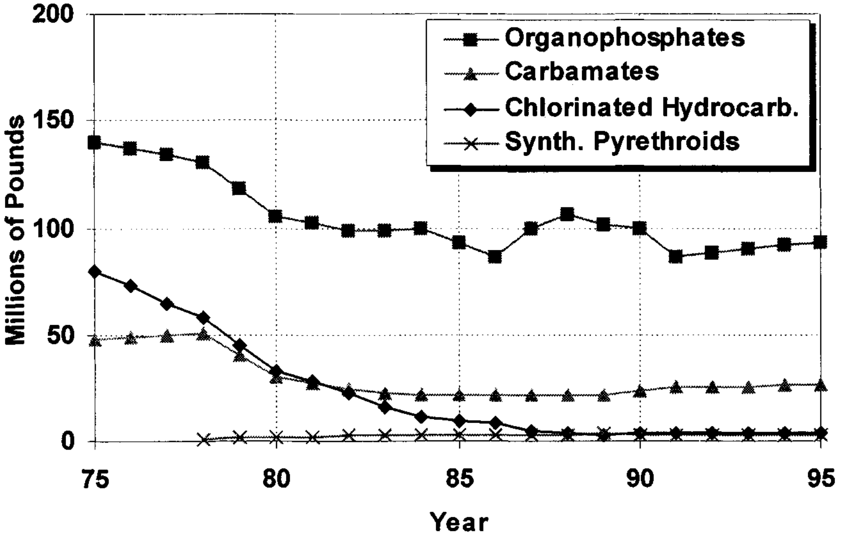


Figure 20.3 U.S. consumption of insecticides. (*Source: Chemical Economics Handbook*)

Table 20.4 Types of Insecticides

Oranophosphates	71%
Carbamates	20
Chlorinated hydrocarbons	3
Synthetic pyrethroids	2
Miscellaneous	4

Source: Chemical Economics Handbook

consumption of types of insecticides through the years. The very dramatic decline of the chlorinated hydrocarbons in the late 1960s and early 1970s, while organophosphates and carbamates increased, is not shown. Most of the chlorinated hydrocarbons are banned from use in the U.S. today, but they still are applied in other countries and historically they are very important, so we will cover them first, even though they are presently only a small percentage of the total consumption of insecticides in the U.S., as shown in Table 20.4.

3.2 Chlorinated Hydrocarbons

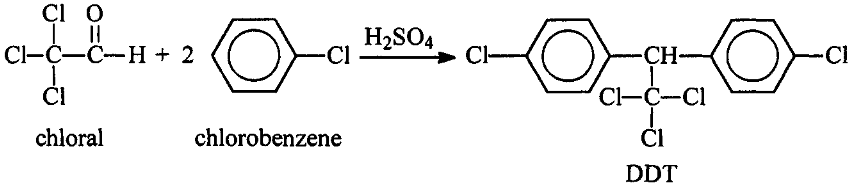
3.2.1 DDT

DDT is no longer being used in large amounts in this country because of its persistence in the environment, although for many uses there were no good substitutes available. *D*ichloro*d*iphenyl*t*richloroethane (DDT) was first made back in 1874 by Zeidler in Germany, but its insecticidal properties were not discovered until 1939 by Dr. Paul Mueller of Geigy Chemical Company in Switzerland. He received the Nobel Prize in medicine and physiology in 1948 for this work. Chloral (trichloroacetaldehyde) can be made from the chlorination and oxidation of ethanol in one step.

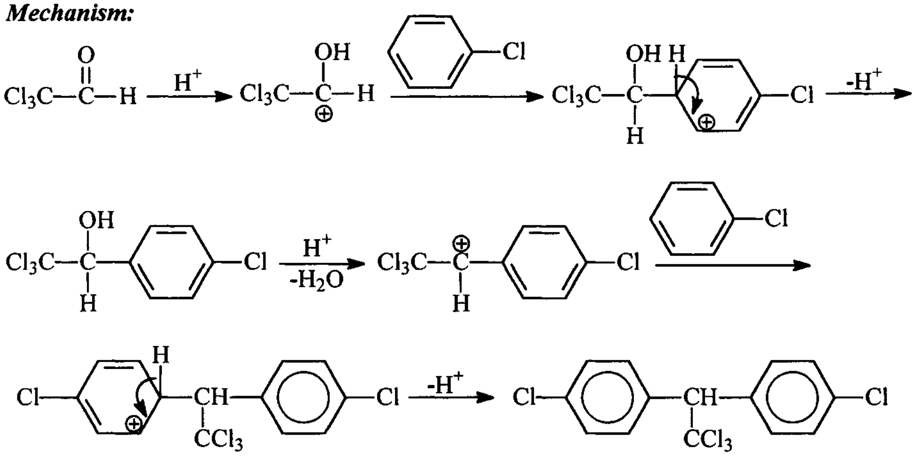
$$CH_3—CH_2—OH + 3Cl_2 + \tfrac{1}{2}O_2 \longrightarrow \underset{\text{chloral}}{Cl_3C—CH{=}O} + 3HCl + H_2O$$

The synthesis of DDT is a good example of an electrophilic aromatic substitution. The chloral is protonated and attacks the aromatic ring to generate a carbocation. Loss of a proton regenerates the aromatic ring.

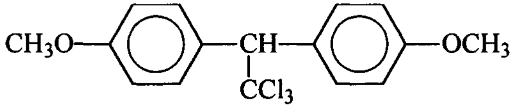
Reaction:



Mechanism:



The commercial product is actually a mixture of about 80% *p,p* isomer and 20% *o,p* isomer. The *p,p* isomer has the most insecticidal properties. Structure-activity relationships have been studied in detail for DDT and its analogs. For good biological activity there must be at least one para chlorine. The *m,m*-dichloro isomer is not active. The activity increases as the para halogen is changed: I (which is inactive) < Br < Cl < F. If the para chlorines are replaced by alkyl groups of about the same size (like CH_3– or CH_3O–), then the compound is still active, but larger R groups show no activity. Methoxychlor has been used as an insecticide. Finally, as the chlorines of the Cl_3C– group are replaced by hydrogens the activity also declines ($Cl_3C– > Cl_2CH– > ClCH_2 > CH_3–$).



methoxychlor

DDT is still used extensively overseas out of necessity. For example, in India malaria cases went from 75 million in the early 1950s to 50 thousand in 1961 thanks to DDT. But when spraying stopped the figure went back up to 6 million in 1976, then down to 2.7 million in 1979 when other insecticides were sprayed. In 1972 the EPA imposed a near total ban on DDT used in the U.S. In 1985 it was added to the list of suspect carcinogens of the National Toxicology Program (NTP).

The use of chlorinated hydrocarbons has declined in the U.S. for three main reasons: (1) concern over the buildup of residues (half-lives of 5-15 years in the environment, especially in the fat tissue of higher animals [10-20 ppm not uncommon]), (2) the increasing tendency of some insects to develop resistance to the materials, and (3) the advent of insecticides that can replace the organochlorines. Domestic consumption of DDT fell from 70 million lb in 1960 to 25.5 million in 1970 to none in 1980 (although worldwide demand is still high). The chlorinated hydrocarbons are a large part of the family of compounds now called POPs (persistent organic pollutants) and efforts are being made for a global elimination of these compounds.

3.2.2 Cyclodienes

All the chlorinated hydrocarbons belonging to this second group of compounds, once used in large amounts, have been banned for use in the U.S. since 1974. They are made by the Diels-Alder reaction, named after two chemists who won the Nobel Prize in 1950 for the discovery of this important reaction. The synthesis of the important insecticides chlordane, heptachlor, aldrin, dieldrin, and endrin are summarized in Fig. 20.4.

3.2.3 Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs), known by their trade marks of Arochlor® (Monsanto U.S.), Phenochlor® (in France), and Clophen® (in Germany) are chemically similar to the chlorinated insecticides. Although not used for this purpose, their existence and persistence in the environment is well established. They were used to make more flexible and flame retardant plastics and are still used as insulating fluids in electrical transformers since there is no substitute in this application. They have been made by Monsanto since 1930 and were first discovered as a pollutant in 1966. U.S. production peaked at 72 million lb in 1970 but in 1975 it was down to 40 million lb/yr because in 1971 Monsanto voluntarily adopted the policy of selling PCBs only for electrical systems. At least 105 PCBs are present in the environment.

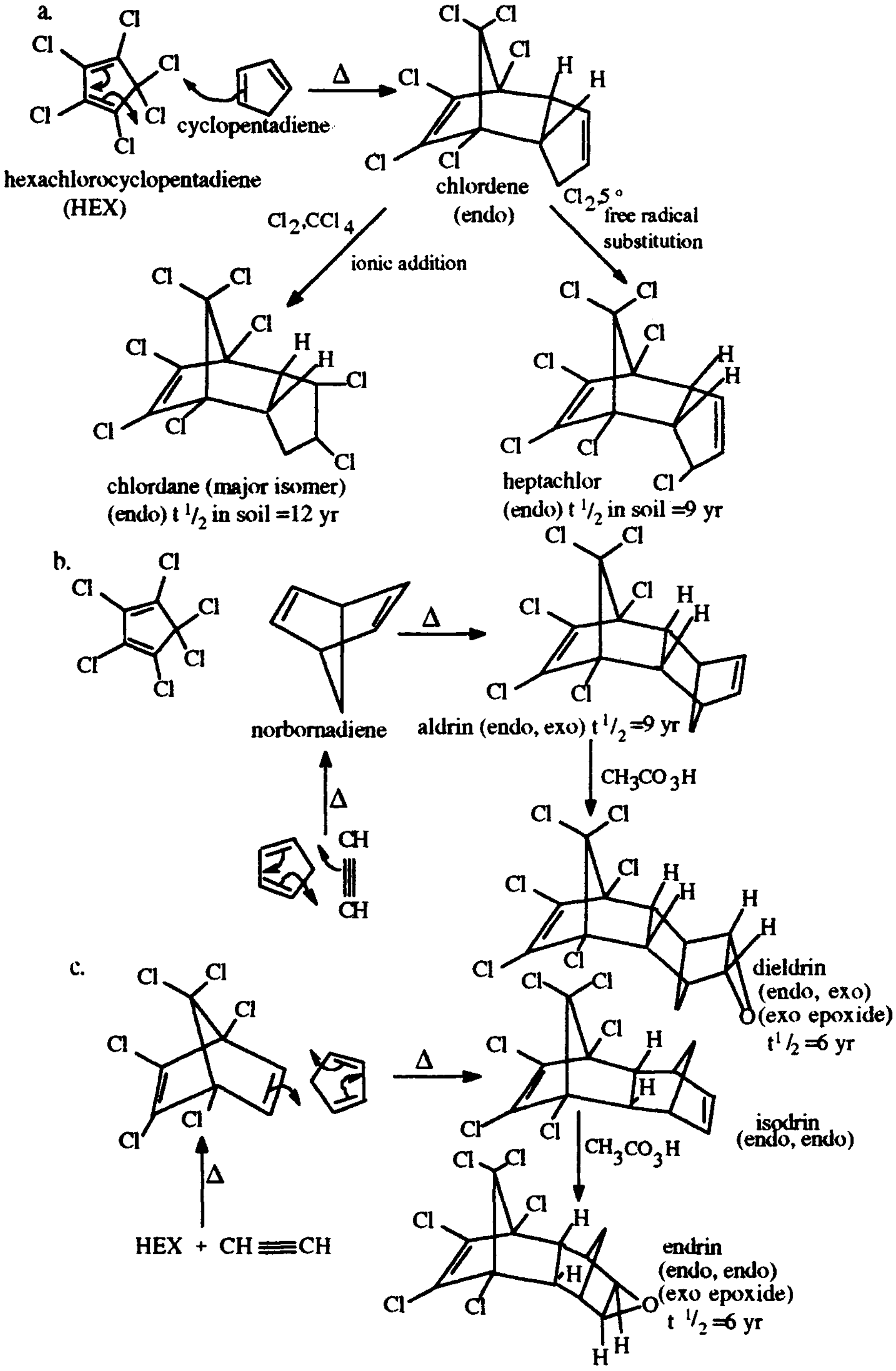
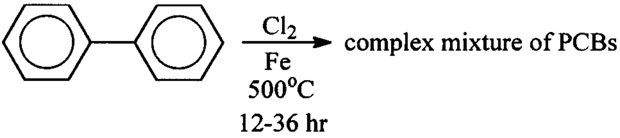
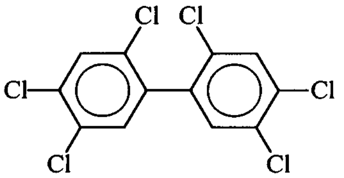
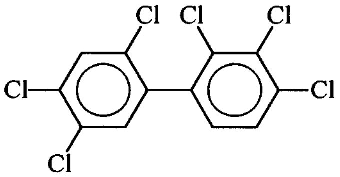


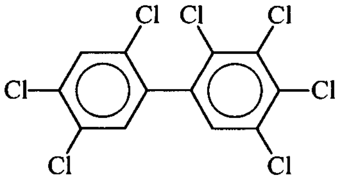
Figure 20.4 Cyclodienes

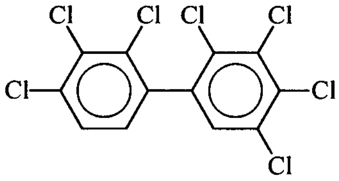
PCBs are made by the chlorination of biphenyl by electrophilic aromatic substitution (know this mechanism!). A typical sample might contain some of the chloro derivatives shown here.



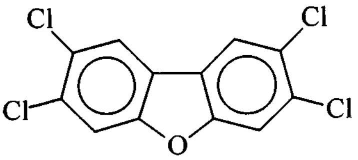








Much work has been done on the PCB problem. Potentially dangerous amounts of PCBs have been found in fish. At the time of this writing the EPA and General Electric are planning a \$500 million cleanup of the Hudson River sediment contaminated with PCBs even after many years of being banned. A very toxic trace contaminant in European PCBs that may be present in Monsanto's PCBs is tetrachlorodibenzofuran, the second most toxic chemical known to humans.

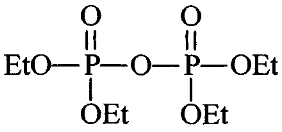


tetrachlorodibenzofuran

The search for the ideal PCB replacement continues, especially for the difficult electrical transformer application. Approximately 324 million lb of PCBs are still present in some 150,000 transformers. Possible substitutes range from mineral oil to high-temperature hydrocarbons, with silicones by far the most popular. There may be as much as a \$2 billion market in replacing PCB-containing transformers, which under 1985 EPA rules cannot be used where they would present a contamination risk in human food or animal feed.

3.3 Organophosphorus Insecticides

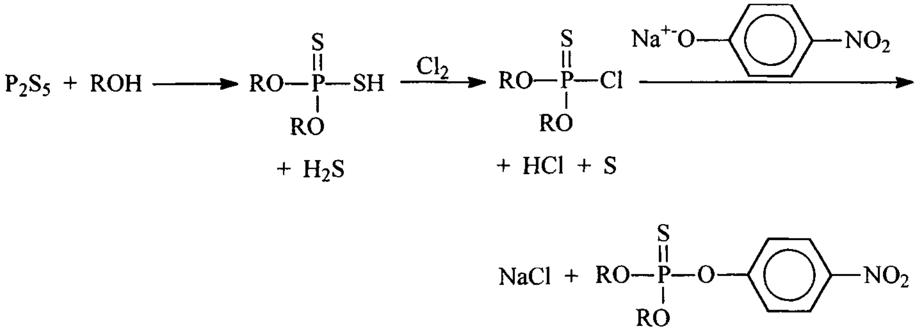
In the 1970s organophosphorus compounds became the leading type of insecticide and they still are, mainly because they are less persistent. Over 50 such compounds are registered in the U.S. today as insecticides. Gerhard Schrader synthesized the first organophosphorus insecticide in Germany in 1938, commonly called *t*etra*e*thyl *p*yro*p*hosphate (TEPP).



$$\mathrm{EtO{-}\overset{\overset{O}{\|}}{\underset{\underset{OEt}{|}}{P}}{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{OEt}{|}}{P}}{-}OEt}$$

TEPP

Methyl parathion was developed around 1948 when the German technology was discovered after the war. Parathion (the ethyl analog) is not so safe and is used to a lesser extent. Both methyl parathion and parathion are synthesized by reacting the sodium salt of *p*-nitrophenol with *O,O*-dialkyl phosphorochloridothioate, which is made from phosphorus pentasulfide, the alcohol, and chlorine.

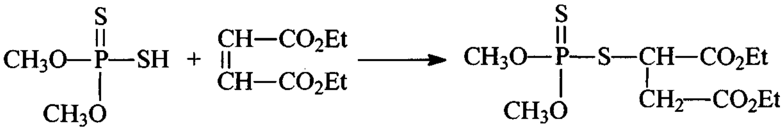


R = CH_3, methyl parathion

R = CH_3—CH_2, parathion

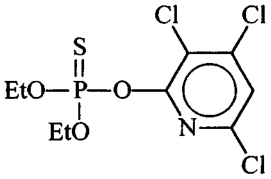
The parathions, although not persistent (half-life of one to ten weeks in the environment), are highly toxic to humans and deaths have been attributable to careless uses. Operators in organophosphate plants must take a blood test once a month. The discovery of the safer malathion by

American Cyanamid in the early 1950s was therefore welcome. Malathion is widely used today. It is synthesized by condensing diethyl maleate with the *O,O*-dimethyl phosphorodithioic acid obtained as previously discussed.

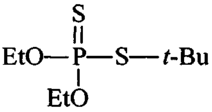


diethyl maleate malathion

Methyl parathion is used primarily on cotton. It was one of the first insecticides restricted under the 1996 Food Quality Protection Act (FQPA), which developed new safety standards for human health, especially that of children. It can no longer be used on many fruits and vegetables. Malathion and parathion are the broadest spectrum organophosphate insecticides. There are many other organophosphate insecticides in use in the U.S. today. Many are produced at the 1-5 million lb/yr level for specific applications. Three other leading organophosphates besides those mentioned already are chlorpyrifos, terbufos, and phorate.

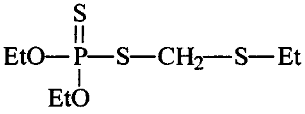


chlorpyrifos



$(EtO)_2P(=S)-S-t\text{-Bu}$

terbufos

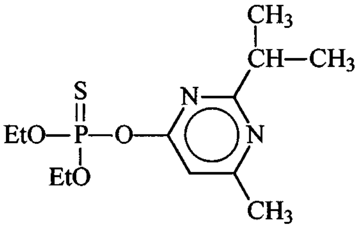


$(EtO)_2P(=S)-S-CH_2-S-Et$

phorate

In 2000 chlorpyrifos, the most commonly used household pesticide product, was outlawed for most household applications, though agricultural use will continue. It has caused unintentional poisoning and may affect brain development in unborn children.

Diazinon, another important organophosphate and the pesticide most widely used by homeowners on lawns, is being targeted for review because



diazinon

Table 20.5 U.S. Consumption of Organophosphates as Insecticides

Name	Million lb
Organophosphates, Total for 50 Compounds	93.3
Chlorpyrifos	18.5
Methyl parathion	14.0
Malathion	14.0
Terbufos	8.4
Phorate	5.5
Parathion	4.7

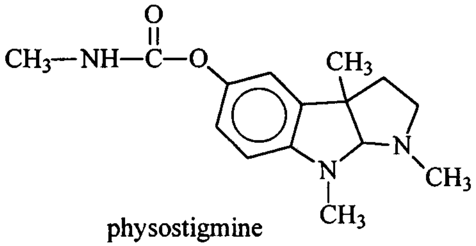
Source: Chemical Economics Handbook

EPA considers it potentially harmful to children. Indoor household use is scheduled to end in 2002, lawn and garden use in 2003. Agricultural applications will continue.

Table 20.5 gives the U.S. consumption of the leading organophosphates and the total used if all 50 are counted.

3.4 Carbamate Insecticides

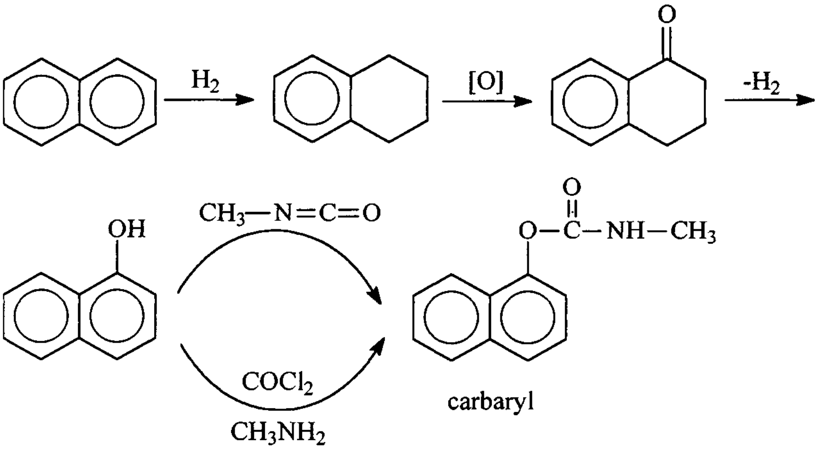
Carbamates are sold at a lesser volume than are organophosphorus compounds. The first carbamate (urethane) insecticides were developed in the late 1940s at Geigy Chemical Co. in Switzerland. Research on carbamates was inspired by the known toxicity of the alkaloid physostigmine, which occurs naturally in a West African bean.



physostigmine

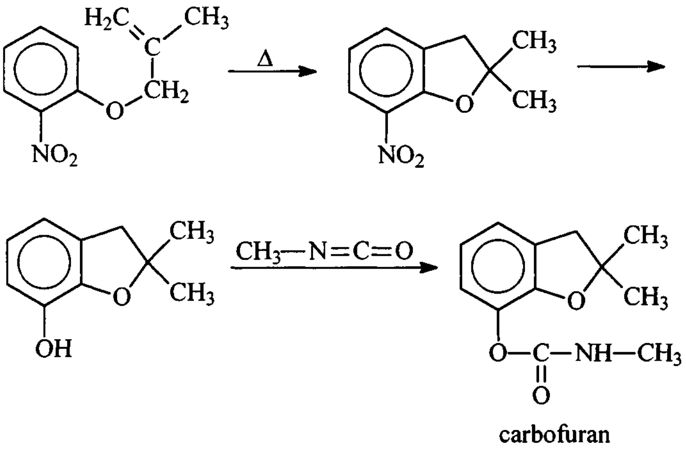
In the 1950s Kolbezen and Metcalf at the University of California-Riverside laid the foundation for Union Carbide's development of carbaryl (Sevin®), the first major carbamate. Still the most important carbamate insecticide, it is made by condensing l-naphthol with methyl isocyanate. The

1-naphthol is made from naphthalene by hydrogenation, oxidation, and dehydrogenation. The naphthalene is obtained from coal tar distillation or from petroleum. Carbaryl finds use in practically all the agricultural crop markets and is popular for home lawn and garden use.

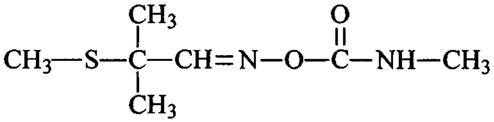


Methyl isocyanate is a very dangerous chemical. It was responsible for the deaths of over 2,500 people, perhaps as many as 10,000 people, in the worst industrial accident ever, that of the carbamate insecticide plant in Bhopal, India on December 3, 1984. It is a very toxic chemical. This tragedy is discussed in more detail in Chapter 25. Methyl isocyanate can be made from phosgene and methylamine, which would circumvent use of the isocyanate. Phosgene is made from chlorine and carbon monoxide, but it is also very toxic and dangerous.

Another important carbamate insecticide is carbofuran, whose synthesis is outlined here.

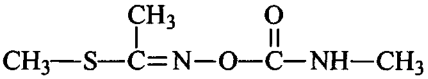


A third important carbamate is aldicarb or Temik®, an insecticide and nematocide for potato and vegetable crops. This chemical has been found in water wells in 11 states above the 1 ppm EPA safety threshold, barring use in some locales in 1982. According to Union Carbide, one manufacturer, humans can safely ingest 500 ppb. But it is one of the most acutely toxic pesticides registered by the EPA. A fourth carbamate insecticide is methomyl.



$$CH_3{-}S{-}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH{=}N{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_3$$

aldicarb



$$CH_3{-}S{-}\overset{CH_3}{\overset{|}{C}}{=}N{-}O{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_3$$

methomyl

Table 20.6 lists the leading carbamate insecticides by U.S. consumption. Carbofuran and aldicarb are also used as nematocides but this is not reflected in the table.

Advantages of the carbamate insecticides are lower toxicity to animals and use immediately up to harvest of crops (half-life is one week). Prolonged protection against insects requires frequent sprayings.

Table 20.6 U.S. Consumption of Carbamates as Insecticides

Name	Million lb
Carbamates, Total for 13 Compounds	24.4
Carbaryl	8.0
Carbofuran	7.0
Aldicarb	3.9
Methomyl	3.2

Source: Chemical Economics Handbook

3.5 Synthetic Pyrethroids

Mention was made of the natural product pyrethrins and the structure of pyrethrin I was given in this chapter, Section 3.1. Because of the unique structures of these cyclopropane-containing natural products and their high insecticidal properties, syntheses of analogs have been studied. The isobutenyldimethylcyclopropanecarboxylic acid moiety, called chrysanthemic acid, has been modified by using different ester groups. As a result a number of synthetic pyrethroids are available for certain specific uses,

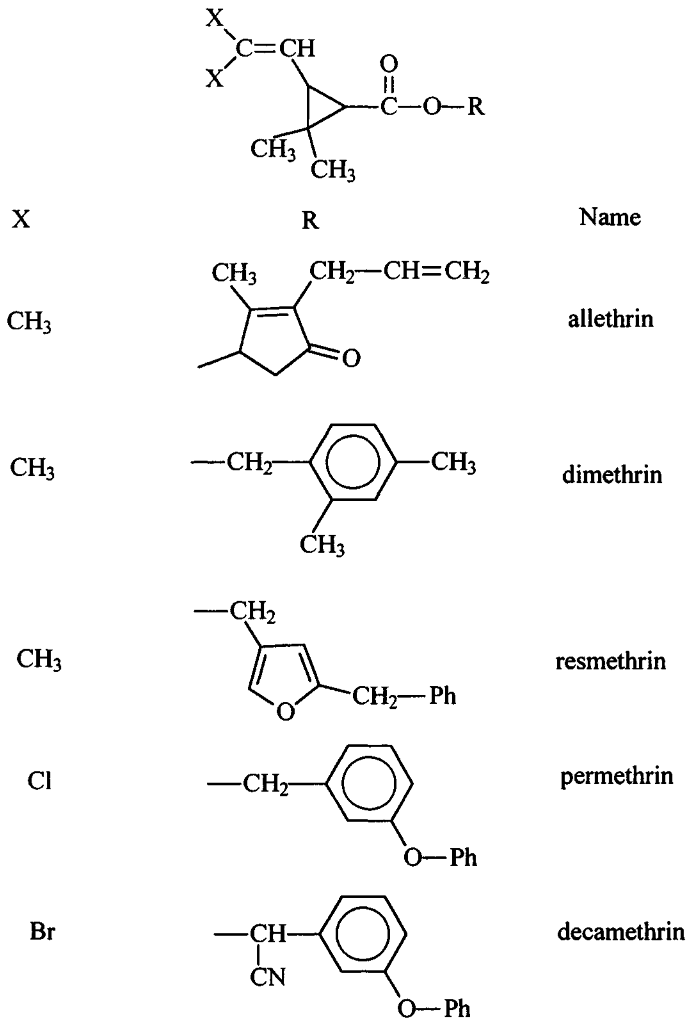


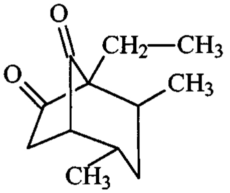
Figure 20.5 Synthetic pyrethroids.

though they are very expensive compared to methyl parathion, carbaryl, terbufos, and carbofuran. Names and structures of some synthetic pyrethroids are given in Fig. 20.5. Their main advantages are (1) few side effects on plants, livestock, and humans; (2) no resistance buildup by insects; and (3) lower quantities needed. The synthetic pyrethroids can have up to 30 times the quickkill power of the natural pyrethrins and longer half-lives. In 1997 the EPA reviewed synthetic pyrethroids for 273 tolerances on food. All of these insecticides met the new standards for the 1996 FQPA. They are now considered major alternatives to organophosphate and carbamate insecticides on major crops, including cotton, corn, sorghum, rice, wheat, and alfalfa.

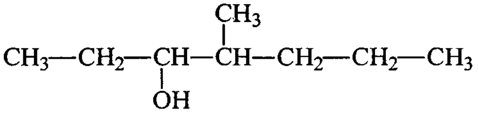
3.6 Third-Generation Insecticides

Many people think the ultimate pesticide should be developed from research now being done on certain insect attractants and juvenile hormones. Isolation of naturally occurring sex attractants (pheromones) and juvenile hormones has been accomplished. The attractants could be used to congregate large numbers of insects in one place for extermination by the already existing insecticides. Alternatively, juvenile hormones have been found that prevent maturation or cause sterility in many pests.

The U.S. Forest Service scientists in New York have isolated and identified chemical sex attractants used by elm bark beetles that are responsible for transmitting the fungus causing Dutch elm disease. Examples of attractants are 2,4-dimethyl-5-ethyl-6,8-dioxabicyclo [3.2.1] octane (called multistriatin) and 4-methyl-3-heptanol. In field trials an artificially produced mixture of the compounds has proved attractive to the elm bark beetle.



multistriatin

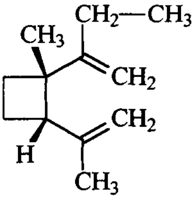


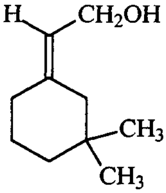
$$CH_3-CH_2-\underset{OH}{CH}-\overset{CH_3}{CH}-CH_2-CH_2-CH_3$$

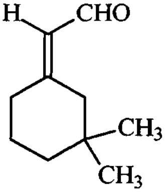
4-methyl-3-heptanol

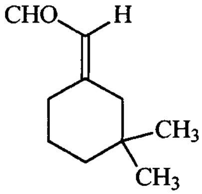
The boll weevil sex attractant is a mixture of four compounds, two alcohols and two aldehydes.

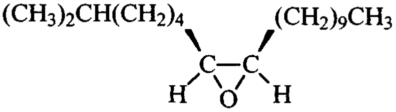
The epoxide disparlure has been isolated as the gypsy moth sex attractant. These pheromones are in experimental use for control of these pests.





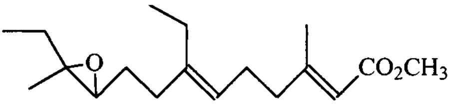




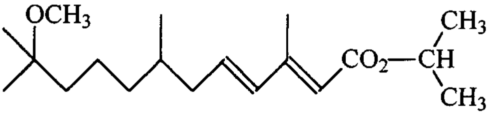


Insects may emit as little as 10^{-15}g of pheromone and a female insect contains typically only 50 mg of the material. The structure is sometimes exacting, as in the case of the pink bollworm, where the ratio of *cis* and *trans* double bonds is species specific to avoid hybridization of insects.

In 1965 the first juvenile hormone was isolated and it was synthesized in 1967. The substance studied was methyl *trans, trans, cis*-10-epoxy-7-ethyl-3, 11-dimethyl-2,6-tridecadienoate from the male silkmoth.



A juvenile hormone was approved for commercial marketing by the EPA. Approved for control of floodwater mosquitoes, Zoecon Corporation of Palo Alto, California, is selling Altosid SR-10, which is isopropyl 11-methoxy-3,7,11-trimethyldodeca-2,4-dienoate, also known as methoprene.



The big advantage of this type of insecticide is its relatively rapid degradation and low toxicity to applicators, fish, birds, beneficial insects, and other wildlife. The price is competitive with more conventional pesticides. No doubt more third generation insecticides will be developed in the future.

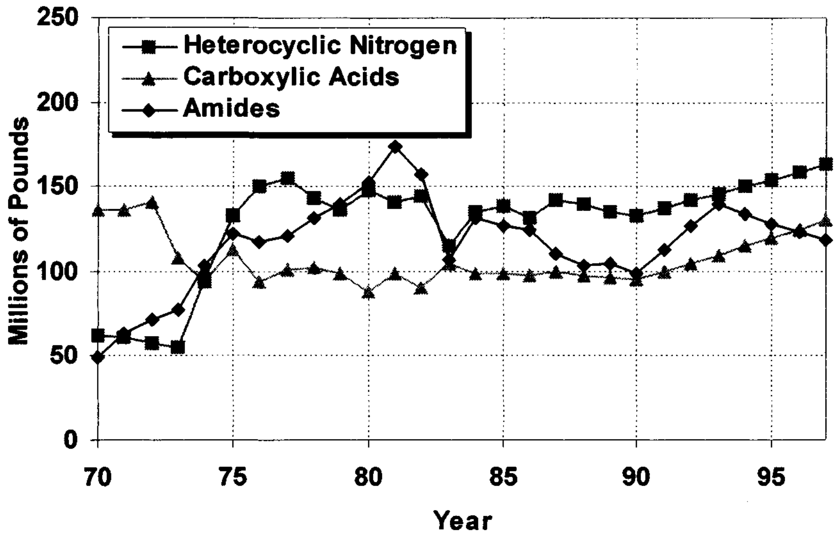


Figure 20.6 U.S. consumption of herbicides. (*Source: Chemical Economics Handbook*)

4. HERBICIDES

The Department of Agriculture has estimated that about 10% of U.S. agricultural products is lost because of weeds. About 1,500 species of weeds cause economic loss. As we mentioned earlier, herbicide use rose dramatically in the 1970s and 1990s, and herbicide consumption is now at 900 million lb/yr with a worth of $6 billion/yr. In 1950 there were only 15 different herbicides; today there are over 180. Herbicides are used mainly on corn, soybeans, wheat, and cotton.

Fig. 20.6 shows the trend in consumption for the three most important types of herbicides. Carboxylic acids have been the standby for many years and were the first type of herbicide. They were replaced as number one by the heterocyclic nitrogen compounds in the 1970s. Carboxylic acids are making a comeback in the 1990s. A close third are the amide herbicides. The present percentage of consumption for herbicides is given in Table 20.7.

Table 20.7 Types of Herbicides

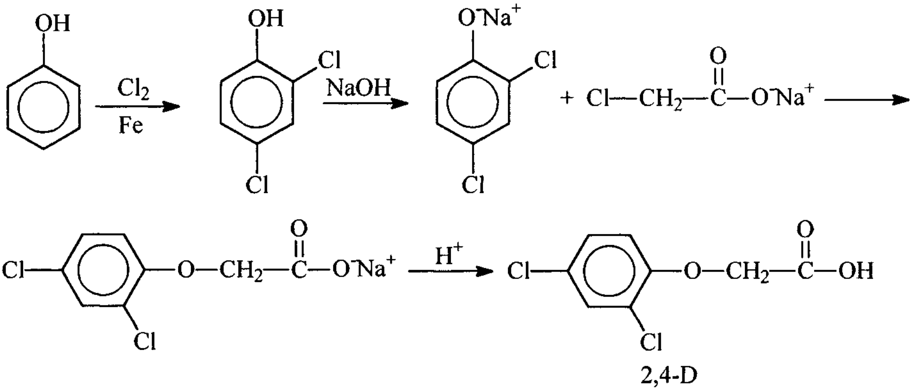
Heterocyclic nitrogens	29%
Carboxylic acids & derivatives	23
Amides	20
Dinitroanilines	10
Miscellaneous	18

Source: Chemical Economics Handbook

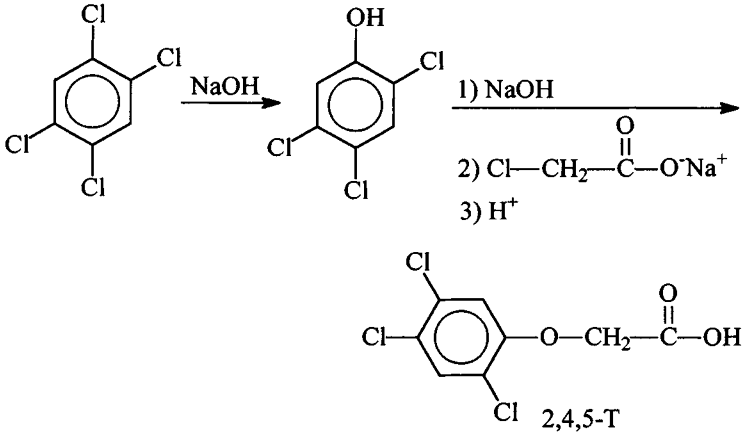
4.1 Carboxylic Acids

Rapid growth of chemical weed control did not occur until after World War II when a herbicide was introduced by Jones in 1945 at the Imperial Chemical Industries of England: 2,4-dichlorophenoxyacetic acid (2,4-D). Its utility has come from its ability to kill selectively broadleaf weeds in cereal grains, corn, and cotton. It does not disturb the soil and is not persistent. 2,4,5-T was launched commercially by American Chemical Paint Co. in 1948 (now Union Carbide) to combat brush and weeds in forests, along highways and railroad tracks, in pastures, and on rice, wheat, and sugarcane.

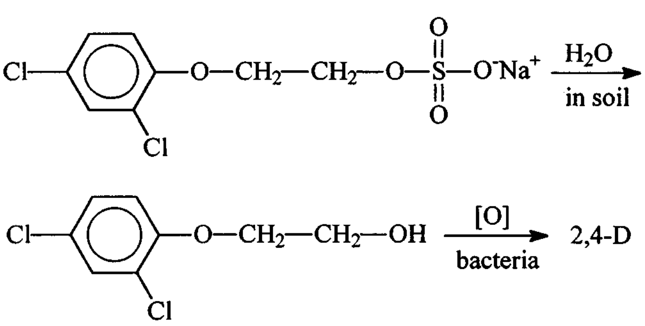
2,4-Dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) dominated the herbicide market up to the late 1960s. These are sometimes called phenoxy herbicides. Phenol is the starting material for 2,4-D. Chlorination via electrophilic aromatic substitution (know the mechanism!) gives 2,4-dichlorophenol. The sodium salt of this compound can react with sodium chloroacetate (S_N2) and acidification gives 2,4-D.



2,4,5-T can be synthesized easily. Chlorination of benzene gives 1,2,4,5-tetrachlorobenzene (why this isomer?) which reacts with caustic to give 2,4,5-trichlorophenol. A conversion similar to the preceding one yields the phenoxyacetic acid 2,4,5-T.

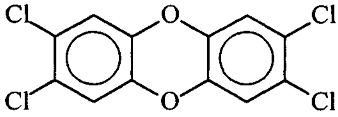


The phenoxy herbicides' inexpensiveness, selectivity, nonpersistency and low toxicity to animals are difficult to beat. Application is usually accomplished by spraying on the leaves. The herbicides cannot themselves be applied to the soil because they are washed away or decomposed by microorganisms in a few weeks. They can be applied by this method using a sulfonic acid derivative that, after hydrolysis in the soil and oxidation by bacteria, can form 2,4-D in the plant. 2,4-D is still the main herbicide used on wheat.



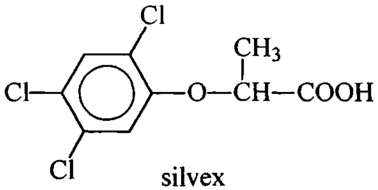
Much publicity has been given to 2,4,5-T. A trace impurity called 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) has been called the most toxic small molecule known to humans. TCDD kills animals and causes birth defects at lower levels than any other chemical tested in the laboratory. In

2001 TCDD was added to the known carcinogen list of the National Toxicology Program.



TCDD

In 1969 Vietnam newspapers claimed use of 2,4,5-T as a defoliant was causing illness, stillbirths, and fetal deformities. Agent Orange (named after the color of its storage drums) contained a 50:50 mixture of the butyl esters of 2,4,5-T and 2,4-D. The U.S. Defense Department stopped using it in 1970. The National Cancer Institute funded a study in 1968 that seemed to indicate that large doses of 2,4,5-T (containing 28 ppm of dioxin) increased the incidence of birth defects in certain strains of mice. The 2,4,5-T marketed more recently contained 0.01 to 0.02 ppm. In 1985 the EPA cancelled all uses of 2,4,5-T as well as another dioxin-containing herbicide, silvex.

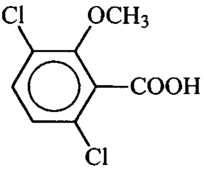


silvex

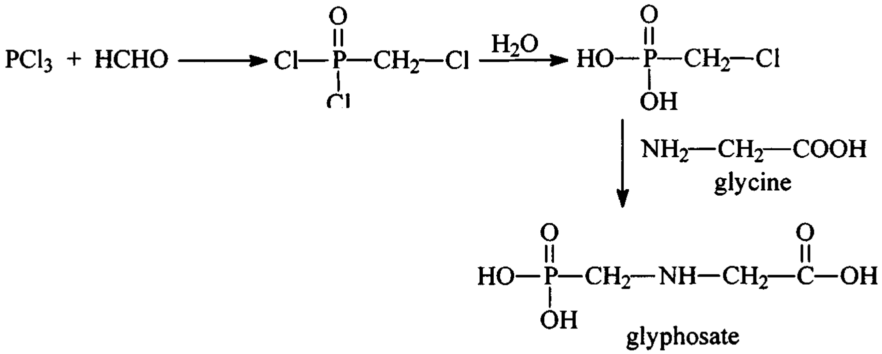
In 1984 a suit involving some 15,000 Vietnam veterans and their dependents against seven chemical companies reached an out-of-court settlement in which the chemical companies agreed to pay $180 million into a trust fund that will be used to pay damages to veterans and their families as their health claims are proven. They have complained of health problems ranging from skin conditions to nervous disorders, cardiovascular effects, cancer, and birth defects. However, the Center for Disease Control in Atlanta found that Vietnam veterans have no greater likelihood of fathering children with serious birth defects than do other American males. The 1976 toxic cloud containing TCDD released in Seveso, Italy did not cause an increase in cancer rate, birth defects, or other diseases, and the signs of chloracne, a skin disfiguring disease, have disappeared from most of the people who suffered from it.

In 1990 the National Cancer Institute reviewed 2,4-D, still one of the most widely used carboxylic acid herbicides. They found that wheat farmers exposed to the herbicide may face an increased risk of cancer. Studies so far have only shown increased cancer risk for heavy users of the weedkiller, not the occasional user, such as homeowners. One of the active ingredients in Ortho Weed-B-Gon® lawn weed killer is 2,4-D. However, 2,4-D is not yet on the known or suspect carcinogen list of the National Toxicology Program.

Other carboxylic acids that have become popular herbicides, though they are not phenoxyacetic acid derivatives, are dicamba and glyphosate or Roundup®. Notice that dicamba does have a methoxy group and two chlorines, so it is similar to 2,4-D. Glyphosate is used on cotton and soybeans. Monsanto, the maker of Roundup®, has genetically engineered cotton and soybeans to develop tolerance to the lower selectivity of this herbicide. It was introduced in 1971 and has since become a major revenue earner. Its structure is novel because it bears no resemblance to any other herbicide except that it is a carboxylic acid. Glyphosate is thought to bind by chelation with metals, such as iron, in the soil. The isopropylamine salt of the acid is used. Its mode of action appears to be interference with the biosynthesis of aromatic acids such as phenylalanine. This in turn inhibits nucleic acid metabolism and protein synthesis. The synthesis of glyphosate involves organophosphorus chemistry, with the intermediate reacting with glycine: hence the name glyphosate.

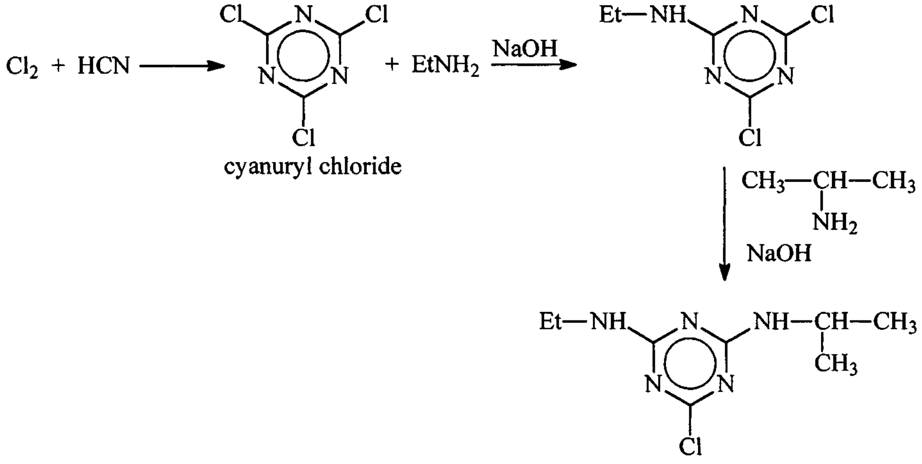


dicamba



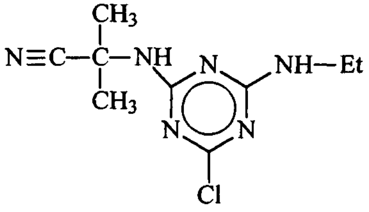
4.2 Heterocyclic Nitrogen Herbicides

The most widely used herbicides today are triazine compounds (three nitrogens in the heterocyclic aromatic ring). Atrazine is used especially on corn but also on pineapple and sugarcane. It is synthesized by reacting cyanuryl chloride successively with one equivalent of ethylamine and one equivalent of isopropylamine. Cyanuryl chloride is made in one step from chlorine and hydrogen cyanide. Cyanazine (Bladex®) is another important triazine. Trazines will kill most types of plants but corn because something in this crop degrades the triazines before their toxic action can take place. Cyanazine may be a carcinogen. It is not on the official list of known or suspected carcinogens of the National Toxicology Program in 2001, but further tests are being conducted. Atrazine is not a carcinogen but it could have developmental effects in children. Some states have limited use of atrazine because it is detected in groundwater. Bentazon is a different type of herbicide. It is a heterocyclic nitrogen compound but not a triazine.

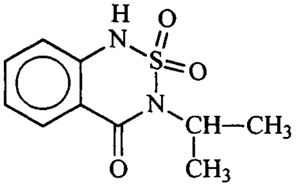


cyanuryl chloride

atrazine



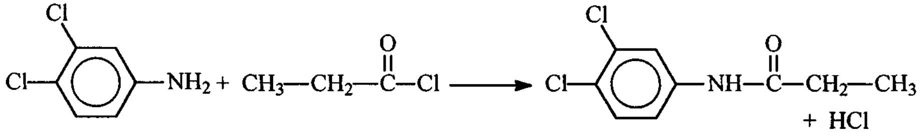
cyanazine



bentazon

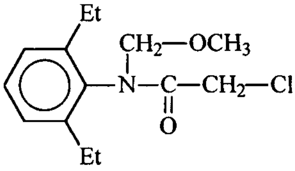
4.3 Amide Herbicides

A number of other herbicides have specific uses. The amide herbicides, of which propanil is typical, are used in large quantities. Propanil is made by the reaction of propionyl chloride and 3,4-dichloroaniline.

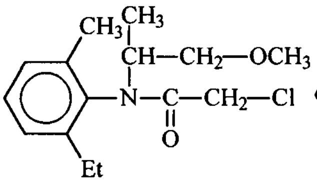


propanil

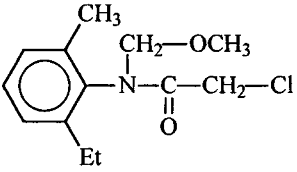
Another common amide herbicide, alachlor (Lasso®), is used on corn and soybeans in large amounts, as well as on potatoes, peanuts, and cotton. In late 1984 the EPA determined that alachlor poses a significant potential cancer risk to persons working with it. Dietary feeding studies showed that alachlor induces tumors in rats and mice. Those wishing to apply the compound are required to wear protective clothing. Aerial spraying is banned. It has been found in surface water and groundwater. Further testing is being conducted but it is not on the official list of known or suspect carcinogens of the National Toxicology Program. Consumption of alachlor was down to 16 million lb in 1997 from 48 million lb in 1993. Metolachlor and acetochlor are amide herbicides with similar structures used in large volume. Their use has rapidly increased in the last few years.



alachlor



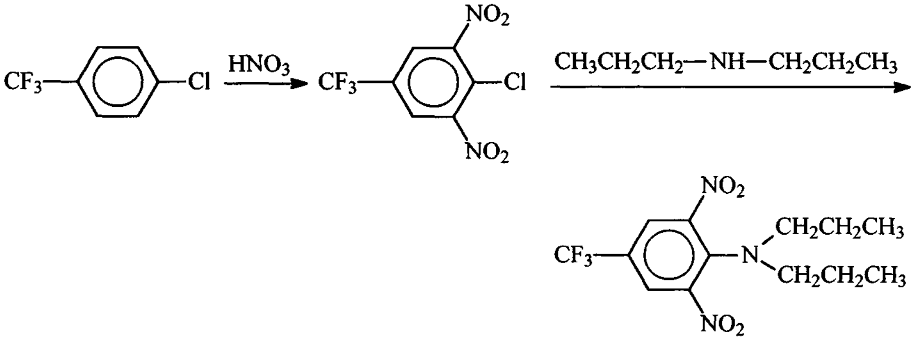
metolachlor



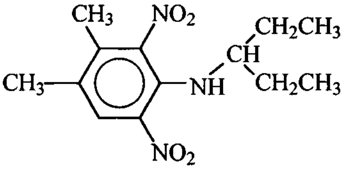
acetochlor

4.4 Dinitroanilines

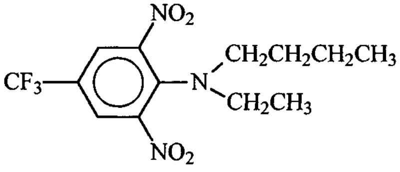
A class of compounds, discovered at Ely Lilly in 1961, are the dinitroanilines, with trifluralin (Treflan®) being an important member. Trifluralin is used on soybeans and cotton. Pendimethalin is a second important dinitroaniline. Benefin is a common crabgrass preventer for home lawns.



trifluralin



pendimethalin



benefin

4.5 Summary

Table 20.8 lists the herbicides discussed here with their annual U.S.

Table 20.8 U.S. Consumption of Herbicides

Name	Million lb
Heterocyclic Nitrogens, total	**163.2**
Atrazine	73.0
Cyanazine	20.0
Bentazon	8.0
Carboxylic Acids, total	**130.0**
Glyphosate	40.0
2,4-D	30.0
Dicamba	10.0
Amides, total	**118.4**
Metolachlor	63.0
Acetochlor	30.0
Alachlor	16.0
Propanil	7.0
Dinitroanilines, total	**62.0**
Pendimethalin	24.0
Trifluralin	23.0

Source: Chemical Economics Handbook

consumption, together with the total for each major type of herbicide. In this chapter we have taken up our first example of a sector of the chemical industry that involves multistep organic syntheses, very diverse organic chemical structures, and final compounds which are unique in their biological action and selectivity. We will see this type of industrial sector again when we study the pharmaceutical industry in Chapter 23. Despite this complexity of chemistry most of the major pesticides fall into one chemical class or another that has been shown to give the desired biological response. Then slight modifications of structures are used for specific applications to maximize the desired effect and minimize the side effects. In summary, the insecticide market is now dominated by the organophosphates and the carbamates. The herbicide market is a little more diverse, but heterocyclic nitrogens, carboxylic acids, amides, and dinitroanilines are the main materials.

Suggested Readings

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 1141-1185.
Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, pp. 339-362.

Chapter 21

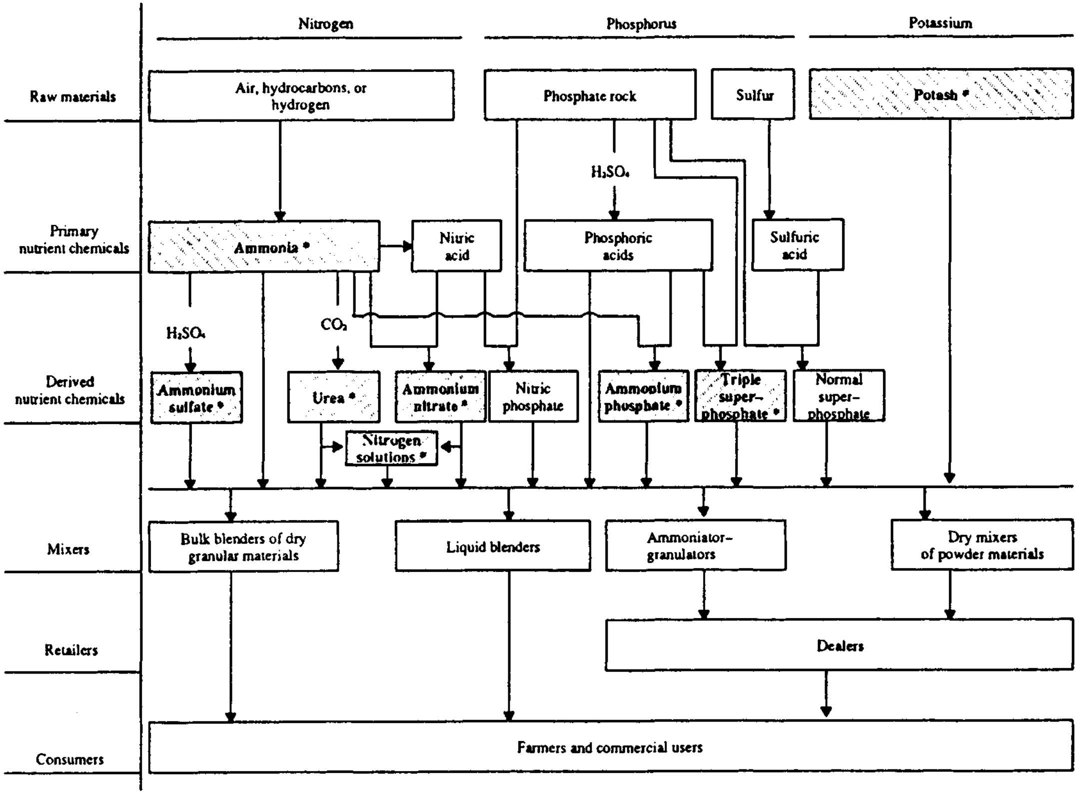
Fertilizers

1. INTRODUCTION

Besides the three basic elements of carbon, hydrogen, and oxygen that are common to all plants, there are 16 other elements known to be essential to good plant growth. Their percentages are given below.

95% basic elements—44% C, 6% H, 45% O
3.5% primary nutrients—2.0% N, 0.5% P, 1.0% K
1.3% secondary nutrients—Ca, Mg, S
0.1% micronutrients—B, Cl, Cu, Fe, Mn, Mo, Zn (Co, F, I in animals also)

This chapter is concerned with the three primary nutrients making up most fertilizers: nitrogen, phosphorus, and potassium. The usual sources of nitrogen are ammonia, ammonium nitrate, urea, and ammonium sulfate. Phosphorus is obtained from phosphoric acid or phosphate rock. Potassium chloride is mined or obtained from brine and the sulfate is mined in small amounts. Potassium nitrate is made synthetically. These chemicals have already been described under inorganic chemicals of the top 50. Sources for the three primary nutrients are given in Fig. 21.1.



* Major direct application materials sold through blender–retailers or dealers.

Figure 21.1 Major fertilizer materials. (*Source:* Kline & Company, Inc.)

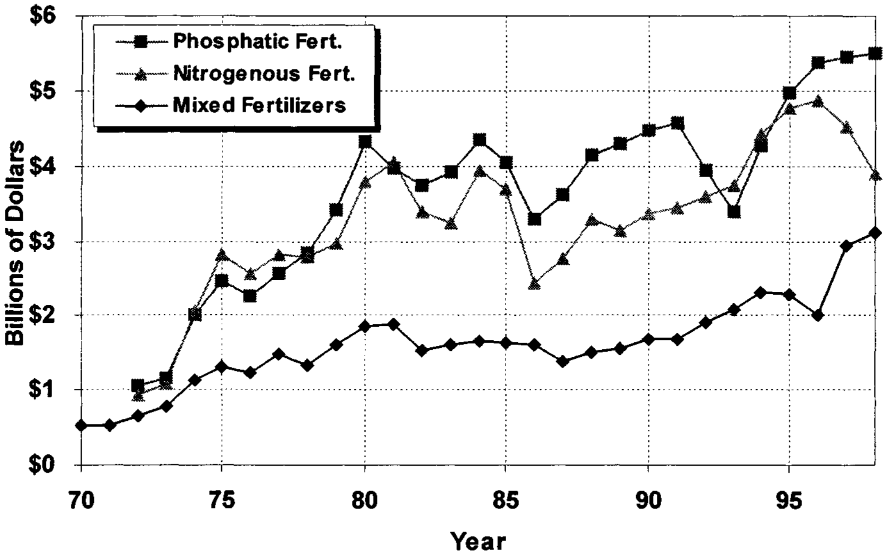


Figure 21.2 U.S. shipments of fertilizers. (*Source: Annual Survey of Manufactures*)

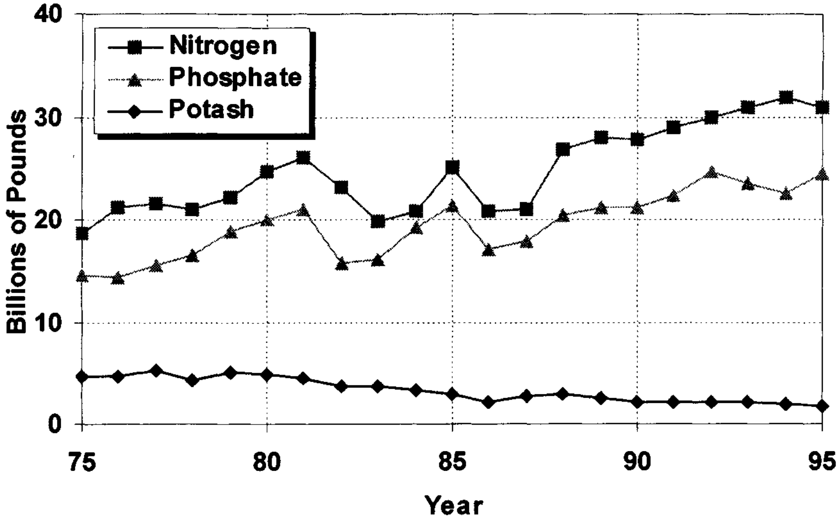


Figure 21.3 U.S. production of fertilizers. (*Source: Chemical Economics Handbook* and UN Food and Agriculture Organization)

2. HISTORY AND ECONOMICS OF FERTILIZERS

Although the modern era of fertilizers began with the work of Justus von Liebig in 1840 and the first U.S. patent for a mixed fertilizer was granted in 1849, the use of large amounts of synthetic fertilizers was popularized only after World War II. Fertilizer consumption increased eight times between 1950 and 1980 worldwide. U.S. shipments of fertilizers is summarized in Fig. 21.2. Phosphatic Fertilizers (NAICS 325312) had a very fast increase from $1 billion in the early 1970s to $4.4 billion in 1980. Since then it has increased only slowly to $5.5 billion. Nitrogenous fertilizers (NAICS 325311) have also had a similar trend to 1980 and have dropped recently to that level now. Mixed Fertilizers (NAICS 325314) have had a more constant increase in the last few years. Fig. 21.3 gives trends in nitrogen, phosphate, and potash fertilizer production. Nitrogen and phosphorus production in billions of pounds have increased slowly through the years except for a few drops in the 1980s. Potash production is always much less and has been steady or decreasing in the last 25 years. Table 21.1 shows the uses of fertilizers on various types of crops. Note that nearly half of all fertilizers is used on one crop: corn. Wheat, hay, soybeans, and cotton consume most of the rest of fertilizers used on crops.

3. FERTILIZER MATERIALS

Fertilizers may contain all three primary nutrients, in which case they are called mixed fertilizers, or they may contain only one active ingredient, called direct application fertilizers. Recently the ratio of direct application to mixed fertilizers is 60:40 in the U.S. Nitrogen and potash are consumed mainly from direct application fertilizers. Phosphate is applied mostly from mixed fertilizers.

Table 21.1 Uses of Fertilizers on Crops

Corn	44%
Wheat	17
Hay	9
Soybeans	6
Pasture and range	5
Cotton	3
Other crops	10
Other feed grains	6

Source: Chemical Economics Handbook

Table 21.2 Percentage of Direct Application Fertilizers

Nitrogen solutions	24%
Anhydrous and aqueous ammonia	22
Potassium chloride	20
Ammonium nitrate	10
Urea	8
Superphosphates	5
Ammonium sulfate	3
Ammonium phosphate	2
Miscellaneous	6

3.1 Direct Application Fertilizers

Table 21.2 lists all important direct application materials and their percentage of direct application fertilizers. Direct application use is increasing mainly because of anhydrous ammonia gas becoming popular. It can be pumped in 3-6 in. beneath the soil during plowing and is absorbed by the soil rapidly. Nitrogen solutions can also be applied in this manner (mixture of free ammonia, ammonium nitrate, urea, and water).

3.2 Mixed Fertilizers

The primary advantage of mixed fertilizers is that they contain all three primary nutrients—nitrogen, phosphorus, and potassium—and require a smaller number of applications. They can be liquids or solids. The overall percentage of the three nutrients must always be stated on the container. The grade designation is $\%N$-$\%P_2O_5$-$\%K_2O$. It is commonly called the *NPK value.* Note that it is an elemental percentage only in the case of nitrogen. Phosphorus and potassium are expressed as oxides. Thus an NPK value of 6-24-12 means that 6% by weight is elemental nitrogen, 24% is phosphorus pentoxide, and 12% is potash. One way of remembering the order is that they are alphabetical according to the English name (*n*itrogen, *ph*osphorus, *po*tassium). A changeover to a grade designation by the three elemental bases is being resisted by the industry.

3.2.1 Nitrogen Sources

The nitrogenous chemicals ammonia, urea, ammonium nitrate, and ammonium sulfate are used as sources of nitrogen in mixed fertilizers. A mixture is also quite popular and is relatively cheap, since the mixed nitrogen solution from which pure urea is made can be used as fertilizer. Nitrogen solutions have their own code number. An example would be 414(19-66-6), meaning 41.4% total nitrogen, 19% free ammonia, 66% ammonium nitrate, and 6% urea with the rest being water. Over 100 nitrogen solutions are marketed. Although the solutions are cheap, the solids do not have a vapor pressure problem and are more easily transported. The present breakdown of nitrogen fertilizer production is ammonia, 40%; nitrogen solutions, 30%; urea, 14%; ammonium nitrate, 8%; and ammonium sulfate, 8%.

3.2.2 Phosphorus Sources

All phosphorus fertilizers come from wet process phosphoric acid or directly from phosphate rock. Normal superphosphate, triple or concentrated superphosphate, and ammonium phosphate are the three common types used. Normal or ordinary superphosphate (NSP or OSP) is mostly monocalcium phosphate and calcium sulfate. It is made from phosphate rock and sulfuric acid and is equated to a 20% P_2O_5 content. It led the market until 1964. The production of normal superphosphate is similar to that for the manufacture of wet process phosphoric acid (Chapter 2, Section 3) except that there is only partial neutralization. Normal superphosphate is no longer used to any great extent. The following reaction is one example of an equation that represents this process.

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 17H_2O + 7H_2SO_4 \longrightarrow$$

$$3[CaH_4(PO_4)_2 \cdot H_2O] + 2HF + 7(CaSO_4 \cdot 2H_2O)$$

normal superphosphate (NSP)

Triple superphosphate (TSP), made from phosphate rock and phosphoric acid, is mostly mono- and dicalcium phosphate. It is equivalent to a 48% P_2O_5 content. It led the market from 1965-1967.

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 14H_3PO_4 \longrightarrow 10CaH_4(PO_4)_2 + 2HF$$

triple superphosphate (TSP)

The ammonium phosphates took over the lead in 1967. Diammonium phosphate (DAP) is made from wet process phosphoric acid of about 40% P_2O_5 content and ammonia. The usual finishing NH_3:H_3PO_4 mole ratio is 1.85-1.94:1. Monoammonium phosphate (MAP) is made with a final NH_3:H_3PO_4 ratio of 1:1. Current production percentages for phosphate fertilizers are DAP, 67%; MAP, 26%; and TSP, 7%.

$$2NH_3 + H_3PO_4 \longrightarrow \underset{\text{(DAP)}}{(NH_4)_2HPO_4}$$

$$NH_3 + H_3PO_4 \longrightarrow \underset{\text{(MAP)}}{NH_4H_2PO_4}$$

3.2.3 Potassium Sources

Most potassium in fertilizers is the simple chloride salt, having a 60-62% K_2O equivalent. Certain crops such as potatoes and tobacco do not like high amounts of chloride. For these crops KNO_3, K_2SO_4, or $K_2Mg(SO_4)_2$ may be used. Florida citrus crops need magnesium nutrients so $K_2Mg(SO_4)_2$ is favored there.

3.2.4 Ammoniation

When an ammonia fertilizer is mixed with a superphosphate there is a chemical reaction that occurs, changing the active ingredient's structure. The following equations illustrate this chemistry.

(1) $H_3PO_4 + NH_3 \longrightarrow NH_4H_2PO_4$

(2) $Ca(H_2PO_4)_2 \cdot H_2O + NH_3 \longrightarrow CaHPO_4 + NH_4H_2PO_4 + H_2O$

(3) $NH_4H_2PO_4 + NH_3 \longrightarrow (NH_4)_2HPO_4$

(4) $2CaHPO_4 + CaSO_4 + 2NH_3 \longrightarrow Ca(PO_4)_2 + (NH_4)_2SO_4$

(5) $NH_4H_2PO_4 + CaSO_4 + NH_3 \longrightarrow CaHPO_4 + (NH_4)_2SO_4$

Reactions (1) and (2) are common for both normal and triple superphosphate. Reaction (3) is important in triple superphosphate because of the lack of large amounts of calcium sulfate. Reaction (5) is important

Table 21.3 Advantages of Fertilizers

Liquids	Solids
Lower capital investment by the company	Less corrosion of equipment
Less labor, handling, and conditioning costs	Better economics of costs of storing smaller volumes
More uniform composition	Solubility restrictions are not present
More uniform distribution on land	No crystallization problems in cold weather

with normal superphosphate because of the large surplus of calcium sulfate in this formulation.

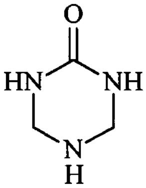
4. LIQUIDS VS. SOLIDS

There are many different types of liquid and solid fertilizers but we give only some generalizations about advantages of each. Liquid fertilizers are a clear solution, a suspension of a solid in a liquid (aided by a suspending agent), or a simple slurry of a solid in a liquid. Solid fertilizers contain no liquid. Table 21.3 summarizes the advantages of liquids and solids.

Mixed solid fertilizers can be made by either direct granulation methods (40%) or bulk blending (40%). Bulk blending is made by mechanical mixing of the separate granular intermediate materials. It is usually done in small plants near the point of use. This technique is employed because the fertilizer can be “tailor-made” to fit the exact requirements of the user. Fluid or liquid fertilizers (clear, suspension, and slurry) account for 20% of all NPK mixed fertilizers.

5. CONTROLLED-RELEASE FERTILIZERS

Much recent research has centered on developing long-lasting slow-release fertilizers to make application requirements less often. Urea-formaldehyde resins in nitrogen fertilizers tie up the nitrogen for a longer time, since degradation of the polymer occurs slowly by sunlight. This type of fertilizer is especially popular for the high nitrogen content of home lawn fertilizers. Sulfur-coated urea (SCU) is also becoming a popular slow-release nitrogen formulation. *sym*-Tetrahydrotriazone, made by reacting urea, formaldehyde, and ammonia, can be added to urea fertilizers.



sym-tetrahydrotriazone

Triazones form ammonium ions much more slowly than urea. Slow-release potassium is also being developed. A coating of sulfur seems to delay its release. For phosphorus $Mg(NH_4)PO_4$ is becoming popular because it has a slower dissolution rate in the soil. Despite the simple chemicals used in most fertilizers, some interesting research and formulation work will keep chemists involved in the industry for some time to come.

Suggested Readings

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 367-407.

Chapter 22

Pulp, Paper, and Wood

1. INTRODUCTION

Although the pulp and paper industry is not part of Chemical Manufacturing, it is one of the major divisions of the chemical process industries. Containing some interesting chemistry, this industry employs many chemists and chemicals. It takes over 400 lb of chemicals to make 1 ton of paper.

Writing paper was first used in Egypt as far back as 2500-2000 BC, made from the papyrus reed. Paper manufacture began in China about AD 105. In 1690 the first American paper mill began its operation. Two recent dates of importance to modern paper technology are 1867, when Tilghman in the U.S. developed the sulfite process, and 1884, when Dahl in Germany discovered the kraft or sulfate process.

The student should review Fig. 7.1 to see the relative size of Paper Manufacturing compared to other chemical process industries. Its 1998 U.S. shipments totalled $156 billion, about one third of the size of Chemical Manufacturing at $424 billion. It is about the same size as Petroleum and Coal at $137 billion. It has undergone a steady increase over the years, even in the 1980s when sectors like Petroleum and Coal suffered a decline. It has not grown as fast as Chemical Manufacturing. U.S. consumption of wood pulp is 67 million tons per year. The paper industry makes approximately 95 million tons of paper and paperboard products annually. This country's production of paper products is more than half the world's production. Per capita consumption of pulp has risen sharply in recent years. In 1940 it was 255 lb of pulp per person in the U.S.; in recent years it is near 600 lb.

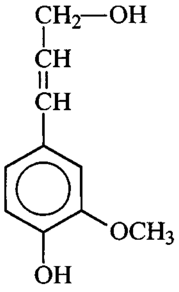
Compare this to 31 lb per person annually in Asia and 11 lb in Africa. There are about 200 pulp mills and 600 paper and paperboard mills in operation now. Some names of companies in this industry in order of sales from first to tenth are International Paper, Georgia-Pacific, Stone Container, Scott Paper, James River, Weyerhaeuser, Champion International, Union Camp, Mead, and Boise Cascade.

2. THE CHEMISTRY OF WOOD

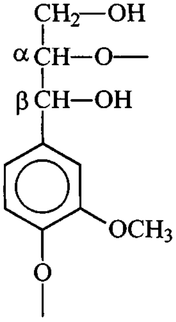
Woody plants are made of strong, relatively thick-walled long cells that make good fibers. The cell wall in these types of plants is a complex mixture of polymers that varies in composition. But it can be roughly divided into 70% polysaccharides and 28% lignin.

The polysaccharides in wood are called holocellulose, or total cellulose carbohydrates. They can be subdivided into (1) cellulose (40%), a high molecular weight linear polymer composed of glucose units with high chemical resistance, and (2) hemicellulose (30%), other polysaccharides besides cellulose that are of lower molecular weight and have lower chemical resistance to acids and alkalies. The sugars in the hemicellulose are mostly xylose, galactose, arabinose, mannose, and glucose.

Lignin has been described as "the adhesive material of wood" because it cements the fibers together for strength. It is a complex cross-linked polymer of condensed phenylpropane units joined together by various ether and carbon linkages. A representative structure of the phenylpropane units in lignin is given in Fig. 22.1. Lignin can be considered to be a polymer of coniferyl alcohol. About 50% of the linkages are β-aryl ethers. Lignin can be degraded with strong alkali, with an acid sulfite solution, and with various oxidizing agents. It is therefore removed from the wood to leave cellulose fibers, commonly called pulp. Although there are many differences between



coniferyl alcohol



β-aryl ethers

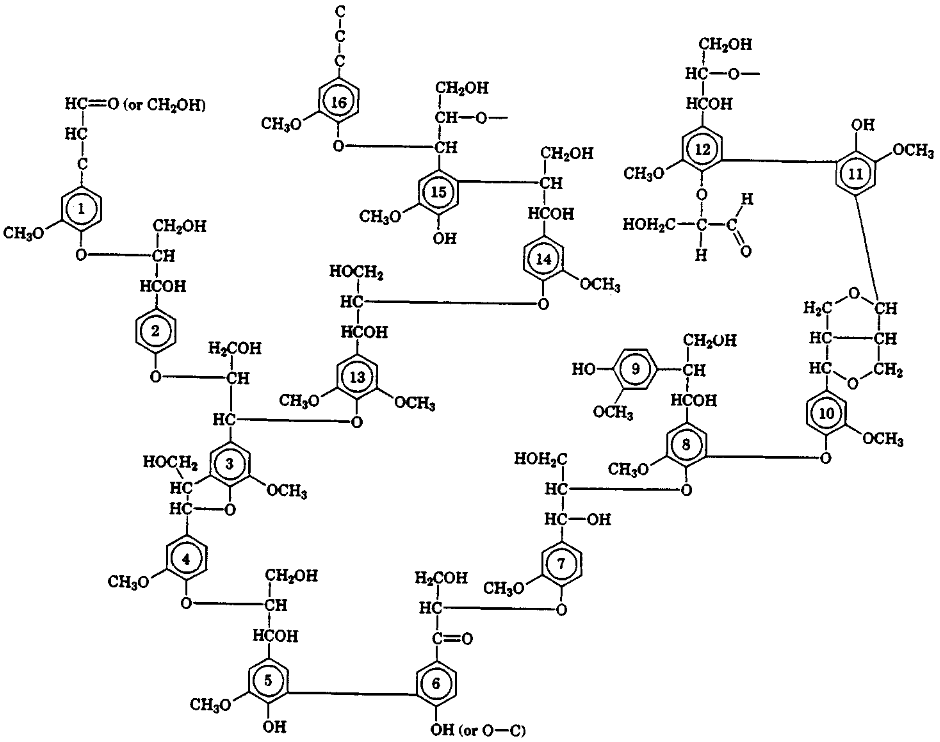


Figure 22.1 Representative structure of lignin. (*Source:* Kirk-Othmer's *Encyclopedia of Chemical Technology*, 4th ed., John Wiley & Sons, 1991-1998. Reprinted by permission of John Wiley & Sons, Inc.)

hardwood and softwood, the hardwoods always have less lignin and more hemicellulose (high in xylose), whereas the softwoods have more lignin and less hemicellulose (which is high in galactose, glucose, and mannose units). Besides the holocellulose and lignin of the cell wall, wood contains about 2% extractives. These can be separated by steam distillation or solvent extraction and will be discussed later. The average composition of most woods is summarized as follows: holocellulose, 70% (including 40% cellulose and 30% hemicellulose); lignin, 28%; and extractives, 2%.

3. PULP MANUFACTURE

The process of pulping, degrading the lignin to a more soluble form so the cellulose fibers can be separated from it, involves some interesting chemistry. The kraft or alkaline sulfate process dominates this part of the industry. Approximately 78% of all pulp is made by the kraft process, 3%

Table 22.1 Relative Weights of Wood Components Before and After Kraft Pulping

Component	Before	After
Cellulose	40	36
Hemicellulose	30	7
Lignin	27	4
Extractives	3	0.5
Total	**100**	**47.5**

by the acid sulfite process, 7% by the neutral sulfite semichemical (NSSC) process, 10% by a nonchemical, mechanical method called groundwood, and 2% by other methods.

3.1 The Kraft Process

Recalling that *kraft* is the German word for *strong* helps remind us that the strongest pulp fibers can be made by this method. Any pulping process lowers the molecular weight of the hemicellulose, depolymerizes the lignin, and gives a much larger percentage of cellulose fibers. Table 22.1 gives the relative weights of these different components before and after this alkaline sulfate treatment.

3.1.1 Inorganic Kraft Chemistry

The important chemistry in the kraft method is divided into inorganic and organic parts. Figure 22.2 summarizes the inorganic chemistry. The inorganic loop is a closed system with the exception of sodium sulfate being added periodically. Only wood enters the loop and only pulp leaves.

Although the digester is shown as containing NaSH, NaOH, and NaS_xH, the typical entering white liquor is analyzed at about 59% NaOH, 27% Na_2S, and 13% Na_2CO_3—Na_2SO_4—Na_2SO_3. Digestion of the wood-white liquor mixture occurs at 170-175°C and 100-135 psi for 2-5 hr. A typical digester is 40 ft high with a diameter of 20 ft and can hold up to 35 tons of wood chips at a 1:4 wood: white liquor weight ratio. The organic chemistry of this digestion process is covered subsequently.

The resulting pulp is separated from the black liquor (colored with organics), which is then oxidized to $Na_2S_2O_3$ (S^{-2} to S^{+2}) and further oxidized in the furnace to Na_2SO_4 (S^{+2} to S^{+6}). The organic material from the digestion process, which we may simplify here as carbon, is oxidized in the furnace to CO_2 (C^0 to C^{+4}) whereas the Na_2SO_4 is reduced back to Na_2S (S^{+6}

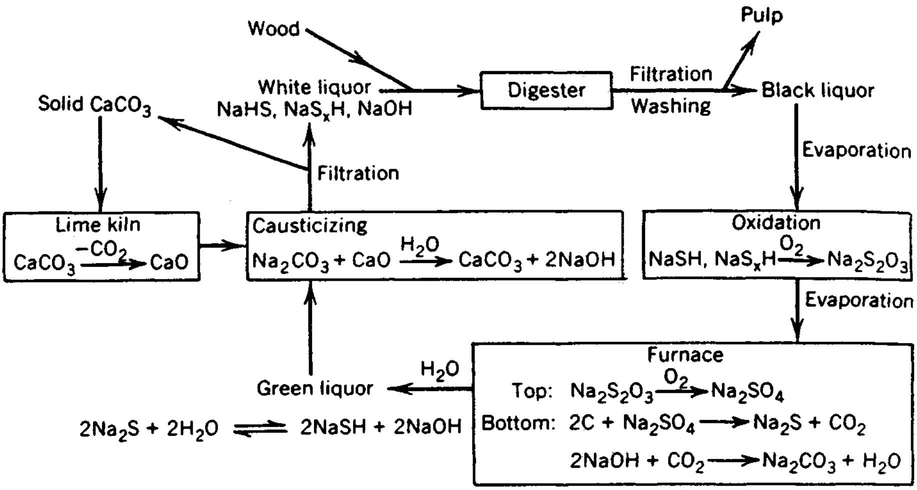
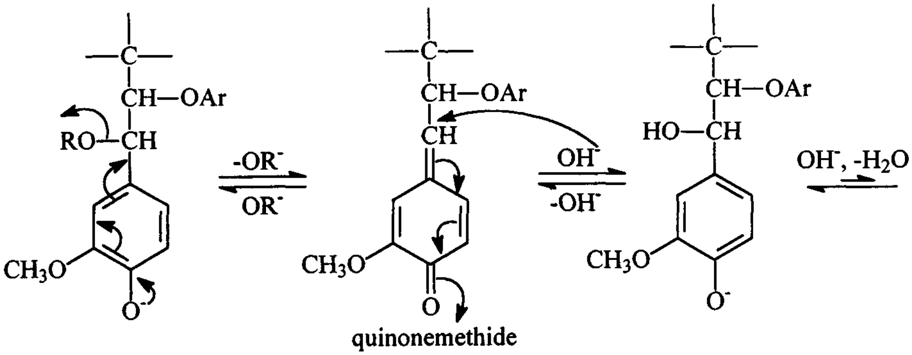


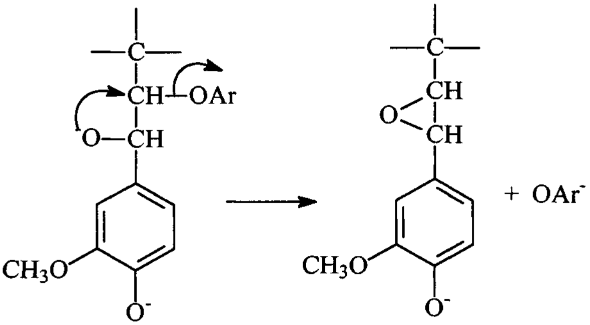
Figure 22.2 Kraft inorganic chemistry.

to S^{-2}), the original oxidation state of sulfur in the process. The CO_2 is absorbed by NaOH to form Na_2CO_3. Water is added to the material from the furnace, forming a green liquor containing NaSH and NaOH. The Na_2CO_3 is reacted with CaO and water to give more NaOH (causticizing) and $CaCO_3$, which is usually filtered and transformed on site back into CaO by a lime kiln.

3.1.2 Organic Kraft Chemistry

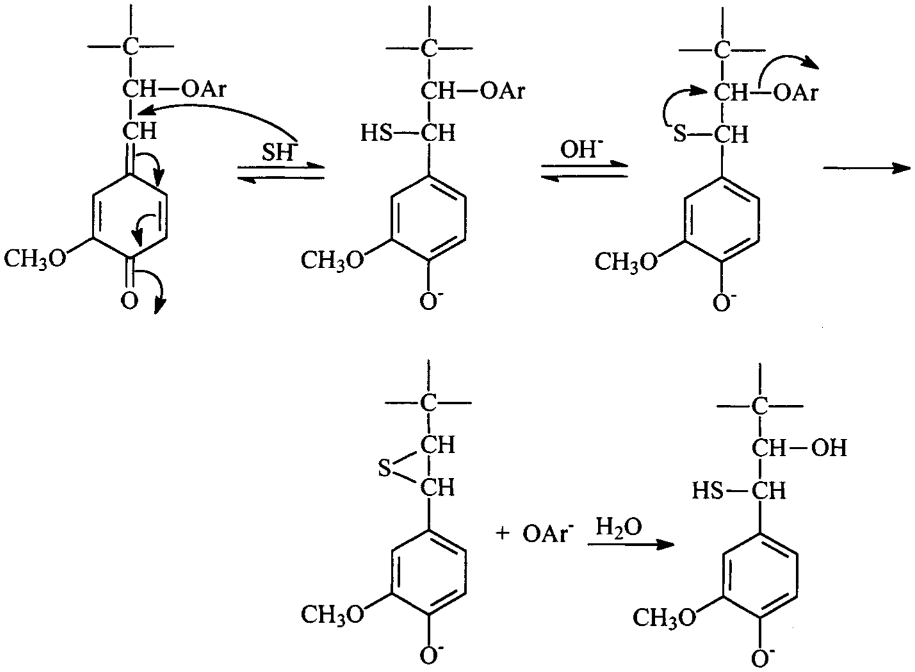
The organic chemistry of the alkali cleavage of lignin is summarized





here. The phenoxide ion expels an alkoxide ion to form a quinonemethide intermediate, which then is attacked by hydroxide ions to form eventually an epoxide ring. Although this is somewhat simplified, it does give an idea of how the degradation begins.

The bisulfide ion present in the kraft process is even a better nucleophile than hydroxide, so when it is present it attacks the quinonemethide intermediate. An episulfide is formed that then hydrolyzes to a thiol-alcohol.



Basic hydrolysis also lowers the molecular weight of the polysaccharides in wood. Two types of hydrolysis occur, peeling and chain cleavage, as

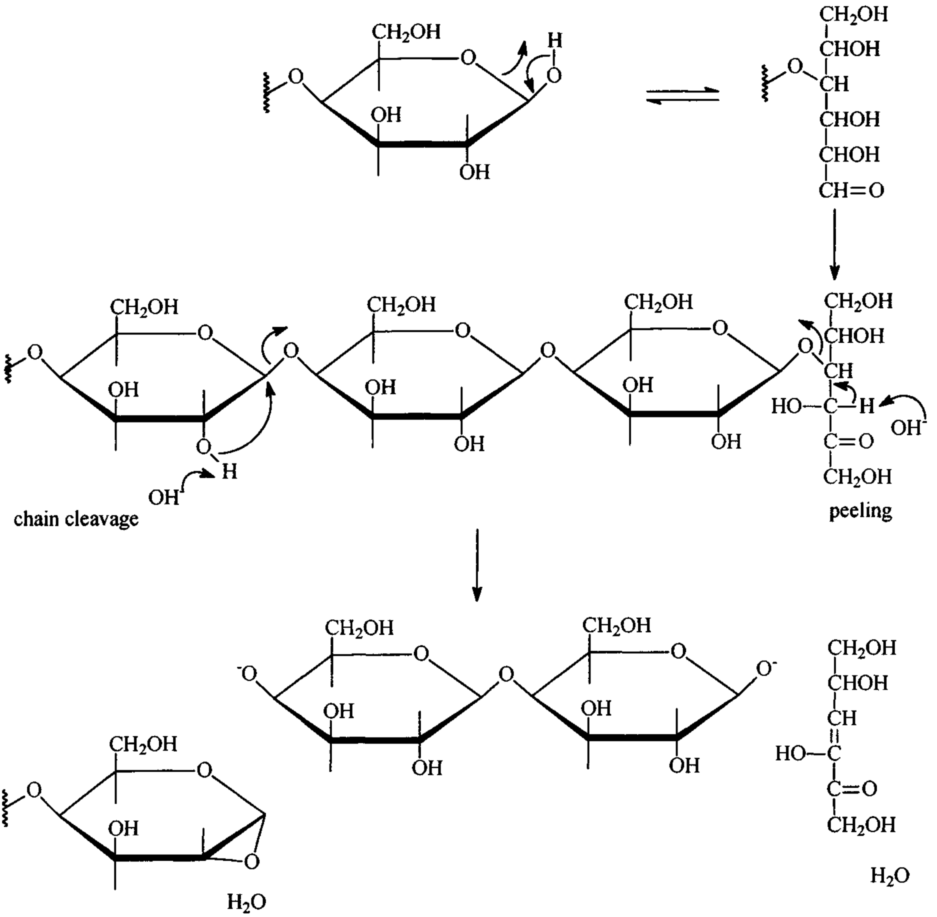


Figure 22.3 Two types of hydrolysis: peeling and chain cleavage.

shown in Fig. 22.3. Some organic materials from the black liquor can be isolated as useful side products. Much of it eventually is oxidized to carbon dioxide in the furnace.

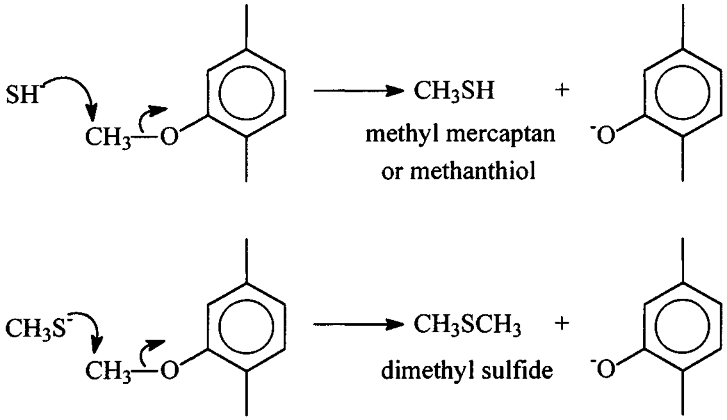
3.1.3 Finishing Kraft Paper

After the crude pulp is obtained from the alkaline sulfate process, it must be bleached in stages with elemental chlorine, extracted with sodium hydroxide, and oxidized with calcium hypochlorite, chlorine dioxide, and

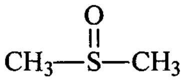
Table 22.2 **Advantages and Disadvantages of Kraft Pulping**

Advantages	Disadvantages
Excellent paper strength	Poor pulp color
Low energy requirements	Low yield—43% after bleaching
Chemical recycling	High capital investment
Little pollution	High bleaching costs
Low chemical cost	Nonrecyclable bleaching effluent
Variety of wood species usable	Strong odors

hydrogen peroxide. This lightens it from a brown to a light brown or even white (difficult) color. Chlorination of the aromatic rings of residual lignin is probably what is occurring although this has not been completely studied. Typical end-uses of kraft pulp are brown bags, paper boxes, and milk cartons. A list of the major advantages and disadvantages of the kraft process versus other pulping methods is given in Table 22.2. Anyone having approached a kraft mill will be familiar with the last-named disadvantage. This odor is caused by methyl mercaptan and dimethyl sulfide, both of which are formed by bisulfide cleavage of methoxy groups in lignin. There is also some H_2S and CH_3SSCH_3, all of which make up the total reduced sulfur (TRS) lost in ppm levels.



Much of the methyl mercaptan and dimethyl sulfide can be oxidized to dimethylsulfoxide (DMSO), a useful side product that is a common polar, aprotic solvent in the chemical industry. This is in fact the primary method of its manufacture, as a kraft by-product. Reports that DMSO is a cure for common body aches and pains, including arthritis, have little scientific foundation and the chemical does not have FDA approval for most medical applications. Caution must be used when handling it because of its extremely high rate of skin penetration.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{S}-CH_3$$

dimethylsulfoxide (DMSO)

Two other important side products of the kraft process are sulfate turpentine and tall oil. The turpentine is obtained from the gases formed in the digestion process. From 2-10 gal of turpentine can be obtained per ton of pulp. Tall oil soap is a black viscous liquid of rosin and fatty acids that can be separated from the black liquor by centrifuging. Acidification gives tall oil. These side products will be discussed later.

3.2 Other Pulp Processes

The acid sulfite process is used to obtain a higher quality paper. It is also more water polluting. Digestion occurs in a mixture of sulfur dioxide and calcium or magnesium bisulfite. The magnesium bisulfite process is better for pollution but still not so good as the kraft process. Sulfite pulp is used for bond paper and high-grade book paper.

In the NSSC process sodium sulfite is buffered with sodium carbonate, bicarbonate, and hydroxide to maintain a slightly alkaline pH during the cook. NSSC hardwood pulp is the premier pulp for corrugating medium and cannot be matched by any other process.

4. BLEACHING AND RECYCLING

There have been many changes in the bleaching process for pulp during the 1990s. Chlorine bleaching has been challenged by environmental concerns and dioxin emission guidelines since studies done in the 1980s showed chlorinated dioxins and other chlorinated organic compounds in the effluent of pulp and paper mills. Discharges of dioxins (see Chapter 20, Section 4.1) in wastewater could be slashed by up to 95% by switching from chlorine to chlorine dioxide, according to the EPA. Furans (see Chapter 20, Section 3.2.3) could be reduced by 99%. In the 1990s some estimates said that elemental chlorine use by the pulp and paper industry were down 54-

70% from 1991-1997. Replacements for chlorine include sodium chlorate (converted at paper mills to chlorine dioxide), hydrogen peroxide, and oxygen, all of which went up in use in the 1990s. These three chemicals are more powerful bleaching agents than chlorine. In 1977 approximately 140 lb of chlorine was used to make one ton of kraft pulp. In 2002 it is estimated that only 30 lb/ton will be needed. Conversion to totally chlorine-free (TCF) or elemental chlorine-free (ECF) paper will continue in the years to come. In 1997 the EPA passed its "Cluster Rule" that directed all bleached paper kraft and soda pulp mills to utilize ECF bleaching, and all sulfite mills to use ECF or TCF technology.

Another way of cutting the need for bleaching is by recycling of final paper products. This is on the increase, with 38% of the paper being recycled in recent years. It is estimated that 50% of paper is potentially recoverable in the near future. Of the 600 paper mills operating in the U.S., 140 of them depend on waste paper recycling. The majority of the recycled paper (about 75%) is used with no attempt to remove inks, dyes, or pigments from the paper. This pulp is poor in color and quality but can be used in paperboard. Deinked grades require special equipment to remove inks, coatings, adhesives, solvents, and surfactants.

5. PAPER MANUFACTURE

Less chemistry is involved in the manufacture of paper once the pulp has been made, but it is a complex process that can be summarized in the following steps:

1. *Beating and refining* the pulp to make the fibers stronger, more uniform, denser, more opaque, and less porous.
2. *Coagulating and coating* the fibers with aluminum sulfate, papermaker's alum.
3. *Adding fillers* to occupy the spaces between the fibers. These fillers are usually inorganic clays, calcium carbonate, or titanium dioxide.
4. *Adding sizing* to impart resistance to penetration by liquids. Most sizing is a soap or wax emulsion precipitated by the alum. This produces a gelatinous film on the fiber and a hardened surface.
5. *Adding wet strength resins* to increase the strength of the paper when wet. Urea-formaldehyde resins are typical.
6. *Dyeing.*

There are many chemicals that are important in the manufacture of paper. These paper additives include pigments and dyes, wet-strength resins, sizes, thickeners, biocides, defoamers, etc. A good estimate of the total commercial value of these additives is at least $1 billion.

6. GENERAL USES OF PAPER PRODUCTS

The following breakdown of paper uses lists most important general applications.

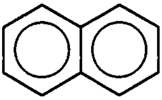
- Paper (50%)
    Newsprint, books, tissue, corrugated boxes, bags, cigarette paper, food containers, plates, wallpaper, disposable clothing
- Paperboard (50%)
    Fiberboard (fibers with added phenolics): panelling, furniture, insulation
    Particleboard (waste wood chips or dust plus a resin): panelling, subflooring, general plywood and lumber replacement
    Paper-base laminates (plies of wood plus a phenolic, urea, or melamine resin): structural and machine parts

7. MISCELLANEOUS CHEMICALS USED ON WOOD

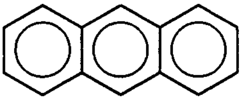
7.1 Preservatives

An interesting industry that has developed out of the necessity for preserving wood is now the second largest wood-related industry. Preservation against fungi, insects, borers, and mildew is accomplished by using one of three important types of preservatives. The first type is creosotes, which are mixtures of aromatic hydrocarbons with organic acids and bases.

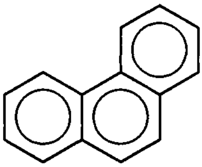
hydrocarbons



naphthalene

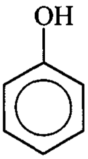


anthracene

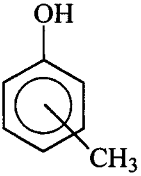


phenanthrene

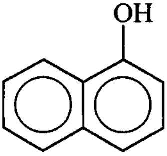
acids



phenol

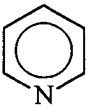


cresols

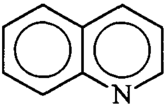


naphthol

bases

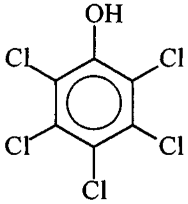


pyridines



quinolines

Secondly, chlorinated phenols, especially pentachlorophenol, is used as a preservative.



pentachlorophenol

Thirdly, inorganic salts of copper, chromium, arsenic, and tin have been used as preservatives. The use of wood preservatives is about 1 billion lb, with 60% being creosotes, 20% pentachlorophenol, and 20% copper compounds. But these are inexpensive chemicals, so commercial value is under $1 billion. Creosotes from coal tar are the most widely used because, in addition to their low price, they are highly toxic to wood-destroying organisms, have a high degree of permanence because of low water solubility and volatility, and are easy to apply and penetrate deeply. In 1984 the EPA ruled that only people holding state pesticide licenses would be able to buy and use all three types of preservatives.

7.2 Flame Retardants

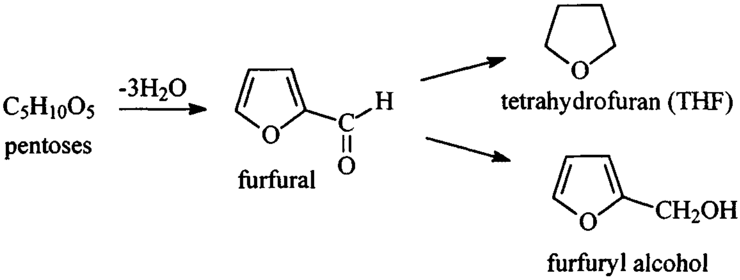
Flame retardants for wood have been developed. They include inorganic compounds such as diammonium phosphate, ammonium sulfate, borax

($Na_2B_4O_7 \cdot 10H_2O$), boric acid, and zinc chloride. The mechanism of flame retardance in wood has no single explanation. It probably includes the following: (1) The fusing of the chemical at high temperatures to form a nonconbustible film that excludes oxygen, (2) the evolution of nonconbustible gases, and (3) the catalytic promotion of charcoal formation instead of volatile combustible gas.

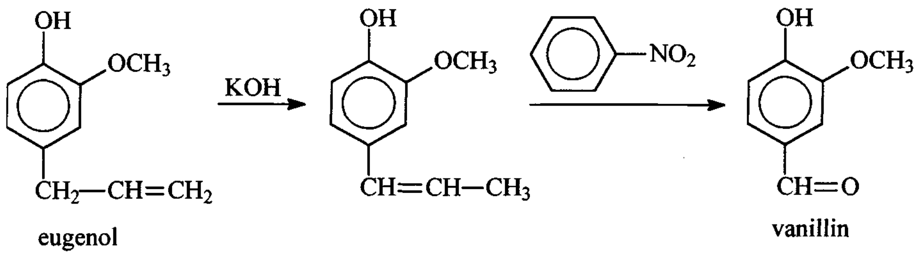
8. CHEMICALS OBTAINED FROM WOOD HYDROLYSIS AND FERMENTATION

Hydrolysis of the polysaccharides in wood to sugars and fermentation of the sugars to ethyl alcohol is no longer an economical process in this country. It cannot compete with alcohol made from ethylene or fermentation of corn.

A number of lower volume chemicals can be obtained from wood hydrolysis. Furfural is formed from the hydrolysis of some polysaccharides to pentoses, followed by dehydration. This process is still used in the Soviet Union. Furfural is used in small amounts in some phenol plastics; it is a small minor pesticide and an important commercial solvent. It can be converted into the common solvent tetrahydrofuran (THF) and an important solvent and intermediate in organic synthesis, furfuryl alcohol.



Vanillin is obtained in the United States from sulfite waste liquor by further alkaline hydrolysis of lignin. It is the same substance that can be obtained from vanilla bean extract and is the common flavoring in foods and drinks. Interestingly, natural and synthetic vanillin can be distinguished from each other by a slight difference in the amount of ^{13}C in their structure since one is biosynthetic in the bean and the other is isolated from a second natural product, wood, by hydrolysis of the lignin. Vanillin is the most important synthetic flavoring agent in the U.S. It can also be made from eugenol, oil of cloves.



9. CHEMICALS OBTAINED FROM WOOD CARBONIZATION AND DISTILLATION

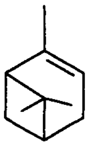
Wood distillation was used previously in the U.S. to make methanol, acetic acid, and acetone. Up to 1-2% per wood weight of methanol, 4-5% acetic acid, and 0.5% acetone can be obtained. Many years ago this was the only source of these compounds. It is no longer competitive with the synthetic processes. Some phenols can be obtained, as well as common gases such as carbon dioxide, carbon monoxide, methane, and hydrogen.

The manufacture of charcoal, especially briquettes, has been increasing in demand. It is the residue after combustion of the volatiles from a hardwood distillation. It consists of elemental carbon and incompletely decomposed organic material and many adsorbed chemicals. Carbonization is usually performed at about 400-500°C. The charcoal has a volatile content of 15-25% and can be made in about 37-46% yield by weight from wood.

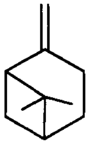
10. NAVAL STORES INDUSTRY

These still important products, produced from softwood pines, were once used by the U.S. Navy in the days of wooden ships and were governed by the 1923 Federal Naval Stores Act.

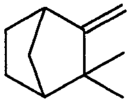
Turpentine is a mixture of $C_{10}H_{16}$ volatile terpenes (hydrocarbons made of isoprene units). There are actually four different types and methods of making turpentine, including steam distillation of wood. The two pinenes, α and β, are major components of turpentine. Other compounds found in abundant amounts are camphene, dipentene, terpinolene, and Δ^3-carene. Although it has been replaced by petroleum hydrocarbons as paint thinners (lower price, less odor), turpentine is still a good solvent and thinner in many specialty applications. The use pattern for turpentine is as follows: synthetic pine oil, 48%; polyterpene resins as adhesives, 16%; toxophene insecticides, 16%; solvent, 11%; and flavor and fragrance essential oils, 9%.



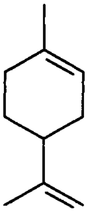
α-pinene



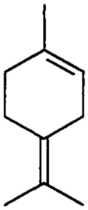
β-pinene



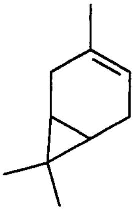
camphene



dipentene

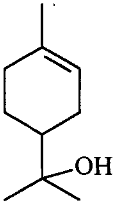


terpinolene

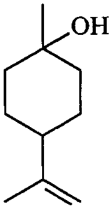


Δ^3-carene

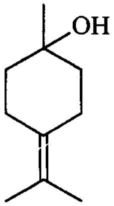
Pine oil is a mixture of terpine-derived alcohols. It can be extracted from pine but is also synthetically made from turpentine, especially the α-pinene fraction, by reaction with aqueous acid. It is used in many household cleaners as a bactericide, odorant, and solvent. The major constituents of pine oil are shown here.



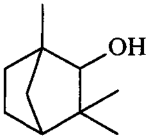
α-terpineol



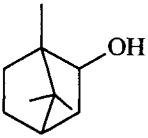
β-terpineol



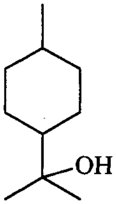
γ-terpineol



α-fenchone

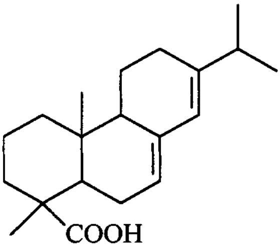


borneol



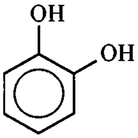
octahydro-α-terpineol

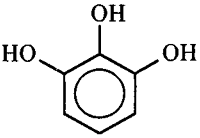
Rosin, a brittle solid, mp 80°C, is obtained from the gum of trees and tree stumps as a residue after steam distillation of the turpentine. It is made of 90% resin acids and 10% neutral matter. Resin acids are tricyclic monocarboxylic acids of formula $C_{20}H_{30}O_2$. The common isomer is l-abietic acid. About 38% of rosin is used as paper size (its sodium salt), in synthetic rubber as an emulsifier in polymerization (13%), in adhesives (12%), coatings (8%), and inks (8%).

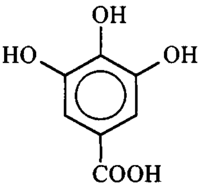

abietic acid

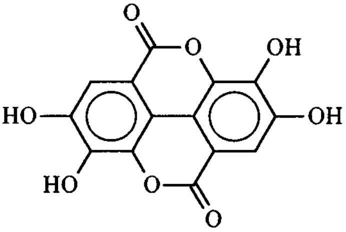
Besides the turpentine, rosin, and pine oil that can be obtained from pines, directly or indirectly by distillation or extraction, the kraft pulp process now furnishes many related side products. Sulfate turpentine can be obtained from the black kraft liquor. Tall oil rosin and tall oil fatty acids can also be isolated from this liquor. "Tall" is the Scandinavian word for pine and is used to differentiate these kraft by-products from those obtained from pine more directly. Tall oil rosin is similar to pine rosin and is used in paper sizing, printing inks, adhesives, rubber emulsifiers, and coatings. Tall oil fatty acids are C_{16} and C_{18} long-chain carboxylic acids used in coatings, inks, soaps, detergents, disinfectants, adhesives, plasticizers, rubber emulsifiers, corrosion inhibitors, and mining flotation reagents. The tall oil obtained from kraft liquor gives about 26% rosin and 29% fatty acids. The market for tall oil is expanding.

The last naval stores chemical that we will mention is tannin, an extract from the wood, bark, or leaves of many trees and plants. This is a mixture of


catechol

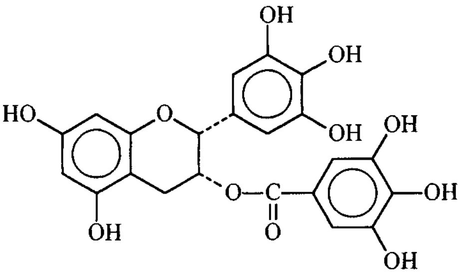

pyrogallol


gallic acid

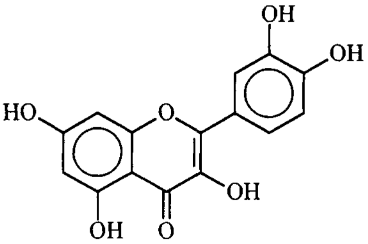

ellagic acid

complex, dark-colored sugar esters of polyhydroxy phenolic compounds related to catechol, pyrogallol, gallic acid, and ellagic acid. There is much variation with the species. Tannin has the ability to combine with proteins of animal skins to produce leather. This tanning process, probably involving hydrogen-bonding to the proteins, keeps the skin soft and pliable so it may be used in many leather products. Almost all tannin used by the U.S. is imported especially from Argentina and Paraguay.

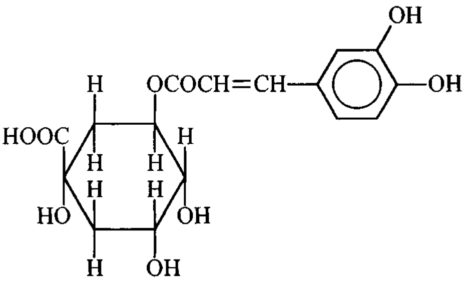
In 1991 it was reported that certain specific phenols and polyphenols, such as ellagic acid, commonly found in vegetables, fruits, and tea (especially green tea), have anticancer properties. Ellagic acid was effective in inhibiting the development of liver tumors. Other phenols, such as epigallocatechin-3-gallate, chlorogenic acid, and quercetin, show anticarcinogenic properties. Studies suggest that a proper diet including these sources of phenols may help reduce the incidence of some cancers, especially esophageal cancer, by as much as 60%. These substances are antioxidants and may have other health benefits such as prevention of heart disease.



(-)-epigallocatechin-3-gallate



quercetin



chlorogenic acid

In Chemical Manufacturing there is a subsector entitled Gum and Wood Chemicals (NAICS 3251911) that covers many of the miscellaneous chemicals that we have discussed here, including charcoal, tall oil, rosin, turpentine, and pine oil. The value of shipments is $960 million. The pulp and paper industry is large and is a prime user of chemicals and chemical processes, so it is good to know some of the basics of this industry and how it interacts with the chemical industry.

Suggested Readings

Austin, *Shreve's Chemical Process Industries*, pp. 602-632.
Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 207-272.

Chapter 23

The Pharmaceutical Industry

1. THE PHARMACEUTICAL INDUSTRY

The pharmaceutical industry is an important segment of the chemical industry not because of its volume of chemicals, which is usually small, but because these chemicals are high priced per volume and because it employs about 30% of all technical personnel in Chemical Manufacturing. The pharmaceutical industry is a technologically intensive industry; it is not uncommon for drug companies to spend 10% of their sales on research expenditures. A typical new drug might take 15 years and $500 million R & D. Only 3 out of 15,000 developmental drugs make it to full market. This includes discovery, animal trials, limited human trials, patent applications, process development, large-scale clinical trials, regulatory approval, and marketing.

Pharmaceuticals and Medicine (NAICS 3254) is a very large segment of the chemical industry at $103 billion, which is 24% of Chemical Manufacturing. Fig. 23.1 gives the trend since 1970 for the three major subsectors, Pharmaceutical Preparations (NAICS 325412), Biological Products and Diagnostics (325413, 325414), and Medicinals and Botanicals (325411). Percentages by shipments are 72% pharmaceutical preparations, 15% biological products and diagnostics, and 13% medicinals and botanicals.

Pharmaceutical preparations are drugs formulated and fabricated into their final form for direct consumption (tablets, capsules, etc.). The industry has grown rapidly in the past 30 years especially in pharmaceutical production. Examples of biological products are bacterial and virus

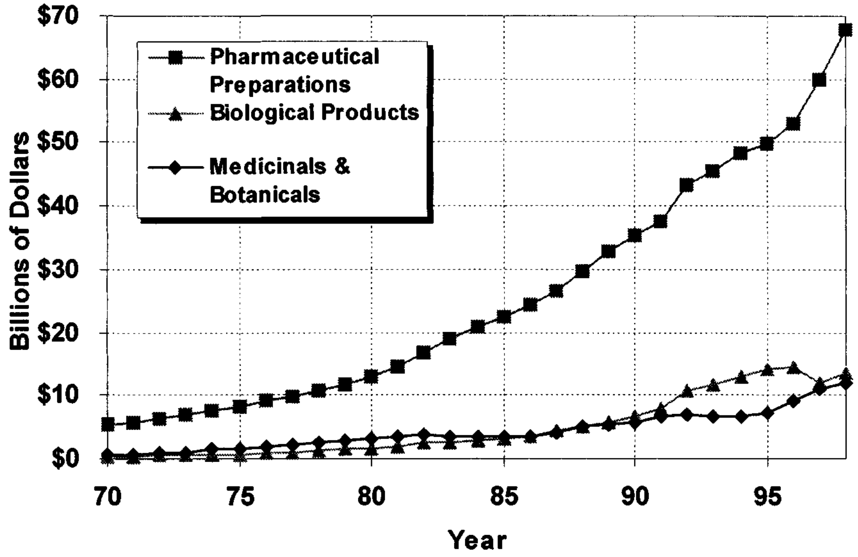


Figure 23.1 U.S. shipments of pharmaceuticals. (*Source: Annual Survey of Manufactures*)

vaccines, serums, plasmas, and other blood derivatives. Medicinals and botanicals include bulk organic and inorganic medicinal chemicals and bulk botanical drugs and herbs. Examples are alkaloids, anesthetics, barbituric acid and derivatives, caffeine, hormones, insulin, morphine, penicillin, quinine, aspirin, sulfa drugs, and vitamins.

The effect of the modern drug industry on the life expectancy in the U.S. can be seen in Table 23.1. In 1900 infectious diseases accounted for 500 deaths per 100,000 Americans; today the figure has dropped to 50. But many problems still face the industry, including most forms of cancer, arthritis, diabetes, senility, and viral diseases, even including the common cold.

There are five basic sources of pharmaceuticals. By dollar value of products, fermentation is probably the most important, whereas by tonnage, chemical synthesis is dominant. Fermentation is used for antibiotics such as penicillins and tetracyclines. Chemical synthesis provides drugs such as the psychotropics and antihistamines. Animal extracts provide hormones. Biological sources lead to vaccines and serums. Vegetable extracts provide steroids and alkaloids. The top ten pharmaceutical companies in order of revenues are the following: Merck, Pfizer, Bristol-Myers Squibb, Johnson &

Table 23.1 Life Expectancy

Year	Life Expectancy
1900	47
1920	56
1970	70
1975	75
1990	75
1999	77

Johnson, Aventis, Glaxo Wellcome, Novartis, Roche, Eli Lilly, and SmithKline Beecham.

Other important general characteristics of the pharmaceutical industry are the following: (1) use of multistage batch processes rather than continuous flow, (2) high level of product purity, (3) management which is usually technically oriented, (4) high promotional costs, (5) use of generic names as well as brand or trademark names, (6) expensive and lengthy drug testing and clinical trials, and (7) strict regulation by the Food and Drug Administration (FDA).

Although some efficacious drugs have been known for centuries, such as the antimalarial quinine first used in 1639, most important discoveries are of more recent origin. Smallpox vaccine was discovered around 1800, morphine in 1820, aspirin in 1894, and phenobarbital in 1912. But the discovery of the antibacterial activity of sulfur drugs in 1932 and penicillin in 1940 started the golden era of rapid expansion and discovery in the industry. Nearly all important drugs today have been discovered since 1940, some very recently.

What are the properties of an “ideal drug”? It should be non-toxic and without side effects. The fatal dose should be many times the therapeutic dose (it should have a maximum therapeutic index). The necessary dose should not require too frequent administration over too long a period (four tablets at 3-hr intervals is hard to remember). The efficiency of the drug should not be seriously reduced by changes in body fluids or by tissue enzymes. A drug should be stable and storable for long periods, even in extreme climates. Finally, it should be possible to dispense it in a variety of forms—pills, soft gelatin capsules, hard capsules, liquids, syrups for children, suppositories, ointments, and solutions for intravenous or intramuscular injection to name a few. Even implantation, time release capsules, and controlled release through membranes are now possible.

2. TYPES OF DRUGS

The pharmaceutical industry is so complex and diverse in its chemistry that it is difficult to know where to start, but actually 100 drugs usually account for over 50% of all prescriptions filled. There are many different ways of subdividing drugs. Drugs that can be bought without a prescription from a doctor are called *over-the-counter* or *proprietary drugs.* Those that require a prescription are called *ethical* or *prescription drugs,* the purity of which are rigidly defined in the U.S. Pharmacopoeia (a drug or chemical this pure is described as USP grade). Drugs may also be divided by either structure or physiological activity. Many different types of chemical structures may still be useful in combating a certain type of illness. We will concentrate on dividing the discussion by physiological use rather than by chemical type: cardiovascular drugs, central nervous system depressants and stimulants, antibacterials, steroids, analgesics, anti-inflammatory agents, and antihistamines.

What are the most important drugs? How can they be ranked? Production totals are not too important in the drug industry. Drugs are manufactured in much smaller quantities than the top 50 chemicals. Each drug has a different effective dose so relative quantities are not important. Drugs vary in cost as well and dollar amounts are not a good reflection of importance. Most workers in the field use total number of prescriptions per year in the U.S. as the best ranking for those requiring a prescription.

The ranking for the year 2000 is given in Table 23.2 for the top 35 drugs, arranged by total prescriptions for a given brand and company. The generic name is also listed. Since the generic name and actual structure is identical for more than one brand name, this ranking may not be ideal either. Hydrocodone (HYCD) is listed for no. 4 and no. 24. Conjugated estrogens are listed under Premarin® (no. 2) and Prempro® (no. 18). Amoxicillin is included under no. 15, 22, 25, and 35. It is difficult to combine totals for all brands of a given generic name. Sometimes many companies sell basically the same drug. If all brands were combined hydrocodone would be no. 1. Other chemicals such as atenolol (no. 30) would be much higher, near no. 5, and furosemide (no. 21) would be near no. 6. In total sales, Prilosec® would be no. 1 at $4.6 billion, followed by Lipitor® at $4.1 billion and Prevacid® at $3.1 billion. The list does not include important high-volume non-prescription drugs. We will arrange our discussion to include the top ten prescription drugs in order giving structure and physiological activity as well as some selected syntheses. This will be followed by an extensive treatment of other drugs in the top 35 and some important selected additional prescription and non-prescription drugs, subdivided by physiological response.

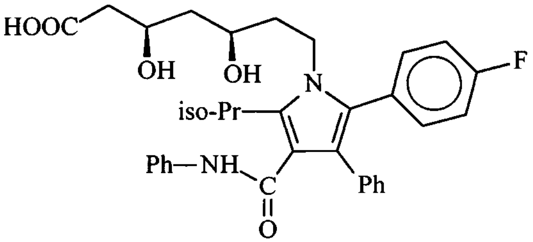
Table 23.2 Top Prescription Drugs

	Brand Name	Generic Name	Pres. (10^6)	Treatment for
1	Lipitor (Parke-Davis)	Atorvastatin	48.8	High cholesterol
2	Premarin (Wyeth-Ayerst)	Conj. estrogens	46.8	Menopause
3	Synthroid (Knoll Pharm)	Levothyroxine	43.5	Hypothyroidism
4	HYCD/APAP (Watson)	Hydrocodone/APAP	36.5	Pain
5	Prilosec (AstraZeneca)	Omeprazole	32.1	Ulcers
6	Norvasc (Pfizer)	Amlodipine	30.8	Hypertension
7	Glucophage (Bristol-Myers)	Metformin	27.4	Diabetes
8	Albuterol (Warrick)	Albuterol	27.4	Asthma
9	Claritin (Schering)	Loratadine	26.5	Allergies
10	Zoloft (Pfizer)	Sertraline	25.2	Depression
11	Celebrex (Pharmacia)	Celecoxib	24.7	Arthritis
12	Prevacid (Tap Pharm)	Lansoprazole	24.5	Ulcers
13	Prozac (Lilly)	Fluoxetine	24.1	Depression
14	Paxil (SmithKline Beecham)	Paroxetine	24.0	Depression
15	Trimox (Apothecon)	Amoxicillin	23.4	Bacteria
16	Zestril (AstraZeneca)	Lisinopril	22.6	Hypertension
17	Zocor (Merck & Co)	Simvastatin	22.4	High cholesterol
18	Prempro (Wyeth-Ayerst)	Conj. est/med. progest.	22.3	Menopause
19	Zithromax Z-Pak (Pfizer)	Azithromycin	22.0	Bacteria
20	Vioxx (Merck & Co)	Rofecoxib	20.5	Arthritis, pain
21	Furosemide (Mylan)	Furosemide	20.4	Hypertension
22	Augmentin (SmithKline)	Amoxicillin/clavulan.	19.8	Bacteria
23	Lanoxin (Glaxo Wellcome)	Digoxin	19.6	Heart failure
24	HYCD/APAP (Malinckrodt)	Hydrocodone/APAP	19.0	Pain
25	Amoxicillin (Teva Pharm)	Amoxicillin	18.4	Bacteria
26	Ortho-Tri-Cy 28 (Ortho)	Norgestinate/ethin. est.	16.8	Contraception
27	Levoxyl (Jones Medical Ind)	Levothyroxine	16.0	Hypothyroidism
28	Zyrtec (Pfizer)	Cetirizine	16.0	Allergies
29	Coumadin (DuPont Pharm)	Warfarin	15.7	Blood Coagulat.
30	Atenolol (Geneva Pharm)	Atenolol	15.5	Hypertension
31	Allegra (Aventis Pharm)	Fexofenadine	14.9	Allergies
32	Cephalexin (Teva Pharm)	Cephalexin	14.7	Bacteria
33	Ambien (Pharmacia)	Zolpidem	14.2	Insomnia
34	Cipro (Bayer Pharm)	Ciprofloxacin	14.0	Bacteria
35	Amoxil (SmithKline)	Amoxicillin	13.8	Bacteria

Source: Pharmacy Times and the Internet

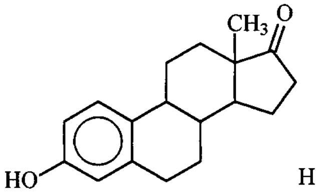
3. THE TOP TEN DRUGS

3.1 Lipitor® (atorvastatin)

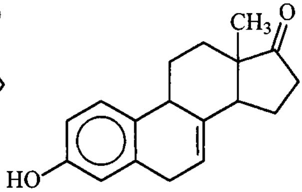


This pyrrole derivative is a synthetic lipid-lowering agent for hyperlipidemia. It is used to reduce elevated total and low-density lipoprotein (LDL) cholesterol levels. It increases levels of high-density lipoprotein (HDL) cholesterol, the "good" cholesterol considered beneficial to heart health. It is also prescribed for atherosclerosis (hardening of the arteries), diabetes-related blood-fat problems, preventing heart attacks and strokes, and reducing the risk of cardiac bypass surgery. A 29% increase in prescriptions from 1999-2000 moved atorvastatin to no. 1.

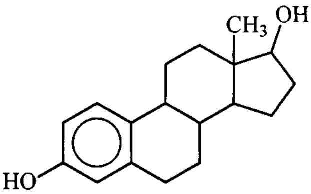
3.2 Premarin® (conjugated estrogens)



estrone



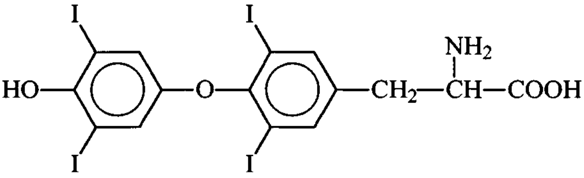
equilin



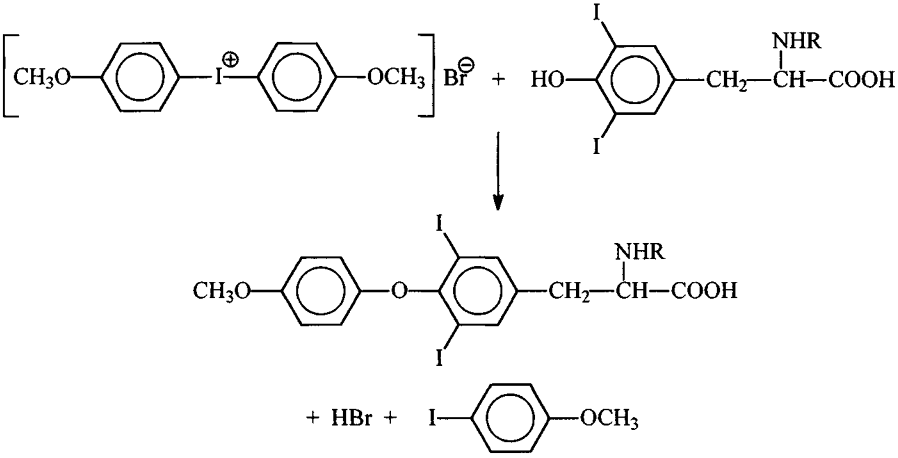
17α–dihydroequilin

After eight years in the no. 1 spot Premarin® fell to no. 2 in 2000. This is a mixture of female sex hormones that occur in the human body and may be extracted from the urine of pregnant mares. The main hormones in the mixture are estrone, equilin, and 17α-dihydroequilin. It is used to alleviate menopausal symptoms and problems. There is a decreased production of estrogens during menopause, which causes a weight increase, hot flashes, and psychological problems. This mixture takes the place of those estrogens. However, there is an increased risk of cancer of the uterus in women who take this for more than a year. For a discussion of other steroid drugs and hormones, see this chapter, Section 7.

3.3 Synthroid® (levothyroxine)

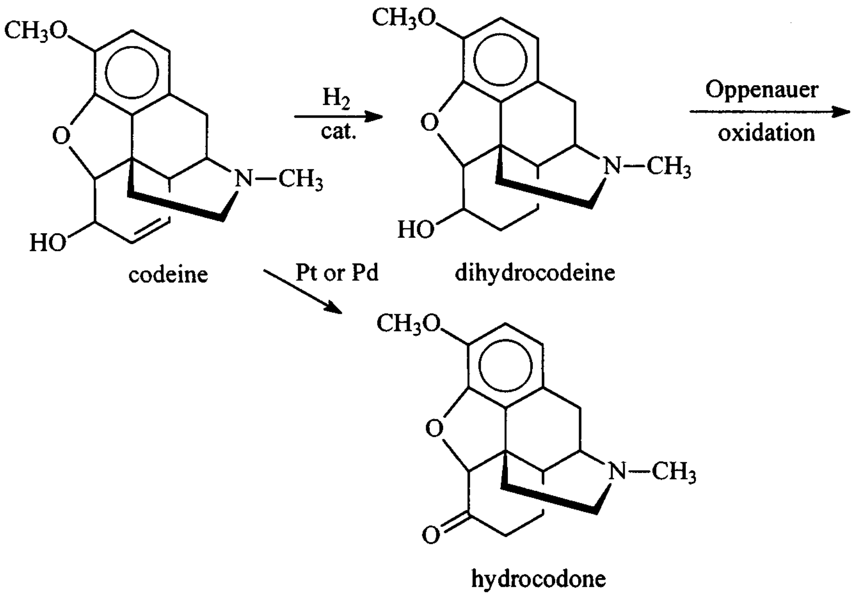


Levothyroxine is used to treat hypothyroidism (an underactive thyroid gland). Thyroid hormone can be made from beef and pork thyroid, but this lacks standardization and it is difficult to control dosage. The synthetic drug is more desirable. Levothyroxine is one of two important thyroid hormones. It is converted into the second important hormone, liothyronine, in the body. The key step in the synthesis of structures such as levothyroxine is the substitution of an iodonium salt by an iodinated phenol. S_N2-like reactions on an aromatic ring are not common, but an iodonium salt provides a good leaving group.



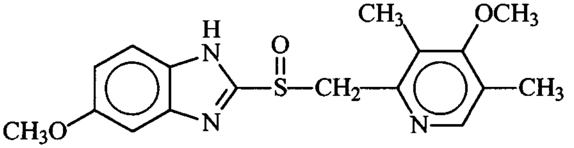
3.4 HYCD/APAP® (hydrocodone with acetaminophen)

Hydrocodone is an opium analgesic (pain reliever) and antitussive (cough suppressant). It is related in structure to other alkaloids used as drugs, such as morphine and codeine (see Section 8). It increased 20% in number of prescriptions for one year. Its synthesis from codeine is by simple reactions.

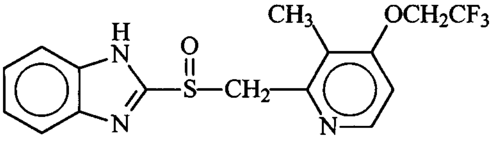


Catalytic reduction of codeine gives dihydrocodeine and Oppenauer oxidation (a ketone such as acetone and an aluminum alkoxide, the ketone being reduced to an alcohol) gives hydrocodone. Hydrocodone can also be prepared directly from codeine with a metal catalyst, which isomerizes the allylic alcohol to a ketone. Codeine is prepared by methylation of morphine, which is isolated from the opium poppy. Hydrocodone is more potent than codeine. Acetaminophen is a mild analgesic and is discussed in Section 8.

3.5 Prilosec® (omeprazole)



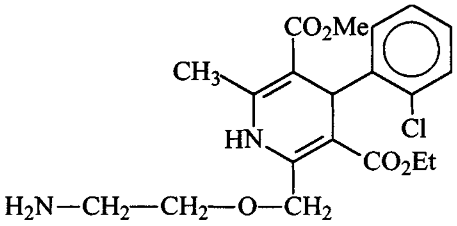
omeprazole



lansoprazole

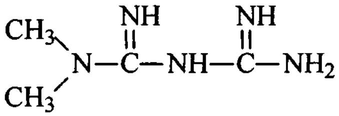
Omeprazole is an antiulcer drug. It is a proton pump inhibitor. This substituted benzimidazole inhibits gastric acid secretion to help acid/peptic disorders and duodenal ulcers. It interferes with the proton pump in the mucous lining of the stomach, the last stage of acid production. It can turn off stomach acid in as little as one hour. Lansoprazole (no. 12) has a similar structure.

3.6 Norvasc® (amlodipine)



Amlodipine is a calcium channel blocker used to treat hypertension and angina pectoris. Calcium channel blockers block the passage of calcium, an essential factor in muscle contraction, into the heart and smooth muscles. Such blockage interferes with the contraction of these muscles, which in turn dilates the veins that supply blood to them. This reduces blood pressure.

3.7 Glucophage® (metformin)



This is an antihyperglycemic drug for non-insulin dependent diabetes. It is a blood glucose regulator. It lowers the amount of glucose produced by the liver, reduces the amount of glucose absorbed from food, and helps cells use glucose. Metformin increased 21% in prescriptions for one year.

3.8 Albuterol

The complete synthesis of albuterol from methyl salicylate is given in Fig. 23.2 and it is a good example of a complex structure obtained from readily available starting materials, although with quite a few steps. Methyl salicylate (oil of wintergreen, **1**) undergoes Friedel-Crafts acylation to give **2**, followed by addition of a benzyl group as a protecting group to give **3**.

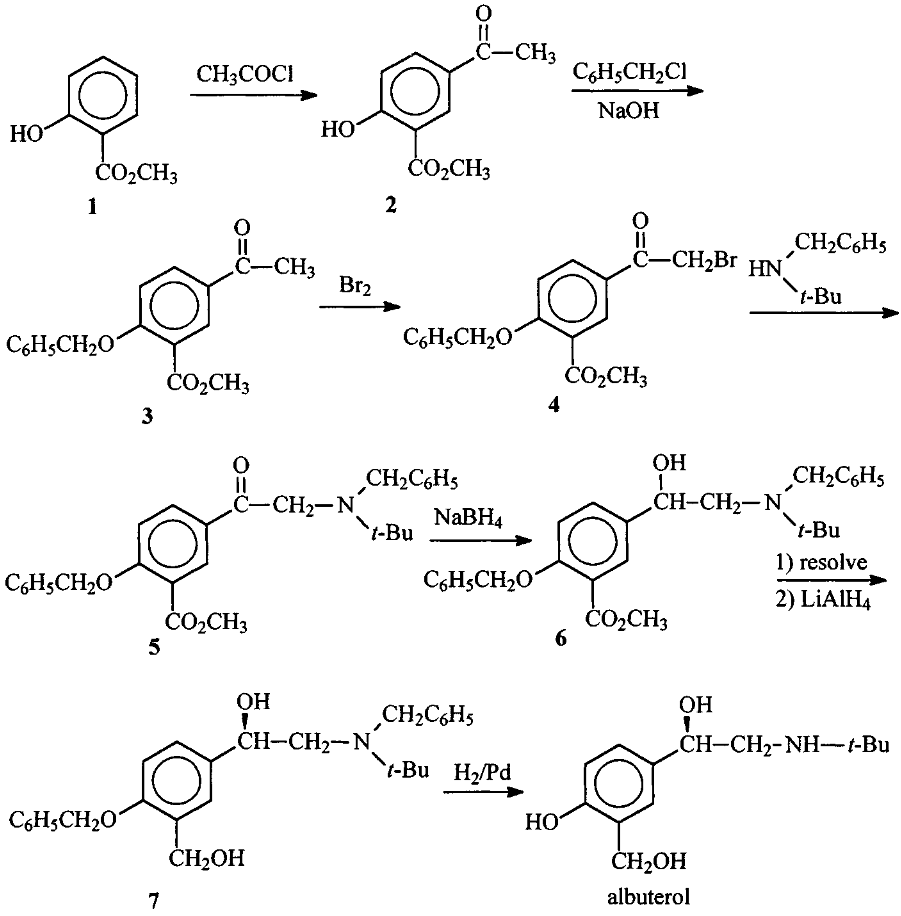


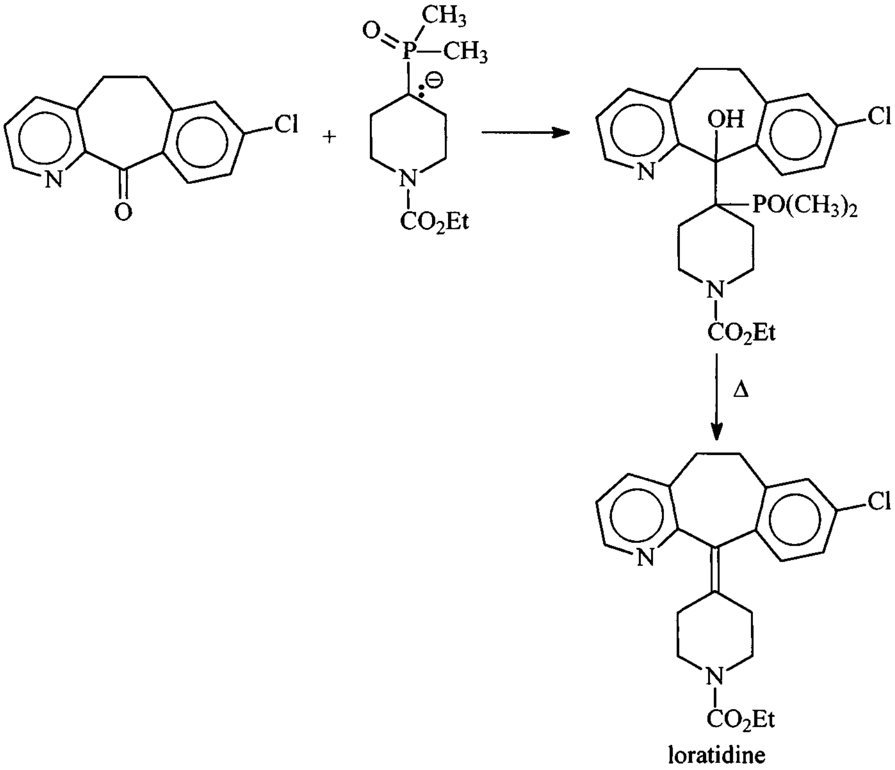
Figure 23.2 Synthesis of albuterol.

Bromination to **4** and substitution of the bromine by an amine gives **5**. Sodium borohydride reduction of the ketone to an alcohol **6** is followed by a resolution with (-)-di-*p*-toluoyltartaric acid and reduction of the ester group with lithium aluminum hydride to give diol **7**. Catalytic debenzylation gives albuterol, sometimes called salbutamol.

Albuterol is a bronchodilator used in inhalation aerosols for the treatment of asthma. It is a β_2-adrenergic drug. The bronchial muscles are controlled by β_2 receptors. Stimulation of the β_2 receptors leads to the relaxation of the bronchial muscles and the opening of the airways. But it must not encourage α stimulation, leading to vasoconstriction, or β_1 stimulation, giving an increased heartbeat rate. Albuterol is a safer alternative to the earlier bronchodilator drugs.

3.9 Claritin® (loratadine)

This drug is an antihistamine (see Section 9 for a detailed discussion) and helps alleviate the symptoms of seasonal allergies. It causes less sedation than most antihistamines and appears to be just as effective. The key step in a recent synthesis is a Wittig-type reaction.



3.10 Zoloft® (sertraline)

A synthesis of sertraline is given in Fig. 23.3. Diethylsuccinate (**1**) is condensed with the diarylketone **2** and base, and dehydration gives **3**, followed by acid-catalyzed hydrolysis and decarboxylation yielding **4**, and hydrogenation to give **5**. The cyclic ketone **6** is made by a Friedel-Crafts acylation-cyclization, followed by the ketone reacting with methylamine and final hydrogenation to give sertraline.

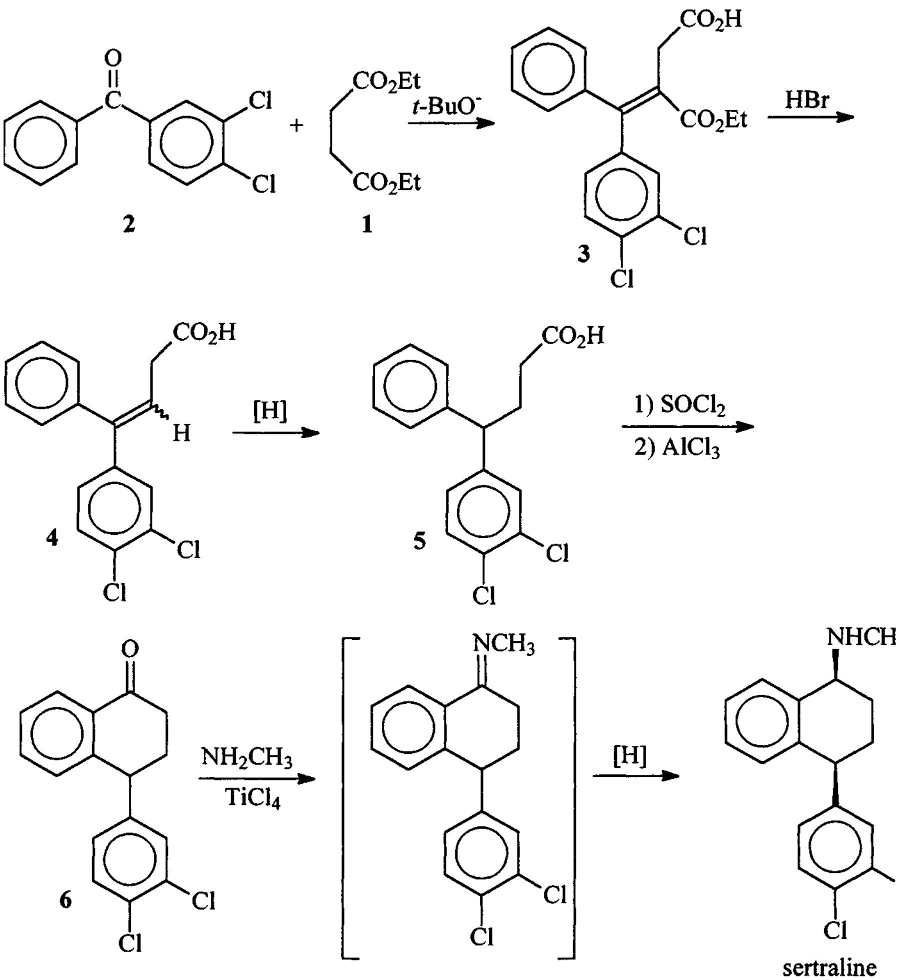


Figure 23.3 Synthesis of sertraline.

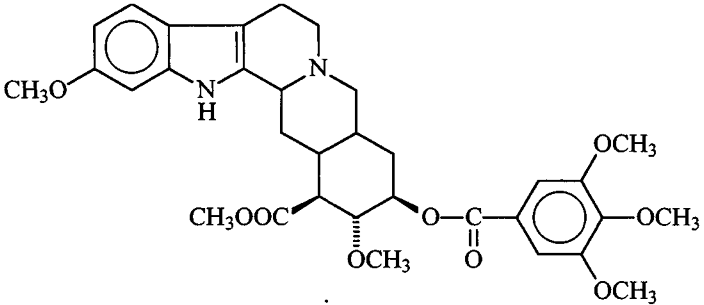
Sertraline is a recent antidepressant that is called a selective serotonin reuptake inhibitor (SSRI). It is chemically unrelated to the older tricyclic antidepressants (see Section 5.3). It works by preventing the movement of the neurohormone serotonin into nerve endings. It can help to improve mood and mental alertness, increase physical activity, and improve sleep patterns. It is prescribed for obsessive-compulsive disorder and obesity. It may offer some advantage over fluoxetine by exhibiting little central nervous system (CNS) action. It has less sedation and anxiety and is shorter acting.

4. CARDIOVASCULAR AGENTS

After highlighting the present top ten pharmaceuticals, let us now cover a number of other important drugs, both prescription and over-the-counter. We will attempt to categorize them by physiological action but will emphasize chemical structure and synthesis where appropriate. Our first type will be drugs affecting the heart. Cardiovascular agents are used for their action on the heart or on other parts of the vascular system. They modify the total output of the heart or the distribution of blood to certain parts of the circulatory system.

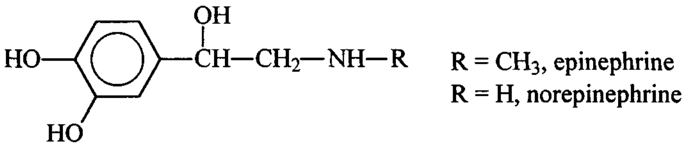
4.1 Antihypertensive Agents

Antihypertensive agents, substances that lower high blood pressure, are an important subclass of cardiovascular agents. Reserpine, an indole alkaloid obtained from the Rauwolfia plant, was the first successful drug to treat high blood pressure and was discovered in 1953. The plant extracts were first used in India to alleviate toothaches. They were brought to the U.S. in 1940. Reserpine was isolated in 1952. Its structure was determined in 1954 and it was proven by total synthesis in 1958. The mode of action of reserpine involves the release of norepinephrine (noradrenaline), responsible for heart contraction, which in turn is destroyed by normal processes to expand the heart and lower the blood pressure.



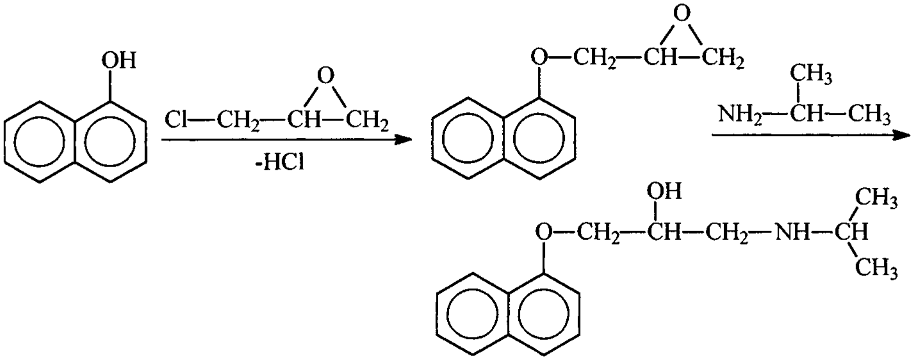
reserpine

Propranolol is another type of antihypertensive agent called a β-adrenergic blocking agent (β-blocker) because it competes with epinephrine



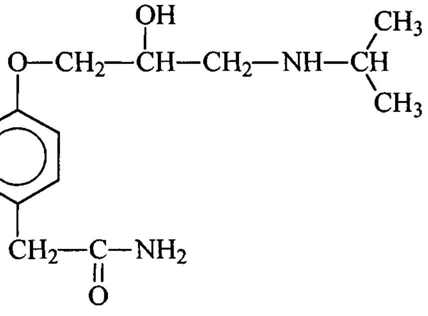
R = CH_3, epinephrine
R = H, norepinephrine

(adrenaline) and norepinephrine at their receptor sites and protects the heart against undue stimulation. Propranolol and many similar derivatives are easily synthesized in two S_N2 substitution reactions from a phenol, epichlorohydrin, and isopropylamine. In the synthesis of propranolol α-naphthol attacks the better leaving group chlorine in the first S_N2 at a primary position of epichlorohydrin. Isopropylamine picks the primary and strained three-membered ring carbon in the second step. Notice that for propranolol, although it blocks the receptor site of epinephrine and norepinephrine, it bears only a vague chemical similarity to these substances.



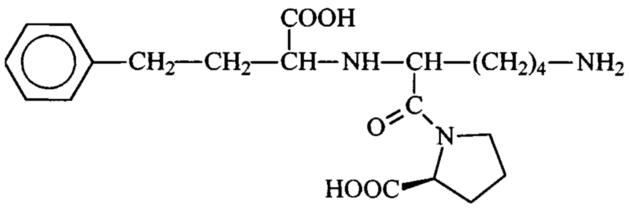
propranolol

Propranolol was the largest selling drug in the U.S. in 1985. Sir James Black of the U.K. won the Nobel Prize in Medicine in 1988 for his discovery of propranolol in 1964, as well as other research. A more common β-blocker now is atenolol (no. 30), synthesized in an analogous manner to propranolol.



atenolol

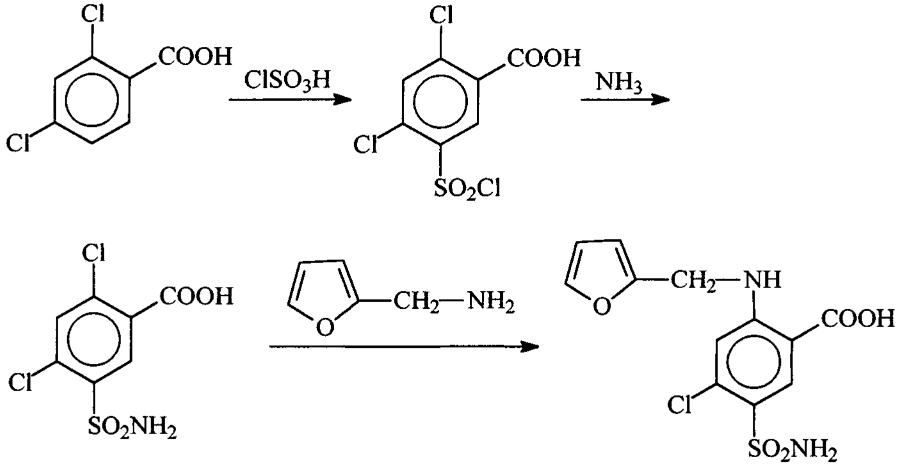
Another type of antihypertensive agent is a calcium channel blocker. This was discussed under amlodipine (no. 6) in Section 3.6. Finally, angiotension-converting enzyme (ACE) inhibitors are used in severe hypertension that does not respond to other drugs. ACE inhibitors work by preventing the conversion of a hormone called angiotension I to another hormone called angiotension II, a potent blood-vessel constrictor. Preventing this conversion relaxes blood vessels, thus reducing blood pressure and relieving the symptoms of heart failure. Lisinopril (no. 16) is an important ACE inhibitor.



lisinopril

4.2 Diuretics

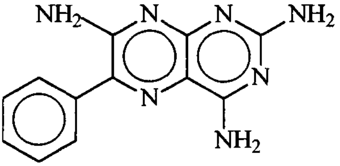
Diuretics are drugs that increase the excretion of urine by the kidney, thereby decreasing body fluids. This alleviates the swelling of tissues that sometimes cause high blood pressure and heart, kidney, and liver failure. Furosemide is the most effective diuretic. It inhibits the readsorption of sodium in the kidney and promotes potassium excretion, two ions intimately involved in water retention for the body. It lowers blood pressure as well. The starting material for its synthesis is 2,4-dichlorobenzoic acid (formed by



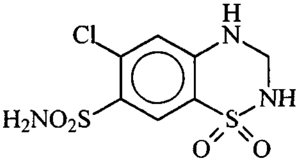
furosemide

chlorination and oxidation of toluene). Reaction with chlorosulfonic acid is an electrophilic aromatic substitution via the species $\oplus SO_2Cl$ attacking ortho and para to the chlorines and meta to the carboxylate. Ammonolysis to the sulfonamide is followed by nucleophilic aromatic substitution of apparently the less hindered chlorine by furfurylamine (obtained from furfural, which is a major product from hydrolysis of many carbohydrates).

Another important diuretic contains both triamterene and hydrochlorothiazide. Triamterene is a diuretic and is known to increase sodium and chloride ion excretion but not potassium ion. It is used in conjunction with a hydrothiazide, which is an excellent diuretic but also gives significant loss of potassium and bicarbonate ions. If the triamterene were not included potassium chloride would have to be added to the diet. Hydrochlorothiazide is an antihypertensive agent as well but, unlike other antihypertensives, it lowers blood pressure only when it is too high, and not in normotensive individuals. These two drugs are made by a number of different manufacturers and do not appear in our top 35 list, but they would rank high if all brands were combined.

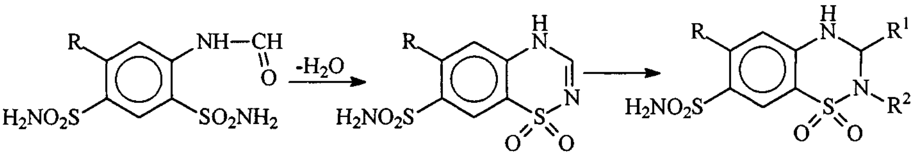


triamterene



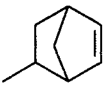
hydrochlorothiazide

A number of thiazides can be synthesized from appropriate sulfonamides by cyclization with dehydration. Conversion to hydrothiazides increases their activity by a factor of ten.



a thiazide

a hydrothiazide

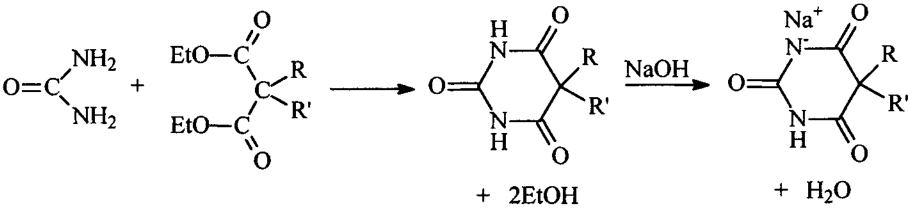
R	R^1	R^2
Cl	H	H
CF_3	H	H
CF_3	$—CH_2Ph$	H
Cl	$—CHCl_2$	H
Cl	$—CH_2Cl$	CH_3
Cl	$—CH_2SCH_2CF_3$	CH_3
Cl		H

5. CENTRAL NERVOUS SYSTEM PHARMACEUTICALS

Although this type of drug has various subclasses based on physiological response, such as tranquilizers, stimulants, depressants, etc., we will subdivide and treat a few of them on the basis of their chemical classes. The leading antidepressant, sertraline (no. 10), was covered in Section 3.10.

5.1 Barbiturates

The barbiturates were widely used as sedative-hypnotic drugs. Barbital was introduced as a drug in 1903. The method of synthesis for thousands of its analogs has undergone little change. Urea reacts with various derivatives of malonic acid, usually a diethyl ester of a dialkyl substituted malonic acid. This is a classic example of a nucleophilic acyl substitution. A derivative of ammonia reacts with esters to form an amide, only in this case a cyclization to a strainless six-membered ring results because of the proximity of the bifunctionality.



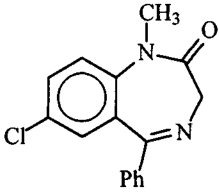
The barbiturates are usually administered as the sodium salts. The N—H bonds are acidic because the anion is resonance stabilized. Although barbituric acid is inactive, a range of activities is obtained that varies with the groups at R and R′. Some of the more important ones are listed below.

Name	**R**	**R′**
Barbituric acid	H	H
Barbital	Et	Et
Phenobarbital	Et	Phenyl
Butabarbital	Allyl	Isobutyl

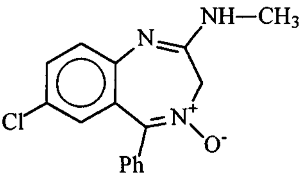
Activity and toxicity both increase with the size of the groups. Branching and unsaturation decrease the duration of action. Phenobarbital and butabarbital are effective. The maximum therapeutic index (tolerated dose/minimum effective dose) is highest when the two groups have a total of six to ten carbons. The mechanism of action is not completely understood, but they in some way reduce the number of nerve impulses ascending to the brain. Major drawbacks of their use are their habit formation and their high toxicity when alcohol is present in the bloodstream. Barbiturates have been replaced by more effective tranquilizers.

5.2 Benzodiazepines

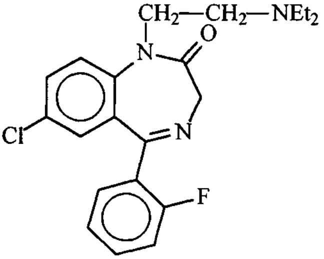
A series of tranquilizers, drugs that relieve anxiety and nervous tension without impairing consciousness, have a benzene ring fused to a seven-membered ring containing two nitrogens. As a group they are called benzodiazepines. The two most successful are diazepam (Valium®) and chlordiazepoxide (Librium®) introduced in 1964 and 1960, respectively. Flurazepam (Dalmane®), first used in 1970, is a hypnotic.



diazepam



chlordiazepoxide



flurazepam

The synthesis of diazepam is outlined in Fig. 23.4. *p*-Chloroaniline (prepared from benzene by nitration, reduction of the nitro group to an amine, and chlorination of the *o,p*-directing aniline) is reacted with benzoyl chloride (from toluene by oxidation to benzoic acid, followed by acid chloride formation) in a Friedel-Crafts acylation. Since the position para to the amino group is taken, acylation occurs ortho to give **1**. Formation of the oxime derivative **2** is followed by methylation and then acetylation of the amino group with chloroacetyl chloride, giving **3**. Heating in base splits out HCl as shown and forms the ring. Reduction of the amine oxide **4** with hydrogen gives diazepam.

Diazepam is used for the control of anxiety and tension, the relief of muscle spasms, and the management of acute agitation during alcohol withdrawal, but it itself may be habit-forming. Chlordiazepoxide has similar uses and its synthesis is somewhat analogous to diazepam. Flurazepam is a hypnotic, useful for insomnia treatment. It is reported to provide 7-8 hr of restful sleep.

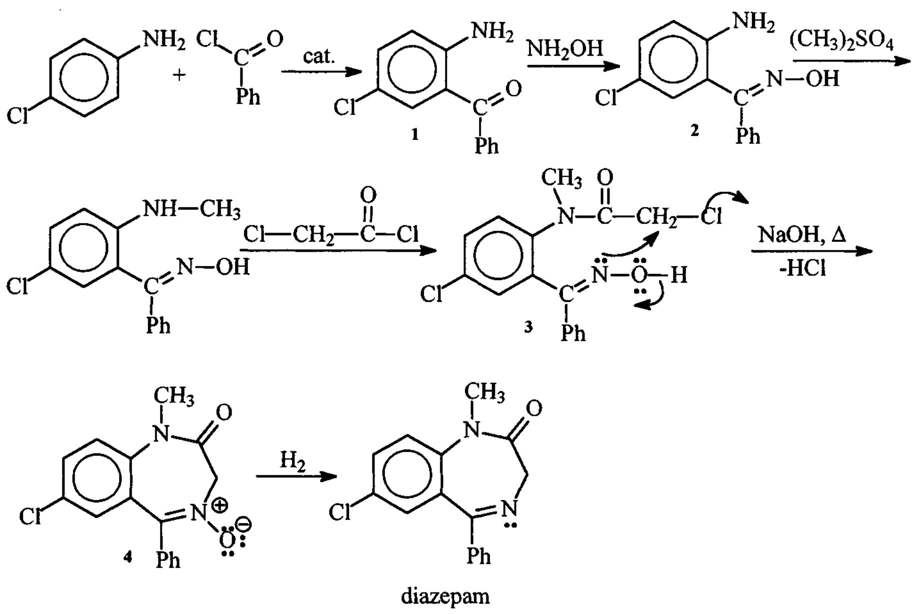
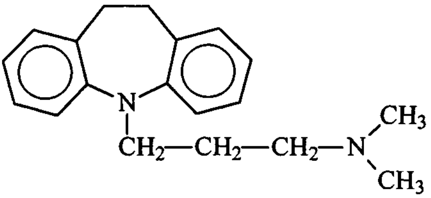
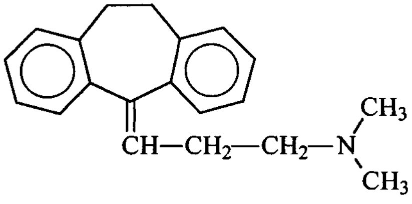


Figure 23.4 Synthesis of diazepam.

5.3 Tricyclic Antidepressants

Certain tricyclic compounds are found to be powerful stimulants, or antidepressants, to the central nervous system. Depressed individuals may respond with an elevation of mood, increased physical activity, mental alertness, and an improved appetite. Imipramine and amitriptyline hydrochlorides are good examples.


imipramine


amitriptyline

The synthesis of amitriptyline starts from the key intermediate dibenzosuberone (which comes from phthalic anhydride) and can proceed by two pathways (Fig. 23.5). Treatment of dibenzosuberone with cyclopropyl

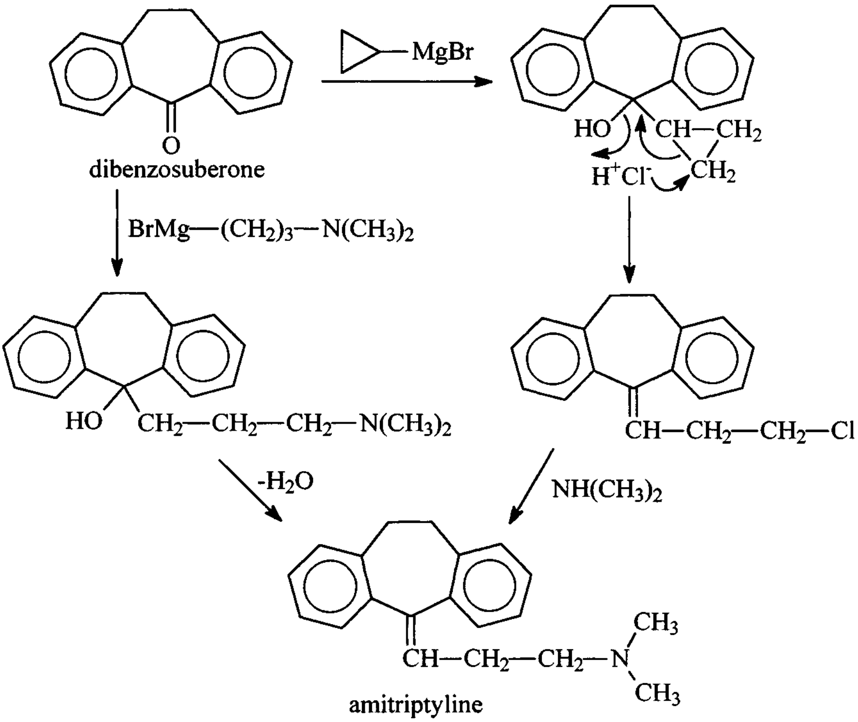


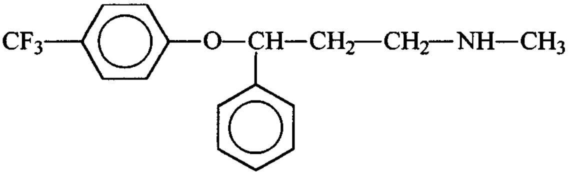
Figure 23.5 Synthesis of amitriptyline.

Grignard gives the tertiary alcohol after hydrolysis. Reaction of the alcohol with hydrochloric acid proceeds with rearrangement and opening of the strained cyclopropane to give a chloride. S_N2 displacement of the chloride with dimethylamine forms amitriptyline. Alternatively, dibenzosuberone can be reacted with dimethylaminopropyl Grignard to form an alcohol, which upon dehydration forms amitriptyline.

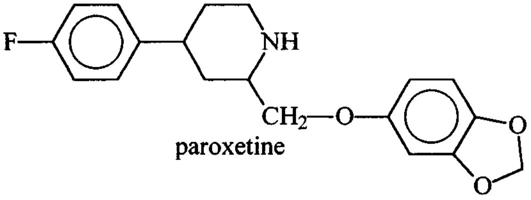
Activity in these tricyclic compounds is restricted to compounds having a two- or three-carbon side chain and methyl-substituted or unsubstituted amino groups in the side chain. Some compounds with substituents on the aromatic ring are active. Finally, the two-carbon bridge linking the aromatic rings may be $-CH_2—CH_2—$ or $-CH=CH—$. Amitriptyline is recommended for the treatment of mental depression, with improvement in mood seen in two to three weeks after the start of medication. Imipramine is used in similar cases.

5.4 Recent Antidepressants

Besides sertraline (no. 10, see Section 3.10) other recently developed antidepressants have become very popular, including two fluorinated compounds, fluoxetine (Prozac®, no. 13) and paroxetine (Paxil®, no. 14).



fluoxetine



paroxetine

Like sertraline, these two drugs are selective serotonin reuptake inhibitors. Fluoxetine is prescribed for depression, bulimic binge-eating and vomiting, obsessive-compulsive disorder, obesity, alcoholism, and anorexia among other ailments. Paroxetine is used for depression and obsessive-compulsive disorder. Interestingly the three top antidepressants are chemically unrelated to each other, except for being amines, and are unrelated to earlier tricyclic antidepressants.

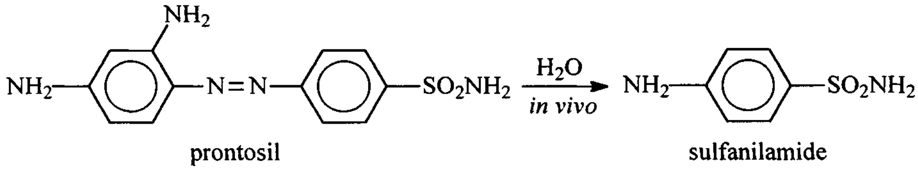
6. ANTIBACTERIAL AGENTS

Before the 1930s bacterial diseases were a major cause of death. Pneumonia and tuberculosis were major killers. Since the advent of the sulfa drugs and penicillins many bacterial diseases have been controlled. The antibacterial drugs will be discussed by type. We will see that some of these are antibiotics, an antibacterial substance produced by a living organism such as a bacterium or fungus, rather than synthesized in the laboratory.

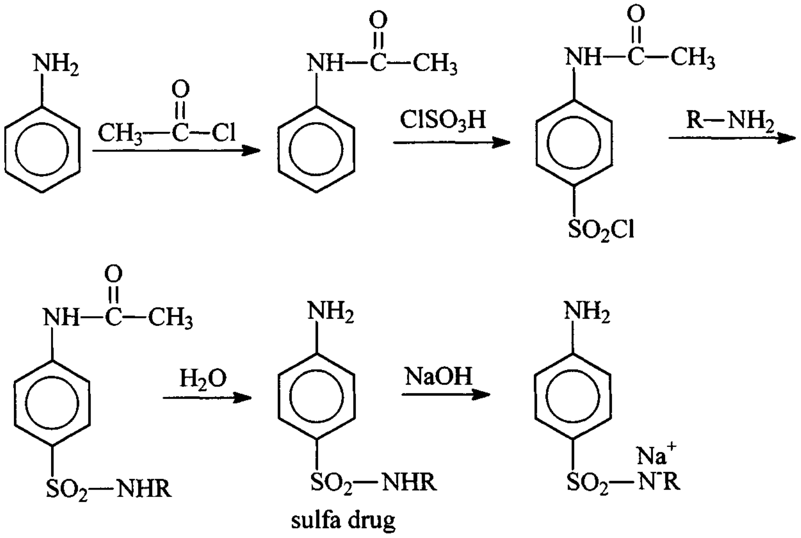
There are four general properties for a good antibacterial agent. It must be selective. Eliminating all species of bacteria from the body may leave the patient prone to superinfection. It should kill bacteria rather than just prevent their multiplication; it should be bactericidal rather than bacteriostatic. Bacteria should not develop resistance to the drug. Lastly, absorption of the drug into the body should be rapid and the desired level maintained in the body for long periods.

6.1 Sulfa Drugs (Sulfonamides)

In 1935 Gerhard Domagk observed that prontosil, an azo dye, was effective against streptococcus bacteria. He won the 1939 Nobel Prize in Medicine for this discovery. Actually hydrolysis of the dye in the body forms the active ingredient *p*-aminobenzenesulfonamide, or sulfanilamide.



Over 5000 sulfonamides have been synthesized and tested. The physiologically active ones are known collectively as sulfa drugs. Most involve variations of groups in place of the hydrogens of the sulfonamide moiety. A general synthesis of these compounds is outlined. Aniline is



protected by acetylation to acetanilide to limit the chlorosulfonylation to the para position. Acetylation deactivates the ring toward multi-electrophilic attack. Various amines react with sulfonyl chloride to give acetylated sulfonamides. Hydrolysis then removes the acetyl group to give the active

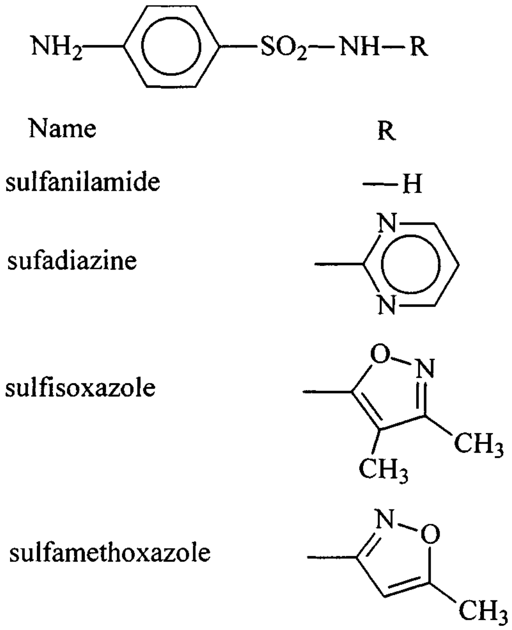
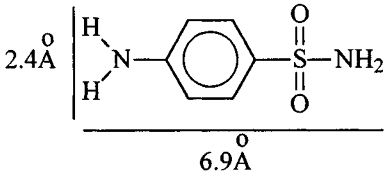


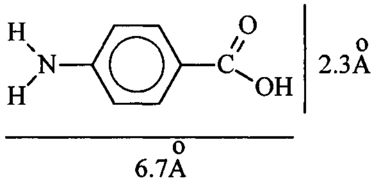
Figure 23.6 Useful sulfa drugs.

drug. Sometimes the drug is administered as its sodium salt, which is soluble in water.

Some common sulfa drugs are pictured in Fig. 23.6 with the appropriate R group designated. Sulfadiazine is probably the best for routine use. It is eight times as active as sulfanilamide and exhibits fewer toxic reactions than most of the sulfonamides. Most of the common derivatives have an R group that is heterocyclic. These groups cause greater absorption into the body, yet they are easily hydrolyzed to the active sulfanilamide.

Unlike many drugs the mode of action of sulfonamides *is* well understood. They are bacteriostatic. Sulfanilamide mimics *p*-aminobenzoic acid (PABA), essential for incorporation into enzymes regulating bacterial growth but nonessential for human growth. The bacteria mistake sulfur for





carbon, form inactive enzymes, and cannot grow. Note that the molecular geometry of sulfanilamide and PABA are similar. If an alkyl, alkoxy, or other functional group is substituted for the *p*-amino group all activity is lost. Groups at the ortho and meta positions cause inactivity.

Sulfonamides are historically important but have been largely replaced by other newer antibacterials. They are still used in urinary infections and in the treatment of bronchitis. The danger of crystal formation in the kidneys is circumvented by administering a mixture of sulfonamides. This changes the solubility characteristics but still has an effect on the bacteria.

6.2 Penicillins

In 1929 Fleming discovered that certain molds contained antibiotics. This initial report was studied in detail by Chain and Florey. All three won the Nobel Prize in Medicine for 1945 because of their discovery of the penicillins. Examination of their general structure shows them to contain a fused ring system of unusual design. A four-membered ring amide, or β-lactam, structure is bonded to a five-membered thiazolidine ring. Over 30 penicillins have been isolated from various fermentation mixtures and over 2000 different R groups have been made synthetically. The most important pharmaceutically are shown in Fig. 23.7. They work by inactivating enzymes that are essential for cell wall development. As a result, the bacteria are enclosed only by a fragile cell membrane and they do not survive.

The free carboxylic acid is not suitable for oral administration, but the sodium or potassium carboxylates of most penicillins are soluble in water and are readily absorbed orally. Salts of penicillins with organic bases have limited water solubility but provide effective blood levels over a long period. Although total syntheses of the penicillins have been reported, they are not yet a viable alternative to large-scale fermentation. Large tanks from 5,000-30,000 gal capacities are used. The penicillin is separated by solvent extraction. The mold grows best at 23-25 °C, pH 4.5-5.0. The fermentation broth is made from corn steep liquor with lactose and inorganic materials added. Sterile air permits growth of the mold over a 50-90-hr period.

The strong acid in the stomach leads to hydrolysis of the amide side chain and a β-lactam opening. An electron-attracting group at the α-position of the amide side chain inhibits the electron displacement involving the carbonyl group and the β-lactam ring, thus making such modifications as penicillin V and ampicillin more acid-stable so they can be taken orally.

For years the most popular penicillin was a natural one, penicillin G, but it is not acid stable and is absorbed poorly through the intestine. Penicillin G can be hydrolyzed in the laboratory to 6-aminopenicillanic acid, which can

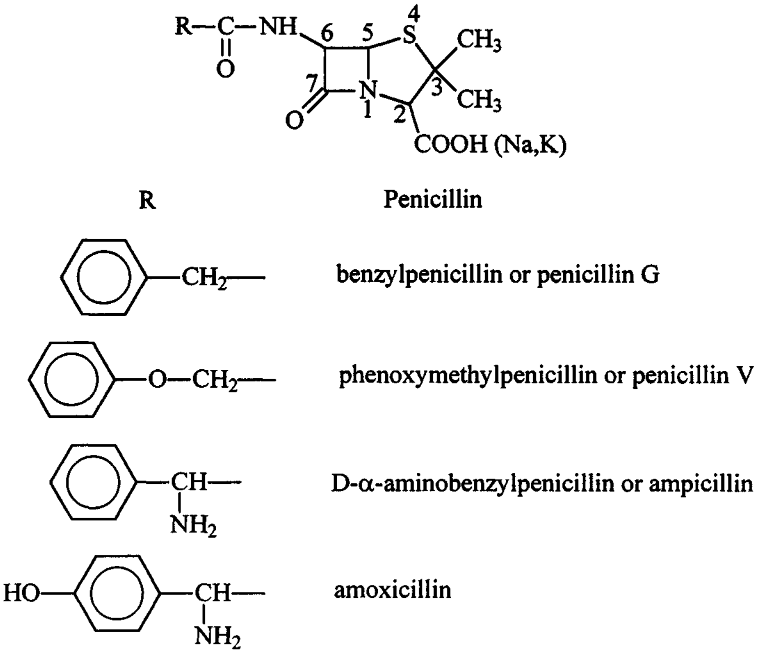


Figure 23.7 Important penicillins.

be acetylated to the more acid-resistant penicillin V and ampicillin, both of which can be taken orally. Ampicillin has a broader spectrum of antibacterial activity than G or V. Amoxicillin (no. 15, 22, 25, and 35) gives more complete absorption through the intestines and causes less diarrhea. There is little or no effect of food on its absorption rate. It has become the most important antibacterial.

6.3 Cephalosporins

The cephalosporins (Fig. 23.8) are β-lactams like the penicillins, but instead of a five-membered thiozolidine ring, they contain a six-membered dihydrothiazine ring. They are otherwise similar in general structure to the penicillins and inactivate enzymes that are responsible for bacterial cell wall formation. Cephalosporin C, which itself is not antibacterial, is obtained from a species of fungus. Chemical modification of this structure to 7-aminocephalosporanic acid by removal of the R—C=O allows the preparation of the active cephalosporins such as cephalexin (no. 32) and cephaloglycin. These are orally active because they have an α-amino-containing R group that is stable to the gastric acid in the stomach. Other

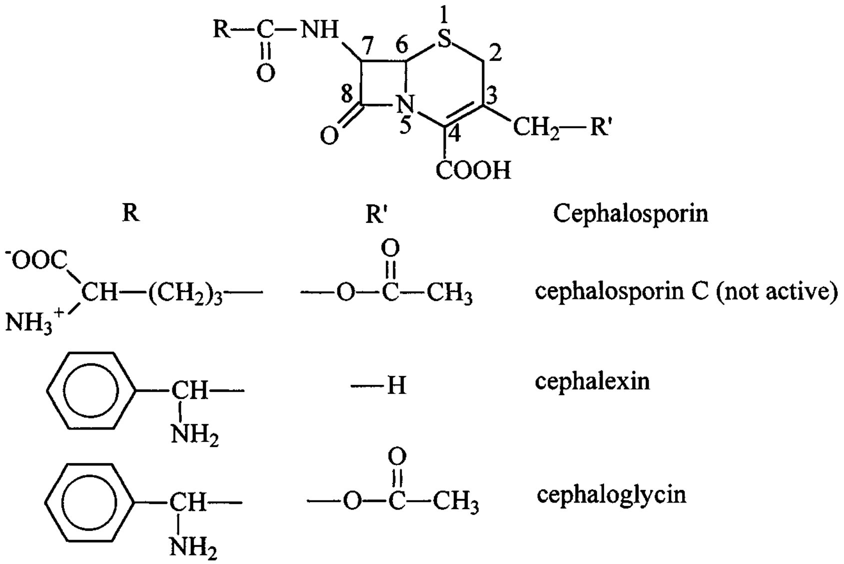
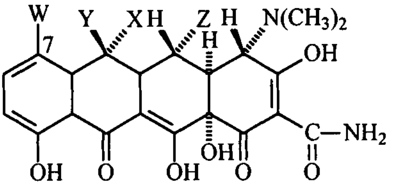


Figure 23.8 Cephalosporins.

cephalosporins are easily made by acylation of the 7-amino group with different acids or nucleophilic substitution or reduction of the 3-acetoxy group.

6.4 Tetracyclines

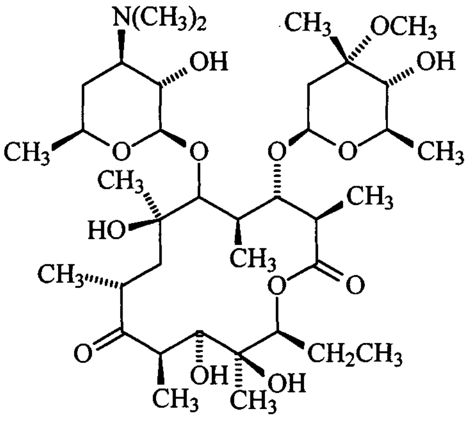
Another group of compounds, the tetracyclines, are made by fermentation procedures or by chemical modifications of the natural product. The hydrochloride salts are used most commonly for oral administration and are usually encapsulated because of their bitter taste. Controlled catalytic hydrogenolysis of chlortetracycline, a natural product, selectively removes the 7-chloro atom and produces tetracycline. Doxycycline and minocycline are other important antibacterials. Tetracycline can be prescribed for people allergic to penicillin. Doxycycline prevents traveler's diarrhea. Tetracyclines help many infections including Rocky Mountain spotted fever, Lyme disease, urinary tract infections, bronchitis, amoebic dysentery, and acne.



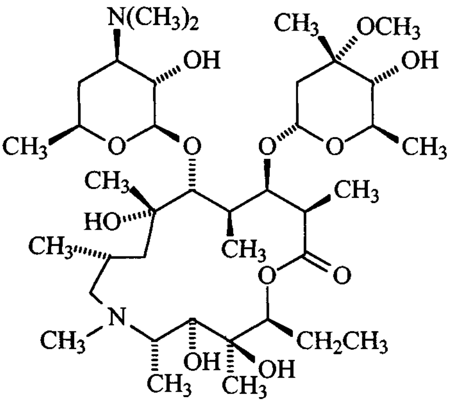
W	X	Y	Z	Name
H	CH_3	OH	H	tetracycline
Cl	CH_3	OH	H	chlortetracycline
H	CH_3	H	OH	doxycycline
$N(CH_3)_2$	H	H	H	minocycline

6.5 The Macrolides

At present more than 30 compounds with large rings have been isolated from fermentation processes. Some have antibacterial properties. Erythromycin and related antibacterials have three common chemical characteristics: (1) a large lactone ring of 12-16 atoms, (2) a ketone group, and (3) an amino sugar. A neutral sugar moiety may also be present. Erythromycin B differs only in one less hydroxyl group. They appear in some way to inhibit protein synthesis in the bacteria. Their activity was reported in 1952, their structure determined in 1957, and their complex stereochemistry found in 1965. Since then they have been the challenge of many chemists who are interested in total synthesis. The natural erythromycin is effective against a number of organisms that have developed resistance to penicillin and tetracycline. It binds with a single high affinity protein site of bacterial ribosomes.



erythromycin A

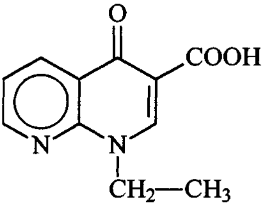


azithromycin (zithromycin)

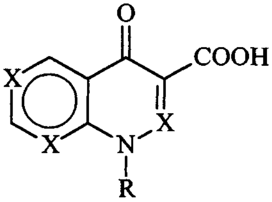
The most used macrolide is now azithromycin (no. 19). It is a significant improvement, begun in 1992, in that it allows cures of antibacterial infection after only five daily doses. It may have better gastric stability as well. This nitrogen-containing macrolide ring, named azalide, contains a methylated nitrogen at position 9 of the 15-membered ring lactone with an attached amino sugar and neutral sugar.

6.6 4-Quinolones

Nalidixic acid, the prototype of this family of drugs, was synthesized as the result of the discovery that an impurity, isolated during the preparation of the antimalarial chloroquine, had significant antibacterial activity. It was introduced into therapy in 1964. It is an example of a general quinolone structure that makes up a dozen antibacterials.



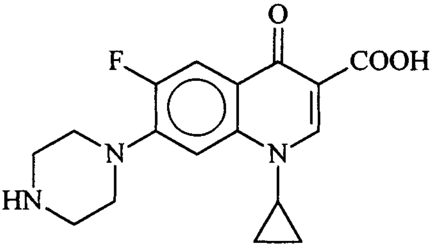
nalidixic acid



general quinolones

X = C or N

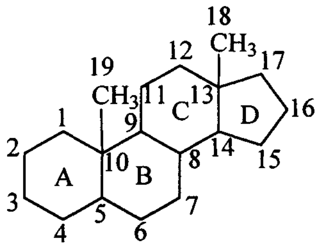
Most of the early quinolones caused gastrointestinal disturbance and other side effects. In 1980 the 6-fluoro analogues were developed, having fewer side effects, requiring smaller dosages, and having reduced development of bacterial resistance. Ciprofloxacin (Cipro®, no. 34) is the leading quinolone antibacterial presently. It is the best cure for anthrax infection and became very newsworthy during the 2001 anthrax scare. All of the quinolones selectively inhibit bacterial DNA synthesis.



ciprofloxacin

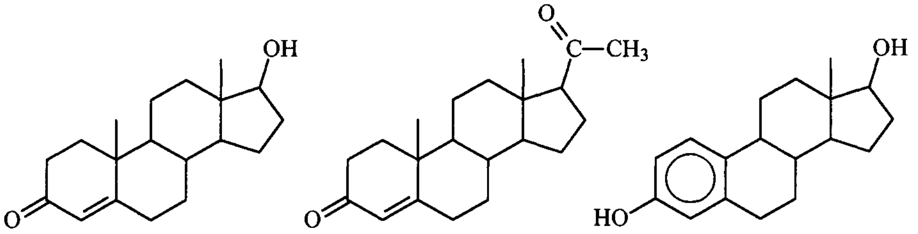
7. STEROIDS

Although we are discussing most drugs by groups in their biological activity, it is convenient to study as a group steroids that are all related chemically but that cause a variety of physiological responses. Steroid drugs include anti-inflammatory agents, sex hormones, and synthetic oral contraceptives. The leading drug to alleviate menopausal symptoms, conjugated estrogens (no. 2), was discussed in Section 3.2. A steroid is a general term for a large number of naturally occurring materials found in many plants and animals. Their general structure includes a fused set of three cyclohexanes and one cyclopentane.



steroids

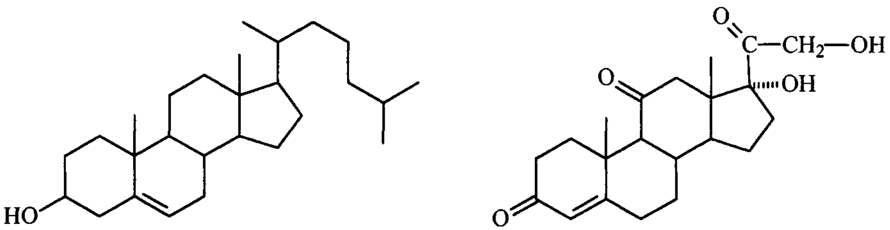
Examples are shown in Fig. 23.9. Stereochemistry is indicated by dotted lines (α-bonds, behind the plane) and solid lines (β-bonds, in front of the plane) of any substituents on the rings. The sex hormones are the molecules mainly responsible for differentiating the sexes. The difference between testosterone and progesterone is a hydroxy versus an acetyl group. The natural sex hormones are used to treat prostate cancer, to alleviate menopausal distress, and to correct menstrual disorders. Other common natural steroids are estradiol, cholesterol, and cortisone. Infamous



testosterone:
an androgen
male sex hormone

progesterone:
a progestogen
female sex hormone

estradiol:
an estrogen
female sex hormone



cholesterol:
cause of gallstones
and heart problems

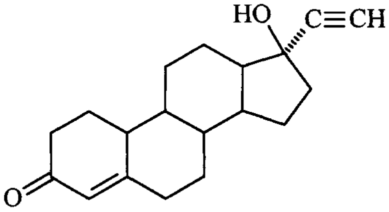
cortisone:
an adrenocortical hormone

Figure 23.9 Important steroids.

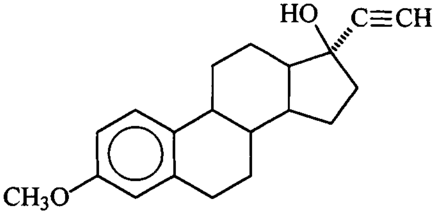
cholesterol causes deposits in the gall bladder and arteries that result in gallstones and some heart attacks. Cortisone is found in the adrenal gland, which is concerned with electrolyte balance and carbohydrate metabolism.

7.1 Oral Contraceptives

The oral contraceptives are synthetic drugs used to mimic the action of the natural progestogens and estrogens. They are combinations of these two types of synthetic derivatives. Note the difference in structure of norethindrone to progesterone and of mestranol to estradiol. The triple bond and other changes at C-17, plus removal of the methyl between rings A and B, allow them to be taken orally by easing the passage of the compound into the blood stream. There is evidence of a relationship between their use and blood clotting, breast cancer, and heart disease. They double the risk of strokes. Some have also been found to actually be abortifacient, preventing pregnancy after conception, rather than before. They induce abortion rather than prevent conception.



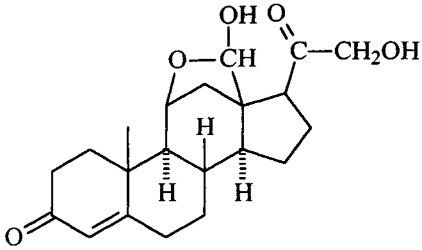
norethindrone



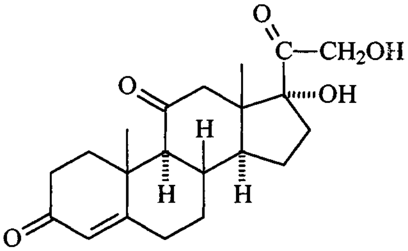
mestranol

7.2 Adrenal Cortex Hormones

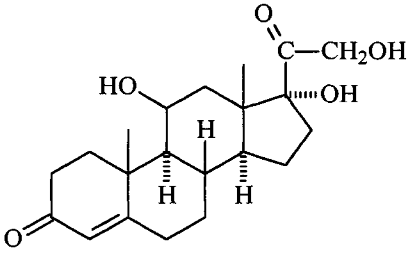
The adrenal glands secrete over 50 different steroids, the most important of which are aldosterone and hydrocortisone. Aldosterone causes salt retention in the body. It is not commercially available. Hydrocortisone is useful for its anti-inflammatory and antiallergic activity. Cortisone and its derivatives have similar activity and it is reduced *in vivo* to hydrocortisone. The two substances are used to treat rheumatoid arthritis. The 11-β-hydroxyl of hydrocortisone is believed to be of major importance in binding to the receptors of enzymes. Anti-inflammatory activity is significantly increased by various substituents: 6α-fluoro, 9α-fluoro, 21-hydroxy, 2α-methyl, 9α-chloro, and a double bond at C-1.



aldosterone



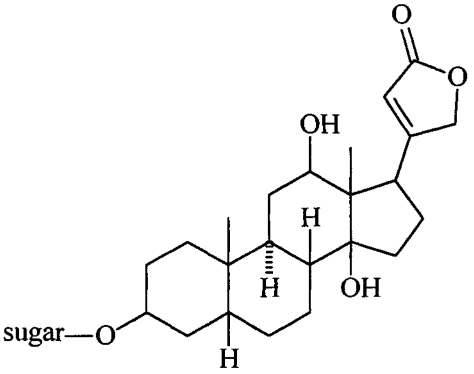
cortisone



hydrocortisone

7.3 Cardiac Steroids

Plants (two species of Digitalis) containing the cardiac steroids have been used as poisons and heart drugs at least since 1500 B.C. Toad skins containing cardiac steroids were good arrow poisons. Cardiac steroids are absolutely indispensable in the modern treatment of congestive heart failure. A commercially available important cardiac steroid is digoxin (no. 23). The cardiac steroids inhibit sodium- and potassium-dependent ATPase, an enzyme responsible for maintaining the unequal distribution of sodium and



digoxin

potassium ions across cell membranes in the heart. It has a steroid structure linked to a trisaccharide sugar moiety.

7.4 Steroid Semisynthesis

The availability of various steroids as drugs is dependent on a combination of three things: isolation of certain steroids economically from natural sources in acceptable yields, conversion into other steroids with the aid of microbial oxidation reactions, and modification with organic synthetic reactions. To sample this fascinating area of research, we will focus on cortisone. Russel E. Marker was the "founding father" of modern steroid chemistry. His synthesis of progesterone from diosgenin in the 1930s is still used commercially today. The bulk of the world's supply of steroid starting material is derived from two species of plants, the Mexican yam and the humble soybean. Diosgenin is isolated from the yam in large amounts. Treatment with acetic anhydride opens the spiran ring as shown in Fig. 23.10. It also acetylates the C-3 hydroxyl to give **1**. Oxidation of the newly formed double bond with chromium trioxide makes the desired acetyl group at C-17 of compound **2**. Treatment with acetic acid hydrolyzes the ester to a hydroxyl at C-16, which then dehydrates to the double bond of compound **3**, called 16-dehydropregnenolone acetate. Selective catalytic hydrogenation of the new double bond follows to give **4**, pregnenolone acetate. The acetate at C-3 is removed by basic hydrolysis to a hydroxy group, which is then oxidized with aluminum isopropoxide (the Oppenauer reaction) to a keto group. The basic reaction conditions isomerize the double bond so that a conjugated α,β-unsaturated ketone is formed, namely, progesterone. The various intermediates shown in this synthesis are currently turned out in tonnage quantity. Other routes to progesterone are commercially used, but this is representative.

Large-scale commercial production of cortisone from progesterone (Fig. 23.11) starts with a microbiologic oxidation with a soil organism, *Rhizopus arrhizus,* to convert progesterone into 1α-hydroxyprogesterone (**5**) in 50% yield. Oxidation of the alcohol with a number of reagents leads to the trione **6**. Condensation with ethyl oxalate gives **7**, which activates the appropriate carbon toward selective bromination to form **8**. A Favorskii rearrangement followed by dehydrohalogenation gives **9**. After the ketone at C-3 is protected as its ketal **10**, reaction with lithium aluminum hydride reduces the ester and the C-11 ketone to the alcohol **11**. Acetylation of one of the alcohol groups (the less hindered primary alcohol) and removal of the protecting group at C-3 then gives **12**. Osmium tetroxide and hydrogen peroxide oxidize the double bond to give hydrocortisone acetate. Oxidation of the alcohol group and hydrolysis of the acetate gives cortisone.

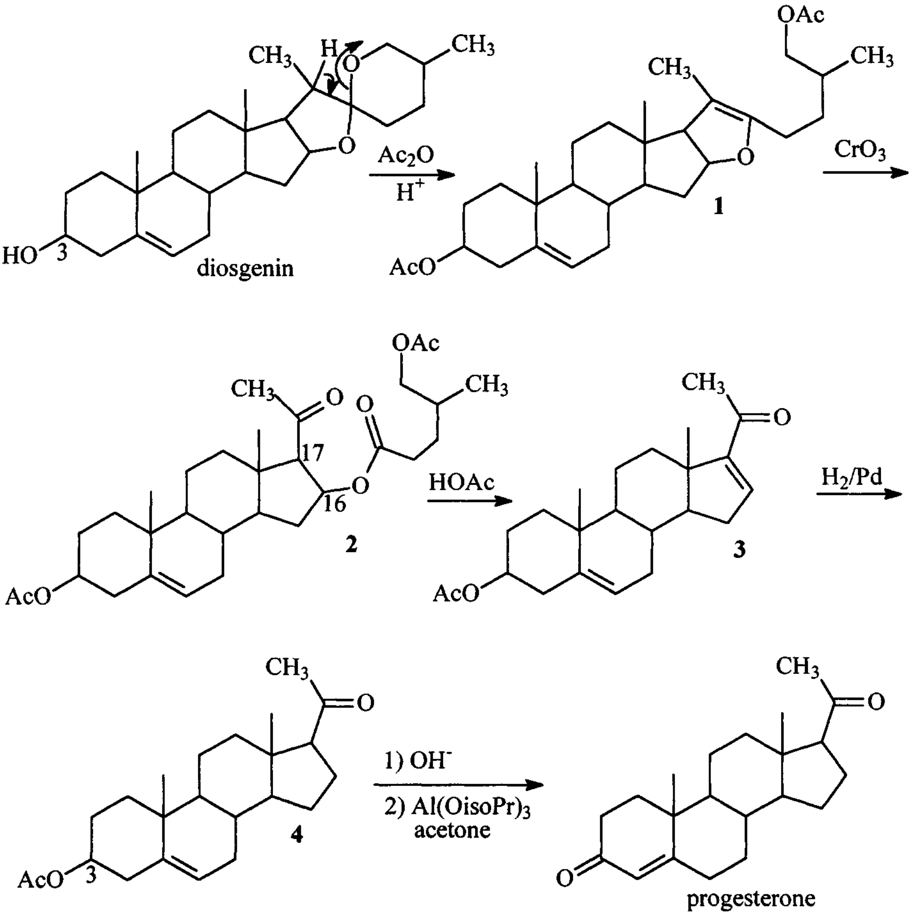


Figure 23.10 Synthesis of progesterone.

8. ANALGESICS AND ANTI-INFLAMMATORY DRUGS

An important class of compounds that have members from both prescription and over-the-counter drugs are those that relieve pain. Aspirin is a common type of analgesic. It is also an antipyretic, that is, it lowers abnormally high body temperatures. A third use is in reducing inflammation caused by rheumatic fever and rheumatoid arthritis. Salicylic acid has been known for its analgesic properties since the early 1800s. Kolbe and

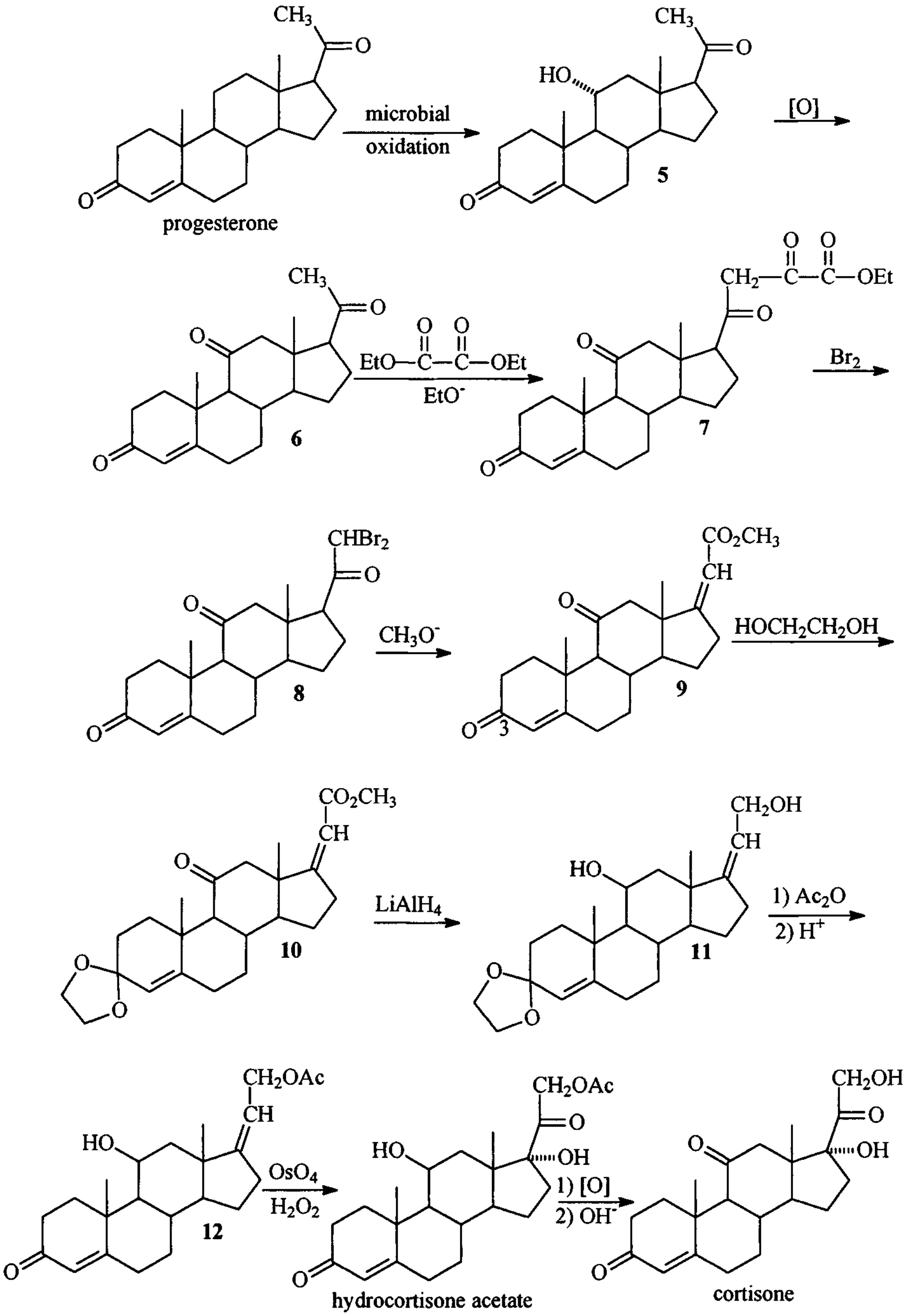
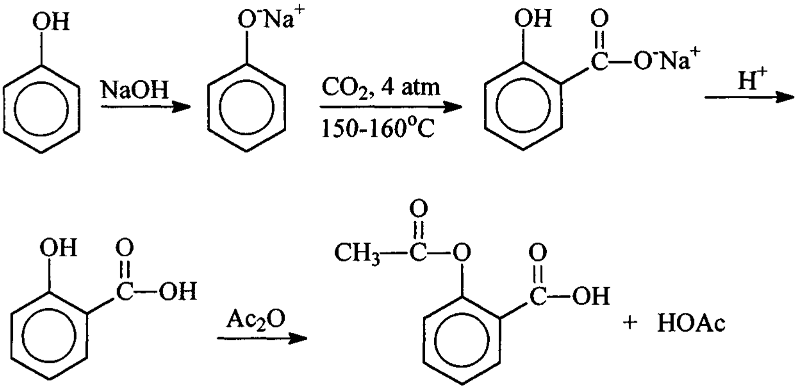


Figure 23.11 Manufacture of cortisone.

Lautermann prepared it synthetically from phenol in 1860. Acetylsalicylic acid was first prepared in 1853 by Gerhardt but remained obscure until Hoffmann discovered its pharmacologic activities in 1899. It was first used in medicine by Dreser, who named it aspirin by taking the "a" from acetyl and adding it to "spirin," the old name for salicylic acid.

The industrial synthesis of aspirin is still based on the original synthesis of salicylic acid from phenol by Kolbe. Reaction of carbon dioxide with sodium phenoxide is an electrophilic aromatic substitution ($O{=}C^{\delta+}{=}O^{\delta-}$) on the ortho-, para-directing phenoxy ring. The ortho isomer is steam-distilled away from the para isomer. Salicylic acid reacts easily with acetic anhydride to give aspirin. Aspirin is a drug manufactured on the scale of other industrial chemicals. Over 20 million lb/yr are produced in the U.S. and it sells for $3.60/lb. In the last step a 500-gal glass-lined reactor is needed to heat the salicylic acid and acetic anhydride for 2-3 hr. The mixture is transferred to a crystallizing kettle and cooled to 3 °C. Centrifuging and drying of the crystals yields the bulk aspirin. The excess solution is stored and the acetic acid is recovered to make more acetic anhydride.



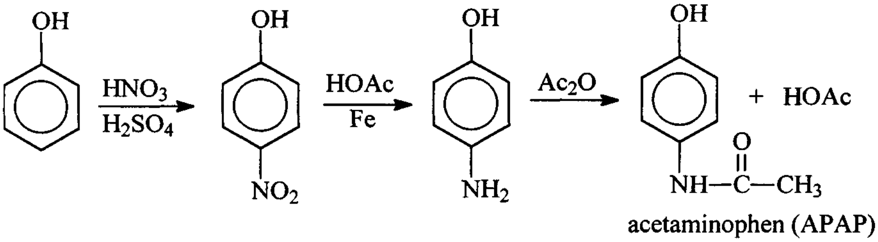
salicylic acid

aspirin

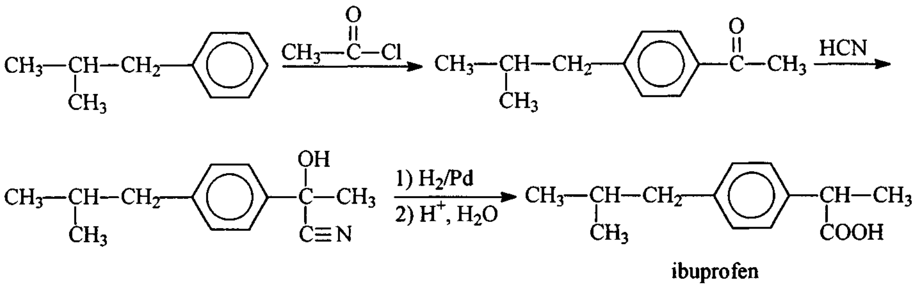
The antipyretic and analgesic actions of aspirin are believed to occur in a certain area of the brain. It is also thought by some that the salicylates exert their analgesia by their effect on water balance. Aspirin is anti-inflammatory because it inhibits the biosynthesis of chemicals called prostaglandins. The irritation of the stomach lining caused by aspirin can be alleviated with the use of mild bases such as sodium bicarbonate, aluminum glycinate, sodium citrate, aluminum hydroxide, or magnesium trisilicate (a common trademark for this type of aspirin is Bufferin®).

Another analgesic, acetaminophen, is a derivative of *p*-aminophenol. Although it is an analgesic and antipyretic, acetaminophen shows little if any anti-inflammatory activity. *p*-Aminophenol itself is toxic but acetylation of the amino group makes it a convenient drug. A common trademark for acetaminophen is Tylenol®. Excedrin® is acetaminophen, aspirin, and caffeine. Acetaminophen now is made at over 60 million lb/yr in the U.S., and sells for $3.30/lb. A common abbreviation for acetaminophen is APAP, since its full name is N-acetyl-*p*-aminophenol. When combined with hydrocodone it is no. 4 and no. 24 on the top prescription drug list (see Section 3.4).

Acetaminophen is easily synthesized from phenol by nitration, reduction of the nitro group to an amine, and acetylation.



A very popular alternative to aspirin and acetaminophen is ibuprofen, which has tradenames such as Motrin® and Advil®. It can be synthesized from isobutylbenzene by a Friedel-Crafts acylation with acetyl chloride, followed by formation of a cyanohydrin. Treatment with H_2/Pd reduces the benzylic hydroxyl to a hydrogen and hydrolysis of the nitrile gives the carboxylic acid. There are at least six published syntheses of ibuprofen. This illustrates the difficulty of knowing which technology a particular company is using. At the other extreme is the proprietary nature of some syntheses, where they have not yet been published.



Ibuprofen has good analgesic and anti-inflammatory action. Ibuprofen is made at approximately 16 million lb/yr in the U.S. Its price is higher than aspirin or acetaminophen and is usually around $9.30/lb. Its common name does tell us something about its structure. There are a number of "profens," or propylphenyl compounds, that are analgesic. They have a three-carbon (propyl) side chain, usually with an acid group included, bonded to a phenyl ("fen") group. "Ibu" stands for the isobutyl side chain of ibuprofen.

The U.S. pain reliever market is estimated at $2.5 billion. Aspirin's share has recently decreased from 60% in 1983 to 28% in 1996, but this share is now stabilized. Acetaminophen has 48% of the market and ibuprofen 24%. Aspirin may be back on the upswing. After earlier reports that it was linked to Reye's syndrome in children, the recent news is that a single aspirin tablet taken every other day halves the risk of heart attacks among healthy men.

A newer drug, naproxen (Naprosyn®, Aleve®), is making the over-the-counter market for analgesics and anti-inflammatory drugs even more complex. There are at least four syntheses of naproxen. In one synthesis (Fig. 23.12) the Willgerodt reaction is used. 2-Methoxynaphthalene (**1**, from naphthalene in three steps) is acylated to **2** and treated with morpholine and sulfur in this interesting reaction to give **3**. Treatment with acid gives a carboxylic acid (**4**). Esterification with methanol (**5**) and methylation with methyl iodide and sodium hydride (**6**), followed by hydrolysis of the ester

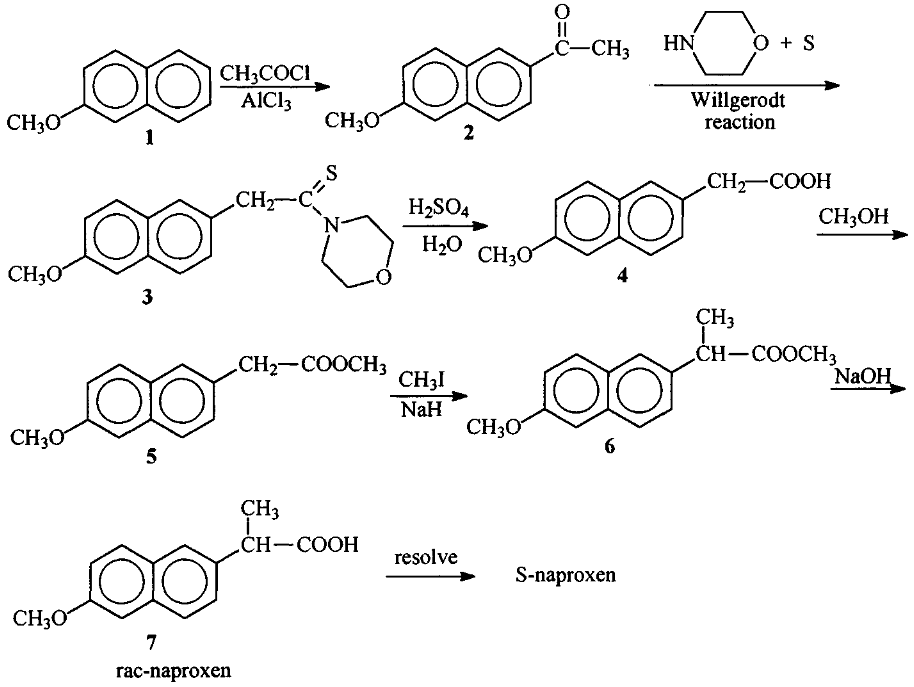
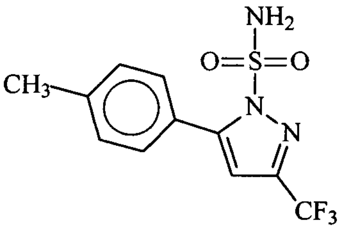


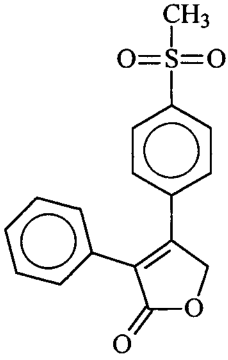
Figure 23.12 Synthesis of naproxen.

protecting group back to the acid, gives racemic naproxen (7). The S enantiomer is the active drug, so the racemic compound is resolved with an alkaloid. Naproxen is being used especially to combat rheumatoid arthritis, tendinitis, migraine, and premenstrual syndrome. It is sometimes administered as the sodium salt.

New anti-inflammatory drugs of the late 1990s to treat arthritis are rapidly growing in importance, including celecoxib (Celebrex®, no. 11) and rofecoxib (Vioxx®, no. 20). Celecoxib grew 41% in prescriptions for one year, and rofecoxib was just introduced in 1999. These are called cyclooxygenase-2 (COX-2) inhibitors. COX-2 is a body enzyme that plays an important role in regulating pain and inflammation. But these drugs do not interfere with COX-1, a related enzyme that helps maintain the stomach's protective lining. So these two substances are less likely to cause gastrointestinal side effects.



celecoxib



rofecoxib

Propoxyphene (Darvon®) is a stronger analgesic but has no antipyretic effects. It is sometimes taken in combination with aspirin and acetaminophen. It has widespread use for dental pain since aspirin is relatively ineffective, but it is not useful for deep pain. It must be prescribed. The starting material for propoxyphene is propiophenone, made from benzene and propionyl chloride by a Friedel-Crafts acylation. It undergoes a Mannich reaction (Fig. 23.13) with formaldehyde and dimethylamine. A Grignard reaction with benzyl magnesium bromide follows. Esterification with propionic anhydride gives propoxyphene. Only one stereoisomer is active physiologically. It is administered as the amine hydrochloride salt.

The discovery of morphine's analgesic activity by Serturner in 1806 started a long series of studies of the alkaloids from the opium poppy, including morphine's first correctly postulated structure in 1925 and its total

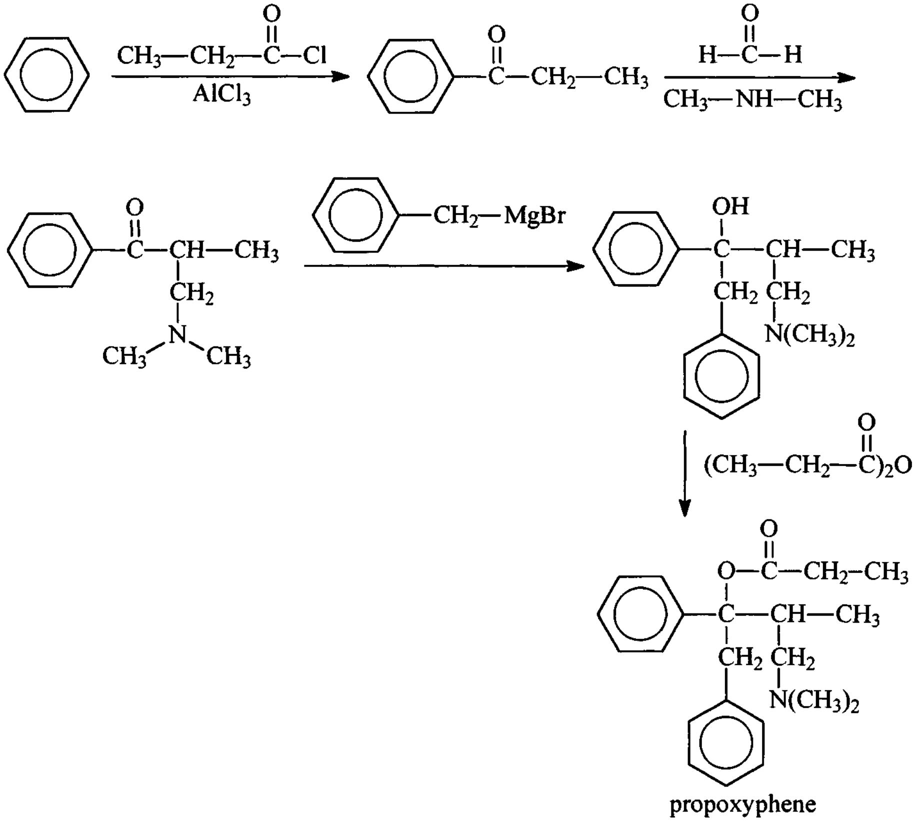
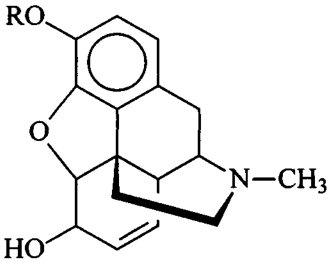


Figure 23.13 Synthesis of propoxyphene.

synthesis in 1952. Codeine is the methyl ether of morphine. The depressant action of the morphine group is the most useful property, resulting in an increased tolerance to pain, a sleepy feeling, a lessened perception to external stimuli, and a feeling of well-being. Respiratory depression and addiction are its serious drawbacks. The important structure-activity relationships that have been defined are (1) a tertiary nitrogen, the group on the nitrogen being small; (2) a central carbon atom, of which none of the valences is connected to hydrogen; (3) a phenyl group connected to the central carbon; and (4) a two-carbon chain separating the central carbon from the nitrogen.

Morphine is isolated from the opium poppy from either opium, the resin obtained by lancing the unripe pod, or from poppy straw. It is isolated by various methods, of which the final step is precipitation of morphine from an acid solution with excess ammonia. It is then recrystallized from boiling



morphine, R = H
codeine, R = CH_3

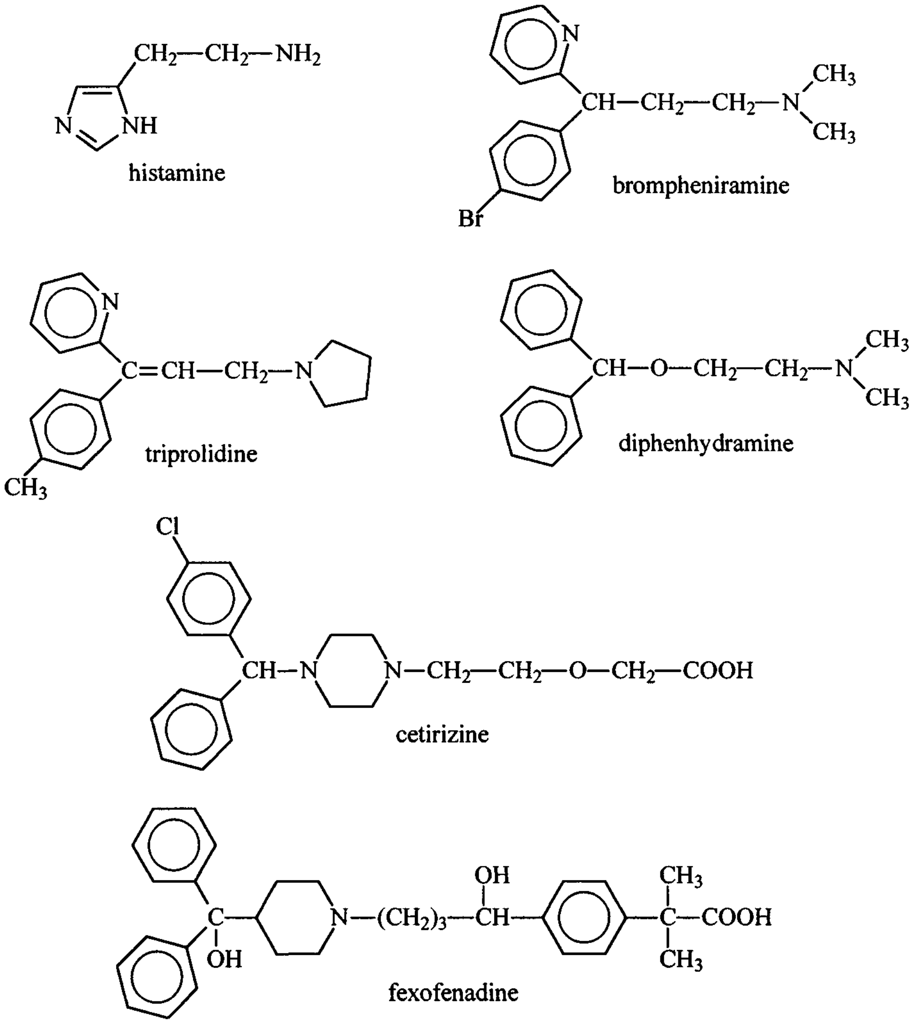
alcohol. Because it causes addiction so readily it is properly termed a narcotic and should be used only in those cases where other pain-relieving drugs are inadequate.

Codeine occurs naturally in opium but the amount is too small to be useful. It is prepared from morphine by methylating the phenolic hydroxyl group with diazomethane, dimethyl sulfate, or methyl iodide. Codeine does not possess the same degree of analgesic potency as morphine but is used as an antitussive, a cough suppressant. Hydrocodone was discussed in Section 3.4. It is made from codeine.

9. ANTIHISTAMINES

These drugs alleviate allergic conditions such as rashes and runny eyes and nose. They are decongestants for swelled sinuses and nasal passages during the common cold. These symptoms are caused by histamine and hence the drugs that get rid of them are antihistamines. They are also sleep inducers. The most popular antihistamines, sold under such tradenames as Dimetapp®, Actifed®, and Benadryl®, have a structure including the group R—X—C—C—N—, where X can be nitrogen, oxygen, or carbon. The mode of action may be considered to be a competition, in tissue, between the antihistaminic agent and histamine for a receptor site. The combining of the antihistaminic agent with the receptive substance at the site of action prevents the histamine from exerting its characteristic effect on the tissue. Fig. 23.14 gives the structures of histamine and some antihistamines. The newer prescribed ones are loratidine (no. 9, see Section 3.9), cetirizine (no. 28), and fexofenadine (no. 31). These last three all have a nitrogen-containing six-membered ring.

These complex molecules can be easily synthesized with some key steps. For instance (Fig. 23.15) diphenhydramine can start with the reaction of diphenylmethane and bromine to give the bromide, followed by reaction



histamine

brompheniramine

triprolidine

diphenhydramine

cetirizine

fexofenadine

Figure 23.14 Important antihistamines.

with dimethylaminoethanol, made from dimethylamine and ethylene oxide. The diphenylmethane is made by a Friedel-Crafts reaction of benzene and methylene chloride or benzene and benzyl chloride.

10. THE FUTURE

The future is fascinating for pharmaceuticals. A big trend now for many drugs is manufacture of the pure enantiomer. Chiral drugs can be made

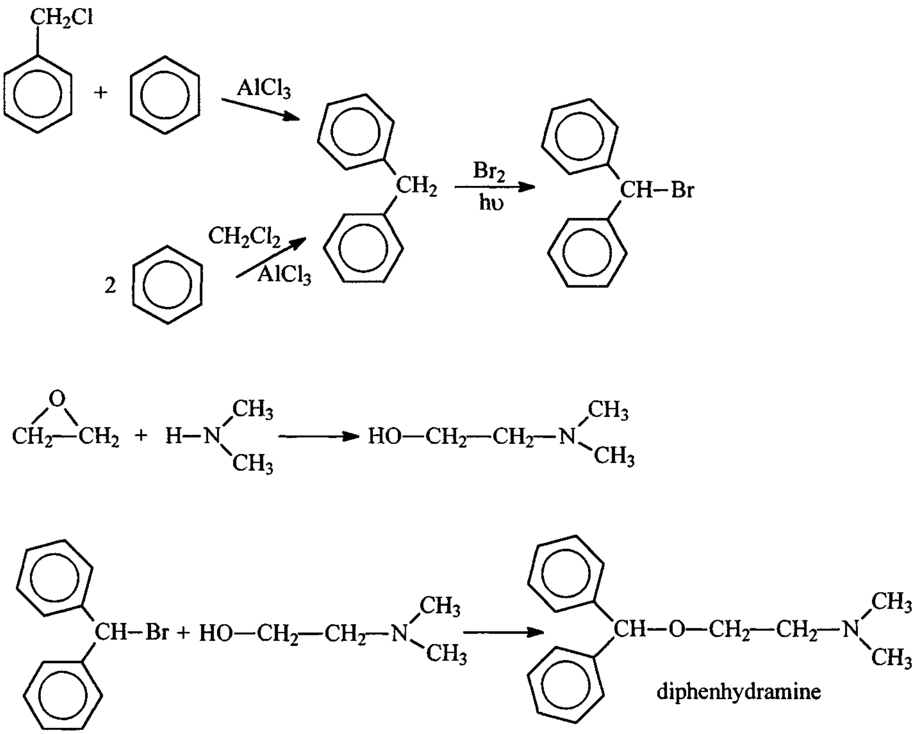


Figure 23.15 Synthesis of diphenhydramine.

either by resolution of a racemic mixture of a structure or by making, using a chiral catalyst or chiral reagent, one enantiomer in large excess over another. Because many drugs are physiologically active for only one of the two enantiomers, with the other being inactive or even harmful, this approach has been very dominant in the research of most pharmaceutical laboratories. The Nobel Prize in Chemistry in 2001 went to three chemists doing enantioselective synthetic work: William Knowles, Ryoji Noyori, and Barry Sharpless. The world market for single enantiomer drugs surpassed $123 billion, about one third of the whole world market. Even a substance as simple as naproxen (Section 8) is now sold as the pure S-enantiomer. R-Fluoxetine (Section 5.4) is now sold as the pure enantiomer of the common antidepressant. In 2001-2002 no less than nine meetings or symposia were devoted to chiral chemistry in one year.

Another recent development in pharmaceuticals is *combinatorial chemistry*. This term is difficult to define, but generally it means the high-throughput synthesis and screening of chemical substances to identify agents with useful properties. Making small amounts of many slightly different compounds enables the medicinal chemist to optimize structure-activity relationships faster. Such things as polymer-supported reagents, microwave heating to reduce reaction times and reagent requirements, automation and instrumentation for synthetic steps, and solid-phase organic synthesis help to make synthesis faster and easier.

High-speed computers have helped the concept of designing drugs by "receptor-fit" models and visualizing them in three-dimensional structures. Quantifying molecular variables such as geometry and electron densities are helpful. Molecular modelling and molecular graphics are useful tools made easier by computers.

This chapter is hopefully a good introduction into the fascinating chemistry and pharmacology of the drug industry. We have tried to summarize representative important types of drugs to give an overall view of the industry. Although many other areas and chemical types could have been included, we mainly emphasized only the most used drugs. Other types of drugs, such as anticancer and antiviral drugs, are rapidly growing in importance and are of course life saving to those who require them. A more complete description of these and other pharmaceuticals is beyond the scope of this text.

Suggested Readings

Gringauz, A. *Introduction to Medicinal Chemistry*; Wiley-VCH: New York, 1997; selected sections.

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 987-1011.

Reuben, B.G.; Wittcoff, H.A. *Pharmaceutical Chemicals in Perspective*; John Wiley & Sons: New York, 1989; selected sections.

Silverman, H.M., Ed. *The Pill Book*, 9th ed.; Bantam Books: New York, 2000; selected sections.

Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, pp. 213-279.

The top 200 prescription drugs are published yearly in a number of pharmaceutical journals, including *Pharmacy Times*, and on the Internet: http://www.rxlist.com/top200.htm.

Chapter 24

Surfactants, Soaps, and Detergents

1. INTRODUCTION TO THE INDUSTRY

A general area of the chemical industry that manufactures most of the surfactants, soaps, and detergents is called Soaps, Cleaning Compounds, and Toilet Preparations (NAICS 3256), one of the seven major divisions of Chemical Manufacturing (see Fig. 20.1 for this summary). This amounts to over $50 billion and is 14% of all Chemical Manufacturing. We will concentrate primarily on a subsector of this division, Soaps and Other Detergents (NAICS 325611), although all subsectors of Soaps, Cleaning Compounds, and Toilet Preparations use surface active (surfactant) chemicals, which are further modified into finished products. Over 5 billion lb of surfactants serve all these sectors. In addition to household and industrial cleaning, oil field applications and personal care products are big users of surfactants.

Fig. 24.1 shows the trend in U.S. shipments of Soaps and Other Detergents (NAICS 325611) along with its further subsections of Household Detergents (3256114), Commercial, Industrial, and Institutional Soaps and Detergents (3256111), and Household Soaps (3256117). Note the rapid increase for Soaps and Detergents in the 1970s, a slower rate of growth in the 1980s, and the near constant market in the early 1990s until 1996. The following important companies have large percentage shares of the U.S. household laundry detergent market: Procter and Gamble (P & G), 43%; Unilever, 21%; Dial, 11%; Huish Detergents, 6%; Church and Dwight, 5%; USA Detergents, 4%; and Colgate-Palmolive, 4%.

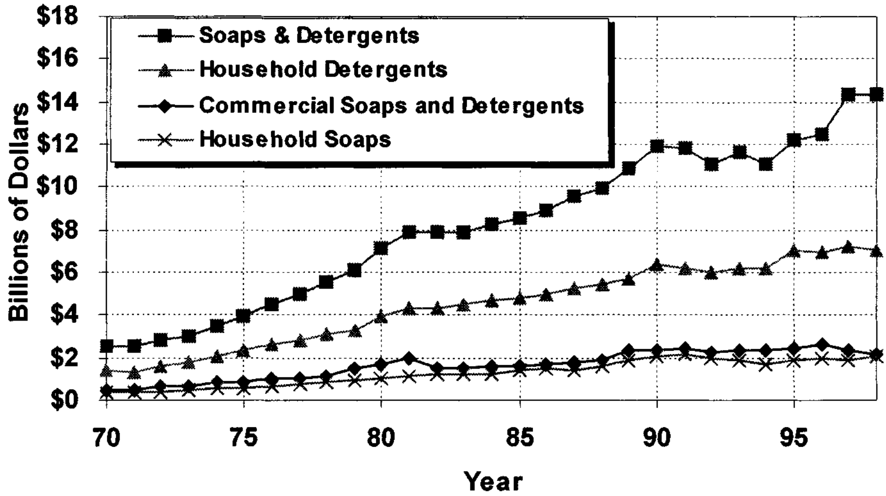


Figure 24.1 U.S. shipments of soaps and detergents. (*Source: Annual Survey of Manufactures*)

Surfactants are chemicals that, when dissolved in water or another solvent, orient themselves at the interface between the liquid and a second solid, liquid, or gaseous phase and modify the properties of the interface. Surfactants are not only important as the active constituent of soaps and detergents but are also vital in the stabilization of emulsions, in fabric softening, in oil well drilling, etc. Surfactants are the most widely applied group of compounds in Chemical Manufacturing. We will concentrate on their use in cleaning, that is, in soaps and detergents.

All surfactants have a common molecular similarity. A portion of the molecule has a long nonpolar chain, frequently a hydrocarbon chain, that promotes oil solubility but water insolubility (the hydrophobic portion—water hating). Another part of the molecule promotes oil insoluble and water soluble properties (the hydrophilic portion—water loving).

Fig. 24.2 summarizes the cleaning action of surfactants. The surfactant lines up at the interface and also forms micelles, or circular clusters of molecules. In both cases the hydrophobic end of the molecule gets away from water molecules and the hydrophilic end stays next to the water molecules (like dissolves like). When grease or dirt come along (primarily hydrophobic in nature) the surfactants surround it until it is dislodged from the substrate. The grease molecules are suspended in the emulsion by the surfactant until they can be washed away with freshwater.

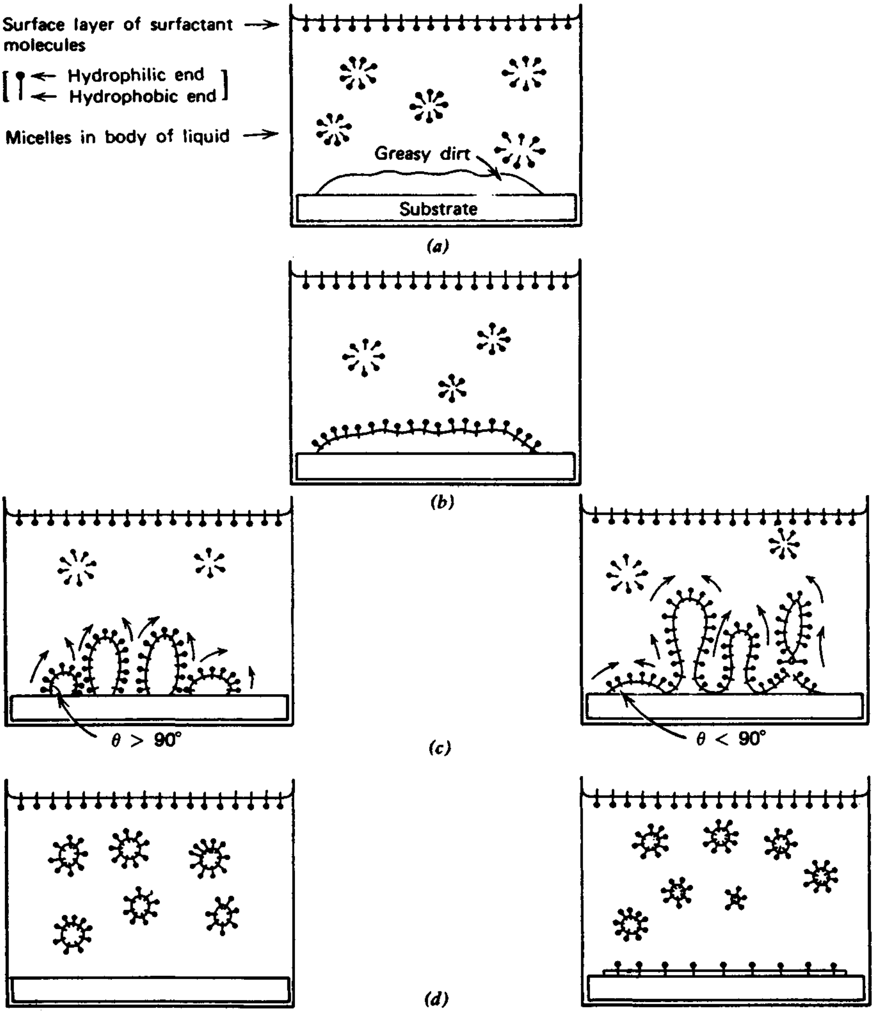


Figure 24.2 "Solubilizing" effect of surface active agents. *(a)* Greasy dirt comes into contact with surfactant solution. *(b)* Hydrophobic ends of surfactant molecules dissolve in the grease. *(c)* The surfactant affects the contact angle θ between the dirt and the substrate. If $\theta <$ 90°, total removal of the grease is impossible. *(d)* Further agitation displaces the greasy dirt as macroscopic particles. These form an emulsion if agitation is sufficient. The particles form the center of micelle-like structures. Removal of grease is seldom complete ($\theta <$ 90° as in the diagrams on the right rather than the simple "rollback" mechanism on the left). Usually the main body of grease is removed from a strongly adsorbed monomolecular or duplex layer of grease. Agitation is an essential part of the process. (*Source:* Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, John Wiley & Sons, 1980. Reprinted by permission of John Wiley & Sons, Inc.)

Table 24.1 U.S. Production of Major Household Surfactants

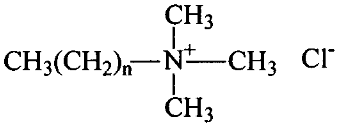
Type	Production (Million lb)	%
Anionics		
Linear alcohol sulfates (AS)	57	2%
Linear alcohol ethoxysulfates (AES)	890	25
Linear alkylbenzenesulfonates (LAS)	661	19
Nonionics		
Nonylphenol ethoxylates (NPE)	462	13
Alcohol ethoxylates (AE or AEO)	1,200	34
Other nonionics	244	7
Total	**3,514**	**100%**

Source: Chemical Economics Handbook

Surfactants can be divided into four general areas. These will be discussed separately: cationics, anionics, nonionics, and amphoterics. Major anionics are soaps, linear alcohol sulfates (AS), linear alcohol ethoxysulfates (AES), and linear alkylbenzenesulfonates (LAS). Major nonionics are nonylphenol ethoxylates (NPE) and alcohol ethoxylates (AE or AEO). Table 24.1 gives the U.S. production of major surfactants used in the household market, which is over half of the total market. We will briefly describe other surfactants, but these five are the most important for household detergents. The 3.5 billion lb of surfactants make over 10 billion lb of household detergents, since other ingredients are added to these complex formulations. Table 24.1 is a little misleading because it is production of surfactant chemicals. Actually the amount of AEO used directly is about 500 million lb, with the rest of the 1,200 million lb used to make AES by sulfonation, which then is used as the surfactant. So the AEO figure in terms of importance as the final surfactant is magnified, though it is a key intermediate in making AES surfactant. We will see how this is possible when the chemistry is covered.

2. CATIONIC SURFACTANTS

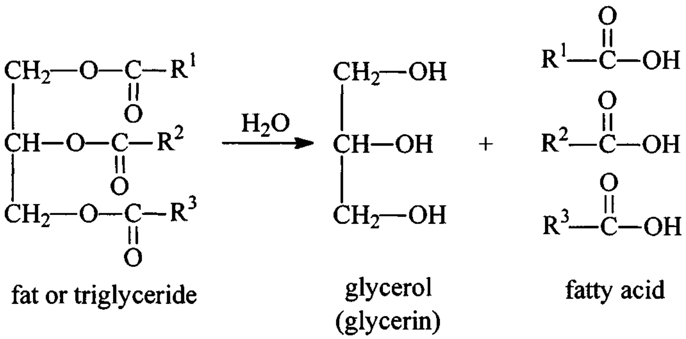
In cationics the long hydrophobic alkyl chain is in the cationic portion of the molecule. Another way of saying this is that the organic part is positive. Practically all industrially important cationics are fatty nitrogen compounds and many are quaternary nitrogen compounds such as tallow fatty acid trimethylammonium chloride. In the more general structure $R^1R^2R^3R^4N^+X^-$, R^1 is a long alkyl chain, the other R's may be alkyl or hydrogen, and X^- is halogen or sulfate.



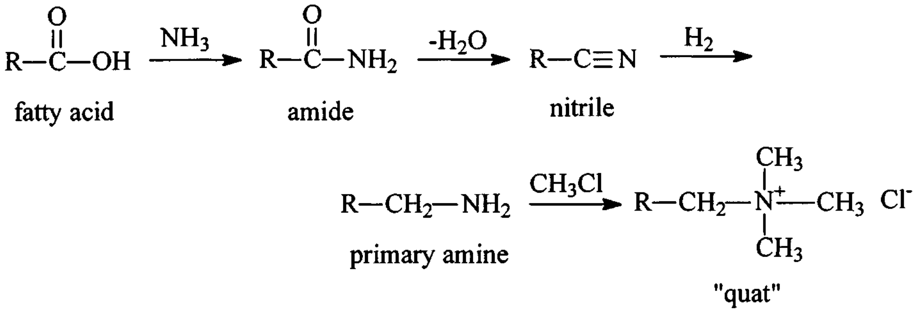
$$CH_3(CH_2)_n{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}{-}CH_3\ \ Cl^-$$

n = 15 or 17

The long hydrocarbon chain is derived from naturally occurring fats or triglycerides, that is, triesters of glycerol having long chain acids with an even number of carbons, being of animal or vegetable origin. A common fat source for cationics is inedible tallow from meat packing plants. If the fatty acid is desired the ester is hydrolyzed at high temperature and pressure, or with a catalyst such as zinc oxide or sulfuric and sulfonic acid mixtures.



The fatty acid is then converted into the "quat" by the following sequence of reactions.



$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH \xrightarrow{NH_3} R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}NH_2 \xrightarrow{-H_2O} R{-}C{\equiv}N \xrightarrow{H_2}$$

$$R{-}CH_2{-}NH_2 \xrightarrow{CH_3Cl} R{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}{-}CH_3\ \ Cl^-$$

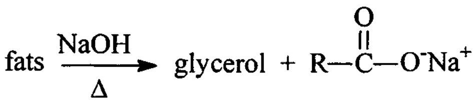
Cationic surfactants are not very good for cleaning because most surfaces carry a negative charge and the cationic portion adsorbs on the surface instead of dissolving the grease. But they do have other important surfactant applications. They inhibit the growth of bacteria, are corrosion inhibitors, are used in ore flotation processes (separating phosphate ore from silica and potassium chloride from sodium chloride), and are good fabric softeners and antistatic agents. They also find use in hair conditioners and other personal care applications.

3. ANIONIC SURFACTANTS

This is by far the most important type of surfactant and will be discussed under separate subtypes. In anionics the long hydrophobic alkyl chain is in the anionic part of the molecule. The organic part is negative.

3.1 Soaps

The first type of cleansing agent, used by humankind for centuries, was soap. Although it has now been supplemented by various synthetic detergents in advanced countries for laundry and household use, it is still preferred for personal hygiene. In less-developed countries it is preferred for laundry use.



$$\text{fats} \xrightarrow[\Delta]{\text{NaOH}} \text{glycerol} + \text{R—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O}^{-}\text{Na}^{+}$$

Soaps are the sodium or potassium salts of certain fatty acids obtained from the hydrolysis of triglycerides. The potassium salts form the "soft soaps" that have become popular recently. The fats used in soap manufacture come from diverse natural sources. Animal tallows and coconut oil are the favored sources of the triglycerides, and quite often mixtures from different sources are used to vary hardness, water solubility, and cleansing action of the final product. Palm, olive, cottonseed, castor, and tall oil are other sources. The side chains are usually C_{12}-C_{18} in length. Manufacturing processes are both batch and continuous. Sometimes the triglyceride is steam-hydrolyzed to the fatty acid without strong caustic and then in a separate step it is converted into the sodium salt. Either way gives a similar result. Soaps have some disadvantages compared to synthetic detergents: they are more expensive, they compete with food uses for fats and oils, and their calcium and magnesium salts formed in hard water are

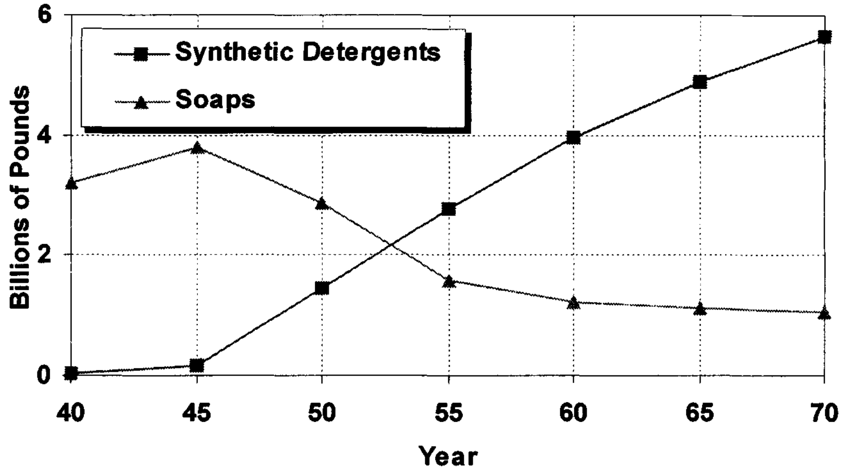


Figure 24.3 U.S. consumption of soaps vs. total synthetic detergents. (*Source: Chemical Economics Handbook*)

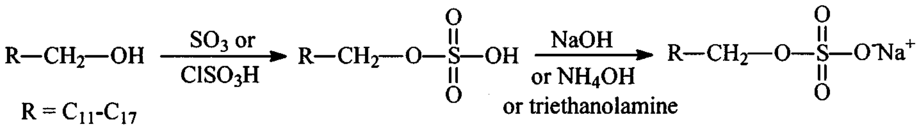
very insoluble and precipitate onto the clothing being washed. They also tend to clog automatic washers. They deteriorate on storage and are unstable in acid solutions. This is why in 1940 only 1% of cleaning agents were detergents; in 1970 they were 85%. Fig. 24.3 shows this historical replacement of soaps by detergents from 1940-1970. However, there will always be that small market for soaps, presently still a significant percentage. Advantages of soaps include greater biodegradability and less toxicity.

3.2 Straight Chain Detergent Intermediates

It is necessary for any soap or detergent to have a high degree of linearity for it to be biodegradable by bacteria. Many synthetic anionic detergents are based on straight chain primary alcohols and α-olefins. New technology allows these materials to be manufactured from ethylene (using Ziegler polymerization catalysts) or from linear alkanes (paraffins), followed by conversion into linear alkyl chlorides by chlorination or linear α-olefins by dehydrogenation, in addition to being formed from naturally occurring straight chains. These processes will be discussed under LAS detergents, but it is important to realize that synthetic long straight-chain compounds are now available.

3.3 Linear Alcohol Sulfates (AS)

Alcohol sulfates (AS) are usually manufactured by the reaction of a primary alcohol with sulfur trioxide or chlorosulfonic acid followed by neutralization with a base. These are high foam surfactants but they are sensitive to water hardness and higher levels of phosphates are required. This latter requirement has harmed the market for this type of detergent, but they are 2% of production for the major household surfactant market. Sodium lauryl sulfate ($R = C_{11}$) is a constituent of shampoos to take advantage of its high-foaming properties.



$$R{-}CH_2{-}OH \xrightarrow[ClSO_3H]{SO_3 \text{ or}} R{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}OH \xrightarrow[\substack{\text{or } NH_4OH \\ \text{or triethanolamine}}]{NaOH} R{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}O^-Na^+$$

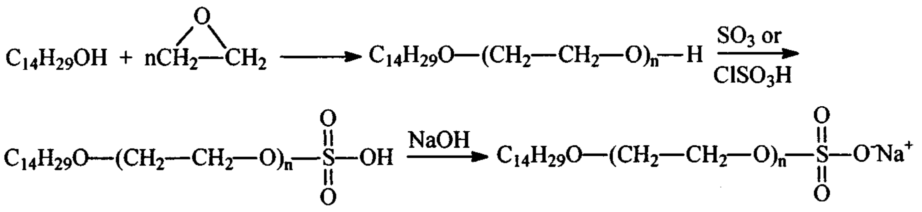
$R = C_{11}\text{-}C_{17}$

The linear alcohols can be made from other long-chain linear materials, but a new process with a triethylaluminum catalyst allows their formation directly from ethylene and oxygen.

$$nCH_2{=}CH_2 + O_2 \xrightarrow{Et_3Al} R{-}CH_2{-}OH$$

3.4 Linear Alcohol Ethoxysulfates (AES)

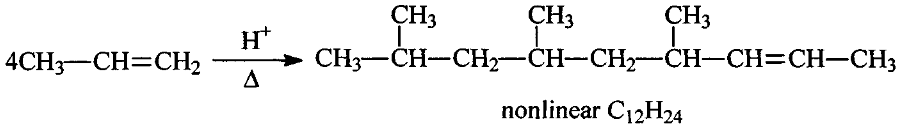
Alcohol ethoxysulfates (AES) are made by reaction of 3-7 mol of ethylene oxide with a linear C_{12}-C_{14} primary alcohol to give a low molecular weight ethoxylate, followed by the usual sulfonation.



They have high foam for shampoos and are "kind to the skin." They are also used in light duty products such as dishwashing detergents. It is the least sensitive of the anionics to water hardness and therefore has benefited in the trend away from phosphates. They have 25% of the production for the major household surfactant market.

3.5 Linear Alkylbenzenesulfonates (LAS)

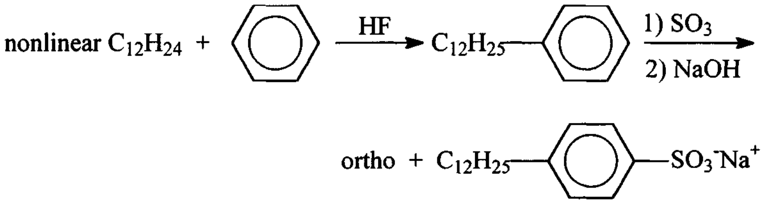
Originally the cheap tetramer of propylene was used as the source of the alkyl group in alkylbenzenesulfonates. This tetramer is not a single compound but a mixture. However, they are all highly branched. For example:



$$4CH_3{-}CH{=}CH_2 \xrightarrow[\Delta]{H^+} CH_3{-}\overset{CH_3}{\overset{|}{CH}}{-}CH_2{-}\overset{CH_3}{\overset{|}{CH}}{-}CH_2{-}\overset{CH_3}{\overset{|}{CH}}{-}CH{=}CH{-}CH_3$$

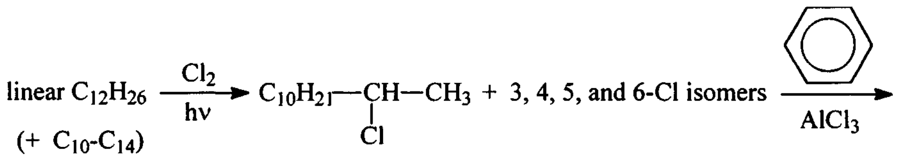
nonlinear $C_{12}H_{24}$

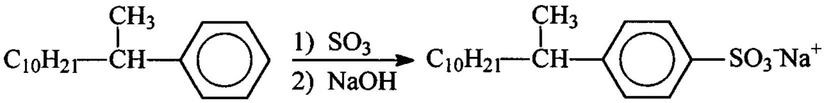
The nonlinear dodecene was then used to alkylate benzene by the Friedel-Crafts procedure. Sulfonation and treatment with caustic completed the process.



This nonlinear alkylbenzenesulfonate formed the basis for the heavy duty household washing powders of the 1950s and early 1960s with excellent cleaning ability. But rivers and lakes soon began foaming since enzymes present in bacteria could not degrade these "hard" detergents because of the highly branched side chain. They were banned in 1965.

Thus *n*-alkanes (C_{10}-C_{14}) separated from the kerosene fraction of petroleum (by urea complexation or absorption with molecular sieves) are now used as one source of the alkyl group. Chlorination takes place anywhere along the chain at any secondary carbon. Friedel-Crafts alkylation followed by sulfonation and caustic treatment gives a more linear alkylbenzenesulfonate (LAS) which is "soft" or biodegradable. The chlorination process is now the source of about 40% of the alkyl group used for the manufacture of LAS detergent.

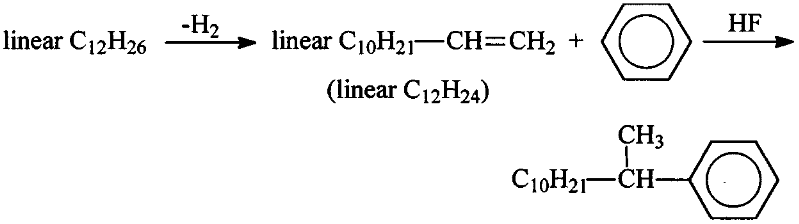




+ 3, 4, 5, and 6-phenyl isomers

C_{10}-C_{14}; 2, 3, 4, 5, 6-isomers; *o* + *p*

The other 60% of the alkyl groups for LAS detergents are made through linear α-olefins. *n*-Alkanes can be dehydrogenated to α-olefins, which then can undergo a Friedel-Crafts reaction with benzene as described above for the nonlinear olefins. Sulfonation and basification gives the LAS detergent.



Alternatively, linear α-olefins can be made from ethylene using Ziegler catalysts to give the ethylene oligomer with a double-bonded end group.

$$6CH_2{=}CH_2 \xrightarrow{\Delta} C_{10}H_{21}{-}CH{=}CH_2$$

$$\text{(linear } C_{12}H_{24})$$

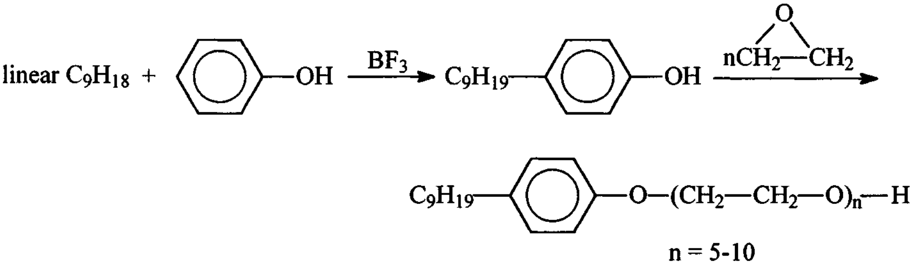
LAS detergents made from the chlorination route have lower amounts of 2-phenyl product. Use of the α-olefins gives greater 2-phenyl content, which in turn changes the surfactant action somewhat. LAS detergents for many years had the highest percentage of the market, but now they own 19% of production for the major household surfactant market.

4. NONIONICS

4.1 Nonylphenol Ethoxylates (NPE)

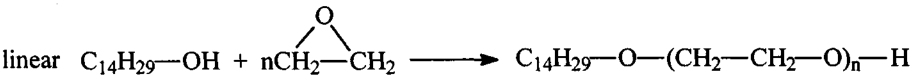
In nonionics the molecule has a nonpolar hydrophobic portion and a more polar, but not ionic, hydrophilic part capable of hydrogen bonding with water. For some years the major nonionics were the reaction products of ethylene oxide and nonylphenol and are called nonylphenol ethoxylates

(NPE). Dehydrogenation of *n*-alkanes from petroleum (C_9H_{20}) is the source of the linear nonene. They still have 13% of the production for the major household surfactant market.



4.2 Alcohol Ethoxylates (AE or AEO)

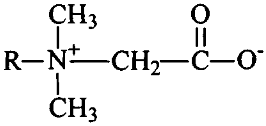
These are polyoxyethylene derivatives of straight-chain primary or secondary alcohols with C_{10}-C_{18}. These linear alcohol ethoxylate nonionics (AE or AEO) are more biodegradable than nonylphenol derivatives and have better detergent properties then LAS. They require fewer phosphates and work well in energy-saving cooler wash water. Nonionics are the fastest growing type of surfactant and now the biggest market in terms of production, holding 34% of production for the major household surfactant market, having surpassed LAS in the 1990s.

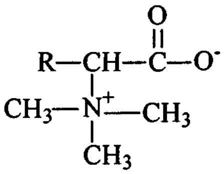


$$\text{linear } C_{14}H_{29}\text{—OH} + nCH_2\text{—}CH_2\ (\text{epoxide}) \longrightarrow C_{14}H_{29}\text{—O—}(CH_2\text{—}CH_2\text{—}O)_n\text{—H}$$

5. AMPHOTERICS

These surfactants carry both a positive and a negative charge in the organic part of the molecule. They have a long hydrocarbon chain as the hydrophobic tail. They may behave as anionics or cationics depending on





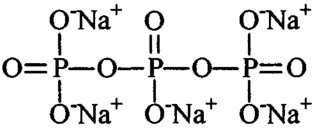
the pH. They are derivatives of amino acids and may have one of two general formulas, where R is linear C_{12}-C_{18}. Amphoterics are used in shampoos. Near pH = 7 they are less irritating and "milder." They can be used with alkalies for greasy surfaces as well as in acids for rusty surfaces.

6. DETERGENT BUILDERS

The finished household soap or detergent is more than just a surfactant. It is a complex formulation that includes bleaches, fillers, processing aids, fabric softeners, fragrances, optical brighteners, foam stabilizers, soil-suspending agents, corrosion inhibitors, foam regulators, solubilizers, antiredeposition agents, dye fixatives, enzymes for stain removal, and opacifying agents. We will not discuss all of these. Recent work on bleaching agents have shown sodium perborate and sodium percarbonate to be replacements of choice for chlorine-containing bleaching agents.

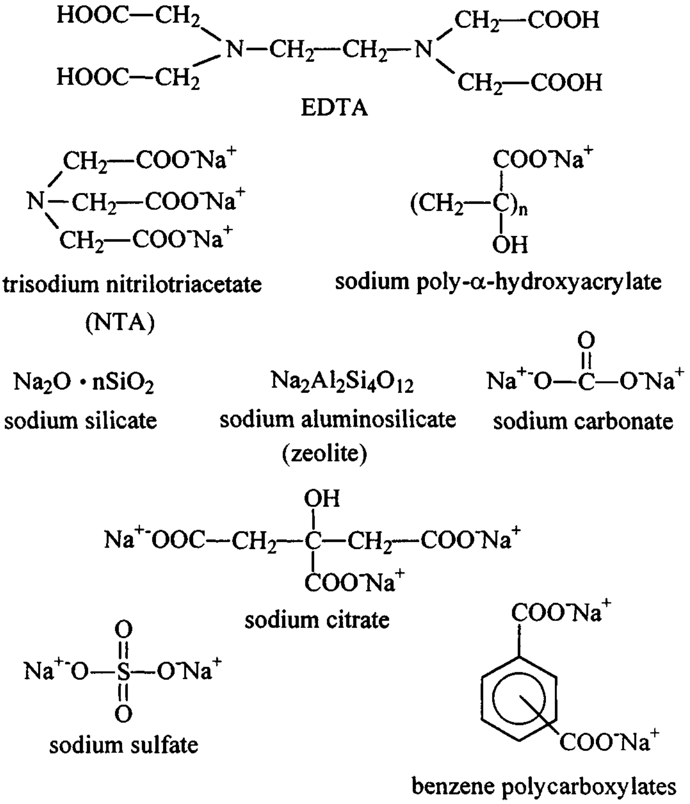
One of the most important and controversial materials in a detergent is the builder, phosphate being a common one. Although the calcium and magnesium salts of dodecylbenzenesulfonic acid are more soluble than those of fatty acids, these ions in solution interfere with the dislodging of dirt from the substrate, and the dirt-suspending power is also affected because of their double positive charge. A chemical must be added to the detergent to sequester or complex the ions. These are called *builders*. Builders are actually an average of 58% by weight of the chemicals found in a detergent, with the surfactants only 36%, and other additives making up the remaining 6%.

The first important commercial builder was sodium tripolyphosphate, $Na_5P_3O_{10}$, first used with Tide® detergent in 1947. Besides sequestering polyvalent metal ions, it prevents redeposition of dirt, buffers the solution to pH = 9-10, kills bacteria, and controls corrosion and deposits in the lines of automatic washers.



$$O{=}\overset{O^-Na^+}{\underset{O^-Na^+}{P}}-O-\overset{O}{\overset{\|}{\underset{O^-Na^+}{P}}}-O-\overset{O^-Na^+}{\underset{O^-Na^+}{P}}{=}O$$

In the late 1960s phosphate builders came to be seen as an environmental problem. Phosphates pass unchanged through sewage works and into rivers and lakes. Since they are plant nutrients they cause blue-green algae to grow at a very fast rate on the surface, causing oxygen depletion. This is called *eutrophication*. The search for phosphate substitutes began, and about half



EDTA

trisodium nitrilotriacetate (NTA)

sodium poly-α-hydroxyacrylate

$Na_2O \cdot nSiO_2$ sodium silicate

$Na_2Al_2Si_4O_{12}$ sodium aluminosilicate (zeolite)

sodium carbonate

sodium citrate

sodium sulfate

benzene polycarboxylates

Figure 24.4 Phosphate substitutes.

the states have banned their use. Currently nearly all laundry detergents do not use phosphates. Phosphate use in laundry detergents declined from 2 billion lb in 1970 to almost zero in 1995. Figure 24.4 lists some of the compounds tried as phosphate substitutes.

Ethylenediaminetetracetic acid (EDTA) is a good sequestering agent but its cost is excessive. Nitrilotriacetate is effective but has been suggested to be teratogenic and carcinogenic so it is not used in the U.S. Sodium citrate is harmless but does not work well. Benzene polycarboxylates are expensive and are not biodegradable. Sodium carbonate is successful except in hard water areas. Commercial use of zeolites and poly-α-hydroxyacrylate has begun. Sodium sulfate occurs as a by-product of any sulfate or sulfonate detergent, but has limited use as a builder, as does sodium silicate. Phosphates have been replaced largely with zeolites and sodium carbonate, with the aid of newer antideposition aids like acrylic polymers. Only about 50% of phosphate came from detergents, with 33% from household wastes and 17% from fertilizer runoff contributing to eutrophication, so we must be watchful of pollution from other sources. The search for phosphate substitutes will probably continue.

Suggested Readings

Chemical and Engineering News, an annual product report entitled "Soaps and Detergents," usually published in a January issue.

Kent, *Riegel's Handbook of Industrial Chemistry*, pp. 1012-1049.

Wittcoff and Reuben, *Industrial Organic Chemicals in Perspective. Part Two: Technology, Formulation, and Use*, pp. 182-212.

Chapter 25

The Chemical Industry and Pollution

1. INTRODUCTION

There are many areas of the chemical industry that must be controlled to avoid ill effects on health and the environment. Throughout this book we have tried to stress individual pollution-related problems. The details of these topics can be found in various chapters. A list of these subjects already discussed is given in Table 25.1. You may wish to review these topics at this time.

The purpose of this chapter is to summarize and generalize the various pollution, health, and environmental problems especially specific to the chemical industry and to place in perspective government laws and regulations as well as industry efforts to control these problems. A brief survey of air and water pollution problems will be given, but these are characteristic of all industry and the topics are too vast to be covered adequately in this book. We will be more concerned with toxic chemical pollution and its control and will spend some time on the Toxic Substances Control Act (TSCA, TOSCA) of 1976 and the Toxic Release Inventory (TRI) list begun in 1988.

Table 25.1 Environmental Problems Discussed Previously

Subject	Chapter	Section
SO_2 in the atmosphere from H_2SO_4 plants	2	2.2.2
Road deicing and its effect on local plant life	5	3
Electrolysis of brine in mercury cells	6	2.2.2
Combustion of petroleum containing sulfur and nitrogen	7	2
Tetraethyllead and contamination of the air	7	4
Disadvantages of burning unleaded gasoline	7	4
Sulfur extraction from petroleum and natural gas	7	5, 9
Chlorofluorocarbons and ozone depletion	12	4
Threshold limit values of organic chemicals	8-13	
Known and suspected organic carcinogens	8-13	
Recycling of plastics	16	5
Recycling of elastomers	18	10
Coatings solvents and air pollution	19	6
Toxicity and persistency of chlorinated pesticides	20	3.2.1
Polychlorinated biphenyls	20	3.2.3
Toxicity of other types of pesticides	20	3,4
Dioxin toxicity and teratogenicity	20	4.1
Pollution problems of various pulping processes	22	3.2
Bleaching and recycling of pulp	22	4
Health risks and side effects of some drugs	23	
Biodegradable vs. nonbiodegradable detergents	24	3.2, 3.5
Phosphate substitutes in detergents	24	6
Phosphate and eutrophication of lakes	24	6

2. GENERAL POLLUTION PROBLEMS

2.1 Air Pollution

Since the advent of the Industrial Revolution there has been an air pollution problem. For years the control of air pollutants was nonexistent. Many industries and governments suggested that "the solution to pollution is dilution," that is, build larger and higher smokestacks to dilute and disperse the fumes before health or the environment are affected. This can no longer be diluted to insignificant concentrations, especially in large metropolitan areas. In 1873 several thousand people died in London because of air pollution. In 1952 another acute air problem in London killed 4,000 people. In 1909 approximately 1,000 deaths were attributed to "smog" in Glascow, Scotland, the first time this word was used. We are all familiar with the continuing battle of the large cities in the U.S. to alleviate the air pollution problem. Recently, the four most important challenges in air pollution control facing all of us (for we are all polluters) are the following:

1. *Acid rain.* Lakes in some areas of the world are now registering very low pH's because of excess acidity in rain. This was first noticed in Scandinavia and is now prevalent in eastern Canada and the northeastern U.S. Normal rainfall is 5.6 (because of CO_2 in the air forming H_2CO_3). However, excessive use of fossil fuels (especially coal) with high sulfur and nitrogen content cause sulfuric and nitric acids in the atmosphere from the sulfur dioxide and nitrogen oxide products of combustion. Some rain in the Adirondack Mountains of upper New York State has been measured with a pH of 3.0. This problem is not specific to the chemical industry but should be of concern to all of us.

$$SO_2 \xrightarrow[H_2O]{O_2} H_2SO_4$$

$$NO_x \xrightarrow[H_2O]{O_2} HNO_3$$

2. *Carbon dioxide content.* The increased burning of fossil fuels in the last couple hundred years is slowly increasing the concentration of carbon dioxide in the atmosphere, which absorbs more infrared radiation than oxygen and nitrogen. Atmospheric carbon dioxide is up more than 10% since 1960. As a result, there is a so-called "greenhouse effect" and the average temperature of the earth may be increasing. The polar ice caps may be melting, oceans may be rising, and more desert areas may be forming. Average global temperatures could rise as much as 2.5-10.4°F during the 21st century unless improvements are made. See the Kyoto agreement in Section 3 under the year 1997. Carbon dioxide is the most important greenhouse gas, but there are five others: methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride.

3. *Lead.* The use of unleaded gasoline is rapidly allowing a solution to this problem. But is the increasing use of aromatic hydrocarbons, necessary for acceptable octane ratings in unleaded gasoline, causing

possible increases in polynuclear aromatic hydrocarbons to be added to our air? Compounds such as benzopyrene are known carcinogens.

4. *CFCs*. This is adequately discussed in Chapter 12, Section 4, but certainly it deserves to be listed here. Chlorine atoms from photodissociation of CFCs in the stratosphere have led to depletion of the ozone layer protecting us from ultraviolet rays. These substances are being phased out. Substitutes have been hard to find. Do we change our way of living by giving up certain products, or do we increase R&D spending to find substitutes more quickly? These questions must be answered.

Things do appear to be improving. In the last few years the level of dust, soot, and other solid particulates in air has decreased. The SO_2 concentration in urban areas has dropped. The CO concentration in urban areas has fallen. In 1970 the Clean Air Amendment allowed the Environmental Protection Agency (EPA) to establish air quality standards and provisions for their implementation and enforcement. This has gone a long way to controlling multi-industrial pollution. This law was strengthened in 1977. The Clean Air Act Amendment of 1990 imposed many new standards. But what have we as individuals done to help? When was the last time we walked instead of drove a car? How many families now get by with *only* one car? How much of our total energy needs are real?

2.2 Water Pollution

A number of critical water problems face us today. We have already discussed information relating to areas of the chemical industry specifically, such as phosphate in detergents and nonbiodegradable detergents. Certainly efforts by general industry must be continued to eliminate local contamination that may occur, whether it be from oil spills or the typical manufacturing plant down the street.

Mercury contamination of water and air has been a known problem for many years, and there is growing concern over it. Methylmercury is an organic form of mercury produced from inorganic mercury by bacteria. Methylmercury accumulates in the food chain and reaches humans, other mammals, and birds through methylmercury-tainted fish. In humans, methylmercury reduces motor skills and dulls the senses of touch, taste, and sight. In severe cases it causes irreversible brain damage and even death. At greatest risk are unborn and young children. Starting in 2000 the EPA began studying mercury emissions from coal- and oil-fired power plants and will regulate them in the future. Other sources of mercury are municipal waste combustors, medical waste incinerators, and hazardous waste combustors. Chlorine-sodium hydroxide plants are smaller generators, but may be a source of 5% of the mercury. That is one reason why mercury chlor-alkali plants are no longer popular.

General sewage problems face every municipal sewage treatment facility regardless of size. Although primary treatment (solid settling and removal) is required and secondary treatment (use of bacteria and aeration to enhance organic degradation) is becoming more routine, tertiary treatment (filtration through activated carbon, applications of ozone, chlorination, etc.) should be set as the ideal for all large urban areas. The 1972 Clean Water Act did some good to improve water quality. It allowed federal funding for sewage treatment, established effluent standards for water quality, and required permits for point-source discharges. The 1987 Clean Water Act did more to guarantee continued progress. Guidelines limiting effluents from chemical plants were developed. Chemical industry facilities are required to sample and monitor stormwater runoff. Wastewater pretreaters that discharge water into sewer systems have requirements. Pollutant standards for sewage sludge are set. States must identify toxic "hot spots" in their water and develop plans to alleviate the problems. In recent years the EPA has found many examples of clear-cut improvements in water quality in the U.S., but much more needs to be done.

3. A CHRONOLOGY OF POLLUTION BY THE CHEMICAL INDUSTRY AND ITS CONTROL

Although general air and water pollution and controls are affected by the chemical industry, these problems and solutions are not unique to our industry. Certainly the area of toxic chemicals is unique. Because this problem is so diverse it is by itself a series of complex pollution problems. We have discussed some of these already (see Table 25.1). We now attempt to summarize these and other toxic chemical problems in chronological order. This includes many examples of pollution caused more specifically by the chemical industry or a closely allied industry as well as the laws and controls that have been enacted by governments and the industry to solve some of these unique problems.

Before 1700: Pollution has been with us a long time. There was copper pollution near Jericho on the west bank of the Jordan river due to *copper smelting* for tool manufacture thousands of years ago. *Deforestation* of many areas near the Mediterranean Sea for the building of ships was a norm. Poor agricultural methods led to soil erosion. In 2500 B.C. Sumerians used *sulfur* compounds to manage insects and in 1500 B.C. the Chinese used natural products to fumigate crops. *Pesticides* began polluting the environment hundreds of years ago. Recent chemical analysis of the Greenland ice sheet has revealed evidence of large-scale atmospheric *lead pollution* dating to A.D. 300 caused by ancient Carthaginian and Roman mines in Spain.

1773: The *LeBlanc* process for making *soda ash* for the growing glass, soap, and paper industries of Europe was discovered in this year. Salt and sulfuric acid were heated to give the salt cake needed to react with limestone in the process. But in addition to the salt cake, large amounts of HCl were also released as a gas into the atmosphere or as hydrochloric acid into water. In 1864 the *Alkali Act* in England became one of the first milestones in pollution control, when the discharge of HCl was forbidden.

$$2NaCl + H_2SO_4 \longrightarrow 2HCl + Na_2SO_4$$

$$CaCO_3 + Na_2SO_4 \longrightarrow Na_2CO_3 + CaSO_4$$

Late 1800s: The *lead chamber process* for manufacturing sulfuric acid was prevalent in this period. *Arsenic* was a common contaminant in the pyrites used as a source of sulfur for this process. Now the cleaner contact process is used and most of the raw material is elemental sulfur.

1906: The Pure Food and Drug Act established the *Food and Drug Administration (FDA)* that now oversees the manufacture and use of all foods, food additives, and drugs. The law was toughened considerably in 1938, 1958, and 1962.

1917: During World War I munitions factory workers making *trinitrotoluene (TNT)* developed *jaundice* from inhaling the dust. Also in 1917 a TNT explosion near Manchester, England killed 41 and wounded 130 additional.

1921: An Oppau, Germany *nitrate plant exploded* killing over 600 people. This was probably the worst ever chemical explosion up to 1984.

1924-25: Illnesses and 15 deaths were recorded at Ethyl Corporation among workers developing *lead gasoline additives*.

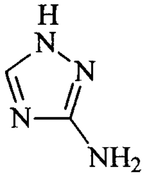
1935: The *Chemical Manufacturers Association (CMA),* a private group of people working in the chemical industry and especially involved in the manufacture and selling of chemicals, established a *Water Resources Committee* to study the effects of their products on water quality.

1947: A French freighter docked in Texas City, Texas caught fire and exploded with 2,500 tons of *ammonium nitrate* on board. Then the nearby Monsanto chemical plant blew up, followed by oil refineries, tin smelters, and tanks filled with chlorine, sulfur, and nitrate. The explosions were more powerful at ground level than the atomic blasts of Hiroshima and Nagasaki. The final toll was 462 dead, 50 missing, 3,000 injured, and $55 million in property damages. This was the worst chemical disaster ever in this country.

1948: CMA established an *Air Quality Committee* to study methods of improving the air that could be implemented by chemical manufacturers.

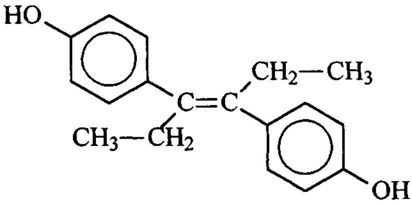
1958: The *Delaney Amendment* to the Food and Drug Act defined and controlled *food additives.* After this passed, any additives showing an increase in cancer tumors in rats, even if extremely large doses were used in the animal studies, had to be outlawed in foods. This controversial law is still being debated today and has been used to ban a number of additives including the artificial sweetener cyclamate. The wording of the Delaney amendment may not be appropriate today. It is possible that some substances may cause cancer in rats at high doses, but not cause a health problem for humans in more common amounts.

1959: Just before Thanksgiving the government announced that it had destroyed *cranberries* contaminated with a chemical, *aminotriazole,* which produced cancer in rats. The cranberries were from a lot frozen from two years earlier when the chemical was still an approved weed killer. The animal studies were not completed until 1959. Even though there was no evidence that the 1959 crop was contaminated, cranberry sales dropped precipitously and public fears about dangerous chemicals in food lingered.



aminotriazole

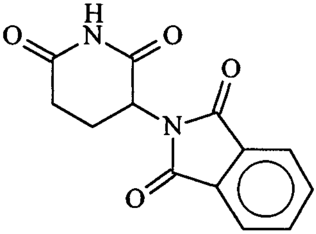
1960: *Diethylstilbestrol (DES),* taken in the late 1950s and early 1960s to



diethylstilbestrol

prevent miscarriages and also used as an animal fattener, was reported to cause vaginal *cancer* in the daughters of these women and caused premature deliveries, miscarriages, and infertility in the daughters.

1962: *Thalidomide,* a prescription drug used as a tranquilizer and flu medicine for pregnant women in Europe to replace dangerous barbiturates that caused 2,000-3,000 deaths per year by overdoses, was found to cause *birth defects.* Thalidomide had been kept off the market in America because a government scientist insisted on more safety data for the drug, but 8,000-10,000 deformities were reported in Europe, especially in Germany. In 1962 the *Kefauver-Harris* Amendment to the Food and Drug Act began requiring that drugs be *proven safe* before being put on the market. For a new use of thalidomide, see 1998.



thalidomide

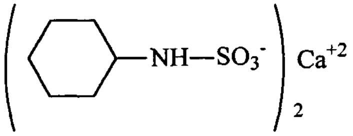
1962: A marine biologist by the name of *Rachel Carson* published her book entitled *Silent Spring* outlining many environmental problems associated with *chlorinated pesticides,* especially DDT. Introduced during World War II, DDT was found to be very effective against insects, was cheap, convenient to use, and had lasting pesticidal action. Its acute toxicity to humans in normal exposure was low. But it was found to accumulate in the body's fatty deposits, had side effects on wildlife, and was very persistent in the environment. Carson's book set off an extensive debate about safety of many different types of toxic chemicals, a debate that is still going on today. Despite some shortcomings *Silent Spring* forced industry to take a hard look at the way their products were affecting the environment. DDT was banned in the U.S. in 1972, and most chlorinated insecticides are now banned.

1965: *Nonlinear, nonbiodegradable synthetic detergents* made from propylene tetramer were banned after these materials were found in large amounts in rivers, so much as to cause soapy foam in many locations. *Phosphates* in detergents were also being investigated for their *eutrophication* effect on lakes. They were later banned in detergents by many states in the 1970s.

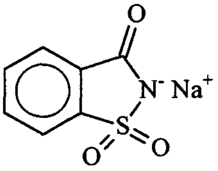
1965: A strange disease was reported in the area around *Minamata Bay* in Japan. Forty-six people died and many more became ill. The illness was due to *mercury poisoning* from a plastics factory. The Chisso Corporation used mercury as a catalyst in making acetaldehyde. Dimethylmercury becomes concentrated up the food chain and the heavy reliance on food from the sea life in the bay caused the epidemic. Mercury became a source of worry in many U.S. rivers and has been monitored closely since then. Chisso was finally found guilty in 1973, and 300 people had died by 1980.

1966: *Polychlorinated biphenyls (PCBs)* were first found in the environment and in contaminated fish. They were banned in 1978 except in closed systems.

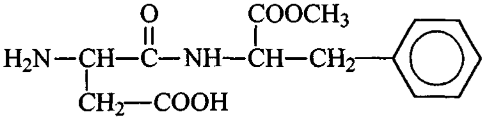
1969: The artificial sweetener *cyclamate* was banned because of a study linking it to *bladder cancer* in rats when large doses were fed. At least 20 subsequent studies have failed to confirm this result but cyclamate remains banned. In 1977 *saccharin* was found to cause cancer in rats. It was banned by the FDA temporarily, but Congress placed a moratorium on this ban because of public pressure. In 1992 it was found that saccharin may cause cancer in rats but not in humans. Saccharin is still available today. A more recent sweetener, aspartame (Nutrasweet®), has also come under attack but has not been proven to be a problem since its introduction in 1981.



calcium cyclamate



sodium saccharin



aspartame

1970: A nationwide celebration, called *Earth Day,* especially on college campuses across the U.S., emphasized respect for the environment and an increased awareness by industry and the public about the effects of many substances on the fragile environment. Over 20 million Americans participated.

1970: The *Clean Air Amendment* was passed. This is described earlier in this chapter. It was strengthened in 1977 and 1990.

1971: After *TCDD (dioxin)* had been found to be a contaminant in the herbicide 2,4,5-T and was tested as a teratogen in rats in 1968, the herbicide was outlawed by the EPA on most food crops. A complete discussion of this chemical and its history is given in Chapter 22, Section 4.1.

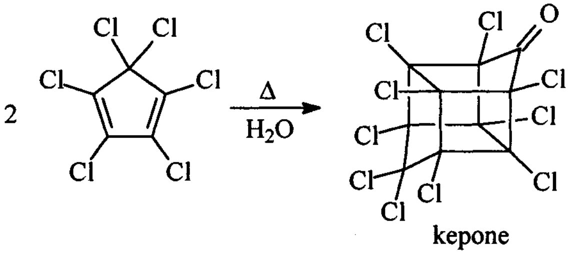
1971: CMA established the *Chemical Emergency Transportation System (CHEMTREC)* to provide immediate information on chemical transportation emergencies. In 1980 this was recognized by the Department of Transportation as the central service for such emergencies.

1972: The *Clean Water Act* was passed. This is discussed earlier in this chapter. It was strengthened in 1987.

1974: A *nylon 6* plant in *Flixborough, England* exploded during the oxidation of cyclohexane to cyclohexanone. Twenty-eight people were killed. Although it was not a pollution problem, it certainly increased public concern about the chemical industry at a time when it was undergoing vigorous scrutiny.

1974: Three workers in a Goodrich *poly(vinyl chloride)* plant in Louisville developed a rare *angiosarcoma of the liver.* This started the investigation of vinyl chloride as a possible carcinogen.

1975: The state of Virginia closed a *kepone* pesticide plant because 70 of the 150 employees were suffering from kepone poisoning. The James River, which furnishes one fifth of all U.S. oysters, was contaminated. Kepone is made by dimerizing hexachlorocyclopentadiene and hydrolyzing to a ketone. Kepone is now banned.



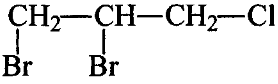
1976: A plant manufacturing 2,4,5-trichlorophenol in *Seveso, Italy* exploded and liberated substantial amounts of *TCDD (dioxin).* Although it caused quite a scare and the town was evacuated, there were no known deaths and no increase in birth defects reported. Some chloracne (a skin disease) occurred and one liver cancer was diagnosed.

1976: *The Toxic Substances Control Act (TSCA or TOSCA) was initiated.* It has far-reaching effects specifically for the chemical industry and will be discussed in detail in the next section. An immediate effect that it had was to direct the EPA to develop rules to limit manufacture and use of *PCBs.*

1976: *The Resource Conservation and Recovery Act (RCRA)* was passed. It became effective in 1980, which governs in detail how generators of chemical wastes manage their hazardous wastes. This includes the generation, handling, transportation, and *disposal of hazardous wastes.*

1977: *Polyacrylonitrile* plastic bottles for soft drinks and beer were taken off the market as possible carcinogens because of migration of acrylonitrile into the drink. Now most plastic food containers of this type are poly(ethylene terephthalate).

1977: Employees in an Occidental Petroleum plant manufacturing *dibromochloropropane (DBCP)* became *sterile.* DBCP was used as a soil fumigant and nematocide. It is now banned.

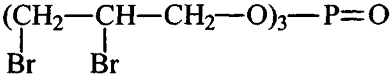


$$\underset{Br}{CH_2}-\underset{Br}{CH}-CH_2-Cl$$

DBCP

1977: *Benzene* was linked to an abnormally high rate of *leukemia* at a Goodyear plant. This further increased the concern with benzene use in industry.

1977: *Tris(2,3-dibromopropyl)phosphate (Tris),* used to treat children's sleepwear to reduce flammability, was banned from use. The chemical was linked to *kidney cancer* in mice and rats and was mutagenic in bacteria. At the time it was used on 40-60% of children's sleepwear, mostly polyester, to enable it to meet federal requirements for flame retardance.



$$(\underset{Br}{CH_2}-\underset{Br}{CH}-CH_2-O)_3-P{=}O$$

Tris

1978: There was a ban on *chlorofluorocarbons (CFCs) as aerosol propellants* because they may react with ozone in the stratosphere, increase the penetration of ultraviolet sunlight, alter the weather, and increase the risk of skin cancer. CFCs are discussed in Chapter 12, Section 4.

1978: An old chemical dump in Niagara Falls, New York, near *Love Canal,* began leaking into the environment. A state of emergency and an evacuation of the neighboring area resulted. This episode helped approve the 1980 "Superfund" law. In 1994, OxyChem agreed to pay New York $98 million.

1980: *Asbestos* dust had been known for years in industry to cause a rare form of *lung cancer* when inhaled. A rule in 1980 caused regulation of asbestos use and repair in school buildings.

1980: The *Comprehensive Environmental Response, Compensation, and Liability Act* established a $1.6 billion, five-year *"Superfund"* to clean up landfills. This was funded by the chemical industry (87.5%) and general government revenues (12.5%). It was expanded in dollar amount and in number of landfills affected later.

1982: Bottles of *Tylenol®,* a common pain reliever, were found to contain *sodium cyanide* that had purposely been placed there. Seven deaths occurred in Chicago. The murderer has never been found. This incident caused stricter packaging guidelines for the pharmaceutical industry. Most drugs now are sealed into their containers with a plastic or metal wrapping that cannot be removed without it being noticed.

1983: Over a two-year period 600 people in Spain died from so-called *"olive oil"* bought from door-to-door salesman. It actually was oil contaminated with toxic chemicals and was to be used industrially only.

1984: On December 3 the *worst* chemical and general *industrial accident* in history occurred in *Bhopal, India.* A Union Carbide plant making carbamate insecticide accidentally added water to one of their underground storage tanks for the very toxic chemical *methyl isocyanate (*MIC) used in the manufacture of their largest selling carbamate, carbaryl or Sevin®. Isocyanates react exothermically with water and methyl isocyanate has a low bp, 39°C. As the tank heated up some of the isocyanate was hydrolyzed with a caustic safety tank, but a large amount escaped into the atmosphere. At least 2,500 people, perhaps as many as 10,000, died that night in the neighborhood next to the plant. As much as 54,000 lb of MIC may have escaped. A detailed reassessment of safety and environmental standards for many chemical plants has resulted. Suits against Union Carbide were filed. In 1989 Carbide agreed to pay a total of $470 million.

1985: Three employees of a silver recovery firm near Chicago were convicted of *murder.* Film Recovery Systems *recovered silver* from used X-ray films using *sodium cyanide.* In 1983 a worker became ill and died. Cyanide level in the blood was a lethal dose. The president and part owner, the plant manager, and the plant foreman were responsible. Plant safety conditions were completely inadequate and much different from that found with any other company, but it is a landmark decision because it was the first time murder was levelled against corporate officials.

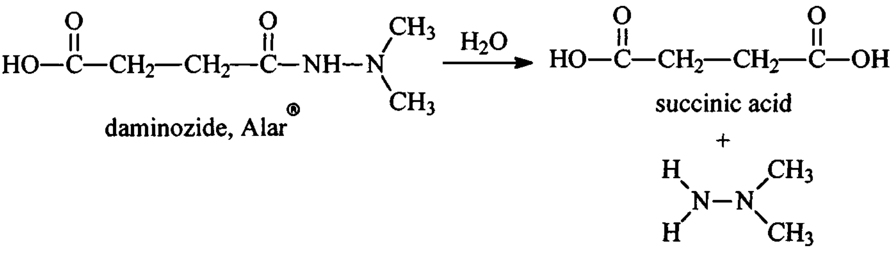
1986: The *Safe Drinking Water Act Amendments* required EPA to set standards for 83 chemicals.

1986: The *Emergency Planning and Community-Right-to-Know Act* was signed into law. Companies involved in the production and handling of hazardous materials must submit *material safety data sheets* (MSDS) or lists of chemicals kept on site. Companies must report inventories of specific chemicals kept in the workplace and an annual release of hazardous materials into the environment.

1986: The *Superfund Amendments and Reauthorization Act* of 1986 established a $9 billion, five-year fund to pay for continued cleanup of 375 hazardous waste sites. Over 30,000 sites have been inventoried, over 1,100 are on the National Priority List for cleanup, hundreds have had short-term cleanups, but only a small number have had complete cleanups.

1988: The *Chemical Diversion and Trafficking Act* contains three key provisions to address the problem of diverting chemicals to make illegal drugs: (1) the seller of chemicals must keep detailed records; (2) sellers must report suspicious purchases and unusual or excessive losses; and (3) the Drug Enforcement Administration is authorized to control export and import transactions.

1989: The *Great Apple Scare* occurred. Alar®, or daminozide, was found in apples and apple products as a residue. It is a growth regulator that keeps apples longer on trees and helps yield more perfectly shaped, redder, firmer fruit. It also maintains firmness in stored apples by reducing ethylene production. Concern about Alar®'s carcinogenicity focussed not on the compound itself, but on a breakdown product, unsymmetrical dimethylhydrazine (UDMH). Heat treatment in apple processing can cause Alar® to break down. Uniroyal, its producer, voluntarily halted sales in the U.S. for food uses.



daminozide, Alar®

succinic acid

UDMH

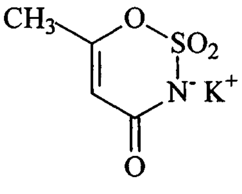
1990: The *Pollution Prevention Act* was passed to focus on preventing pollution at the source rather than dealing with remediation or capture of pollutants. This led the EPA to start its *Green Chemistry Program* in 1991. See this chapter, Section 7.

1989-91: A recent series of *four serious explosions* over these three years, though unrelated to each other, caused renewed concern over plant safety. In 1989 one of the world's largest HDPE plants, owned by Phillips 66 in Pasadena, TX, exploded when ethylene and isobutane leaked from a pipeline. Twenty were killed. In 1990 an Arco Chemical Co. plant in Channelview, TX had an explosion in the petrochemicals complex which killed 17. A treatment tank of wastewater and chemicals blew up. These two accidents in the Houston area caused more deaths than the previous ten years combined. A 1991 explosion in Sterlington, LA of an Argus Chemical nitroparaffin plant resulted in eight deaths. Nitroparaffins are used in pharmaceuticals, fine chemicals, cosmetics, and agrochemicals. Also in 1991 an explosion of an Albright & Wilson Americas plant in Charleston, SC killed six. Ironically Antiblaze 19®, a phosphonate ester and flame retardant used in textiles and polyurethane foam, was being manufactured from trimethyl phosphite, dimethyl methylphosphonate, and trimethyl phosphate.

1996: The *Food Quality Protection Act (FQPA)* requires the EPA to conduct a review of pesticides that pose the most danger to human health. The EPA must make sure the pesticides meet new safety standards specifically designed to protect children.

1997: The EPA passed its *"Cluster Rule"* that requires kraft and soda pulp mills to utilize *elemental chlorine-free (ECF) bleaching* and all sulfite mills to use ECF or *totally chlorine-free (TCF) bleaching.*

1998: *Acesulfame-K* was approved as a new artificial sweetener for Pepsi One. It was the first sweetener approved since aspartame in 1981.



acesulfame-K

1998: The world was hotter than at any time in the last 600 years. *Global warming* is likely human-made, due to the massive burning of fossil fuels since the industrial revolution.

1998: *Thalidomide* (see also 1962) was placed back on sale to treat *leprosy*. It may also alleviate the symptoms of *AIDS* and some cancers.

2000: Governments from around the world agreed to eliminate or minimize use of toxic chemicals that persist in the environment, now called *persistent organic pollutants (POPs)*, which include many chlorinated hydrocarbons such as DDT and PCBs. The accord allows some developing countries to continue using DDT for controlling malaria. It also allows use of PCBs in electrical equipment until 2025, provided the equipment is maintained to prevent leaks.

2001: *TCDD (dioxin)*, long considered as a very toxic chemical, was reclassified as a known human carcinogen (see also 1971).

4. THE TOXIC SUBSTANCES CONTROL ACT (TSCA)

Probably the law that has specifically affected the chemical industry the most is the Toxic Substances Control Act (TSCA). Since it was signed on October 11, 1976 and became effective on January 1, 1977, it has caused many changes in the industry and will create further modifications in the years to come. The basic thrust of the law is threefold: (1) to develop data on the effects of chemicals on our health and environment, (2) to grant authority to the EPA to regulate substances presenting an unreasonable risk, and (3) to assure that this authority is exercised so as not to impede technological innovation.

TSCA is a "balancing-type law." It is concerned with unreasonable risks. It attempts to balance risks versus benefits for all chemicals and uses. The EPA administrator must consider (1) effects on health, (2) effects on the environment, (3) benefits and availability of substitutes, and (4) economic consequences.

Specific bans on chemicals or uses have not been the most important outcome of TSCA. Only one type of chemical, PCBs, was specifically targeted in the original law and they are now outlawed in most of their uses. EPA administration of the law in its early years led to a ban of chlorofluorocarbons as aerosol propellants, restrictions on dioxin waste disposal, rules on asbestos use, and testing rules on chlorinated solvents. It has led to a central bank of information on existing commercial chemicals, procedures for further testing of hazardous chemicals, and detailed permit requirements for submission of proposed new commercial chemicals.

After TSCA was passed the EPA began a comprehensive study of all commercial chemicals. Of the 55,000 chemicals made commercially only 9.9% of them are made at the 1 million lb/yr or more level. These account for 99.9% of all chemical production. Detailed records are now available through the TSCA Chemical Substance Inventory, which has information on 62,000 chemicals. Material Safety Data Sheets (MSDS) have been published for thousands of chemicals.

Many government and private organizations are involved in determining the safety of chemicals, including the EPA, the Occupational Safety and Health Administration, and the Department of Health and Human Services. They provide lists of dangerous chemicals and descriptions of the dangers. The EPA's current list of Extremely Hazardous Substances contains 357 chemicals. The 9th Report on Carcinogens published by the National Toxicology Program of the Department of Health and Human Services lists 65 substances that are Known to be Human Carcinogens. It also lists 242 substances Reasonably Anticipated to be Human Carcinogens. Many of these lists and MSDSs are available on the Internet.

The EPA requires companies to submit premanufacturing notices (PMNs) 90 days before a chemical's manufacture is started. EPA may stop the manufacture or prohibit certain uses. The PMN must include detailed information. They were initiated in 1979. Some 1,100 were filed from 1979-1981 and the number now averages 700 new PMNs per year. About 1-7% are chemicals of concern. The PMN system has been criticized by many in the industry. There has been a 54% decline in new chemical introductions since PMNs have been initiated. Eventually it may concentrate new product development into large companies that can afford the extra testing and administrative costs.

The cost of TSCA administration is high. Hundreds of people are now employed in the Office of Toxic Substances. Direct public and private costs total millions of dollars and there may be other indirect costs that cannot be estimated. Certainly some things could be done to get more for our money. The PMN system could be modified to spend less time on low-risk chemicals. The ability to regulate existing chemicals should be increased. Voluntary compliance by industry should be stressed because it is cheaper and more efficient, but this must obviously be backed up by the possibility of regulatory action by the government.

The final verdict is still out on whether TSCA is sufficient to maintain adequate control of toxic chemicals. The years ahead may show that further regulation, legislation, and enforcement are necessary or that less is optimum to avoid restrictions on innovation. No doubt, just as now, a variety of opinions will exist.

5. TOXIC RELEASE INVENTORY (TRI)

In 1988 the EPA began requiring companies to report the amount of toxic chemical release to the environment. Originally listed for 328 chemicals, the list has grown to over 600 chemicals. This Toxic Release Inventory (TRI) includes chemical releases, transfers, and disposal. Over the years that it has been in existence the total amount of chemicals has fallen. In the manufacturing industries there has been a 46% decrease over the 12-year history of the program. Unfortunately the downward trend in the manufacturing sector (including the chemical industry) was overwhelmed by hundred of millions of lb of increases in TRI releases by mining just from 1998 to 1999 alone. Thus TRI chemicals for all industries collectively increased 5.0% from 1998 to 1999, rising from 7.38 billion lb to 7.75 billion lb. Chemical industry releases declined 2.4% from 687 million lb to 670 million lb in this same year. Interestingly, chemical wholesale distributors had an increase in release for 1998 to 1999, especially in air emissions of solvents. Chemical producers did better than even the manufacturing sector as a whole and had decreased emissions.

TRI data on substances released by chemical manufacturers show nitrate compounds topped the list in 1999. They were discharged mainly into surface waters, and another third were injected underground. Second was ammonia, mainly emitted into the air, with some injected underground. Methanol was third mostly into the air. Carbon disulfide was fourth, discharged mainly into the air, and chromium compounds were fifth, disposed on land. The amounts are listed in Table 25.2.

Overall, the chemical industry ranked third among sectors that must report to TRI. Metal mining was first, accounting for more than half of all total TRI releases of 7.5 billion lb, with nearly 4 billion lb, released to land. Electric utilities were second. Half of their emissions were hydrochloric acid aerosols from fossil fuel combustion. Percentages of TRI releases are given in Table 25.3. Overall, we should feel good, since the chemical

Table 25.2 TRI Releases by Chemical Manufacturers, Million Lb

Nitrate compounds	123
Ammonia	100
Methanol	47
Carbon disulfide	27
Chromium compounds	25

Source: EPA and *Chemical and Engineering News*

Table 25.3 TRI Releases by Sector

Metal mining	51%
Electrical utility	15
Chemical	9
Primary metal	8
Solvent recovery	4
Miscellaneous	13

Source: EPA and *Chemical and Engineering News*

industry releases have fallen from nearly 800 million lb in 1995 to close to 600 million lb in 1999. The chemical industry releases are mainly air emissions and underground injection, though some are water discharges and releases to land.

6. HIGH PRODUCTION-VOLUME (HPV) CHEMICALS

The chemical industry has initiated a voluntary program with its high production-volume (HPV) chemicals, those manufactured in or imported into the U.S. in volumes of 1 million lb or more per year. In 1998 the EPA, the Chemical Manufacturers Association, and the Environmental Defense Fund issued a challenge to 900 companies to sponsor environmental and health testing for 2,800 HPV chemicals and to make the data available to the public by 2004. Many larger companies are participating, nearly 200 companies for 1,100 compounds by 1999. The primary concern to small companies is the cost, which has been estimated to be $270,000 per compound. The total cost to industry will be $500 million. It will be interesting to see how well this program succeeds and what information this program will provide.

7. ARE THINGS BETTER TODAY?

Since the beginning of the environmental movement in the 1960s many people have asked repeatedly if we better off environmentally today and, if so, can we do even more than we have done? In some respects we see a bad side. The chemical industry still has a large amount of toxic chemical emissions. Pollution control is getting more expensive. On the brighter side, chemical industry releases are decreasing annually. It is spending more money on pollution control. From 1986-2000 electrical productivity, measured as the amount of electricity needed to produce a unit of production, declined 21% in the chemical industry. There are more employers working with environmental problems. The chemical industry is a safe industry.

Another bright spot is that "green chemistry" is becoming more and more popular. It is defined as the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment. Green chemistry interest started in earnest with the 1990 Pollution Prevention Act. There are many principles of green chemistry. Waste prevention is better than having to treat or clean up waste after it has been created. This can include using less toxic chemicals, making safer but still effective chemicals, using less hazardous solvents, requiring less energetic processes, employing catalysts rather than stoichiometric reagents, having materials that will decompose easily to non-polluting degradation products in the environment, and requiring safer processes.

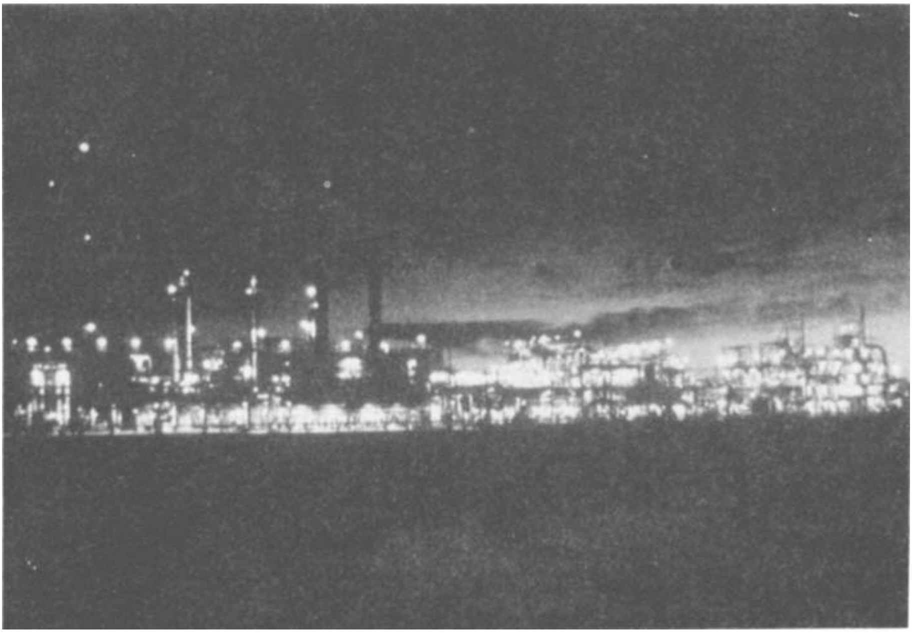


Figure 25.1 Sunset on a chemical plant. (Courtesy of BP Chemicals, Alvin, Texas)

In summary, it does appear that dramatic improvements have been made in pollution control by the chemical industry, but we need to try harder if we are to be even more successful at improving our environment.

Suggested Readings

Chemical and Engineering News, selected articles, 1980-2001.

Davis, L.N. *The Corporate Alchemists*; William Morrow & Co.: New York, 1984.

Ingle, G.W., Ed. "TSCA's Impact on Society and the Chemical Industry," ACS Symposium Series; ACS: Washington, DC, 1983.

Appendix—Subjects for Further Study

This book contains some information on approximately 90% of the chemical and related industries. This material can be covered well in a one-semester course. Examples of special areas of industrial chemistry are listed below and are ideal for study via written or oral reports, or for self-study. Good starting points for these are the Kirk-Other or Ullmann encyclopedias.

Asbestos
Battery technology
Cancer drugs
Catalysts in industry
Ceramics
Coal technology
Cosmetics
Dyes and pigments
Explosives
Fermentation processes
Fibers, specialty
Flame retardants
Flavors
Food additives
Fragrances
Fuel cells
Glass
History of industrial chemistry
Industrial solvents
Metals and alloys
Nuclear power
Oils, waxes, and fats
Photographic products
Plasticizers
Plastics additives
Plastics, specialty, engineering
Pollution control technology
Portland cement
Steel Manufacture
Sugars
Sweeteners, artificial
Synthetic fuels
Vitamins
Zeolites

List of Important References

There are a variety of useful sources for obtaining information on industrial chemistry. The following list is not exhaustive. In the book an attempt has been made to specify appropriate reading for each chapter. Some references are given in shortened form at the end of each chapter by citing the author's name and book title. These references, as well as some of the others the author has found useful, are given below.

Books

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Austin, G.T. *Shreve 's Chemical Process Industries*, 5th ed.; McGraw-Hill: New York, 1984.

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Heaton, A. *The Chemical Industry*, 2nd ed.; Blackie Academic and Professional: New York, 1994.

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Kent, J.A. *Riegel's Handbook for Industrial Chemistry*, 9th ed.; Van Nostrand Reinhold: NewYork, 1992.

Kroschwitz, J.I. *Concise Encyclopedia of Polymer Science and Engineering*; John Wiley & Sons: New York, 1990.

Lowenheim, F.A.; Moran, M.K. *Faith, Keyes, and Clark's Industrial Chemicals*, 4th ed.; John Wiley: New York, 1975.

Reddy, M.A.; Darnay, A.J. *Market Share Reporter*; Gale Research: Detroit, 1995.

Reddy, M.A.; Lazich, R.S. *World Market Share Reporter*; Gale Research: New York, 1995.

Reuben, B.G; Burstall, M.L. *The Chemical Economy*; Longmans: London, 1973.

Reuben, B.G.; Wittcoff, H.A. *Pharmaceutical Chemicals in Perspective*; John Wiley: New York, 1989.

Silverman, H.M., Ed. *The Pill Book*; 9th ed.; Bantam Books: New York, 2000.

Stocchi, E. *Industrial Chemistry*, vol. 1; Ellis Horwood: New York, 1990.

Szmant, H.H. *Organic Building Blocks of the Chemical Industry*; John Wiley: New York, 1989.

Thompson, R. *Industrial Inorganic Chemicals*; 2nd ed.; Royal Society of Chemistry: Cambridge, 1996.

Ulrich, H. *Raw Materials for Industrial Polymers*; Oxford University Press: New York, 1988.

Weissermel, K.; Arpe, H.J. *Industrial Organic Chemistry*; 2nd ed.; VCH: New York, 1993.

White, H.L. *Introduction to Industrial Chemistry*; John Wiley: New York, 1986.

Wittcoff, H.A.; Reuben, B.G. *Industrial Organic Chemicals*; John Wiley: New York, 1996.

Wittcoff, H.A.; Reuben, B.G. *Industrial Organic Chemicals in Perspective. Part One. Raw Materials and Manufacture*; John Wiley: New York, 1980.

Wittcoff, H.A.; Reuben, B.G. *Industrial Organic Chemicals in Perspective. Part Two. Technology, Formulation, and Use*; John Wiley: New York, 1980.

Wiseman, P. *Petrochemicals*; Ellis Horwood Limited: Chichester, 1986.

Multi-Volume Works

Chemical Economics Handbook; Stanford Research Institute International: Menlo Park, CA.

Kirk-Othmer's *Encyclopedia of Chemical Technology*, 4th ed.; John Wiley: New York.

Ullmann's *Encyclopedia of Industrial Chemistry*; VCH: New York.

Periodicals

Chemical and Engineering News; American Chemical Society: Washington, DC. Contains many interesting articles each week and valuable annual series including "Facts and Figures for the Chemical Industry," "Facts and Figures for Chemical R&D," "ACS Salary Survey," "Employment Outlook," "Top 50 Chemicals" (up to 1996), "Top 75 Chemical Producers," and "Global Top 50 Chemical Producers."

Chemical Marketing Reporter; Schnell Publishing Co.: New York. Contains many informative articles in each issue and up-to-date chemical prices each week.

Chemical Week; McGraw-Hill: New York. Similar to *Chemical and Engineering News*.

"Chemical Profiles," a weekly series in *Chemical Marketing Reporter*. This series is also available on the Internet:
http://www.chemexpo.com/news/newsframe.cfm?framebody=/news/profile.cfm

Government Documents

Annual Survey of Manufactures; U.S. Department of Commerce, Bureau of the Census, each year.

Statistical Abstract of the United States; U.S. Department of Commerce, Bureau of the Census, each year.

Synthetic Organic Chemicals; U.S. Department of Commerce, International Trade Commission, each year until 1995.

U.S. Industrial Outlook; U.S. Department of Commerce, International Trade Commission, each year.

The Internet

ChemExpo is the chemical industry's source for over 20,000 chemicals, latest news, chemical profiles, business briefs, a directory of chemical products and companies, forums, a calendar of events, a business card exchange, and a column on people and jobs.

http://www.chemexpo.com

Chemistry and Industry magazine has a web site that contains news and features from the current issue, plus hundreds of articles from past issues. It has a searchable database of jobs in chemistry, a list of meetings, and daily science news.

http://ci.mond.org

The Council on Chemical Research has a homepage that leads to various kinds of lecture material on chemistry and chemical engineering which have an industrial perspective.

http://www.udel.edu/ccr/

A chemical engineering page has relevant text on various topics involving industrial chemistry.

http://www.che.ufl.edu/WWW-CHE/index.html

The *Annual Survey of Manufactures*, covering values of shipments for all areas of industry, as well as other interesting data, is published by the U. S. Census Bureau.

http://www.census.gov/ftp/pub/econ/www/ma0300.html

An *Industrial Products Overview* by the U. S. Census Bureau covers many chemical products.

http://www.census.gov/ftp/pub/econ/www/industry.html

Full texts of U.S. patents, 1994 to present, are available.

http://www.uspto.gov/

ACS Information can be obtained easily and covers a multitude of information on chemistry, chemists, chemical education, and the chemical industry.

http://www.acs.org/portal/Chemistry

Over 750 homepages of chemical companies can be linked from an alphabetical list at one homepage.

http://www.claessen.net/chemistry/comp_en.html

A searchable hazardous chemicals database is available from the University of Akron.

http://ull.chemistry.uakron.edu/erd/index.html

The *Journal of Chemical Education* has useful information on many topics related to teaching chemistry.

http://jchemed.chem.wisc.edu/

Material Safety Data Sheets contain health and safety information on thousands of chemicals. These are available at a number of locations. Some of the sites are alphabetical by chemical name. Some allow the user to key in a chemical name. Here are some examples.

Vermont Safety Information http://hazard.com/msds2/

Oxford University http://physchem.ox.ac.uk/msds/

Denison University http://www.denison.edu/sec-safe/safety/msdsres.shtml

University of Kentucky has a valuable list of places on the Internet to find information on chemicals, including MSDS's.
http://www.ilpi.com/msds/index.html

Pesticide information is readily obtainable on the Extoxnet.
http://ace.orst.edu/info/extoxnet/

A list of carcinogens is published by the National Toxicology Program.
http://ntp-server.niehs.nih.gov/main_pages/ntp_8roc_pg.html

Chemfinder gives information and manufacturers for any searched chemical.
http://chemfinder.cambridgesoft.com/

A list of the Top 200 Prescription Drugs in the U. S. is available.
http://www.rxlist.com/top200.htm

Prof. Bassam Shakhashiri of the University of Wisconsin puts a chemical description on an Internet page each week.
http://www.scifun.chem.wisc.edu/chemweek/ChemWeek.html

Videotapes

Available from Films for the Humanities & Sciences, Princeton, NJ.

Chemicals from NaCl	*Soaps*
Polyethylene	*Glues*
Out of the Air	*Limestone*

Man-made Macromolecules, Open University, BBC-TV.

Manufactured Fibers, American Fiber Manufacturers Association, Washington, DC.

Vinyl the Versatile Plastic: Issues and Answers, The Vinyl Environmental Resource Center, Akron, OH.

Audio Courses

Jonnard, A. *Business Aspects of Chemistry*; American Chemical Society Audio Course: Washington, DC, 1974.

Wittcoff, H. *Industrial Organic Chemistry*; American Chemical Society Audio Course: Washington, DC, 1979.

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