

Basic Concepts from Organic Chemistry

5.1 | INTRODUCTION

The fundamental information that environmental engineers and scientists need concerning organic chemistry differs considerably from that which the organic chemist requires. This difference is due to the fact that chemists are concerned principally with the synthesis of compounds, whereas environmental engineers and scientists are concerned, in the main, with how the organic compounds in liquid, solid, and gaseous wastes can be destroyed and how they react in the environment. Another major difference lies in the fact that the organic chemist is usually concerned with the product of the reaction: the by-products of a reaction are of little interest to him or her. Since few organic reactions give better than 85 percent yields, the amount of by-products and unreacted raw materials that represent processing wastes is of considerable magnitude. In addition, many raw materials contain impurities that do not enter the desired reaction and, of course, add to the organic load in waste streams. A classical example is formaldehyde, which normally contains about 5 percent of methanol unless special precautions are taken in its manufacture. Unfortunately, organic chemists have presented very little information on the nature of the by-products of reactions to aid environmental engineers and scientists in solving industrial and hazardous waste problems. Fortunately, this is changing because of the large liabilities that companies now face from discharge of environmental pollutants. Awards are now being given for “green chemistry,” that is, for changing the ways chemicals are produced in order to reduce the environmental harm they or their production cause.

The environmental engineer and scientist, like the biochemist, must have a fundamental knowledge of organic chemistry. It is not important for either to know a multiplicity of ways of preparing a given organic compound and the yields to be expected from each. Rather, the important consideration is how the compounds react in the atmosphere, in the soil, in water, and in treatment reactors, especially when serving as a source of energy for living organisms. It is from this viewpoint that organic chemistry will be treated in this chapter, and considerations will be from the viewpoint of classes rather than individual compounds.

History

Organic chemistry deals with the compounds of carbon. The science of organic chemistry is considered to have originated in 1685 with the publication by L  mery¹ of a chemistry book that classified substances according to their origin as mineral, vegetable, or animal. Compounds derived from plants and animals became known as *organic* and those derived from nonliving sources were inorganic.

Until 1828 it was believed that organic compounds could not be formed except by living plants and animals. This was known as the *vital-force theory*, and belief in it severely limited the development of organic chemistry. W  hler,² in 1828, by accident, found that application of heat to ammonium cyanate, an inorganic compound, caused it to change to urea, a compound considered organic in nature. This discovery dealt a death blow to the vital-force theory, and by 1850 modern organic chemistry became well established. Today about 13 million organic compounds are known.³ Many of these are products of synthetic chemistry, and similar compounds are not known in nature. Approximately 70,000 organic chemicals are in commercial use.

Elements

All organic compounds contain carbon in combination with one or more elements. The hydrocarbons contain only carbon and hydrogen. A great many compounds contain carbon, hydrogen, and oxygen, and they are considered to be the major elements. Minor elements in naturally occurring compounds are nitrogen, phosphorus, and sulfur, and sometimes halogens and metals. Compounds produced by synthesis may contain, in addition, a wide variety of other elements.

Properties

Organic compounds, in general, differ greatly from inorganic compounds in seven respects:

1. Organic compounds are usually combustible.
2. Organic compounds, in general, have lower melting and boiling points.
3. Organic compounds are usually less soluble in water.
4. Several organic compounds may exist for a given formula. This is known as isomerism.
5. Reactions of organic compounds are usually molecular rather than ionic. As a result, they are often quite slow.
6. The molecular weights of organic compounds may be very high, often well over 1000.
7. Most organic compounds can serve as a source of food for bacteria.

¹Nicholas L  mery (1645–1715), French physician and chemist.

²Friedrich W  hler (1800–1882), German chemist.

³R. Chang, "Chemistry," 7th ed., McGraw-Hill, New York, 2002.

Sources

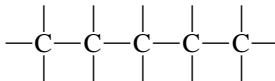
Organic compounds are derived from three sources:

1. *Nature*: fibers, vegetable oils, animal oils and fats, alkaloids, cellulose, starch, sugars, and so on.
2. *Synthesis*: A wide variety of compounds and materials prepared by manufacturing processes.
3. *Fermentation*: Alcohols, acetone, glycerol, antibiotics, acids, and the like are derived by the action of microorganisms upon organic matter.

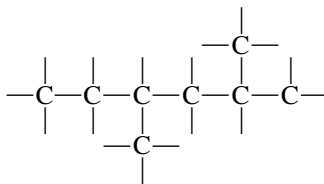
The wastes produced in the processing of natural organic materials and from the synthetic organic and fermentation industries constitute a major part of the industrial and hazardous waste problems that environmental engineers and scientists are called upon to solve.

The Carbon Atom

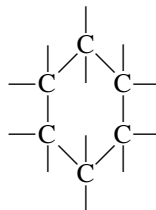
A question commonly asked is: How is it possible to have so many compounds of carbon? There are two reasons. In the first place, carbon normally has four covalent bonds (four electrons to share). This factor alone allows many possibilities, but the most important reason is concerned with the ability of carbon atoms to link together by covalent bonding in a wide variety of ways. They may be in a continuous open chain,



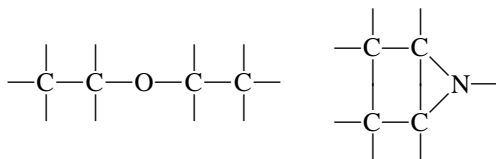
or a chain with branches,



or in a ring,



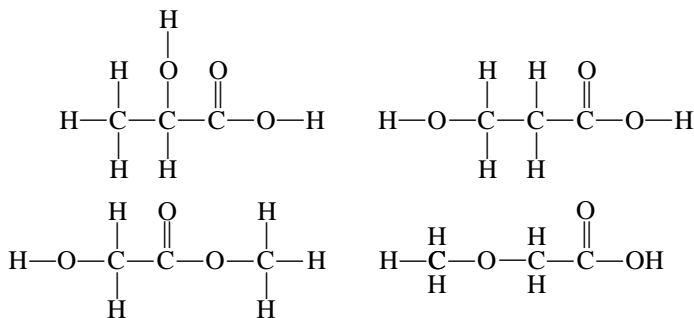
or in chains or rings containing other elements,



These examples will serve to show the tremendous number of possibilities that exist.

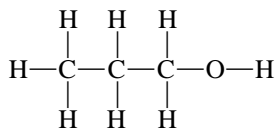
Isomerism

In inorganic chemistry, a molecular formula is specific for one compound. In organic chemistry, most molecular formulas do not represent any particular compound. For example, the molecular formula $C_3H_6O_3$ represents at least four separate compounds and therefore is of little value in imparting information other than that the compound contains carbon, hydrogen, and oxygen. Four compounds having the formula $C_3H_6O_3$ are

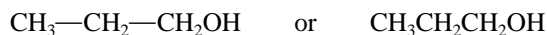


Compounds having the same molecular formula are known as *isomers*. In the case just cited, the first two isomers are hydroxy acids, the third is an ester of a hydroxy acid, and the fourth is a methoxy acid. To the organic chemist, each of the formulas represents a chemical compound with definite physical and chemical properties. The term *structural* formulas is applied to molecular representations as drawn for the four compounds. They are as useful to a chemist as blueprints are to an engineer.

In many cases structural formulas may be simplified as *condensed* formulas so as to use only one line. Thus, the formula



may be written as



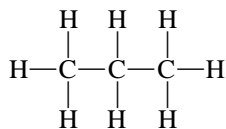
thereby saving a great deal of space.

There are three major types of organic compounds, the *aliphatic*, *aromatic*, and *heterocyclic*. The *aliphatic* compounds are those in which the characteristic groups are linked to a straight or branched carbon chain. The *aromatic* compounds have these groups linked to a particular type of six-member carbon ring that contains three alternating double bonds. Such rings have peculiar stability and chemical character and are present in a wide variety of important compounds. The *heterocyclic* compounds have a ring structure with or without the alternating double-bond structure of aromatic compounds, and in which at least one member is an element other than carbon.

ALIPHATIC COMPOUNDS

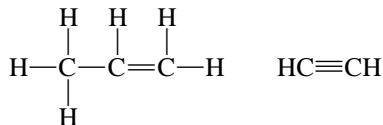
5.2 | HYDROCARBONS

The hydrocarbons are compounds of carbon and hydrogen. There are two types, saturated and unsaturated. Saturated hydrocarbons are those in which adjacent carbon atoms are joined by a single covalent bond and all other bonds are satisfied by hydrogen.



A saturated compound

Unsaturated hydrocarbons have at least two carbon atoms that are joined by more than one covalent bond and all remaining bonds are satisfied by hydrogen.



Unsaturated compounds

Saturated Hydrocarbons

The saturated hydrocarbons form a whole series of compounds starting with one carbon atom and increasing one carbon atom, stepwise. These compounds are called *alkanes*, or the *methane series*. The principal source is petroleum. Gasoline is a mixture containing several of them; diesel fuel is another such mixture.

The hydrocarbons serve as feedstocks for the preparation of a wide variety of organic chemicals. This knowledge serves as the basis of the great petrochemical industry within the petroleum industry. Saturated hydrocarbons are quite inert toward most chemical reagents. For this reason they were termed “paraffins” by early chemists (from the Latin *parum affinis*, meaning “little affinity”).

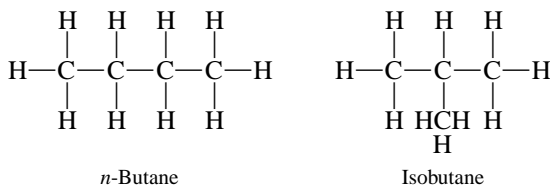
Methane (CH₄) is the simplest hydrocarbon. It is a gas of considerable importance to environmental engineers and scientists since it is a major end product of the anaerobic treatment process as applied to sewage sludge and other organic

waste materials. It is a component of marsh gas and of natural gas and, in a mixture with air containing from 5 to 15 percent methane, it is highly explosive. This property allows its use as fuel for gas engines. Methane is commonly called “firedamp” by miners and makes their work particularly hazardous. Methane is also considered to be an important greenhouse gas; its concentration in the stratosphere affects the earth’s heat balance, and thus temperature. On a per molecule basis, it is 21 times more effective at trapping heat in the atmosphere than carbon dioxide, the primary greenhouse gas.

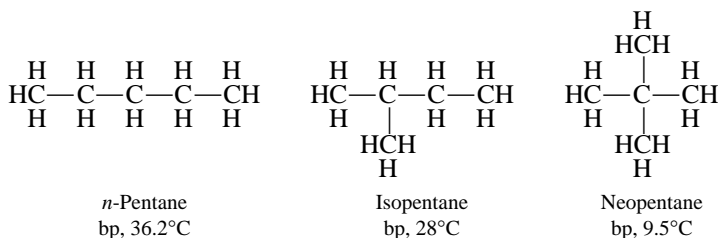
Ethane ($\text{CH}_3\text{—CH}_3$) is the second member of the series.

Propane ($\text{CH}_3\text{—CH}_2\text{—CH}_3$) is the third member of the series.

Butane (C_4H_{10}) is the fourth member of the series and is of interest because it occurs in two isomeric forms:



Pentane (C_5H_{12}) is the fifth member of the series and exists in three isomeric forms:



The third isomer of pentane might also be called tetramethylmethane or dimethylpropane, as the reader will shortly recognize.

As the number of carbon atoms increases in the molecule, the number of possible isomers increases accordingly. There are five possible isomers of *hexane* (C_6H_{14}) and 75 possible isomers of *decane* ($\text{C}_{10}\text{H}_{22}$).

Physical Properties Table 5.1 lists the names and physical constants of the *normal* saturated hydrocarbons of 1 to 10 carbon atoms per molecule. The term “normal” applies to the isomer that has all its carbon atoms linked in a *straight chain*. The others are referred to as *branched-chain* compounds. The branched form of butane and the simplest branched form of pentane are commonly given the prefix *iso-*.

The saturated hydrocarbons are colorless, practically odorless, and quite insoluble in water, particularly those with five or more carbon atoms. They dissolve read-

Table 5.1 | Physical constants of some normal alkanes

Name	Formula	Mp, °C	Bp, °C	Sp. gr., 20°/4°*	Calcd. no. of isomers
Methane	CH ₄	-182.4	-161.5	0.423 ^{-162°}	1
Ethane	C ₂ H ₆	-182.8	-88.6	0.545 ^{-89°}	1
Propane	C ₃ H ₈	-187.6	-42.1	0.493 ^{25°}	1
Butane	C ₄ H ₁₀	-138.2	-0.5	0.573 ^{25°}	2
Pentane	C ₅ H ₁₂	-129.7	36.0	0.626	3
Hexane	C ₆ H ₁₄	-95.3	68.7	0.655	5
Heptane	C ₇ H ₁₆	-90.6	98.5	0.684	9
Octane	C ₈ H ₁₈	-56.8	125.6	0.699 ^{25°}	18
Nonane	C ₉ H ₂₀	-53.5	150.8	0.718	35
Decane	C ₁₀ H ₂₂	-29.7	174.1	0.730	75

*Density of compound at 20°C (or at the temperature noted by superscript) over the maximum density of water, which is at 4°C.

Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

ily in many organic solvents. At room temperature all members through C₅ are gases, those from C₆ to C₁₇ are liquids, and those above C₁₇ are solids. Data in Table 5.1 show that as molecular size increases, the melting and boiling points of alkanes increase. Solubility in water in general decreases with increasing size. Such relationships are important in understanding the behavior of organic compounds in the environment and in engineered reactors (Sec. 5.34).

Homologous Series It will be noted from Table 5.1 that each successive member of the series differs from the previous member by CH₂. When the formulas of a series of compounds differ by a common increment, such as CH₂, the series is referred to as being a *homologous series*. Such compounds can be expressed by a general formula. That for the alkane series is C_nH_{2n+2}.

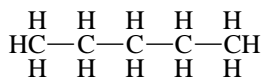
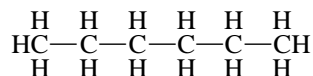
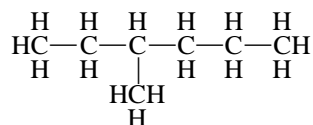
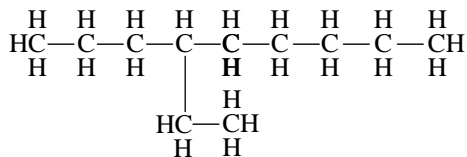
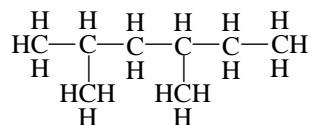
Radicals The inert character of the alkanes has been mentioned; however, they may be made to react under the proper conditions, and a wide variety of compounds results. It becomes necessary, therefore, to establish some form of nomenclature to identify the products formed. When one hydrogen is replaced from a molecule of an alkane, the *-ane* ending is dropped and a *-yl* is added. The names of some radicals are shown in Table 5.2. The system serves quite well for the normal compounds but is of little value in naming derivatives of the isomers.

Nomenclature The alkanes are characterized by names ending in *-ane*. The straight-chain compounds are termed *normal* compounds. The branched-chain

Table 5.2 | Names of alkane-series radicals (alkyl groups)

Parent compound	Radical	Formula
Methane	Methyl	CH ₃ —
Ethane	Ethyl	C ₂ H ₅ —
Propane	<i>n</i> -Propyl	C ₃ H ₇ —
Propane	Isopropyl	(CH ₃) ₂ CH—
<i>n</i> -Butane	<i>n</i> -Butyl	C ₄ H ₉ —

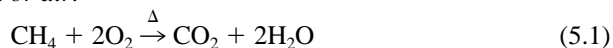
compounds and the derivatives of both straight- and branched-chain compounds are difficult to name with any degree of specificity. The IUPAC system, as proposed by the International Union of Pure and Applied Chemistry, is commonly used. In this system the compounds are named in terms of the longest continuous chain of carbon atoms in the molecule. A few examples will illustrate the method.

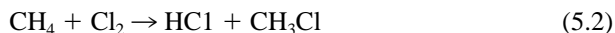
*n*-Pentane*n*-Hexane3-Methylhexane
(an isomer of heptane)4-Ethylnonane
(an isomer of undecane)2,4-Dimethylhexane
(an isomer of octane)

It will be noted that a chain is numbered from the end nearest the attached radical. The rule is to make the numbers as small as possible. The IUPAC system is applied to other compounds as well as to hydrocarbons.

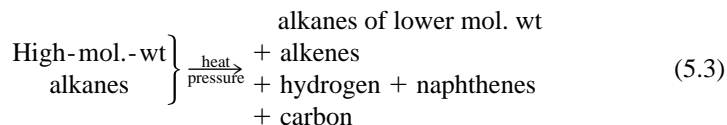
Chemical Reactions Strong bases, acids, or aqueous solutions of oxidizing agents do not react with saturated hydrocarbons at room temperature. At elevated temperatures, strong oxidizing agents, such as concentrated sulfuric acid, oxidize the compounds to carbon dioxide and water. Other reactions of importance are as follows:

1. *Oxidation with oxygen or air:*

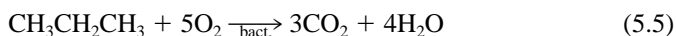


2. *Substitution of hydrogen by halogens:*

This reaction does not ordinarily occur in aqueous solutions and therefore is of little significance in environmental engineering and science.

3. *Pyrolysis or cracking:* High-molecular-weight hydrocarbons may be broken into smaller molecules by heat treatment. The process is used in the petroleum industry to increase the yield of light boiling fractions, suitable for sale as gasoline or for chemical synthesis. Heat treatment results in disruption of the large molecules as follows:4. *Biological oxidation:* Hydrocarbons are oxidized by certain bacteria under aerobic conditions. The oxidation proceeds through several steps. The first step is very slow biologically and involves conversion to alcohols with attack occurring on terminal carbon atoms, i.e., omega oxidation.

Through additional oxidative steps, which will be discussed in Chap. 6, microorganisms convert the hydrocarbon to carbon dioxide and water and derive energy in the process.

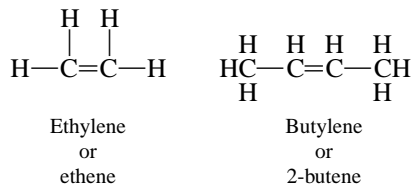


Such reactions, particularly the intermediate steps, are of great interest to environmental engineering and science.

Unsaturated Hydrocarbons

The unsaturated hydrocarbons are usually separated into four classes.

Alkenes Each member of the alkane group except methane can lose hydrogen to form an unsaturated compound or alkene. The alkenes all contain one double bond between two adjacent carbon atoms,



and their names all end in *-ylene* (older nomenclature) or *-ene*. The alkenes are also called *olefins*. Alkenes, particularly ethene, propene, and butene are formed in great quantities during the cracking or pyrolysis of petroleum.

The names, formulas, and physical constants of a number of important alkenes are given in Table 5.3. In naming specific alkenes, the IUPAC system

Table 5.3 | Physical constants of selected alkenes

IUPAC name	Formula	Mp, °C	Bp, °C	Sp. gr., 20°C/4°C*	Calcd. no. of isomers
Ethene	CH ₂ =CH ₂	-169	-103.7	0.568 ^{-104°}	1
Propene	CH ₂ =CHCH ₃	-185.2	-47.6	0.505 ^{25°}	1
1-Butene	CH ₂ =CHCH ₂ CH ₃	-185.3	-6.2	0.588 ^{25°}	3
1-Pentene	CH ₂ =CH(CH ₂) ₂ CH ₃	-165.2	29.9	0.640	5
1-Hexene	CH ₂ =CH(CH ₂) ₃ CH ₃	-139.7	63.4	0.673	13
1-Heptene	CH ₂ =CH(CH ₂) ₄ CH ₃	-119.7	93.6	0.697	27
1-Octene	CH ₂ =CH(CH ₂) ₅ CH ₃	-101.7	121.2	0.715	66
1-Nonene	CH ₂ =CH(CH ₂) ₆ CH ₃	-81.3	149.9	0.725 ^{25°}	153
1-Decene	CH ₂ =CH(CH ₂) ₇ CH ₃	-66.3	170.5	0.741	377

*Density of compound at 20°C (or at the temperature noted by superscript) over the maximum density of water, which is at 4°C.

Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

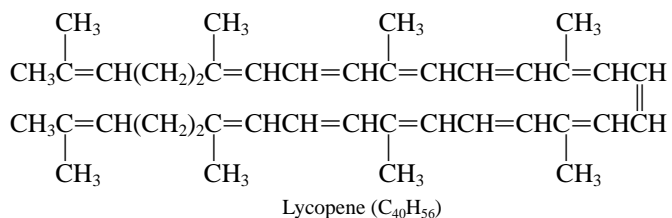
must be employed on all compounds with over three carbon atoms. The nomenclature becomes quite complicated with branched-chain isomers. Fortunately, there is little reason to differentiate between normal and branched-chain compounds in this series.

Diolefins When aliphatic compounds contain two double bonds in the molecule, they are called alkadienes, some times dienes for short. The compound 1,3-butadiene is an important example:



It has been used to make polymers.

Alkadienes Some organic compounds contain more than two double bonds per molecule. The red coloring matter of tomatoes, lycopene, and the yellow coloring matter of carrots are examples.



These compounds are of interest because of their occurrence in industrial wastes produced in the preparation of vegetables for canning. The oxidant (e.g., chlorine) demand of such wastes is extremely high.

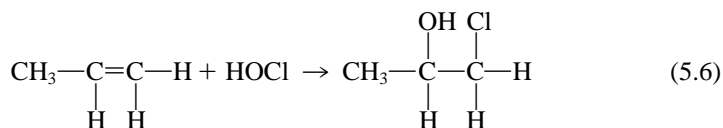
Alkynes The alkynes have a triple bond between adjacent carbon atoms.



These compounds are found to some extent in industrial wastes from certain industries, particularly those from the manufacture of some types of synthetic rubber.

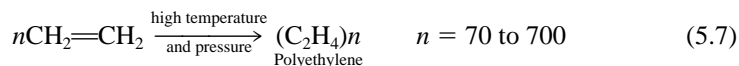
Chemical Reactions Unsaturated linkages occur in many types of organic compounds and exhibit many properties in common, regardless of the type of compound in which they exist. Unsaturated compounds undergo several reactions with relative ease.

1. *Oxidation:* The compounds are easily oxidized in aqueous solution by oxidizing agents such as potassium permanganate. A glycol is the normal product.
2. *Reduction:* Under special conditions of temperature, pressure, and catalysis, hydrogen may be caused to add at double or triple bonds. This reaction is of considerable importance commercially in the conversion of vegetable oils to solid fats. Many vegetable shortenings are made by this process.
3. *Addition:* Halogen acids, hypochlorous acid, and halogens will add across unsaturated linkages.



The reaction with hypochlorous acid is most important. Industrial wastes containing appreciable amounts of unsaturated compounds exhibit high chlorine-demand values because of such reactions.

4. *Polymerization:* Molecules of certain compounds having unsaturated linkages are prone to combine with each other to form polymers of higher molecular weight.

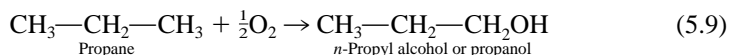
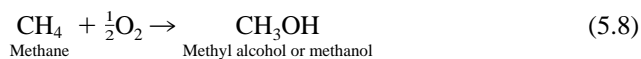


Similar reactions serve as the basis for many industrial products, e.g., synthetic resins, synthetic fibers, synthetic rubber, and synthetic detergents. Industrial wastes from such industries can be expected to contain a wide variety of polymers and usually exhibit a high chlorine demand. Historically such wastes were treated by chlorination. This practice is currently discouraged because the chlorinated organic compounds so formed have adverse impacts to human health and the environment.

5. *Bacterial oxidation:* It is generally considered that organic compounds possessing unsaturated linkages are more prone to bacterial oxidation than corresponding saturated compounds because of the ease of oxidation at the double bonds.

5.3 | ALCOHOLS

Alcohols are considered the primary oxidation product of hydrocarbons.

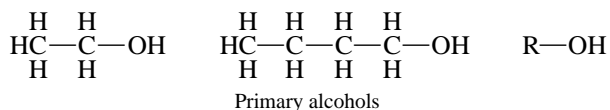


They cannot be prepared in this manner, however, because the reaction cannot be stopped with alcohols as the end product. Nevertheless, the reaction illustrates an initial step in biological degradation of hydrocarbons under aerobic conditions.

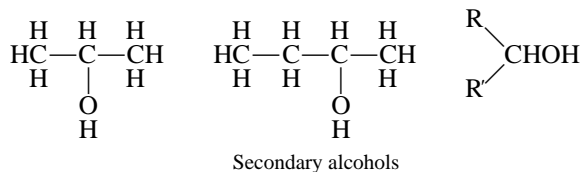
Alcohols may be considered as *hydroxy alkyl* compounds. For convenience, the alkyl group in alcohols and other organic compounds is often represented by R—, and the general formula for alcohols is R—OH. The OH group does not easily ionize; consequently, alcohols are neutral in reaction. The chemistry of alcohols is related entirely to the OH group.

Classification

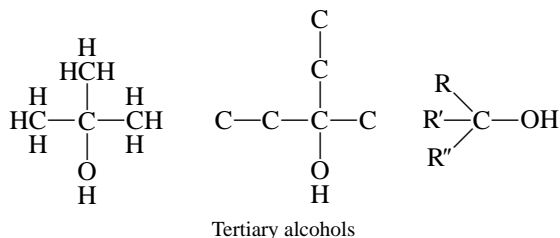
Alcohols are classified into three groups: primary, secondary, and tertiary, depending upon where the OH group is attached to the molecule. If the OH group is on a terminal (primary) carbon atom, it is a *primary* alcohol.



If the OH group is attached to a carbon atom that is joined to two other carbon atoms, it is a *secondary* alcohol, and the carbon atom to which it is attached is a *secondary carbon atom*.



If the OH group is attached to a carbon atom that is joined to three other carbon atoms, it is a *tertiary* alcohol, and the carbon atom to which it is attached is a *tertiary carbon atom*.

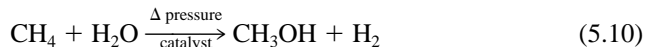


The chemistry of the primary, secondary, and tertiary alcohols differs considerably (e.g., bacterial oxidation of tertiary alcohols is much more difficult than of primary alcohols). Therefore, it is important to know how to differentiate among them.

Common Alcohols

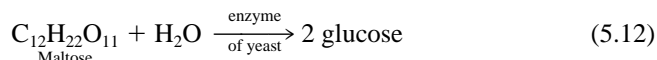
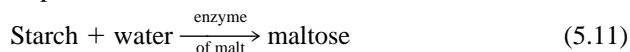
The alcohols of greatest commercial importance are methyl, ethyl, isopropyl, and *n*-butyl.

Methanol (CH₃OH) Methanol (also called methyl alcohol) is used to a considerable extent for synthesis of organic compounds. It has been used as an antifreeze for automobiles. It is prepared mainly by synthesis from natural gas and steam as follows:

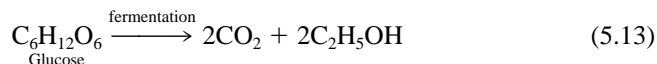


but may be manufactured from carbon monoxide and hydrogen.

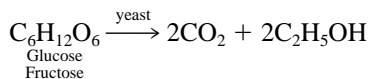
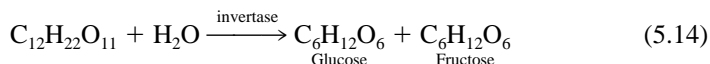
Ethanol (CH₃CH₂OH) Ethanol (ethyl alcohol) is used for the synthesis of organic compounds, the production of beverages, and the manufacture of medicines. Recently it has found use as a fuel oxygenate for reformulated gasoline (Sec. 3.8). It is prepared largely by fermentation processes. Alcohol intended for beverages is often manufactured by the fermentation of starch derived from a variety of materials, such as corn, wheat, rye, rice, and potatoes. The reactions involved are as follows:



Fermentation of the glucose yields carbon dioxide and alcohol.



Wine is produced from the fermentation of sugars in grapes. Industrial alcohol is produced largely from the fermentation of solutions containing sugars that are difficult to reclaim, such as molasses and, sometimes, even spent sulfite liquor.



The residues remaining after distillation of the desired product, ethanol, constitute some of the most potent industrial wastes in terms of strength with which the environmental engineer has to deal.

Isopropanol (CH₃CHOHCH₃) Isopropanol (isopropyl alcohol) is widely used in organic synthesis, and considerable amounts are sold as “dry gas” to prevent separation of water in the fuel tanks of automobiles. It is prepared by hydration of propylene derived from the cracking of petroleum.

***n*-Butanol (CH₃CH₂CH₂CH₂OH)** Normal butanol (*n*-butyl alcohol) is used to prepare butyl acetate, an excellent solvent. It is often referred to as “synthetic banana oil” because of its odor which resembles natural banana oil, amyl acetate. Normal butanol is prepared from cornstarch by a fermentation process utilizing a particular microorganism, *Clostridium acetobutylicum*. Considerable amounts of acetone

and some ethanol and hydrogen are produced during the fermentation. The liquid wastes remaining after distillation of the desired products are classed as industrial wastes, and their treatment and ultimate disposal usually fall to the lot of the environmental engineer. They are similar in character to the residues from the production of ethanol but offer less promise of by-product recovery. While methanol, ethanol, and isopropanol are completely miscible with water, *n*-butanol has a somewhat limited solubility in water.

Physical Properties of Alcohols

The short-chain alcohols are completely soluble in water due in part to the increased polarity caused by the hydroxyl group. As with alkanes and alkenes, as alcohol molecular size increases, melting and boiling points increase while water solubility decreases. The miscibility of C₁–C₃ alcohols makes them useful as cosolvents for remediation of contaminated subsurface environments (Sec. 3.8). Alcohols with more than 12 carbon atoms are colorless waxy solids and very poorly soluble in water. The physical constants of several alcohols are given in Table 5.4.

Nomenclature

The alcohols of commercial significance are usually called by their common names. The IUPAC system must be employed, however, to differentiate among isomers and to name the higher members, such as hexadecanol. In this terminology, the names of all alcohols end in *-ol*. The formulas, common names, and IUPAC names of several alcohols are given in Tables 5.4 and 5.5. In this system, the longest carbon chain containing the hydroxyl group determines the name. The locations of alkyl groups and the hydroxyl group are described by number; e.g., isobutanol is described as 2-methyl-1-propanol.

Table 5.4 | Physical constants of normal primary alcohols

Name of radical	IUPAC name of alcohol	Formula	Mp, °C	Bp, °C	Sp. gr., 20°/4°*	Calcd. no. of isomers
Methyl	Methanol	CH ₃ OH	−97.6	64.6	0.791	1
Ethyl	Ethanol	C ₂ H ₅ OH	−114.1	78.2	0.789	1
Propyl	1-Propanol	C ₃ H ₇ OH	−126.1	97.2	0.800 ^{25°}	2
Butyl	1-Butanol	C ₄ H ₉ OH	−89.8	117.7	0.810	4
Pentyl	1-Pentanol	C ₅ H ₁₁ OH	−78.9	137.9	0.814	8
Hexyl	1-Hexanol	C ₆ H ₁₃ OH	−44.6	157.6	0.814	17
Heptyl	1-Heptanol	C ₇ H ₁₅ OH	−34	176.4	0.822	39
Octyl	1-Octanol	C ₈ H ₁₇ OH	−15.5	195.1	0.826 ^{25°}	89
Nonyl	1-Nonanol	C ₉ H ₁₉ OH	−5	213.3	0.827	211 [†]
Decyl	1-Decanol	C ₁₀ H ₂₁ OH	6.9	231.1	0.830	507

*Density of compound at 20°C (or at the temperature noted by superscript) over the maximum density of water, which is at 4°C.

[†]These numbers are for all the isomers of a given carbon content.

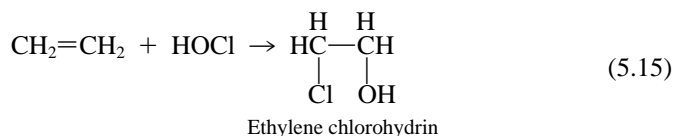
Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

Table 5.5 | Nomenclature of alcohols

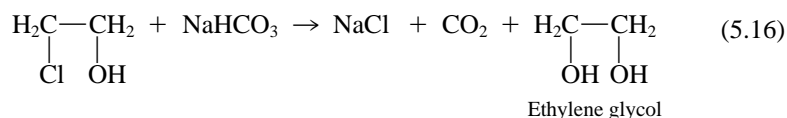
Formula	Common name	IUPAC name
CH ₃ OH	Methyl alcohol	Methanol
C ₂ H ₅ OH	Ethyl alcohol	Ethanol
CH ₃ CH ₂ CH ₂ OH	<i>n</i> -Propyl alcohol	1-Propanol
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CHOH} \\ \diagup \\ \text{CH}_3 \end{array}$	Isopropyl alcohol	2-Propanol
CH ₃ CH ₂ CH ₂ CH ₂ OH	<i>n</i> -Butyl alcohol	1-Butanol
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CHCH}_2\text{OH} \\ \diagup \\ \text{CH}_3 \end{array}$	Isobutyl alcohol	2-Methyl-1-propanol
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{CHOH} \\ \diagup \\ \text{CH}_3 \end{array}$	<i>sec</i> -Butyl alcohol	2-Butanol
$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ (\text{CH}_3)_3\text{COH} \end{array}$	<i>tert</i> -Butyl alcohol	2-Methyl-2-propanol

Polyhydroxy Alcohols

Those alcohols having two hydroxyl groups per molecule are known as *glycols*. The principal glycol of commercial significance is *ethylene glycol* (1,2-ethanediol), which is prepared from ethene. Ethene adds hypochlorous acid to form ethylene chlorohydrin.

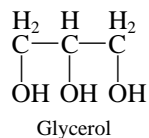


and treatment of the chlorohydrin with sodium bicarbonate produces ethylene glycol.



It is used extensively as a nonevaporative, radiator antifreeze compound.

Glycerol or glycerin is a trihydroxy alcohol (1,2,3-trihydroxypropane).



It was formerly produced in large quantities in the soap industry through saponification of fats and oils. Presently, considerable amounts are produced by chemical synthesis. Glycerol is used in a wide variety of commercial products: foods, cosmetics, medicines, tobaccos, and so on. It is used for the manufacture of nitroglycerin, an important component of dynamite.

Chemical Reactions of Alcohols

Alcohols undergo two types of reactions of special interest.

Ester Formation Alcohols react with acids, both inorganic and organic, to form esters. Inorganic hydroxy acids yield “inorganic” esters:



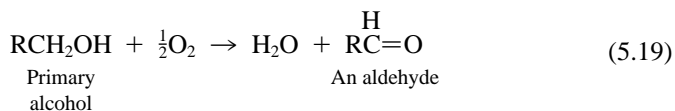
Organic acids yield organic esters:



Organic esters are discussed in Sec. 5.6.

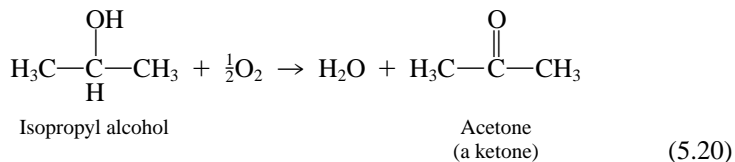
Oxidation Most alcohols are readily oxidized by strong oxidizing agents and by many microorganisms. The product of the oxidation depends upon the class of alcohol involved.

Primary alcohols are oxidized to aldehydes. The general equation is



Care must be used in selecting the oxidizing agent, or the aldehyde may be oxidized still further to an acid.

Secondary alcohols are oxidized to ketones.



The ketones are not easily oxidized and can usually be recovered completely.

Tertiary alcohols are not oxidized by ordinary agents in aqueous solution. When attacked by very strong oxidizing agents, they are converted to carbon dioxide and water.

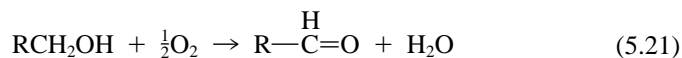
Microorganisms oxidize primary and secondary alcohols readily under aerobic conditions. The end products are carbon dioxide and water, but aldehydes and ketones are believed to exist as intermediates. Present evidence indicates that tertiary alcohols are very resistant to microbial degradation and are oxidized initially through terminal methyl groups, as with the hydrocarbons.

5.4 | ALDEHYDES AND KETONES

Aldehydes are the oxidation products of primary alcohols (ROH). *Ketones* are the oxidation products of secondary alcohols.

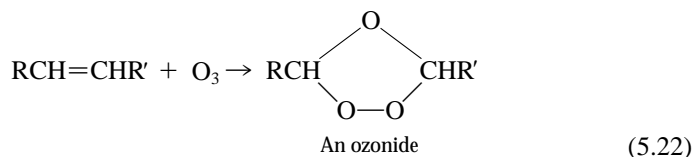
Aldehydes

The oxidation of primary alcohols to aldehydes is as follows:

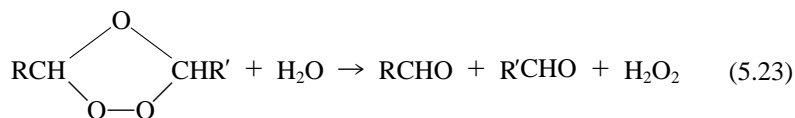


All aldehydes have the characteristic *carbonyl* group, $-\overset{\text{H}}{\text{C}}=\text{O}$. The general structural formula for an aldehyde is $\text{R}-\overset{\text{H}}{\text{C}}=\text{O}$, where R represents any alkyl group: CH_3- , C_2H_5- , and so on.

Aldehydes can also be formed from unsaturated hydrocarbons by ozonation. The hydrocarbons are first converted to an ozonide by ozone.



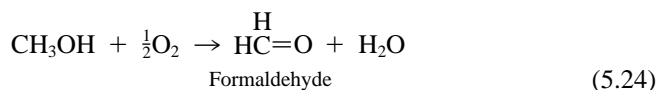
The ozonides react readily with water to form aldehydes.



These reactions are particularly significant in air pollution, where aldehydes are formed when unsaturated hydrocarbons discharged in automobile exhausts combine with ozone catalytically produced by reactions of oxygen with sunlight in the presence of oxides of nitrogen. The aldehydes so formed cause eye irritation, one of the most serious problems associated with air pollution. The oxides of nitrogen required for catalyzing ozone formation are produced in great quantities during high-temperature combustion of fossil fuels in steam power plants and internal combustion engines. Automobile and truck engine exhaust gases are a particularly significant source because of wide distribution at ground level where contact with human, animal, and plant life is most probable.

Although a wide variety of aldehydes can be formed from primary alcohols, only a few are of commercial importance. Aldehydes can also be produced by reduction of carboxylic acids.

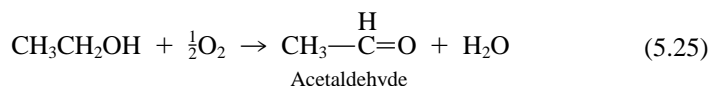
Formaldehyde Formaldehyde is formed by the oxidation of methanol.



It is used extensively in organic synthesis. It is very toxic to microorganisms, and, because of this property, it is used in embalming fluids and fluids used for the preservation of biological specimens. Industrial wastes containing formaldehyde were considered at one time to be too toxic for treatment by biological methods.

Through dilution of such wastes to reduce the concentration of formaldehyde below 1500 mg/L, it was found that microorganisms could use the formaldehyde as food and oxidize it to carbon dioxide and water. This experience has led to the concept of *toxicity thresholds* in industrial waste treatment practice. It means that below certain concentrations all materials are nontoxic. The completely mixed activated sludge system is designed to take advantage of this concept.

Acetaldehyde Acetaldehyde is formed by the oxidation of ethanol.

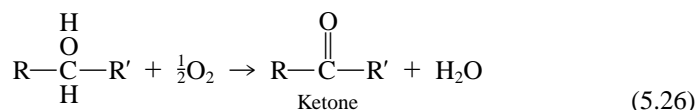


It is used extensively in organic synthesis. A major industrial use involves its condensation with formaldehyde to produce pentaerythritol [$\text{C}(\text{CH}_2\text{OH})_4$], an important intermediate for the production of a wide variety of products, including aldehyde resin paints. Development of a biological treatment process for the formaldehyde-bearing industrial wastes from the manufacture of pentaerythritol led to the concept of toxicity threshold mentioned earlier.

A wide variety of aldehydes are of commercial interest. The names and formulas of several of them are given in Table 5.6. The IUPAC names of all aldehydes end in *-al*.

Ketones

Ketones are prepared by the oxidation of secondary alcohols.

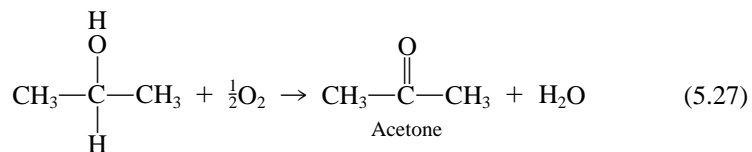


Ketones have two alkyl groups attached to the carbonyl group, $-\overset{\text{O}}{\text{C}}-$, while aldehydes have one R group and a hydrogen atom. The R groups in ketones may be the same or different.

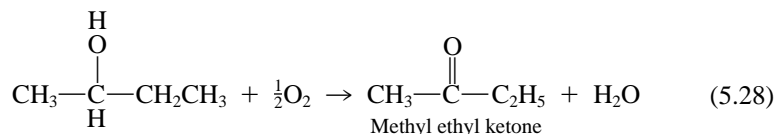
Table 5.6 | Common aldehydes

Common name	IUPAC name	Formula
Formaldehyde	Methanal	HCHO
Acetaldehyde	Ethanal	CH_3CHO
Propionaldehyde	<i>n</i> -Propanal	$\text{C}_2\text{H}_5\text{CHO}$
Butyraldehyde	<i>n</i> -Butanal	$\text{C}_3\text{H}_7\text{CHO}$
Valeraldehyde	<i>n</i> -Pentanal	$\text{C}_4\text{H}_9\text{CHO}$
Caproaldehyde	<i>n</i> -Hexanal	$\text{C}_5\text{H}_{11}\text{CHO}$
Heptaldehyde	<i>n</i> -Heptanal	$\text{C}_6\text{H}_{13}\text{CHO}$
Acrolein		$\text{CH}_2=\text{CHCHO}$
Citral		$\text{C}_9\text{H}_{15}\text{CHO}$
Citronellal		$\text{C}_9\text{H}_{17}\text{CHO}$

Acetone Acetone (dimethyl ketone) is the simplest ketone and is produced by the oxidation of isopropyl alcohol (2-propanol).



Methyl ethyl ketone Methyl ethyl ketone is prepared by the oxidation of 2-butanol.

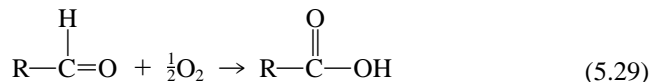


Ketones are used as solvents in industry and for the synthesis of a wide variety of products. The names of a few ketones are given in Table 5.7.

Chemical Properties of Aldehydes and Ketones

Aldehydes and ketones differ in ease of oxidation.

1. Aldehydes are easily oxidized to the corresponding acids.



2. Ketones are more difficult to oxidize. This is because there is no hydrogen attached to the carbonyl group. As a result, further oxidation must initiate in one of the alkyl groups, the molecule is cleaved, and two or more acids are produced.

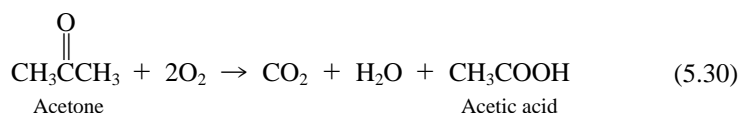
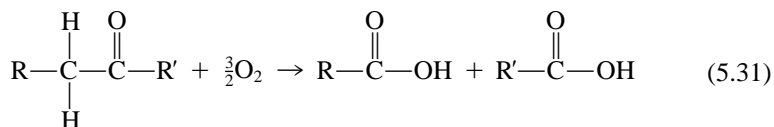


Table 5.7 | Common ketones

Common name	IUPAC name
Acetone	Propanone
Methyl ethyl ketone	Butanone
Diethyl ketone	3-Pentanone
Methyl propyl ketone	2-Pentanone
Methyl isopropyl ketone	3-Methyl-2-butanone
<i>n</i> -Butyl methyl ketone	2-Hexanone
Ethyl propyl ketone	3-Hexanone
Dipropyl ketone	4-Heptanone
Dibutyl ketone	5-Nonanone

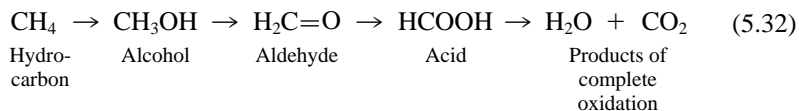
In the case of acetone, carbon dioxide and acetic acid are formed. Theoretically, formic acid should be formed, but it is so easily oxidized that it is generally converted under the prevailing conditions to carbon dioxide and water. Higher ketones such as diethyl ketone (3-pentanone) are oxidized as follows:



Oxidation of both aldehydes and ketones to organic acids is accomplished readily by many microorganisms. However, since the organic acids serve as a good food supply, the ultimate end products under aerobic conditions are carbon dioxide and water.

5.5 | ACIDS

Acids represent the highest oxidation state that an organic compound can attain. Further oxidation results in the formation of carbon dioxide and water, which are classed as inorganic compounds, and the organic compound is considered completely destroyed.



Organic acids typically contain the $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{OH} \end{array}$ group. This is called the *carboxyl* group and is commonly written $-\text{COOH}$. Acids with one carboxyl group are known as *monocarboxylic* acids, and those with more than one are *polycarboxylic* acids. In addition, derivatives of phenol (Sec. 5.14) can act as acids. The acids may be saturated or unsaturated. Some contain hydroxy groups within the molecule.

Saturated Monocarboxylic Acids

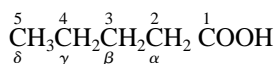
A wide variety of saturated monocarboxylic acids occur in nature as constituents of fats, oils, and waxes. Unsaturated acids are also found in these materials, and, as a result, both types are commonly known as *fatty* acids. The majority of the fatty acids derived from natural products have an even number of carbon atoms and usually have a straight-chain or normal structure.

Physical Properties The first nine members, C_1 to C_9 , are liquids. All the others are greasy solids. Formic, acetic, and propionic acid have sharp penetrating odors;

the remaining liquid acids have disgusting odors, particularly butyric and valeric. Butyric acid gives rancid butter its characteristic odor. Industrial wastes from the dairy industry must be treated with considerable care to prevent formation of butyric acid and consequent odor problems. The “volatile acids” (C_1 to C_5) are quite soluble in water.

The names, formulas, and physical constants of the important saturated acids are given in Table 5.8. All the acids are considered weak acids from the viewpoint of ionization. Formic acid is the strongest of all.

Nomenclature The common names are usually used for most of the acids, except for those with 7, 8, 9, and 10 carbon atoms. The IUPAC names are given in Table 5.8. In naming derivatives of acids, the IUPAC system is frequently abandoned for a system using Greek letters to identify the carbon atoms. In this system the carboxyl group is the reference point, and carbon atoms are numbered from it as follows:



The carbon atom next to the carboxyl group is *alpha*, the next *beta*, then *gamma*, *delta*, and so on. The terminal carbon atom is also referred to as being in the *omega* position. The α -amino acids are particularly important compounds and are discussed in Sec. 5.22.

Unsaturated Monocarboxylic Acids

The principal unsaturated monocarboxylic acids are as follows:

Acrylic Acid ($\text{CH}_2=\text{CHCOOH}$) Acrylic acid is used extensively because of its ability to polymerize, a characteristic of many compounds with unsaturated link-

Table 5.8 | Physical constants of some normal monocarboxylic acids

Common name	IUPAC name	Formula	Mp, °C	Bp, °C	Sp. gr., 20°/4°*	pKa at 25°
Formic	Methanoic	HCOOH	8.3	101	1.220	3.75
Acetic	Ethanoic	CH ₃ COOH	16.6	117.9	1.045 ^{25°}	4.756
Propionic	Propanoic	C ₂ H ₅ COOH	-20.7	141.1	0.993	4.87
Butyric	Butanoic	C ₃ H ₇ COOH	-5.7	163.7	0.958	4.83
Valeric	Pentanoic	C ₄ H ₉ COOH	-34	186.1	0.939	4.83 ^{20°}
Caproic	Hexanoic	C ₅ H ₁₁ COOH	-3	205.2	0.927	4.85
Enanthic	Heptanoic	C ₆ H ₁₃ COOH	-7.5	222.2	0.918	4.89
Caprylic	Octanoic	C ₇ H ₁₅ COOH	16.3	239	0.911	4.89
Pelargonic	Nonanoic	C ₈ H ₁₇ COOH	12.3	254.5	0.905	4.96
Capric	Decanoic	C ₉ H ₁₉ COOH	31.9	268.7	0.886 ^{40°}	
Palmitic	Hexadecanoic	C ₁₅ H ₃₁ COOH	63.1	351.5	0.853 ^{62°}	
Stearic	Octadecanoic	C ₁₇ H ₃₅ COOH	68.8	232	0.941	

*Density of compound at 20°C (or at the temperature noted by superscript) over the maximum density of water, which is at 4°C.

Source: D. R. Linde (ed.): “Handbook of Chemistry and Physics,” 82nd ed., CRC Press LLC, Boca Raton, 2001.

ages. Derivatives of the acid are used to form colorless plastics such as Lucite and Plexiglas.

Oleic Acid [$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$]

Linoleic Acid [$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$]

Linolenic Acid [$\text{CH}_3(\text{CH}_2\text{CH}=\text{CH})_3\text{CH}_2(\text{CH}_2)_6\text{COOH}$]

Oleic, linoleic, and linolenic acids are normal constituents of the glycerides of most fats and oils. A glyceride is the ester (Sec. 5.6) formed by combining glycerol (Sec. 5.3) with these acids. Oleic acid is considered to be an essential acid in the diet of humans and animals. Linoleic and linolenic acids as glycerides are important constituents of linseed and other drying oils. Their value for this purpose is dependent upon the multiple double bonds that they possess.

Chemical Properties of Acids The chemical properties of acids are determined largely by the carboxyl group. All form metallic salts that have a wide range of commercial use. In addition, the unsaturated acids have chemical properties characterized by the double bond, as described under unsaturated hydrocarbons in Sec. 5.2. The unsaturated acids may be reduced with hydrogen to give corresponding saturated acids.

Organic acids serve as food for many microorganisms and are oxidized to carbon dioxide and water. Ease and rate of oxidation are believed to be enhanced by the presence of unsaturated linkages. The rate of biological attack on high-molecular-weight fatty acids is often limited by their solubility in water. This is a particular problem in sludge digesters where fatty materials tend to float and segregate themselves in a scum layer.

Polycarboxylic Acids

The most important of the polycarboxylic acids are those that have two carboxyl groups, one on each end of a normal chain of carbon atoms. The most important acids are listed in Table 5.9.

Adipic acid is of some interest because it is used in the manufacture of nylon fiber and may be expected to occur in the industrial wastes of that industry.

Table 5.9 | Dicarboxylic acids

Name	Formula
Oxalic	$(\text{COOH})_2$
Malonic	$\text{CH}_2(\text{COOH})_2$
Succinic	$(\text{CH}_2)_2(\text{COOH})_2$
Glutaric	$(\text{CH}_2)_3(\text{COOH})_2$
Adipic	$(\text{CH}_2)_4(\text{COOH})_2$
Pimelic	$(\text{CH}_2)_5(\text{COOH})_2$
Suberic	$(\text{CH}_2)_6(\text{COOH})_2$

Hydroxy Acids

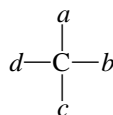
Hydroxy acids have OH groups attached to the molecule other than in the carboxyl group. Thus, they act chemically as acids and as alcohols. A number of the hydroxy acids have special names. Some examples are

HOCH ₂ COOH	Hydroxyacetic acid, glycolic acid
CH ₃ CHOHCOOH	α -Hydroxypropionic acid, lactic acid
HOCH ₂ CH ₂ COOH	β -Hydroxypropionic acid, hydracrylic acid
HOCH ₂ CH ₂ CH ₂ COOH	γ -Hydroxybutyric acid

Lactic acid, α -hydroxypropionic acid, is of special interest since it is formed during bacterial fermentation of milk and therefore is a normal constituent of industrial wastes from the dairy industry. Whey from cheese making contains considerable amounts of lactic acid. It is the principal acid in *sauerkraut* juice and prevents spoilage of the sauerkraut.

Lactic acid is also of interest because it possesses the property of *optical activity*. One form of lactic acid is *levorotatory*, which rotates polarized light in the counterclockwise direction (levo means “to the left”). The other form is *dextrorotatory*, which rotates polarized light in a clockwise fashion (dextro means “to the right”). In the past, *l* was used to name the levorotatory form while *d* was used to name the dextrorotatory form. Current convention is to use a minus sign (–) for the *l* form and a plus sign (+) for the *d* form.

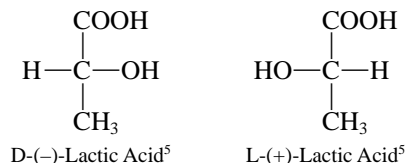
Many organic compounds are optically active. In order to be optically active, a compound must generally possess at least one *asymmetric* carbon atom. An asymmetric carbon atom is one having four dissimilar groups attached to it, as follows:



Such compounds are not superposable on their mirror images. Many other objects lack symmetry and cannot be superposed on their mirror image. For example, the left and right hands are mirror images of each other, but cannot be made to coincide at every point with each other. Objects, including molecules, that are nonsuperposable on their mirror image are said to be *chiral*. With molecules, the asymmetric carbon atom is termed the *chiral center*. Chiral compounds may have more than one chiral center. The different chiral forms of a molecule are called *enantiomers*. Chiral compounds are of environmental significance in that their enantiomers can differ in biological activity or biodegradability. The most sensational case is that of the drug thalidomide. The (+) enantiomer was employed as a sedative and antinausea drug around 1960. As is the case with most commercially available chiral molecules, thalidomide was sold as a *racemic* mixture [approximately equal amounts of the (+) and (–) enantiomers; such mixtures carry the symbol (\pm)]. Unfortunately, the (–) enantiomer caused serious birth defects in children born to pregnant women taking the drug during pregnancy.

Environmental engineers and scientists have recently begun to use the properties of chiral molecules to better understand the fate of organic pollutants.⁴

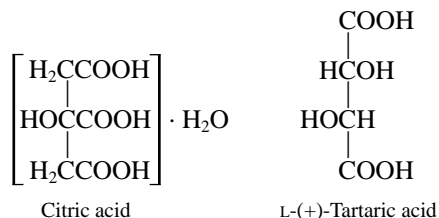
Lactic acid has one chiral center, and two optically active enantiomers are possible.



It is the L form of lactic acid that is commonly produced in living organisms.

Hydroxy Polycarboxylic Acids

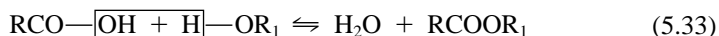
There are several hydroxy polycarboxylic acids.



Tartaric acid occurs in many fruits, especially grapes, and is present in canning and winery wastes. Citric acid is the major acid of all citrus fruits: oranges, lemons, limes, and grapefruit. It is, of course, a major component of the liquid wastes of the citrus industry.

5.6 | ESTERS

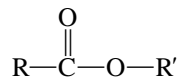
Esters are compounds formed by the reaction of acids and alcohols, similar to the reactions of acids and bases to form salts in inorganic chemistry. The reaction between low-molecular-weight organic acids and alcohols is never complete. Hydrolysis occurs and a reversible reaction results. The reaction may be represented by the general equation



⁴J. J. Ridal et al., Enantiomers of α -Hexachlorocyclohexane as Tracers of Air-Water Gas Exchange in Lake Ontario, *Env. Sci. Tech.*, **31**: 1940–1945, 1997.

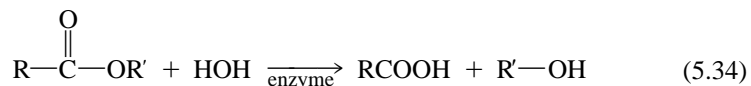
⁵The symbols D and L are used to describe the configuration of the groups surrounding the asymmetric carbon and are not to be confused with the + or – designations. Additional configuration information is conveyed by the use of R and S symbols. Details concerning this terminology are beyond the scope of this text. The reader should refer to the organic chemistry texts listed at the end of this chapter for the finer points of chiral nomenclature.

The general formula of an ester is



A wide variety of esters are used in chemical manufacturing. Most esters have highly pleasing odors. Butyl acetate smells like banana oil (amyl acetate) and is used for solvent purposes. Many esters are used in flavoring extracts and perfumes.

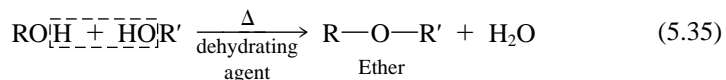
Esters have been used to some extent as immiscible solvents in the separation and purification of antibiotics. Considerable quantities often reach the sewer system and become an industrial waste problem. Enzymes liberated by many microorganisms hydrolyze esters to yield the corresponding acid and alcohol.



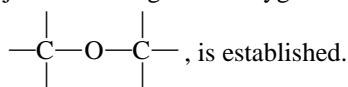
The acid and alcohol serve as bacterial food and are oxidized to carbon dioxide and water, as discussed in Secs. 5.3 and 5.5.

5.7 | ETHERS

Ethers are formed by treatment of alcohols with strong dehydrating agents. In the reaction, one molecule of water is removed from two molecules of alcohol.



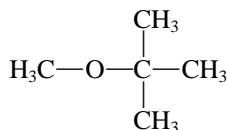
The two fragments of the alcohol join to form an ether. The alkyl groups are joined through an oxygen atom; thus, a carbon-to-oxygen-to-carbon bond,



Ethers are used widely as solvents. The low-molecular-weight ethers are highly flammable. When left exposed to air, they are prone to form peroxides that are extremely explosive, particularly when recovery by distillation is practiced and the distillation is allowed to go to dryness. Diethyl ether has been used widely as an anesthetic.

Ethers are generally resistant to biological oxidation. Fortunately, most are relatively insoluble in water and can be separated from industrial wastes by flotation or decantation procedures.

An important ether is methyl *tert*-butyl ether (MTBE).



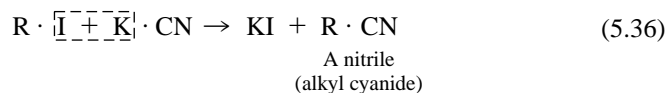
MTBE was first used in the late 1970s as an octane enhancer when lead additives to gasoline were being phased out. More recently it has been added to gasoline as a fuel oxygenate to help reduce carbon monoxide emissions from gasoline combustion. MTBE is very soluble in water, volatile, not strongly sorbed to particulate matter, and relatively nonbiodegradable. Thus, upon release to the environment, it is very mobile. Through leaking storage tanks, pipelines, and other uncontrolled releases to the environment, MTBE has been found in a large number of surface waters and groundwaters. Although the health effects associated with MTBE exposure are not yet completely known, action levels as low as $20 \mu\text{g/L}$ have been set due to taste and odor considerations.⁶ Because of these problems, there is a proposed ban on the use of MTBE as a fuel additive. Ethanol is an alternative for MTBE as a fuel additive. However, it has its own set of potential problems (Sec. 3.8).

5.8 | ALKYL HALIDES AND OTHER HALOGENATED ALIPHATIC COMPOUNDS

The *alkyl halides* are aliphatic compounds in which a halogen is attached to an alkyl carbon. These are to be distinguished from other halogenated aliphatics where the halogen is attached to a double-bonded carbon. Both types of compounds are discussed here. Halogenated aliphatic compounds are used extensively in organic synthesis, and a few of them have important industrial uses. Many are toxic to humans and are of significant environmental concern. They are among the most frequently found hazardous chemicals at abandoned waste sites, refuse disposal areas, and industrial and municipal wastewaters. The U.S. federal government has set drinking water maximum contaminant levels (MCLs) for some of these compounds and is proposing MCLs for others. These are listed in Table 34.1. Most of the halogenated aliphatic compounds are volatile and thus may be significant air pollutants.

Simple Alkyl Halides

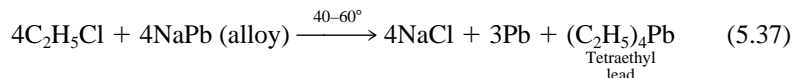
The alkyl halides are of great value in organic synthesis because they react with potassium cyanide to form compounds with an additional carbon atom.



The nitrile formed can be hydrolyzed to an acid and then reduced to an alcohol, if desired. The alcohol can be converted to an alkyl halide and the process repeated. In this manner the organic chemist can increase the length of carbon-chain compounds one atom at a time.

⁶R. Johnson, et al., MTBE—To What Extent Will Past Releases Contaminate Community Water Supply Wells, *Env. Sci. Tech.*, **34**(9): 210A–217A (2000).

Methyl chloride (CH_3Cl), also called chloromethane, and ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$), also called chloroethane, were used extensively as refrigerants in the past. Chloroethane is used in the manufacture of tetraethyl lead, great quantities of which were previously used in the production of high-octane, antiknock gasolines.



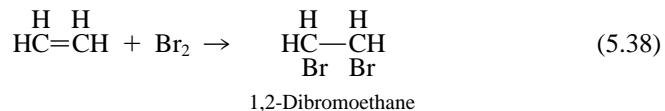
During combustion the lead is converted to lead oxide and is emitted in the exhaust gases, creating a lead pollution problem. The lead also fouls catalytic devices being used to reduce the quantity of unburned fuel discharged to the atmosphere. For these reasons use of leaded gasoline has been eliminated in the United States and is being eliminated in Europe.

Vinyl chloride ($\text{CH}_2=\text{CHCl}$), also called monochloroethene, is used in large quantities to produce a wide variety of polyvinylchloride (PVC) products. It is also formed biologically through reduction of polyhalogenated ethenes. Through this route it is frequently found in contaminated groundwaters and in gases emanating from sanitary landfills. This compound is very volatile and is a known carcinogen. A drinking water MCL of $2 \mu\text{g/L}$ has been established (Table 34.1). Because of its volatility, vinyl chloride is a potentially significant air pollutant.

Polyhalogen compounds

A wide variety of *polyhalogen* compounds are used for industrial purposes. Because of a variety of public and environmental health problems, use of several of these compounds is being discouraged. The challenge is to find environmentally friendly substitutes.

1,2-Dibromoethane This compound has also been called ethylene dibromide (EDB), although it is not actually an alkene. 1,2-Dibromoethane is formed from ethene by addition of bromine.



1,2-Dibromoethane has many industrial uses and has been used as a pesticide in agricultural areas and as an ingredient in ethyl gasoline. In the early 1980s, it was discovered in fumigated fruits and vegetables, and several grain products, causing some commercial products to be removed from stores. It is a commonly detected groundwater contaminant. Because of its potential health effects, a drinking water standard of $0.05 \mu\text{g/L}$ has been established (Table 34.1).

Dichloromethane (CH_2Cl_2) Dichloromethane, sometimes called methylene chloride, is a volatile liquid that has been used as an industrial solvent, in paint strippers, to decaffeinate coffee, and in the making of polyurethane products. It can be pro-

duced from the chlorination of methane, as can all the chlorinated methanes. Dichloromethane is quite soluble in water, more dense than water, and is fairly volatile. A drinking water MCL of $2 \mu\text{g/L}$ has been established.

Chloroform (CHCl_3) Chloroform (trichloromethane) was one of our first anesthetics (1847) and was widely used until about 1920. It is used in industry as a solvent for oils, waxes, and so on. It is nonflammable. Chloroform has been found present in microgram per liter to milligram per liter concentrations in drinking water supplies as a result of chlorination for disinfection. It is formed through reaction of chlorine with organics of biological origin commonly present in natural waters. Because it is a potential carcinogen, an MCL in drinking water has been established for the sum total of chloroform and other trihalomethanes (THMs) of $80 \mu\text{g/L}$.

Carbon Tetrachloride (CCl_4) Carbon tetrachloride (tetrachloromethane) has been widely used as a fire extinguisher in small units (Pyrene) and as a solvent. It is a toxic compound, and its use should be restricted to well-ventilated areas. Its use as a fire extinguisher is fraught with some danger. In contact with hot iron and oxygen, it is converted to phosgene (COCl_2), a highly toxic gas. For this reason, trained fire fighters use other types of fire-fighting equipment. An MCL for carbon tetrachloride has been established at $5 \mu\text{g/L}$.

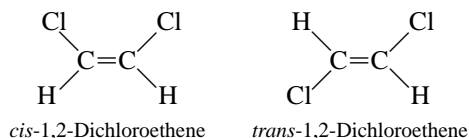
Halogenated Ethanes Several halogenated ethanes, particularly some chlorinated ethanes, are of environmental significance. For the most part, these compounds are used as industrial solvents. They are volatile, heavier than water, and have varying solubilities in water. Some are important because they are products formed during the transformation (chemical and biological) of other halogenated compounds. These aspects are further discussed in Sec. 5.34 and Chap. 6.

1,1,1-Trichloroethane (CCl_3CH_3) is a widely used industrial solvent and is a commonly detected groundwater contaminant. 1,2-Dichloroethane ($\text{CH}_2\text{ClCH}_2\text{Cl}$) is also an industrial solvent. Drinking water MCLs are in place for both of these compounds ($200 \mu\text{g/L}$ and $5 \mu\text{g/L}$, respectively), and for 1,1,2-trichloroethane ($\text{CHCl}_2\text{CH}_2\text{Cl}$), another industrial solvent ($5 \mu\text{g/L}$).

Halogenated Ethenes As with the halogenated ethanes, it is the chlorinated ethenes that are of most environmental significance. They are volatile solvents, heavier than water, and have varying solubilities in water. Transformation reactions can convert parent chlorinated ethenes into other ethenes. A classical example is the reductive dechlorination of trichloroethene to dichloroethene, and then to vinyl chloride.

Trichloroethene (TCE: $\text{CCl}_2=\text{CHCl}$), also called trichloroethylene, is a nonflammable, volatile liquid that has been used as an industrial solvent and degreaser, a dry-cleaning solvent, and in many household products. In the past it was used to decaffeinate coffee. It is one of the most commonly found groundwater pollutants. 1,1-Dichloroethene ($\text{CCl}_2=\text{CH}_2$), also called 1,1-dichloroethylene, is also a solvent and has been found in the environment as a transformation product of both TCE and 1,1,1-trichloroethane. There are drinking water MCLs for both TCE ($5 \mu\text{g/L}$) and 1,1-dichloroethene ($7 \mu\text{g/L}$).

The chlorinated ethenes with the formula $\text{CHCl}=\text{CHCl}$ are examples of a special type of isomerism called *geometric isomers*. In *cis*-1,2-dichloroethene the chlorines are on the same side of the molecule while in *trans*-1,2-dichloroethene the chlorines are on the opposite side of the molecule:



It is important to note that the physical properties can be different for geometric isomers and thus their behavior in the environment and in engineered reactors can be different. For example, the following are given for the *cis* and *trans* isomers of 1,2-dichloroethene (values are for 20°C except for boiling point):

Property	<i>cis</i> isomer	<i>trans</i> isomer
Boiling point, °C	60.3	47.5
Density, g/cm ³	1.2837	1.2565
Vapor pressure, atm	0.24	0.37
Henry's constant, atm/M	7.4	6.7
Water solubility, mg/L	3500	6300

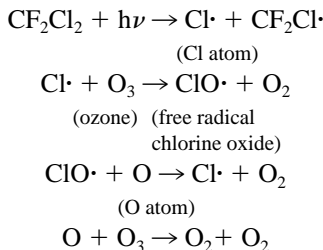
Both *cis*- and *trans*-1,2-dichloroethene have been found in the environment as biological transformation products of TCE. Drinking water MCLs have been established for both (70 and 100 $\mu\text{g/L}$, respectively).

Tetrachloroethene ($\text{CCl}_2=\text{CCl}_2$), also called perchloroethene (PCE), is a widely used industrial solvent and is a commonly found groundwater pollutant. It is a regulated drinking water contaminant with an MCL of 5 $\mu\text{g/L}$.

Dibromochloropropane (DBCP) Although there are nine possible isomers of dibromochloropropane ($\text{C}_3\text{H}_5\text{Br}_2\text{Cl}$), it is 1,2-dibromo-3-chloropropane ($\text{CH}_2\text{BrCHBrCH}_2\text{Cl}$) that is most environmentally significant. This isomer has been widely used as a pesticide and is frequently detected in groundwater. It is thought to cause cancer and adverse reproductive outcomes, and for these reasons a drinking water MCL has been established (0.2 $\mu\text{g/L}$).

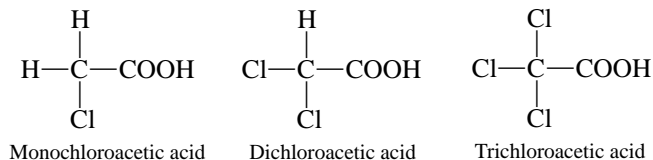
Chlorofluorocarbons (CFCs) Chlorofluorocarbon compounds are one- and two-carbon compounds containing chlorine and fluorine. They are sometimes called by their trade name, Freons. For many years these compounds have been widely used as refrigerants, solvents, and aerosol propellants. They were used because of their stability and their nonflammable and nontoxic properties. The most commonly used CFCs are CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $\text{CCl}_2\text{FCClF}_2$ (CFC-113), $\text{CClF}_2\text{CClF}_2$ (CFC-114), and CClF_2CF_3 (CFC-115). Recently, CFCs have been shown to be involved in the destruction of the stratos-

pheric ozone layer, the “ozone hole” effect, via the following reactions with ultraviolet radiation.

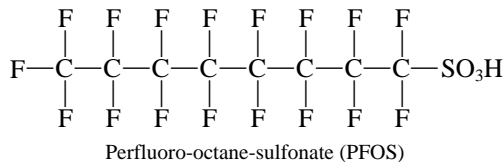


Chlorofluorocarbons are also known to be greenhouse gases. Because of their role in ozone destruction and the greenhouse effect, manufacture and use of chlorofluorocarbons is being eliminated worldwide.

Haloacetic Acids (HAA) Another important group of halogenated aliphatic compounds is the haloacetic acids. They are produced during chlorination of drinking waters that contain natural organic matter. An MCL of 60 $\mu\text{g}/\text{L}$ has been established for the sum of five haloacetic acids (HAA5), mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids.



Perfluorinated Compounds Another class of halogenated compounds of emerging concern are the *perfluorinated* compounds. Here, all C—H bonds are replaced by C—F bonds. These bonds are very stable and tend to persist in the environment. Perfluorinated compounds have been used in fabric protectors and in a variety of products ranging from paper plates to semiconductor coatings to airplane hydraulic fluid. A particular group of these compounds that are of emerging concern are those that either use perfluoro-octane-sulfonate (PFOS) in their manufacture or break down to this compound.



These compounds are known to bioaccumulate and are being found in blood samples from humans and animals far from their known sources.⁷ Laboratory toxicity

⁷J. P. Giesy and K. Kannan, Global Distribution of Perfluorooctane Sulfonate in Wildlife, *Env. Sci. Tech.*, **35**: 1339–1342 (2001).

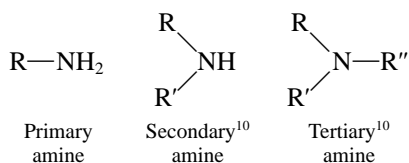
studies are showing that these compounds are toxic, causing a variety of effects in the livers of test animals, and perhaps carcinogenic.^{8,9}

5.9 | SIMPLE COMPOUNDS CONTAINING NITROGEN

The simple aliphatic compounds containing nitrogen are of three types: amines, amides, and nitriles (cyanides). Other nitrogen-containing compounds of environmental significance include nitrosamines and isocyanates.

Amines

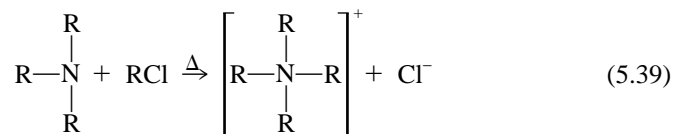
The amines are alkyl derivatives of ammonia. They are of three types: primary, secondary, and tertiary.



In *primary amines*, one hydrogen atom of ammonia is replaced by an alkyl group such as CH_3- , C_2H_5- , and so on. In *secondary amines*, two hydrogen atoms of ammonia are replaced by alkyl groups, and in *tertiary amines*, all three hydrogens are replaced. The amines, like ammonia, are all basic in reaction. The basicity increases from primary to tertiary.

The amines are found in certain industrial wastes, particularly those from the fish and beet-sugar industries. It is well known that deamination reactions (removal of ammonia) are easily accomplished with primary amines, and somewhat less easily with secondary amines.

Tertiary amines combine with alkyl halides to form *quaternary ammonium salts* as follows:



The compounds formed are actually chloride salts and ionize to form a quaternary ammonium ion and a chloride ion. The quaternary ammonium salts have bactericidal properties that can be enhanced by the proper choice of the R groups. They

⁸R. Renner, Growing Concern Over Perfluorinated Chemicals, *Env. Sci. Tech.*, **35**: 154A–160A (2001).

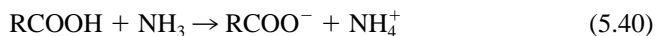
⁹R. Renner, Perfluorinated Compounds Linked to Carcinogenicity in Vitro, *Env. Sci. Tech.*, **35**: 180A (2001).

¹⁰R, R', R'' represent alkyl groups. They may all be different or all alike.

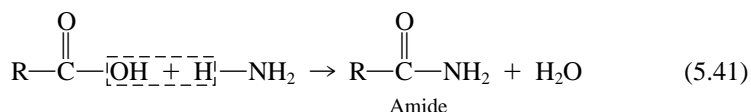
are therefore of interest to public health professionals, who find them useful as disinfecting agents in food- and beverage-dispensing establishments. They are also used as disinfectants in the laundering of babies' diapers to control infections of bacteria responsible for the rapid hydrolysis of urea. Solutions of the quaternary ammonium salts are sold for disinfecting purposes under a variety of trade names.

Amides

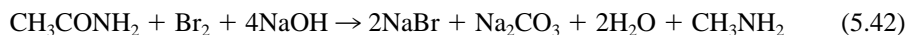
The amides may be considered as being derived from organic acids and ammonia under special conditions. The ordinary reaction between ammonia and an organic acid, of course, produces an ammonium salt.



Under special conditions, an amide results.



Amides are of considerable significance to organic chemists in synthetic work. When they are caused to react with a halogen (Hofmann reaction), an atom of carbon is lost from the amide, and an amine with one less carbon atom is formed.



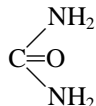
This constitutes a method of reducing a length of a carbon chain by one atom.

Amides as such are of little importance to the environmental engineer, but the

amide group $\left(\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \right)$ is related to an important group of compounds con-

taining the *peptide linkage* $\left(\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\text{H} \right)$, as discussed in Sec. 5.22.

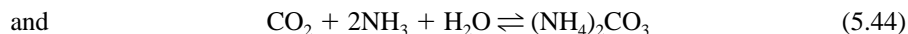
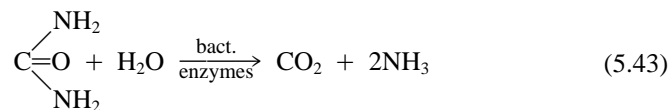
Urea,



is an amide of considerable importance because of its many commercial uses and because it is a normal constituent of urine. It is a constituent of many agricultural fertilizers and is used in the manufacture of synthetic resins.

Although urea was originally considered an organic compound and its accidental production from ammonium cyanate by Wöhler is considered to have initiated the study of organic chemistry, it is in effect an inorganic compound since it cannot be used by saprophytic bacteria as a source of energy. In aqueous solutions contain-

ing soil bacteria, urea is hydrolyzed to carbon dioxide and ammonia. These combine to form ammonium carbonate in the presence of water.



The penetrating odor at latrines, privies, and some urinals is due to bacterial infections and their action on urea with subsequent release of free ammonia to the atmosphere. The use of disinfectants will control the decomposition of urea and, thereby, control odors.

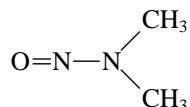
Nitriles

Nitriles, or organic cyanides, are important compounds of industry. They have the general formula $\text{R}-\text{CN}$, and the R group may be saturated or unsaturated. The names and formulas of a few nitriles of industrial importance are given in Table 5.10.

The nitriles are used extensively in the manufacture of synthetic fibers and can be expected to be present in industrial wastes of that industry. Some are quite toxic to microorganisms.

Nitrosamines

Nitrosamines, or *N*-nitroso compounds, have the general formula $\text{R}_2-\text{N}-\text{N}=\text{O}$ and are environmentally significant because they have been shown to cause cancer. They can be formed in the environment through the action of microorganisms and have been detected in beer and whiskey as well as a variety of foods. In the past these compounds had been used as industrial solvents. Of particular recent concern is *N*-nitrosodimethylamine (NDMA).



N-Nitrosodimethylamine (NDMA)

NDMA has been used in rocket fuel production and for a variety of industrial purposes. It has been found in a variety of foods and can also be formed naturally

Table 5.10 | Important nitriles

Name as nitrile	Name as cyanide	Formula
Acetonitrile	Methyl cyanide	CH_3-CN
Propionitrile	Ethyl cyanide	$\text{CH}_3-\text{CH}_2-\text{CN}$
Succinonitrile	—	$\text{CN}-\text{CH}_2-\text{CH}_2-\text{CN}$
Acrylonitrile	Vinyl cyanide	$\text{CH}_2=\text{CH}-\text{CN}$

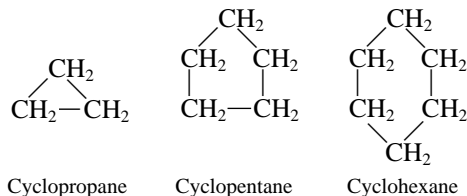
in the environment.¹¹ It is classified as a “probable” human carcinogen. NDMA has been detected in surface waters and treated wastewaters and drinking waters. Recent evidence suggests that NDMA can be formed as a disinfection by-product during chloramination with dimethylamine (DMA) as the precursor.¹²

Isocyanates

Isocyanates have the general formula $R-N=C=O$ and are widely used industrial chemicals. Methyl isocyanate ($CH_3-N=C=O$) was the material involved in the Bhopal, India, chemical plant explosion in which over 1000 people were killed and many thousands were affected to various degrees. The volatility of these compounds makes them potent potential air pollutants.

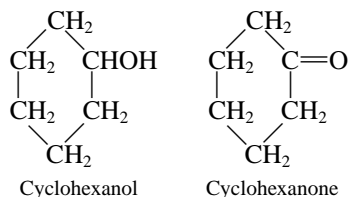
5.10 | CYCLIC ALIPHATIC COMPOUNDS

A number of *cyclic aliphatic* hydrocarbons are known. Many of these occur in petroleum and are known as naphthenes.



They are characterized by having two atoms of hydrogen attached to each carbon in the ring; i.e., they are saturated.

A wide variety of cyclic alcohols and ketones are known. Examples are cyclohexanol and cyclohexanone.



5.11 | MERCAPTANS OR THIOALCOHOLS

Mercaptans or *thioalcohols* are aliphatic compounds that contain sulfur. They have a structure similar to alcohols, except that oxygen is replaced by sulfur.



¹¹M. Alexander, “Biodegradation and Bioremediation,” 2nd ed., Academic Press, San Diego, 1999.

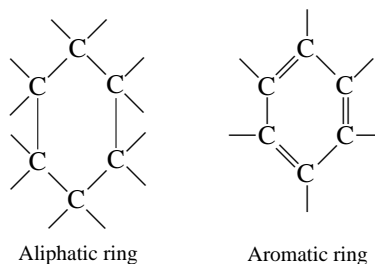
¹²I. Najm and R. R. Trussell, NDMA Formation in Water and Wastewater, *J. American Water Works Assoc.*, **93**(2): 92–99 (2001).

Mercaptans are noted for their disagreeable odor and are found in certain industrial wastes, particularly those from the pulping of wood by the Kraft or sulfate process. They are considered to be quite toxic to fish. The odor of skunks is largely due to butyl mercaptan.

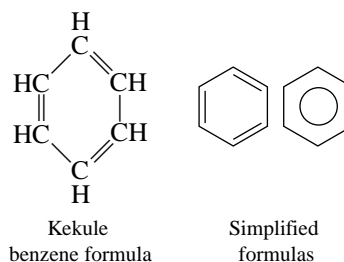
AROMATIC COMPOUNDS

5.12 | INTRODUCTION

The *aromatic* organic compounds are all ring compounds or have cyclic groups of aromatic nature in their structure. The carbon atoms in these ring compounds have only one covalent bond, in contrast to those in aliphatic compounds with two.



The simplest aromatic ring is made up of six carbon atoms and is known as the benzene ring. *Benzene* (C_6H_6) is known as the *parent compound* of the aromatic series. Hydrocarbons based on the benzene ring as a structural unit are also called *arenes*. The benzene ring is usually represented by the Kekule formula.

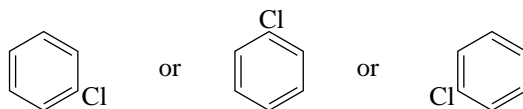


This formula shows double bonds between alternate carbon atoms in the ring. The double bonds, however, are not like those in the aliphatic series. For example, halogens will not add to such bonds. For purposes of simplicity, most chemists represent the benzene ring as one of the simplified formulas shown.

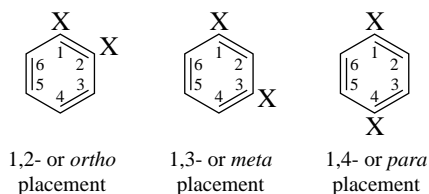
Nomenclature

It is important to note that carbon atoms are not shown in the simplified benzene formula. Also, each carbon atom in a ring is like all others, and therefore, when substitution occurs on one carbon atom, the same compound is formed as though sub-

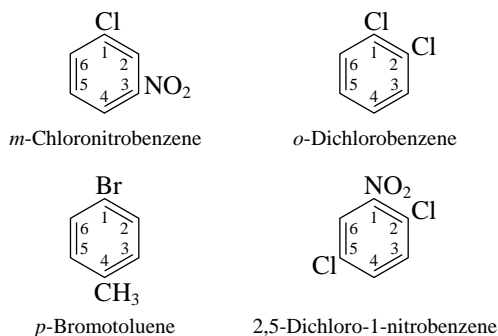
stitution had occurred on any of the other five carbon atoms. Thus, for monochlorobenzene (C_6H_5Cl) there is only one compound, no matter how the structural formula is written.



When substitution occurs on two or more carbon atoms of a benzene ring, it becomes necessary to establish some system of nomenclature. Two systems are used.



Di-substituted compounds, such as dichlorobenzene, are commonly referred to as *ortho*, *meta*, or *para*, depending on the point of substitution. If substitution is on adjacent carbon atoms, the term *ortho* is used; if on carbon atoms once removed, the term *meta* is used; and if on carbon atoms opposite each other, the term *para* is used. Tri- and other poly-substituted compounds must be named by another system. In this system, the carbon atoms of the benzene ring are numbered in a clockwise manner. Examples are



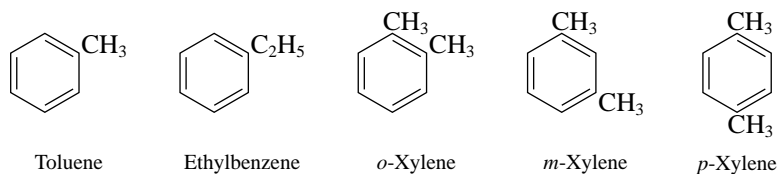
When the benzene ring is attached to aliphatic compounds, the products are also called *phenyl* derivatives, the phenyl group being C_6H_5- . Thus ethyl benzene is also phenyl ethane.

5.13 | HYDROCARBONS

Two series of homologous aromatic hydrocarbons are known: the benzene and the polyring series.

Benzene Series

The benzene series of homologous compounds is made up of alkyl substitution products of benzene. They are found along with benzene in coal tar and in many crude petroleum. Table 5.11 lists the benzene-series hydrocarbons of commercial importance. *Toluene*, or methylbenzene, is the simplest alkyl derivative of benzene. *Xylene* is a dimethyl derivative of benzene.



It exists in three isomeric forms: ortho-xylene, meta-xylene, and para-xylene. All are isomeric with ethylbenzene in that they have the same general formula, C_8H_{10} . Together with benzene, these compounds are commonly referred to as the BTEX group.

The benzene-series hydrocarbons are used extensively as solvents and in chemical synthesis, and are common constituents of petroleum products (e.g., gasoline). Although they are relatively insoluble in water, wastewaters and leachates containing 10 to as high as 1000 mg/L for the BTEXs have been observed. These compounds are frequently detected in groundwaters, with a major source being leaking underground gasoline storage tanks.

The benzene-series compounds have been implicated in several human health effects, most notably cancer. Benzene is known to cause leukemia. The current drinking water MCLs are 5 $\mu\text{g/L}$ for benzene, 700 $\mu\text{g/L}$ for ethylbenzene, 1 mg/L for toluene, and 10 mg/L for the sum total of the xylenes.

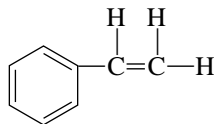
Styrene (phenyl ethene), a benzene derivative, is an environmentally significant compound. It is used as a monomer in the production of a wide variety of poly-

Table 5.11 | Benzene-series hydrocarbons

Name	Formula	Mp, °C	Bp, °C	Sp. gr., 20°/4°
Benzene	C_6H_6	5.5	80.0	0.877
Toluene	$C_6H_5CH_3$	-94.9	110.6	0.867
<i>o</i> -Xylene	$C_6H_4(CH_3)_2$	-25.2	144.5	0.880 ^{10°}
<i>m</i> -Xylene		-47.8	139.1	0.864
<i>p</i> -Xylene		13.2	138.3	0.861
Ethylbenzene	$C_6H_5C_2H_5$	-94.9	136.1	0.867

Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

styrene products (e.g., plastics, synthetic rubber). A drinking water MCL of 100 $\mu\text{g}/\text{L}$ has been set for styrene.

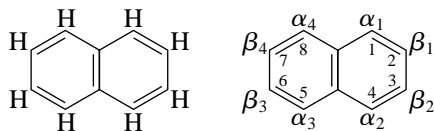


Styrene

Polyring Hydrocarbons

A wide variety of polycyclic aromatic hydrocarbons (PAHs) are known. A few examples will illustrate the possibilities.

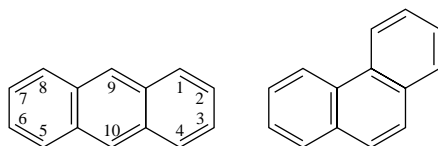
Naphthalene (C_{10}H_8) *Naphthalene* is a white crystalline compound derived from coal tar and was formerly used to produce mothballs.



Naphthalene

It has been displaced largely from this market by paradichlorobenzene. A new system of nomenclature is applied to this type of compound. Carbon atoms adjacent to those shared in common by the two rings are known as α -carbon atoms and the others are known as β -carbon atoms. The carbon atoms shared by the two rings do not have hydrogen attached to them and so are given no designation. The specific name, naphthalene, should not be confused with naphthene (Sec. 5.10).

Anthracene ($\text{C}_{14}\text{H}_{10}$) and Phenanthrene ($\text{C}_{14}\text{H}_{10}$) *Anthracene* and *phenanthrene* are isomers.

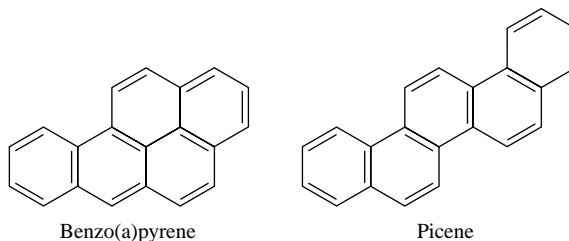


Anthracene

Phenanthrene

Their formulas illustrate the possible ways in which polycyclic aromatic hydrocarbons may occur. Many other more complex compounds, such as *benzo(a)pyrene*

and *picene*, are known. Benzo(a)pyrene is a potent carcinogen, and has a drinking water MCL of $0.2 \mu\text{g/L}$.



It should be remembered that hydrogen atoms occur on all carbon atoms of these compounds that are not common to two rings.

Naphthalene and anthracene are widely used in the manufacture of dye-stuffs. The phenanthrene nucleus is found in important alkaloids, such as morphine, vitamin D, sex hormones, and other compounds of great biological significance.

PAHs are associated with combustion products, and are believed to be the cause of the first recognized chemically related cancer that was found in chimney sweeps in the late eighteenth century. They are common residual contaminants at sites where coal was used to manufacture consumer gas (also called coal gas or town gas) in the early twentieth century, and where creosote, which is manufactured from coal, has been used to preserve wood. The larger compounds (five or more aromatic rings) tend not only to be carcinogenic, but are also the more difficult ones for bacteria to degrade.

Chlorinated Aromatic Hydrocarbons

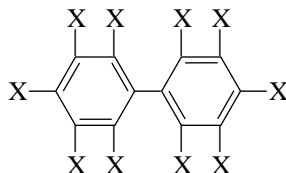
There are many chlorinated aromatic hydrocarbons (also called aryl halides) of importance. They are common industrial chemicals that through their widespread use and relative environmental persistence have become significant environmental problems, much in the same manner as the chlorinated aliphatic compounds. In general, as chlorine atoms are added to the benzene ring, water solubility decreases hydrophobicity increases, and the molecule's vapor pressure decreases. Two of the most important classes are the chlorinated benzenes and the polychlorinated biphenyls.

Chlorinated Benzenes Chlorinated benzenes are benzenes with one or more of the hydrogens replaced with chlorine. They are widely used industrial chemicals that have solvent and pesticide properties. Like the chlorinated aliphatics, they have been found at abandoned waste sites and in many wastewaters and leachates. They are fairly volatile, slightly to moderately soluble, and hydrophobic.

Chlorobenzene (monochlorobenzene) has a drinking water MCL of $100 \mu\text{g/L}$. There are three dichlorobenzene isomers: 1,2-dichlorobenzene (ortho isomer), 1,3-dichlorobenzene (meta isomer), and 1,4-dichlorobenzene (para isomer). The current MCLs are $75 \mu\text{g/L}$ for *p*-dichlorobenzene and $600 \mu\text{g/L}$ for *o*-dichlorobenzene; the meta isomer is not regulated at this time. There are also three trichlorobenzene isomers: 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, and 1,3,5-trichlorobenzene. A drinking water MCL of $70 \mu\text{g/L}$ has been established for 1,2,4-trichlorobenzene.

Hexachlorobenzene (C_6Cl_6) has been used in the synthesis of several chlorinated benzenes and is a commonly found groundwater contaminant. Its MCL is $1 \mu g/L$.

Polychlorinated Biphenyls (PCBs) Polychlorinated biphenyls are chlorinated benzenes with the general structure:



where X can be either a chlorine or a hydrogen. There are 209 possible PCBs (called congeners). Groups of congeners with similar average numbers of chlorine atoms are typically described with the name Aroclor and a corresponding number, for example, Aroclor 1260. PCBs are very stable compounds of low vapor pressure and high dielectric constants. They were widely used as coolants in transformers and capacitors, plasticizers, solvents, and hydraulic fluids. PCBs are very hydrophobic and tend to bioconcentrate. Significant concentrations of PCBs have been found in higher levels of the food chain (e.g., fish and birds). Because of human health and environmental effects associated with PCBs, their manufacture in the United States was banned in 1977. The drinking water MCL for total PCBs is $0.5 \mu g/L$. PCBs have recently been implicated as *endocrine disruptors*. Endocrine-disrupting chemicals (EDC), also called hormonally active agents, are those chemicals that have been reported to be associated with adverse reproductive and developmental effects in humans and wildlife. Additional discussion of EDCs is given in Sec. 5.32. The disposal of PCB wastes is strictly controlled and continues to be problematical. Some PCB congeners have been shown to be degraded by microorganisms; the more highly chlorinated congener ones by anaerobic microorganisms, and the less chlorinated ones by aerobic microorganisms. Transformation rates, however, tend to be very slow such that the compounds are generally considered to be highly resistant to biodegradation.

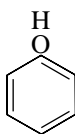
5.14 | PHENOLS

The phenols are among the most important of the aromatic compounds.

Monohydroxy Phenols

There are several monohydroxy phenols of interest.

Phenol (C_6H_5OH) The monohydroxy derivative of benzene is known as *phenol*.



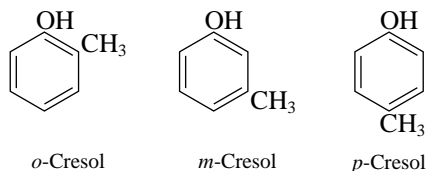
Phenol

Its formula and name indicate that it might correspond in the aromatic series to alcohols in the aliphatic series. This is not the case, however. Phenol is also known as carboic acid. It ionizes to yield H^+ to a limited extent ($K_A = 1.2 \times 10^{-10}$), and in concentrated solution is quite toxic to bacteria. It has been used widely as a germicide, and disinfectants have been rated in terms of "phenol coefficients," i.e., relative disinfecting power with respect to phenol. The system is considered archaic at the present time.

Phenol is recovered from coal tar, and considerable amounts are manufactured synthetically. It is used extensively in the synthesis of organic products, particularly phenolic-type resins. It occurs as a natural component in industrial wastes from the coal-gas, coal-coking, and petroleum industries as well as in a wide variety of industrial wastes from processes involving the use of phenol as a raw material.

Biological treatment of wastes containing more than 25 mg/L of phenol was considered impossible some years ago. However, research and much practice have demonstrated that phenol will serve as food for aerobic bacteria without serious toxic effects at levels as high as 500 mg/L. Studies with it and with formaldehyde have established the concept of toxicity thresholds. At levels below the threshold, bacteria use the material as food, but above the threshold they find it too toxic for use as food and reproduction of the organisms. Phenol has also been shown to be highly degradable even by anaerobic bacteria, and at levels of up to 2000 mg/L.¹³

Cresols and Other Alkylphenols The next higher homologs of phenol are cresols.



They are found in coal tar and have a higher germicidal action than phenol. They are less toxic to humans. *Lysol* is a mixture of cresols which is sold as a household and sickroom disinfectant. Cresols are the major constituents of "creosote" which is used extensively for the preservation of wood.

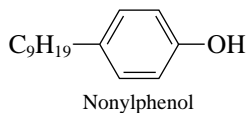
Industrial wastes containing cresols are somewhat difficult to treat by biological methods. Research with aerobic¹⁴ and anaerobic¹⁵ microorganisms has shown the pure cresols to be relatively nontoxic at concentrations of 250 mg/L. The toxicity of crude cresols is believed, therefore, to be due to other compounds.

¹³D. J. W. Blum, R. Hergenroeder, G. F. Parkin, and R. E. Speece, Anaerobic Treatment of Coal Conversion Wastewater Constituents: Biodegradability and Toxicity, *J. Water Pollution Control Federation*, **58**: 122–131 (1986).

¹⁴R. E. McKinney, H. D. Tomlinson, and R. L. Wilcox, Metabolism of Aromatic Compounds in Activated Sludge, *Sewage and Ind. Wastes*, **28**: 547–557 (1956).

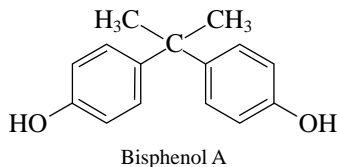
¹⁵Blum et al., Anaerobic Treatment of Coal Conversion Wastewater Constituents: Biodegradability and Toxicity, *J. Water Pollution Control Federation*, **58**: 122–131 (1986).

Alkylphenols have recently been implicated as endocrine disruptors. Alkylphenols are combined with ethylene oxide (Secs. 5.17 and 5.25) to produce alkylphenol ethoxylates, which are used as surfactants in products such as detergents, paints, and pesticides. Action by naturally occurring bacteria degrade these molecules releasing the alkylphenols. These compounds have been found in effluents from wastewater treatment plants, wastewater plant sludges, and natural waters.^{16,17} Nonylphenol is believed to be one of the more potent potential endocrine disruptors.¹⁸

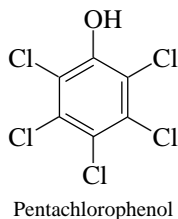


The nonyl group may be highly branched, making the compound resistant to biodegradation.

Another phenol that has been implicated as an important endocrine disrupter is bisphenol A.¹⁹ Bisphenol A is an important intermediate in the production of a wide variety of industrial products including polymers such as polycarbonate plastics, dyes, epoxy coatings, and flame retardants.



Chlorinated Phenols Chlorinated phenols have been used as wood preservatives. The most commonly used phenol for this purpose is pentachlorophenol.



The drinking water MCL for pentachlorophenol is 1 $\mu\text{g/L}$.

¹⁶B. E. Erickson, Alkylphenols in Sewage Sludge Applied to Land, *Env. Sci. Tech.*, **36**(1): 10A–11A, 2002.

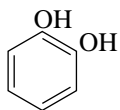
¹⁷C. Maczka et al., Evaluating Impacts of Hormonally Active Agents in the Environment, *Env. Sci. Tech.*, **34**(5): 136A–141A, 2000.

¹⁸Maczka et al., Evaluating Impacts of Hormonally Active Agents in the Environment.

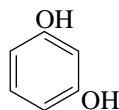
¹⁹*Ibid.*

Polyhydroxy Phenols

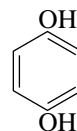
Three isomeric dihydroxy phenols are known. All have been shown²⁰ to be readily oxidized by properly acclimated microorganisms.



Benzene-1,2-diol,
pyrocatechol,
catechol

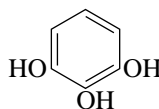


Benzene-1,3-diol,
resorcinol



Benzene-1,4-diol,
hydroquinone

Pyrogallol *Pyrogallol*, 1,2,3-trihydroxybenzene, is known as *pyrogallic acid*.



Pyrogallol

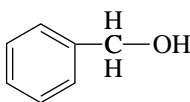
It is easily oxidized and serves as a photographic developer. Pyrogallol is a minor constituent of spent tan liquors. When they are discharged to streams containing iron, inky black ferric pyrogallate is formed.

5.15 | ALCOHOLS, ALDEHYDES, KETONES, AND ACIDS

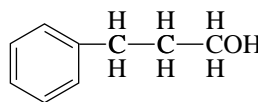
The aromatic alcohols, aldehydes, ketones, and acids are all formed from alkyl derivatives of benzene or one of its homologs. The active group is always in the alkyl group, and therefore the chemistry of the aromatic alcohols, aldehydes, ketones, and acids is very similar to that of the corresponding aliphatic compounds. Common names are usually employed with these compounds, but they may be more properly named as phenyl derivatives of aliphatic compounds.

Alcohols

The aromatic alcohols compose a homologous series. They are phenyl methyl, phenyl ethyl, phenyl *n*-propyl, phenyl isopropyl, and so on.



Benzyl alcohol,
phenyl methyl alcohol



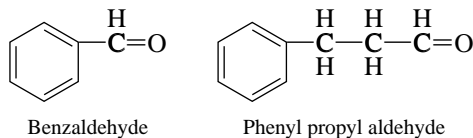
Phenyl *n*-propyl alcohol

²⁰Blum et al., Anaerobic Treatment of Coal Conversion Wastewater Constituents: Biodegradability and Toxicity, *J. Water Pollution Control Federation*, **58**: 122–131 (1986).

The aromatic alcohols are subject to chemical and biological oxidation. Oxidation of primary alcohols produces aldehydes and oxidation of secondary alcohols produces ketones.

Aldehydes

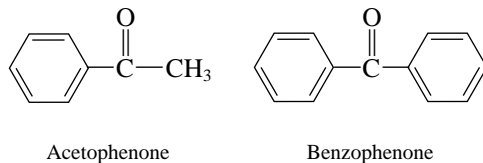
The aromatic aldehydes are important compounds in chemical synthesis.



They are easily oxidized to the corresponding acids. Many of the more complex aldehydes have fragrant odors: coumarin, anisaldehyde, vanillin, and so on.

Ketones

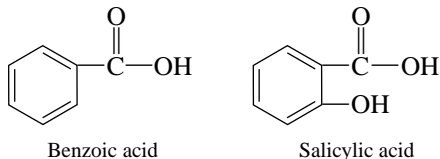
The aromatic ketones are of two types: those that have one phenyl group attached to the carbonyl group and those that have two.



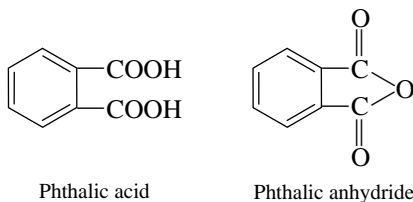
Chemical and biological oxidation results in disruption of the molecule, with the formation of lower-molecular-weight acids and, probably, carbon dioxide.

Acids

A wide variety of aromatic, monocarboxylic acids is known. Oxidation of benzaldehyde produces benzoic acid. Sodium benzoate is used as a food preservative. Salicylic acid is used to prepare aspirin.

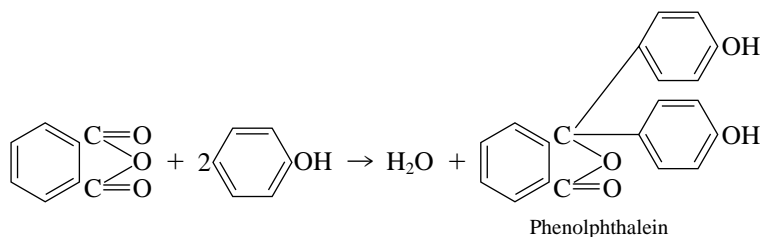


Oxidation of naphthalene produces an important dicarboxylic acid, phthalic acid.



It and its anhydride are important in the manufacture of a variety of organic compounds. Phthalates are used as plasticizers in the production of a wide variety of plastics. A drinking water MCL of $6 \mu\text{g/L}$ has been set for di (2-ethylhexyl) phthalate. Phthalates have also been implicated as endocrine disruptors.

Phenolphthalein, used as a pH indicator in the laboratory, is another example.



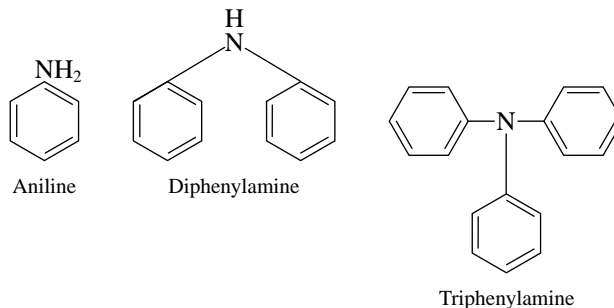
Most aromatic acids are subject to biological oxidation. The normal end products are carbon dioxide and water. However, some phthalates are resistant to biodegradation.

5.16 | SIMPLE COMPOUNDS CONTAINING NITROGEN

The aromatic compounds containing nitrogen are derivatives either of ammonia or of nitric acid. The former are called *amines*, and the latter are called *nitro* compounds. In addition, many complex nitrogen compounds exist that are outside the scope of this book.

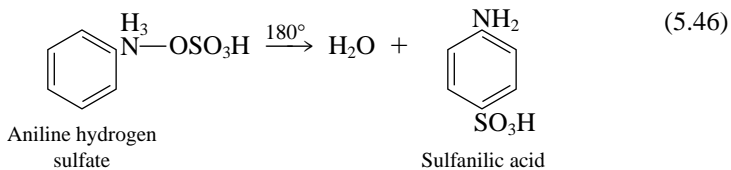
Amines

The aromatic amines are of two types: those in which the phenyl or other aromatic group is attached directly to nitrogen and those in which the nitrogen occurs in an attached alkyl group. There are three phenyl derivatives of ammonia: primary, secondary, and tertiary amines.

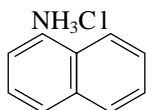


The primary form is called aniline and the secondary form is diphenylamine. They are both basic in character, react with strong acids to form salts, and are important

compounds in organic synthesis. Aniline dyes are derived from aniline. Sulfanilic acid, used in the colorimetric determination of nitrites, is made from aniline.



1-Naphthylamine HCl is an important compound in water analysis.

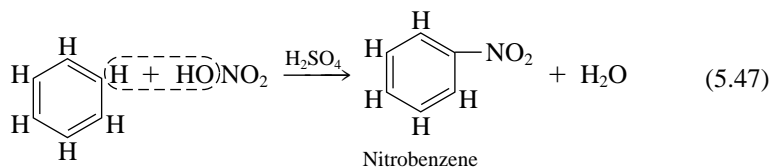


A derivative, N-(1-naphthyl)-ethylenediamine dihydrochloride is used in conjunction with sulfanilic acid in the determination of nitrite nitrogen.

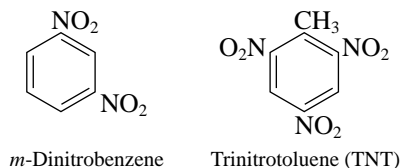
Benzylamine ($\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$) is an example of an aromatic amine that has the $-\text{NH}_2$ group attached to the aliphatic part of the molecule. These compounds are not important commercially.

Nitro Compounds

Nitric acid reacts with benzene and other aromatic compounds to form *nitro* compounds. The reaction is as follows:



A dehydrating agent, usually sulfuric acid, must be present to remove the water that is formed. One additional nitro group may be added under proper conditions. The principal product is *m*-dinitrobenzene,



as the presence of the first nitro group directs the second into the meta position. Trinitrobenzene is very difficult to prepare.

Nitration of toluene results in the formation of trinitrotoluene, or TNT. The first nitro group is directed into the ortho position by the methyl group, and additional nitro groups attach in the meta position with respect to the first nitro group. TNT is

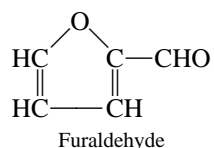
widely used as an ingredient of military explosives. It is relatively resistant to aerobic biological degradation. However, it is fairly easily reduced to the corresponding amine under reducing conditions.

HETEROCYCLIC COMPOUNDS

5.17 | HETEROCYCLIC COMPOUNDS

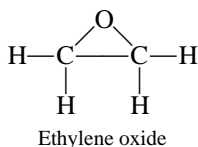
Heterocyclic compounds have one other element in the ring in addition to carbon. A wide variety of compounds exists; some are aliphatic in character, and some are aromatic. Many are of great biological importance, and several are of significance in environmental engineering and science.

Furaldehyde, or *furfural*, is an example of an aliphatic heterocyclic compound having a five-membered ring containing oxygen. It is produced from pentose sugars by dehydration. Commercially, it is made from oat hulls and corn cobs, waste products of the cereal industry.



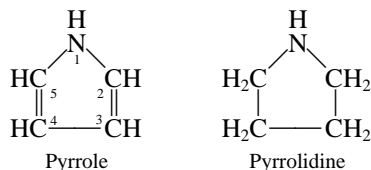
Both were formerly disposed of by burning. Manufacture of furfural yields some liquid wastes of concern to environmental engineers. Furfural has been shown to be biodegradable.

Epoxides are three-membered rings where oxygen is bonded with two carbons. Several epoxides are environmentally significant. For example, ethylene oxide,



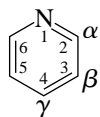
is a toxic epoxide that has been used in chemical synthesis [e.g. alkylphenol ethoxylates (Sec. 5.14) and synthetic detergents (Sec. 5.26)] and as a sterilizing agent and pesticide. It is a regulated air pollutant. In general, epoxides are very reactive. They have been shown to be important intermediates in the biotransformation of several organics, for example, trichloroethene.

Pyrrole and *pyrrolidine* are examples of heterocyclic compounds having five-membered rings containing nitrogen.



The pyrrole or pyrrolidine ring occurs in the structure of many important natural compounds, e.g., nicotine, cocaine, chlorophyll, and hemoglobin.

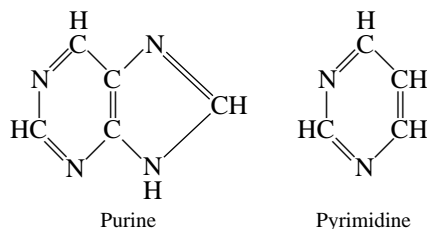
Pyridine is an example of a six-membered aromatic heterocyclic compound with nitrogen contained in the ring.



Pyridine

It is an especially vile-smelling liquid. It is used as a denaturant in ethyl alcohol, to make it unpalatable, and in chemical synthesis. It is weakly basic in character and forms salts with strong acids. *Nicotinic acid* is a derivative of pyridine, having a carboxyl group in the β position. It is a key component of a coenzyme, NAD, which is present in all cells and involved in oxidation of organic matter. Nicotinic acid is a vitamin required by humans and many other mammals, a deficiency in the diet of humans causing pellagra.

Purine and *pyrimidine* are two other ring compounds containing nitrogen and of immense biological importance.

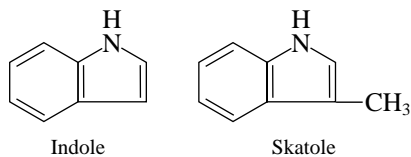


Purine

Pyrimidine

Important derivatives of purine are *adenine* and *guanine*, and of pyrimidine are *cytosine*, *uracil*, and *thymine*. These compounds or *bases* form the major components of nucleic acids, which carry the genetic information for all life (see Sec. 6.14). In addition, they are components of key biological molecules such as ATP, the primary carrier of chemical energy in all cells, and coenzyme A, which is necessary for fatty acid degradation.

Indole and *skatole* are examples of heterocyclic compounds that possess a benzene nucleus condensed with a pyrrole nucleus.



Indole

Skatole

Both possess unpleasant odors and are produced during the putrefaction of protein matter. Under controlled conditions, such as exist in well-operated sludge digesters, very little indole or skatole is formed.

Other heterocyclic nitrogen compounds of interest include the explosives RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-

1,3,5,7-tetrazocine). These compounds have been found as soil or groundwater contaminants at a number of U.S. Department of Defense facilities. They are slightly soluble in water but are not particularly hydrophobic; they have low vapor pressures and are not very biodegradable under most conditions found in the natural environment. They have been detected in a number of groundwater supplies and present environmental engineers and scientists with challenging remediation problems.



5.18 | DYES

The subject of *dyes* is of such magnitude and complexity that a discussion of various types will not be presented here. The environmental engineer and scientist concerned with the treatment of textile wastes, and possibly a few others, will be confronted with the need to learn more about these materials. Recourse for information should be made to standard organic chemistry texts or treatises on dyes. The sulfur dyes are noted for their toxic properties.

THE COMMON FOODS AND RELATED COMPOUNDS

5.19 | GENERAL

The term *food* is applied to a wide variety of organic materials that can serve as a source of energy for living organisms. In the case of bacteria, these compounds range from hydrocarbons through various oxidation products, including organic acids. In the case of higher animals and humans, the principal or common foods are restricted to *carbohydrates*, *fats*, and *proteins*. Other organic compounds such as ethanol, certain aldehydes, and many acids serve as food or energy sources also. The latter are sometimes referred to as exotic foods, as they are not considered part of an essential diet but are added to increase palatability or for other reasons.

5.20 | CARBOHYDRATES

The term *carbohydrate* is applied to a large group of compounds of carbon, hydrogen, and oxygen in which the hydrogen and oxygen are in the same ratio as in water, i.e., two atoms of hydrogen for each atom of oxygen. The processing of car-

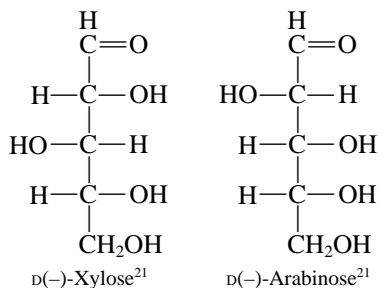
bohydrate materials occurs in the lumber, paper, and textile industries, as well as in the food industry. Wastes from these industries are major problems and tax the ingenuity of environmental engineers and scientists to find satisfactory solutions.

Carbohydrates may be grouped into three general classifications, depending upon the complexity of their structure: (1) simple sugars, or *monosaccharides*; (2) complex sugars, or *disaccharides*; (3) *polysaccharides*. In general, the *-ose* ending is used to name carbohydrates.

Simple Sugars, or Monosaccharides

The simple sugars, or *monosaccharides*, all contain a carbonyl group in the form of an aldehyde or a keto group. Those with aldehyde groups are known as *aldoses* and those with keto groups are known as *ketoses*. They are also glycols, as they possess several OH groups. Two series of simple sugars are of importance commercially: the *pentoses* are five-carbon-atom sugars and the *hexoses* are six-carbon-atom sugars.

Pentoses Pentoses have the general formula $C_5H_{10}O_5$. Two pentoses are of commercial importance, and both are *aldopentoses*. *Xylose* is formed by the hydrolysis of pentosans, which are commonly found in waste organic materials such as oat hulls, corn cobs, and cottonseed hulls. Considerable amounts of xylose are formed in the pulping of wood through the hydrolysis of hemicellulose. *Arabinose* is produced by the hydrolysis of gum arabic or wheat bran.

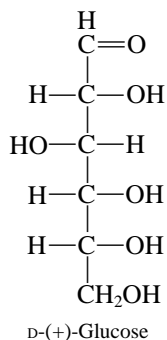


Both xylose and arabinose are used in bacteriological work in media used to differentiate among various bacteria. Certain bacteria can ferment one but not the other, and vice versa. Mixed cultures of bacteria, such as those derived from the soil or waste, convert both sugars to carbon dioxide and water. The pentose sugars are not fermented by yeast under anaerobic conditions; therefore, they cannot be used to produce ethanol. They do serve as an energy source for yeast under aerobic conditions, however, and advantage is taken of this fact in one method of treating spent sulfite liquors from the pulping of wood.

Hexoses There are four important hexose sugars with the general formula $C_6H_{12}O_6$. *Glucose*, *galactose*, and *mannose* are all *aldoses*, and *fructose* is a *ketose*.

²¹All sugars are optically active. The nomenclature is somewhat complicated, however, and details should be obtained from a standard text on organic chemistry.

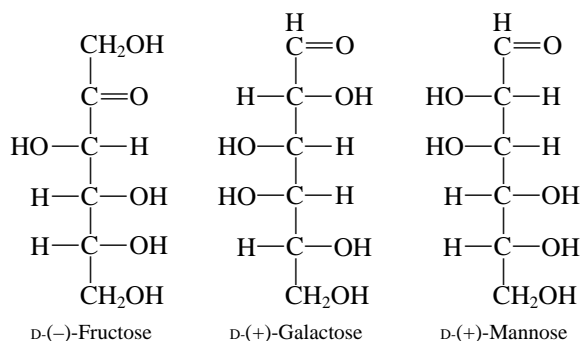
Glucose Glucose is the most common of the aldohexose sugars. It is found naturally in fruit juices and in honey. It is manufactured in great quantity by the hydrolysis of corn starch. It is the principal component of corn syrup. Both corn syrup and glucose are used extensively in candy manufacture. Glucose is much less sweet than ordinary sugar and replaces it for many purposes.



Glucose is the only hexose sugar that can be prepared in relatively pure form by the hydrolysis of disaccharides or polysaccharides. All the other hexose sugars occur in combination with glucose.

Fructose Fructose is the only significant ketohexose and occurs naturally in honey. When cane or beet sugar is hydrolyzed, one molecule of fructose and one molecule of glucose are formed from each molecule of sucrose.

Galactose and Mannose Galactose and mannose do not occur in free form in nature. Galactose is produced by the hydrolysis of lactose, more commonly called milk sugar. Glucose is formed simultaneously. Mannose is produced by the hydrolysis of ivory nut, and glucose is formed at the same time.



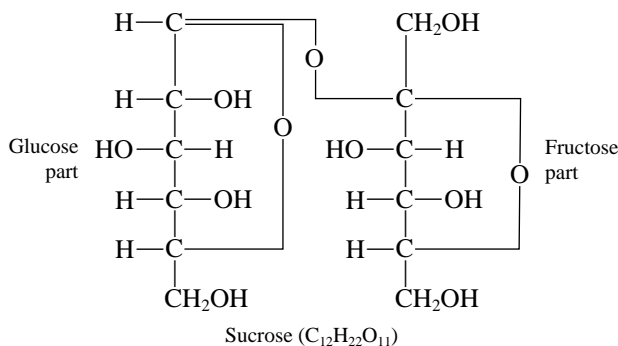
Glucose and galactose are of particular interest. Glucose is always one of the products and may be the sole product when di- or polysaccharides are hydrolyzed. It is therefore found in a wide variety of industrial wastes. Galactose is formed from the hydrolysis of lactose, or milk sugar, and is found in wastes from the dairy industry. Both sugars are readily oxidized by aerobic bacteria to form acids, and the oxi-

dition may stop at that point because of the unfavorable pH conditions produced by the acids unless precautions are taken to control the pH by means of buffers or alkaline materials. Lactic acid is an important intermediate in the oxidation of galactose. Both sugars are fermented rapidly under anaerobic conditions, with acid formation.

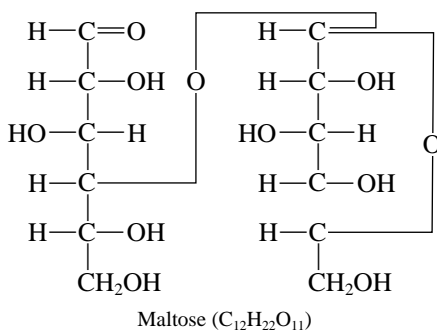
Complex Sugars, or Disaccharides

There are three important sugars with the general formula $C_{12}H_{22}O_{11}$: *sucrose*, *maltose*, and *lactose*. All disaccharides may be considered as consisting of two hexose sugars hooked together in one molecule. Hydrolysis results in cleavage of the molecule and formation of the hexoses.

Sucrose Sucrose is the common sugar of commerce. It is derived largely from sugarcane and sugar beets. The sap of such trees as the sugar maple contains considerable sucrose. Hydrolysis of the sucrose molecule results in the formation of one molecule of glucose and one molecule of fructose.



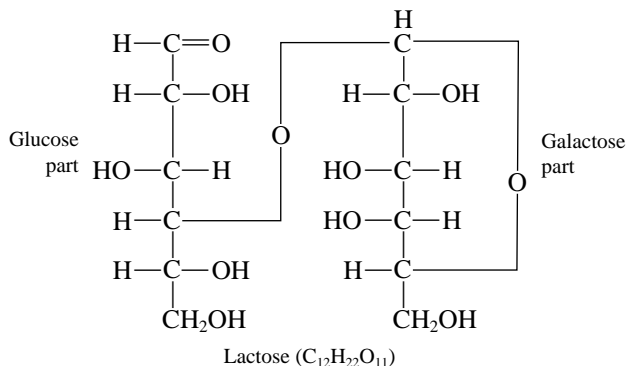
Maltose Maltose is made by the hydrolysis of starch, induced by *diastase*, an enzyme present in barley malt. The starch may be derived from a wide variety of sources, and its hydrolysis by diastase results in commercial maltose, which is used in infant foods and in malted milk.



Maltose is readily hydrolyzed to yield two molecules of glucose.

Alcohol production by fermentation processes uses starch from a wide variety of sources. The starch is converted to maltose by the enzyme from barley malt. Enzymes from the yeast hydrolyze maltose to glucose and convert the glucose to alcohol and carbon dioxide (Sec. 5.3).

Lactose Lactose, or milk sugar, occurs in the milk of all mammals. Upon hydrolysis, the molecule is split to yield a molecule of glucose and a molecule of galactose.

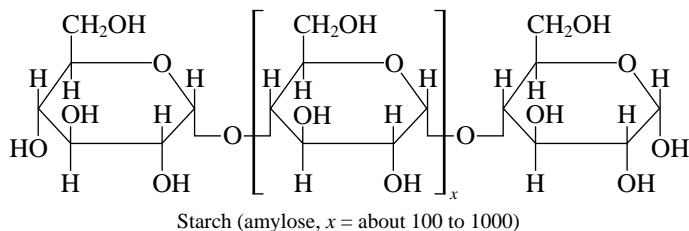


Lactose is used in infant foods and in candy making. Dried skimmed-milk solids contain about 60 percent lactose.

Polysaccharides

The polysaccharides are all condensation products of hexoses or other monosaccharides. Glucose and xylose are the most common units involved. Three polysaccharides are of interest: *starch*, *cellulose*, and *hemicellulose*. None of them have the characteristic sweet taste of sugar because of their insolubility and complex molecular structure.

Starch Starch has the general formula (C₆H₁₀O₅)_x. It occurs in a wide variety of products grown for food purposes (corn, wheat, potatoes, rice, etc.). It is the cheapest foodstuff and serves mainly in human nutrition as a source of energy. Starch is used in fermentation industries to produce a wide variety of products. The structure of the starch molecule is not known definitely. Its hydrolysis yields glucose as the only monosaccharide, and its general formula may be indicated as follows:



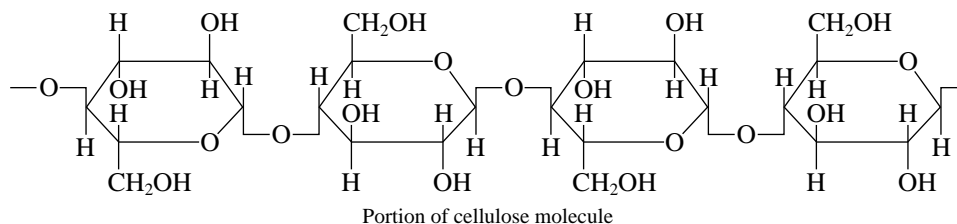
Starch consists of two major fractions. One fraction, consisting of glucose units connected in a straight chain, is termed *amylose*, and the other fraction, consisting

of glucose units attached to form branched chains, is termed *amylopectin*. The amylose molecule contains 100 to 1000 glucose units. Amylose is soluble in water and absorbs up to 20 percent of its own weight in iodine to form the blue complex used as an indicator in iodimetric analysis (Sec. 11.4). The amylopectin molecule, not shown, is much larger and contains about 500 to 5000 glucose units. It is not as soluble in water as amylose.

The glucose units in starch are connected by what is termed an *alpha* linkage. This linkage is readily hydrolyzed by enzymes common to all mammals as well as to microorganisms, and hence they are able to use starch as food.

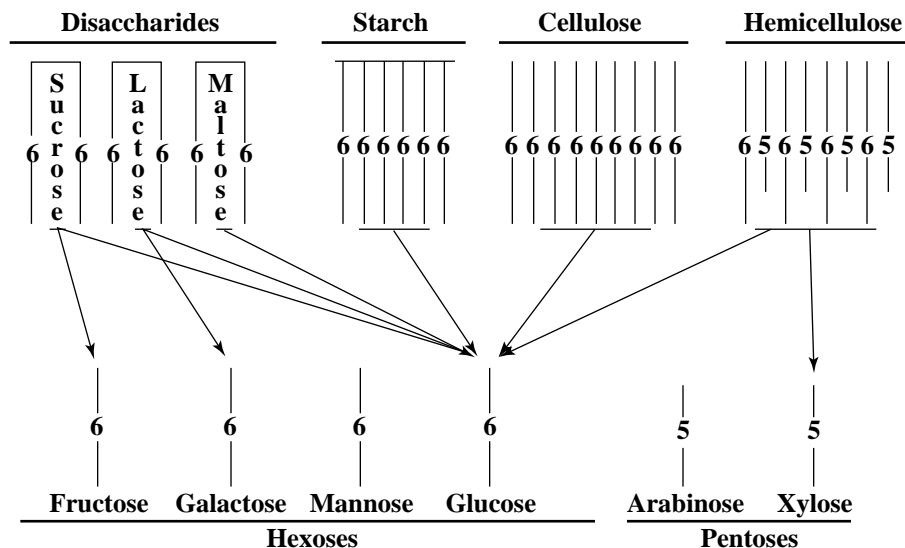
The industrial wastes produced from the manufacture of starch, from the processing of carbohydrate foods, and from the industrial uses of starch can be readily treated by biological processes.

Cellulose Cellulose forms the structural fiber of many plants. Cotton is essentially pure cellulose. High-grade cellulose can be produced from wood through the sulfite and sulfate pulping processes. Like starch, cellulose consists of glucose subunits. However, these units are connected by what is termed *beta* linkage, and mammals, including humans, do not have enzymes capable of promoting the hydrolysis of this linkage. Therefore, cellulose passes through the digestive tract unchanged. Certain animals, especially ruminants (cud-chewing animals) such as the cow, have bacteria in the digestive tract that can hydrolyze the beta link. This is a convenient arrangement, for the animal can digest the bacterial fermentation products and thus derive nourishment indirectly from cellulose. The beta linkage for cellulose is indicated as follows:



Industrial wastes from the paper industry usually contain considerable amounts of cellulose in suspension. This is particularly true of the wastes from the manufacture of low-grade papers involving the reuse of waste paper. Most of the wastes from other industries processing cellulose contain very little cellulose. The principal contaminants are inorganic compounds, derivatives of cellulose, and other organic compounds. Since certain bacteria can hydrolyze cellulose, biological treatment of cellulose containing wastes is possible. However, treatment by aerobic processes is slow. Since most of the cellulose will settle to produce a sludge, preliminary treatment by sedimentation is practiced, and the sludges produced are disposed of by anaerobic digestion or by physical methods such as filtration, centrifugation, and incineration.

Hemicelluloses The hemicelluloses are compounds that have characteristics somewhat like cellulose. They are composed of a mixture of hexose and pentose units, however, and upon hydrolysis yield glucose and a pentose, usually xylose.

**Figure 5.1**

Summary of hydrolytic behavior of carbohydrates.

Most natural woods contain cellulose, hemicellulose, and lignin, along with resins, pitch, and so on. In the pulping process, the lignin, hemicellulose, resins, and so on, are dissolved, leaving cellulose as the product. As a result, spent pulping liquors contain considerable amounts of glucose and xylose as well as other organic substances, principally derivatives of lignin. The lignin derivatives, which have highly complex aromatic structures, are very resistant to biological degradation. Glucose, xylose, and other organic substances are converted to carbon dioxide and water by yeast or bacteria under aerobic conditions. Yeast may be used to ferment the glucose to alcohol under anaerobic conditions, but the xylose, a pentose, is not fermentable to alcohol.

Summary of Hydrolytic Behavior of Carbohydrates

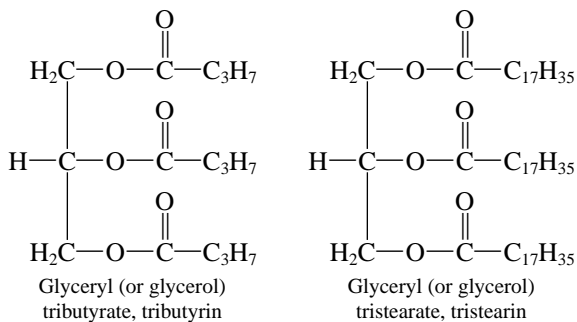
The hydrolytic behavior of carbohydrates is presented in a simplified graphic form in Fig. 5.1. All di- and polysaccharides yield glucose. Sucrose yields fructose, lactose yields galactose, and hemicellulose yields xylose in addition to glucose.

5.21 | FATS, OILS, AND WAXES

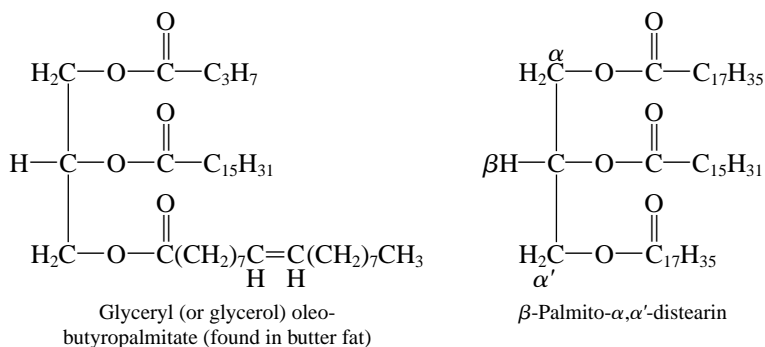
Fats, oils, and waxes are all esters. Fats and oils are esters of the trihydroxy alcohol, glycerol, while waxes are esters of long-chain monohydroxy alcohols. All serve as food for humans, as well as bacteria, since they can be hydrolyzed to the corresponding fatty acids and alcohols.

Fats and Oils

Fats and oils are both glycerides of fatty acids. The fatty acids are generally of 16- or 18-carbon atoms, although butyric, caproic, and caprylic acids are present to a significant extent as components of the esters of butterfat. The acids may also be unsaturated. Oleic and linoleic are important acids in cottonseed oil. Linseed oil contains large amounts of linoleic and linolenic acids. The glycerides of fatty acids that are liquid at ordinary temperatures are called *oils* and those that are solids are called *fats*. Chemically they are quite similar. The oils have a predominance of short-chain fatty acids or fatty acids with a considerable degree of unsaturation, such as linoleic or linolenic.



The fatty acids in a given molecule of a glyceride may be all the same, as just shown, or they may all be different.



The principal acids composing the glycerides of fats and oils are shown in Table 5.12.

The relative amounts of the major fatty acids contained in various fats and oils are shown in Table 5.13.

Fats and oils undergo three types of chemical reactions of interest: hydrolysis, addition, and oxidation.

Table 5.12 | Acids of fats and oils

Name	Formula	Mp, °C	Source
Butyric	C ₃ H ₇ COOH	-5.7	Butter
Caproic	C ₅ H ₁₁ COOH	-3	Butter, coconut oil
Caprylic	C ₇ H ₁₅ COOH	16.3	Palm oil, butter
Capric	C ₉ H ₁₉ COOH	31.9	Coconut oil
Lauric	C ₁₁ H ₂₃ COOH	43.2	Coconut oil, spermaceti
Myristic	C ₁₃ H ₂₇ COOH	53.9	Nutmeg, coconut oil
Palmitic	C ₁₅ H ₃₁ COOH	63.1	Palm oil, animal fats
Stearic	C ₁₇ H ₃₅ COOH	69.6	Animal and vegetable fats, oils
Arachidic	C ₂₀ H ₄₀ O ₂	76.5	Peanut oil
Behenic	C ₂₂ H ₄₄ O ₂	81.5	Ben oil
Oleic	C ₁₈ H ₃₄ O ₂	13.4	Animal and vegetable fats, oils
Erucic	C ₂₂ H ₄₂ O ₂	34.7	Rape oil, mustard oil
Linoleic	C ₁₈ H ₃₂ O ₂	-12	Cottonseed oil
Linolenic	C ₁₈ H ₃₀ O ₂	-11	Linseed oil

Source: D. R. Linde (ed.): "Handbook of Chemistry and Physics," 82nd ed., CRC Press LLC, Boca Raton, 2001.

Table 5.13 | Acid content of fats and oils (percent)

Name	Oleic	Lino- leic	Lino- lenic	Stearic	Myristic	Palmitic	Ara- chidic
Butter ^d	27.4			11.4	22.6	22.6	
Mutton tallow	36.0	4.3		30.5	4.6	24.6	
Castor oil ^b	9	3		3			
Olive oil	84.4	4.6		2.3	Trace	6.9	0.1
Palm oil	38.4	10.7		4.2	1.1	41.1	
Coconut oil ^c	5.0	1.0		3.0	18.5	7.5	
Peanut oil ^d	60.6	21.6		4.9		6.3	3.3
Corn oil ^e	43.4	39.1		3.3		7.3	0.4
Cottonseed oil	33.2	39.4		1.9	0.3	19.1	0.6
Linseed oil	5	48.5	34.1				
Soybean oil ^f	32.0	49.3	2.2	4.2		6.5	0.7
Tung oil ^g	14.9			1.3		4.1	

^aContains caproic, 1.4 percent; caprylic, 1.8 percent; capric, 1.8 percent; butyric, 3.2 percent; lauric, 6.9 percent.

^bContains about 85 percent of ricinoleic acid, 12-hydroxy-9-octadecenoic acid (mp, 17°),
 $\text{CH}_3(\text{CH}_2)_5\text{CHOHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$.

^cContains caprylic, 9.5 percent; capric, 4.5 percent; lauric, 51 percent.

^dContains 2.6 percent lignoceric acid.

^eContains 0.2 percent lignoceric acid.

^fContains 0.1 percent lignoceric acid.

^gContains 79.7 percent eleostearic acid.

Source: From E. Wertheim and H. Jeskey, "Introductory Organic Chemistry," 3rd ed., McGraw-Hill, New York, 1956. Table reproduced by permission of the authors.

Hydrolysis Since fats and oils are esters, they undergo hydrolysis with more or less ease. The hydrolysis may be induced by chemical means, usually by treatment with NaOH, or by bacterial enzymes that split the molecule into glycerol plus fatty acids. Hydrolysis with the aid of NaOH is called *saponification*. Hydrolysis by bacterial action may produce *rancid* fats or oils and renders them unpalatable. Rancid butter and margarine are notorious for their bad odor.

Addition The fats and oils containing unsaturated acids add chlorine at the double bonds, as other unsaturated compounds do. This reaction is often slow because of the relative insolubility of the compounds. It may represent a significant part of the chlorine demand of some wastes, and chlorinated organics will be produced during chlorination, some of which may be of health concern.

Oils that contain significant amounts of oleic and linoleic acids may be converted to fats by the process of *hydrogenation*. In this process hydrogen is caused to add at the double bonds, and saturated acids result. Thus, low-priced oils such as soybean and cottonseed can be converted into margarine, which is acceptable as human food. Many cooking fats or shortenings are made in the same manner. The hydrogenation can be controlled to produce any degree of hardness desired in the product.

Oxidation The oils with appreciable amounts of linoleic and linolenic acids or other highly unsaturated acids, such as linseed and tung oil, are known as *drying oils*. In contact with the air, oxygen adds at the double bonds and forms a resinlike material. The drying oils are the major component in all oil-based paints.

Waxes

Waxes, with the exception of paraffin wax, are esters of long-chain acids and alcohols of high molecular weight. *Beeswax* is an ester of palmitic acid and myricyl alcohol ($C_{15}H_{31}COOC_{31}H_{63}$). It also contains cerotic acid ($C_{25}H_{51}COOH$). Spermaceti is obtained from the heads of sperm whales and is principally an ester of palmitic acid and cetyl alcohol ($C_{15}H_{31}COOC_{16}H_{33}$). Cetyl esters of lauric and myristic acids are also present to a limited extent.

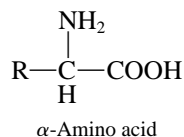
5.22 | PROTEINS AND AMINO ACIDS

Proteins are complex compounds of carbon, hydrogen, oxygen, and nitrogen. Phosphorus and sulfur are present in a few. They are among the most complex of the organic compounds produced in nature and are widely distributed in plants and animals. They form an essential part of protoplasm and enzymes, and are a necessary part of the diet of all higher animals, in which they serve to build and repair muscle tissue. Like polysaccharides, which may be considered to be made up of glucose units, proteins are formed by the union of α -amino acids. Since more than 20 different amino acids are normally found present in proteins, the variety of proteins is considerable.

Amino Acids

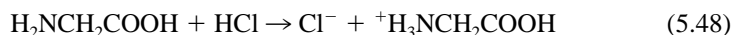
The α -amino acids are the building blocks from which proteins are constructed. Most plants and bacteria have the ability to synthesize the amino acids from which they build proteins. Animals are unable to synthesize certain of the amino acids and must depend upon plants to supply them in the form of proteins. Such amino acids are considered to be indispensable.

The amino acids that occur in proteins all have an amino group attached to the alpha carbon atom and are therefore called α -amino acids.

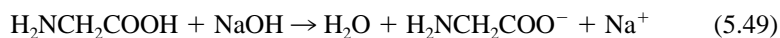


Chemistry of Amino Acids The free amino acids behave like acids and also like bases because of the amino group that they contain. Thus, they are *amphoteric* in character and form salts with acids or bases.

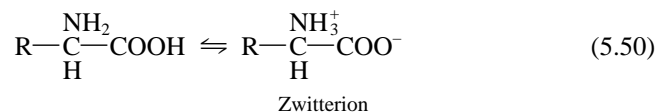
Salt formation with an acid:



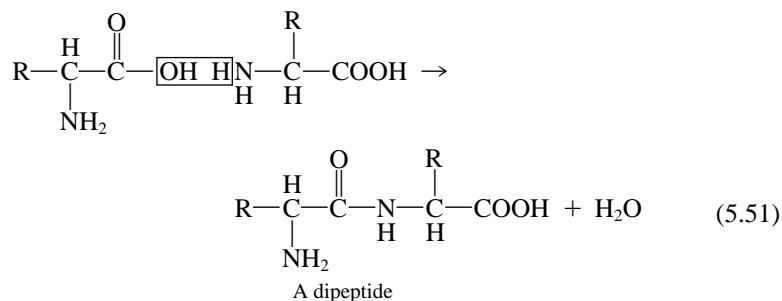
Salt formation with a base:



The amino acids having one amino and one carboxyl group are essentially neutral in aqueous solution. This is considered to be due to a case of self-neutralization in which the hydrogen ion of the carboxyl group migrates to the amino group and a positive-negative (dipolar) ion known as a *zwitterion* results.

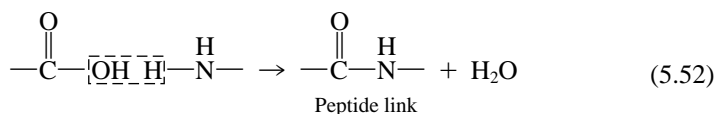


In Sec. 5.9 it was shown that organic acids can react with ammonia to form amides. The amino and carboxyl groups of separate amino acid molecules can react in the same manner.



It is this ability to form linkages between the amino and carboxyl groups that allows the large complex molecules of proteins to be formed. In the example given in Eq. (5.51), the resulting molecule contains one free amino and one free carboxyl group. Each can combine with another molecule of an amino acid. In turn, the resulting molecule will contain free amino and carboxyl groups, and the process can be repeated, presumably, *ad infinitum*. Biochemical processes, however, direct the synthesis to produce the type and size of protein molecules desired.

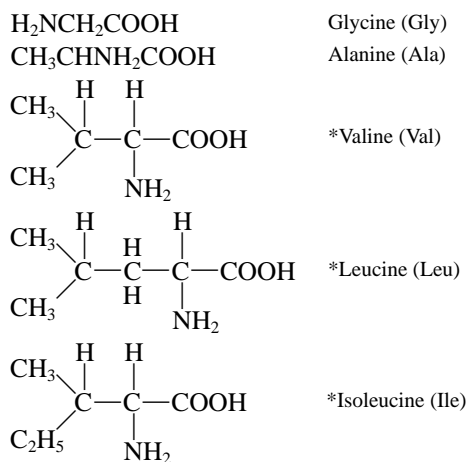
The molecule formed by the union of two molecules of amino acids is known as a *dipeptide*; if there are three units, the name is *tripeptide*; if more than three units, the compound is called a *polypeptide*. The particular linkage formed when amino acids join is called the *peptide link* and is formed by loss of water between an amino and a carboxyl group.

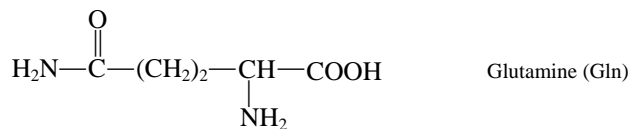
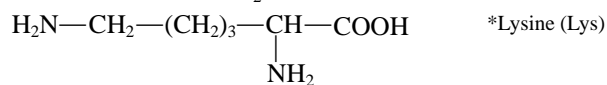
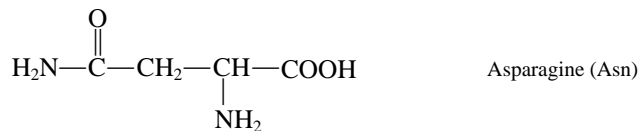
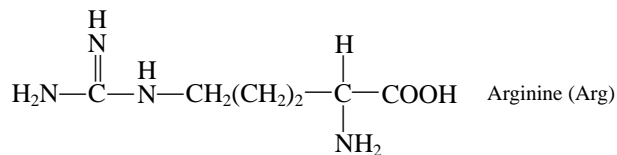
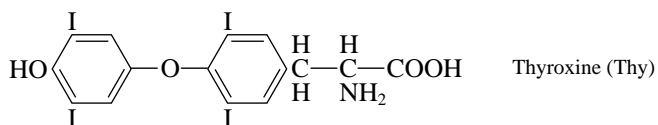
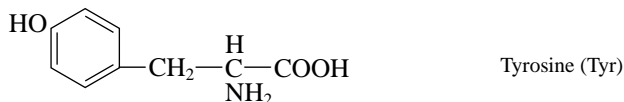
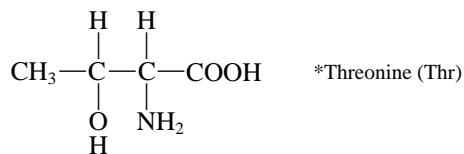


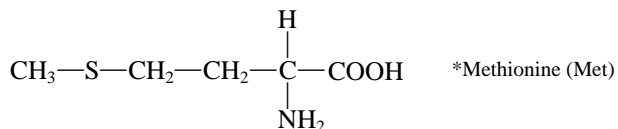
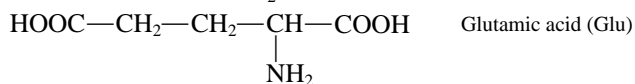
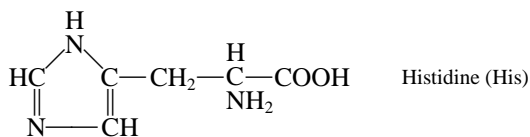
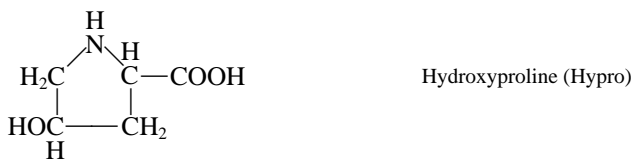
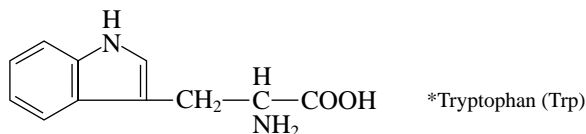
Classes of Amino Acids About 20 different α -amino acids can generally be isolated by the hydrolysis of protein matter. The simplest have one amino group and one carboxyl group per molecule. Some have sulfur in the molecule. Some have two amino groups and one carboxyl group and consequently are basic in reaction. Some have one amino group and two carboxyl groups and are acidic in reaction. Others have aromatic or heterocyclic groups.

All the amino acids, except glycine, are optically active. In the following list, those marked with an asterisk are considered indispensable in human nutrition. The generally used abbreviation for each amino acid is noted after the name.

Monoamino monocarboxy acids



Monocarboxy diamino acids**Aromatic homocyclic acids****Monoamino monocarboxy monohydroxy acids**

Sulfur-containing acids**Dicarboxy monoamino acids****Heterocyclic acids**

Proteins from different sources yield varying amounts of the different amino acids upon hydrolysis. The protein from a given source, however, normally yields the same amino acids and in the same ratio. All proteins yield more than one amino acid.

Proteins

Proteins constitute a very important part of the diet of humans, particularly in the form of meats, cheeses, eggs, and certain vegetables. The processing of these materials, except for eggs, results in the production of industrial wastes that can generally be treated by biological processes.

Properties of Proteins Protein molecules are very large and have complex chemical structures. Insulin, which contains 51 amino acid units per molecule, was the first protein for which the precise order of the atoms in the molecule was discovered. For this significant achievement, Frederick Sanger at the University of Cambridge received the Nobel prize in 1958. Among the large number of proteins for which the order of atoms is now known are ribonuclease with 124 amino acids, tobacco mosaic virus protein with 158 amino acids, and hemoglobin with 574 amino acid units. Hemoglobin has a molecular weight of 64,500 and contains 10,000 atoms of hydrogen, carbon, nitrogen, oxygen, and sulfur, plus 4 atoms of iron. The iron atoms are more important than all the rest as they give blood its ability to combine with oxygen. Some protein molecules are thought to be 10 to 50 times larger than that of hemoglobin.

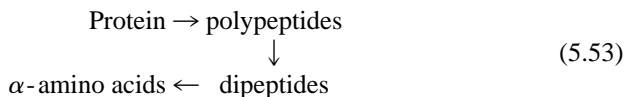
All proteins contain carbon, hydrogen, oxygen, and nitrogen. Regardless of their source, be it animal or vegetable, the ultimate analysis of all proteins falls within a very narrow range, as shown here:

	Percentage
Carbon	51–55
Hydrogen	6.5–7.3
Oxygen	20–24
Nitrogen	15–18
Sulfur	0.0–2.5
Phosphorus	0.0–1.0

The nitrogen content varies from 15 to 18 percent and averages about 16 percent. Since carbohydrates and fats do not contain nitrogen, advantage is taken of this fact in food analysis to calculate protein content. The value for nitrogen as determined by the Kjeldahl digestion procedure (Sec. 25.3), when multiplied by the factor 100/16 or 6.25, gives an estimate of the protein content. This procedure is sometimes used to estimate the protein content of domestic and industrial wastes and of sludges from their organic nitrogen (Sec. 25.3) content. There are several other nitrogen-containing organics in such wastes, however, and so such estimates should be considered only as crude approximations.

Biological Treatment of Protein Wastes In general, satisfactory treatment of wastes containing significant amounts of proteins requires the use of biological processes. In these processes, the first step in degradation of the protein is considered to be hydrolysis, induced by hydrolytic enzymes. The hydrolysis is considered to progress in steps in reverse manner to those in which proteins are synthesized.

Hydrolysis Products of Proteins

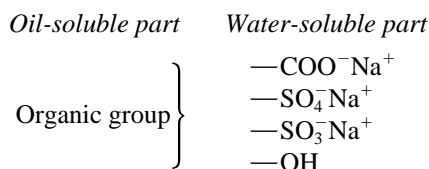


The α -amino acids are then deaminated by enzymic action, and free fatty and other acids result. The free acids serve as food for the microorganisms, and they are converted to carbon dioxide and water.

DETERGENTS

5.23 | DETERGENTS

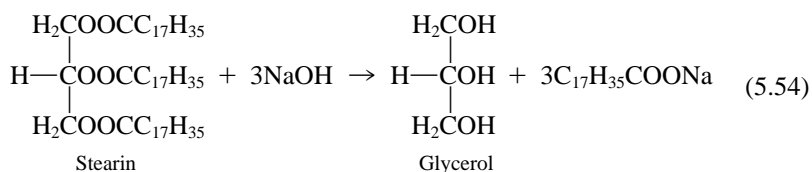
The term *detergent* is applied to a wide variety of cleansing materials used to remove soil from clothes, dishes, and a host of other things. The basic ingredients of detergents are organic materials that have the property of being “surface active” in aqueous solution and are called surface-active agents or *surfactants*. All surfactants have rather large polar functional groups. One end of the molecule is particularly soluble in water and the other is readily soluble in oils. The solubility in water is due to carboxyl, sulfate, hydroxyl, or sulfonate groups. The surfactants with carboxyl, sulfate, and sulfonate groups are all used as sodium or potassium salts.



The nature of the organic part of the molecule varies greatly with the various surfactant types.

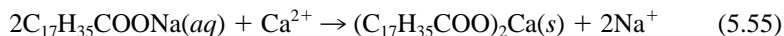
5.24 | SOAPS

Ordinary *soaps* are derived from fats and oils by *saponification* with sodium hydroxide. Saponification is a special case of hydrolysis in which an alkaline agent is present to neutralize the fatty acids as they are formed. In this way the reaction is caused to go to completion.



The fats and oils are split into glycerol and sodium soaps. The nature of the soap depends upon the type of fat or oil used. Beef fat and cottonseed oil are used to produce low-grade, heavy-duty soaps. Coconut and other oils are used in the production of toilet soaps.

All sodium and potassium soaps are soluble in water. If the water is hard, the calcium, magnesium, and any other ions causing hardness precipitate the soap in the form of metallic soaps.



Soap must be added to precipitate all the ions causing hardness before it can act as a surfactant, usually indicated by the onset of frothing upon agitation.

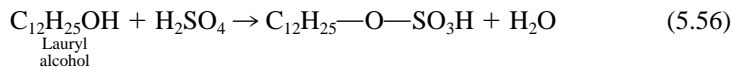
5.25 | SYNTHETIC DETERGENTS

Since 1945 a wide variety of synthetic detergents have been accepted as substitutes for soap. Their major advantage is that they do not form insoluble precipitates with the ions causing hardness. Most commercially available products contain from 20 to 30 percent surfactant (active ingredient) and 70 to 80 percent *builders*. The builders are usually sodium sulfate, sodium tripolyphosphate, sodium pyrophosphate, sodium silicate, and other materials that enhance the detergent properties of the active ingredient. The use of phosphate has been curtailed because of its role in eutrophication. The synthetic surfactants are of three major types: *anionic*, *nonionic*, and *cationic*.

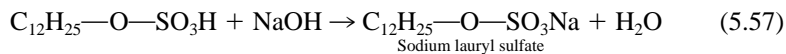
Anionic Detergents

The anionic detergents are all sodium salts and ionize to yield Na^+ plus a negatively charged, surface-activated ion. The common ones are all sulfates and sulfonates.

Sulfates Long-chain alcohols when treated with sulfuric acid produce sulfates (inorganic esters) with surface-active properties. Dodecyl or lauryl alcohol is commonly used.

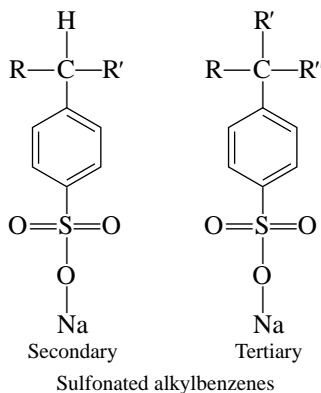
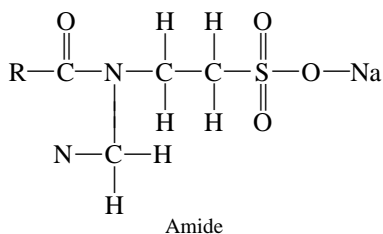
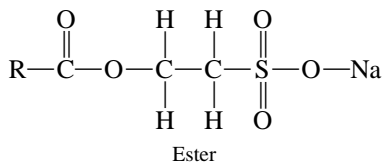


The sulfated alcohol is neutralized with sodium hydroxide to produce the surfactant.



The sulfated alcohols were the first surfactants to be produced commercially. The sulfated alcohols are used in combination with other synthetic detergents to produce blends with desired properties.

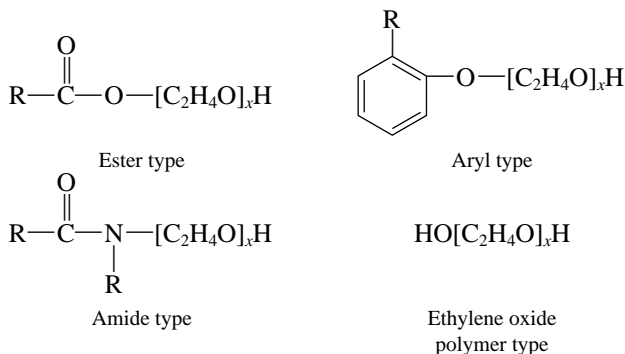
Sulfonates The principal sulfonates of importance are derived from esters, amides, and alkylbenzenes.



The esters and amides are of organic acids with 16 or 18 carbon atoms. In the past the alkylbenzene sulfonates (ABS) were derived largely from polymers of propylene, and the alkyl group, which averaged 12 carbon atoms, was highly branched. These materials are now made largely from normal (straight-chain) paraffins, and thus the alkane chain is not branched and the benzene ring is attached primarily to secondary carbon atoms. These latter materials have been labeled LAS (linear alkyl sulfonate).

Nonionic Detergents

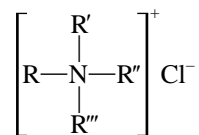
The *nonionic* detergents do not ionize and have to depend upon groups in the molecule to render them soluble. All depend upon polymers of ethylene oxide ($\text{C}_2\text{H}_4\text{O}$) (polyethoxylates) to give them this property.



Nonylphenol (Sec. 5.14) and octylphenol with a variable number of ethylene oxides are important members of the aryl class.

Cationic Detergents

The *cationic* detergents are salts of quaternary ammonium hydroxide. In quaternary ammonium hydroxide, the hydrogens of the ammonium ion have all been replaced with alkyl groups. The surface-active properties are contained in the cation.



A cationic detergent

The cationic detergents are noted for their disinfecting (bactericidal) properties. They are used as sanitizing agents for dishwashing where hot water is unavailable or undesirable. They are also useful in the washing of babies' diapers, where sterility is important. If diapers are not sterilized by some means, bacterial infestations may occur that release enzymes that will hydrolyze urea to produce free ammonia [Eq. (5.43)]. The high pH resulting is harmful to the tender skin of babies, and the odor of free ammonia is unpleasant to all.

Biological Degradation of Detergents

Detergents vary greatly in their biochemical behavior, depending on their chemical structure.²² Common soaps and the sulfated alcohols are readily used as bacterial food. The synthetic detergents with ester or amide linkages are readily hydrolyzed. The fatty acids produced serve as sources of bacterial food. The other hydrolysis product may or may not serve as bacterial food, depending upon its chemical structure. The synthetic detergents prepared from polymers of ethylene oxide appear susceptible to biological attack. However, recent evidence has demonstrated they are only partially transformed, leaving an alkyl aromatic compound that can be chlorinated or brominated during chlorine disinfection. As noted previously, the alkylphenols are suspected endocrine disruptors. The alkyl-benzene sulfonates derived from propene were highly resistant to biodegradation, and their persistence resulted in excessive foaming in rivers and groundwaters in the 1950s. This presented some of the first evidence of the potential harmful environmental consequences of synthetic organic chemicals. For this reason, the detergent manufacturing industry changed to the production of LAS surfactants. LAS is readily degradable under aerobic conditions, and its use has helped relieve the most serious problems of detergent foaming. However, unlike common soap, it is resistant

²²C. N. Sawyer and D. W. Ryckman, Anionic Detergents and Water Supply Problems, *J. Amer. Water Works Assoc.*, **49**: 480 (1957).

to degradation under anaerobic conditions. Currently, there is a United States EPA secondary standard of 0.5 mg/L for foaming agents. Enforcement of secondary standards by states is optional.

PESTICIDES

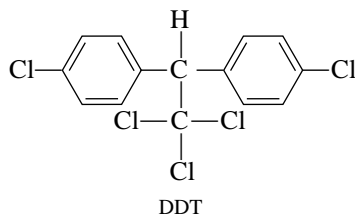
5.26 | PESTICIDES

Pesticides are materials used to prevent, destroy, repel, or otherwise control objectionable insects, rodents, plants, weeds, or other undesirable forms of life. Common pesticides can be categorized chemically into three general groups, inorganic, natural organic, and synthetic organic. They may also be classified by their biological usefulness, viz., insecticides, herbicides, algicides, fungicides, and rodenticides.

The synthetic organic pesticides gained prominence during World War II, and since then their numbers have grown into the thousands, while the total annual production has increased to about 1.5 billion pounds of active ingredients. They are used mainly for agricultural purposes. The synthetic organic pesticides are best classified according to their chemical properties, since this more readily determines their persistence and behavior when introduced into the environment. The major types of synthetic pesticides are the chlorinated hydrocarbons, the organic phosphorus pesticides, and the carbamate pesticides. An additional category of current interest is the s-triazine pesticides. There are many other types of synthetic pesticides.

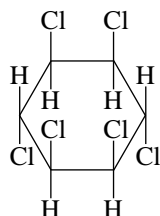
5.27 | CHLORINATED PESTICIDES

Chlorinated pesticides are of many types and have been widely used for a variety of purposes. DDT proved to be an extremely versatile insecticide during World War II when it was used mainly for louse and mosquito control. It is still one of the major pesticides used internationally, although use in the United States has been banned for quite some time for environmental reasons. DDT is a chlorinated aromatic compound with the following structure:



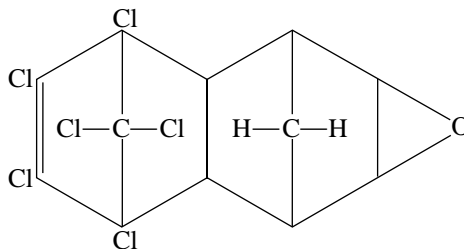
Technical grade DDT contains three isomers, the above isomer representing about 70 percent of the total. It has the long technical name 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane.

When benzene and chlorine react in direct sunlight, the addition product benzene hexachloride or BHC is formed. Several stereoisomers are produced, but the gamma isomer called *lindane* is by far the most effective as an insecticide.



γ -Benzene hexachloride (lindane)

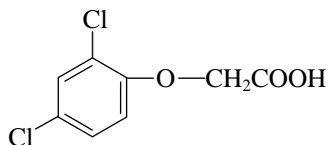
Two other formerly widely used chlorinated insecticides are endrin and dieldrin. They are isomers, and their structural formulas appear the same:



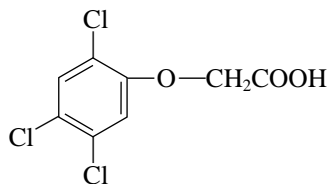
Dieldrin or endrin

However, their spatial configurations are significantly different, as are their insecticidal properties.

Chlorinated pesticides are also used as herbicides. Two of the most common are 2,4-D and 2,4,5-T.



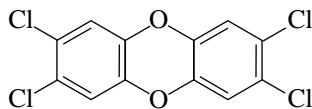
2,4-Dichlorophenoxyacetic acid
(2,4-D)



2,4,5-Trichlorophenoxyacetic acid
(2,4,5-T)

These two herbicides are effective in destroying certain broad-leaf plants while not killing grasses. They have also been used for aquatic-plant control in lakes, ponds, and reservoirs. Dioxin, an extremely toxic organic to humans, is a side product contaminant in 2,4,5-T, which has led to restrictions in its use. Dioxins are also formed

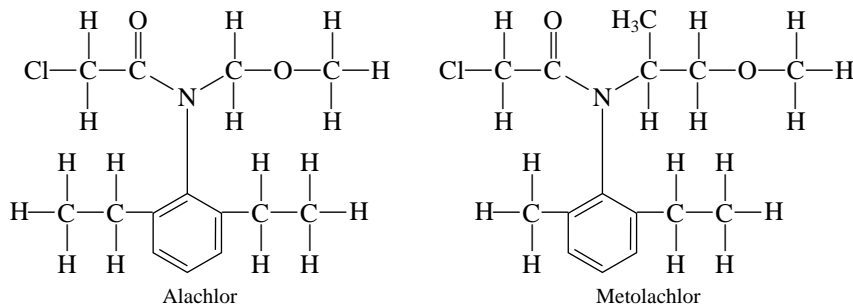
during the combustion of chlorinated organic compounds. The most toxic dioxin is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD):



2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD)

Because of its extreme toxicity, a very low drinking water MCL of $3 \times 10^{-5} \mu\text{g/L}$ has been established for this dioxin.

The family of compounds called the chloroacetamides are also commonly used as herbicides for control of broad-leaf weeds. Two of the most common examples are alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl)-acetanilide] and metolachlor [2-chloro-6'-ethyl-N-(2-methoxy-1-methyl-ethyl)acet-*o*-toluidine]. These herbicides are used primarily for weed control in the production of corn and soybeans.



Alachlor

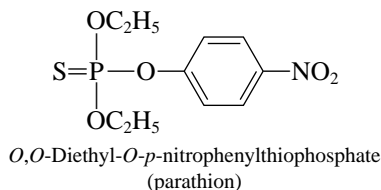
Metolachlor

Other chlorinated or halogenated pesticides of significance are aldrin, chlordane, toxaphene, heptachlor, methoxychlor, DDD, EDB, DBCP, and 1,2-dichloropropane; all have been used as insecticides, fungicides, or nematocides. All halogenated pesticides are considered to be of significant concern because of their persistence and high potential for creating harm to humans and the environment. For this reason aldrin and dieldrin are now banned from use in the United States, and many of the other chlorinated pesticides have been greatly restricted in usage.

5.28 | ORGANIC PHOSPHORUS PESTICIDES

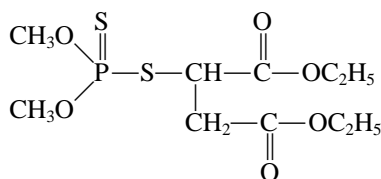
The organic phosphorus pesticides became important as insecticides after World War II. These compounds were developed in the course of chemical warfare research in Germany and in general are quite toxic to humans as well as to pests. *Parathion* is an important pesticide, which was introduced into the United States

from Germany in 1946. It is an aromatic compound and contains sulfur and nitrogen as well as phosphorus in its structure, so do many of the organic phosphorus pesticides.



Parathion has been particularly effective against certain pests such as the fruit fly. However, it is also quite toxic to humans and extreme caution must be exercised in its use.

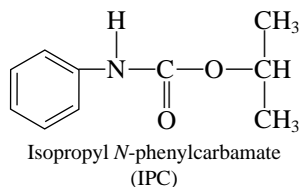
Malathion is highly toxic to a variety of insects, but unlike many organic phosphorus pesticides, it has low toxicity to mammals. This has made it particularly successful and it is widely used.



Other organic phosphorus pesticides of significance are methyl parathion, glyphosate, demeton, guthion, systox, metasystox, chlorthion, disyston, and dicapthion.

5.29 | CARBAMATE PESTICIDES

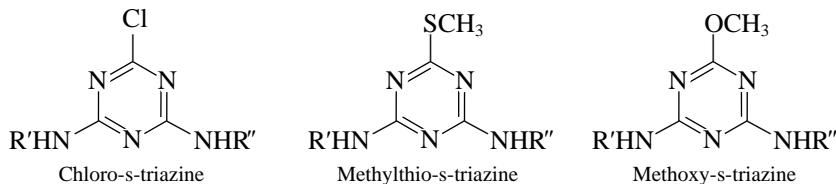
Carbamate pesticides are amides having the general formula $RHNCOOR'$. One that has received wide usage is isopropyl *N*-phenylcarbamate (IPC).



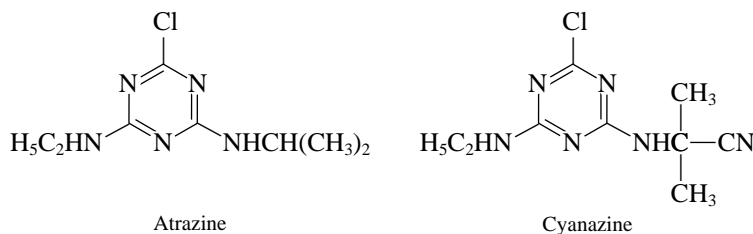
IPC is a herbicide that is effective for the control of grasses, without affecting broad-leaf crops. Other carbamates of importance are aldicarb, carbaryl (Sevin®), carbofuran, ferbam, and captan. Carbamates in general appear to have low toxicity to mammals.

5.30 | s-TRIAZINES

The class of compounds called the s-triazines are primarily used as herbicides in agricultural regions and are of three general types: (1) chloro s-triazines, (2) methylthio s-triazines, and (3) methoxy s-triazines:



Two of the most commonly used s-triazines are atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and cyanazine [2-chloro-4-ethylamino-6-(1-cyano-1-methylethylamino)-s-triazine].



Atrazine is currently one of the most widely used herbicides, is difficult to degrade biologically, and is a commonly detected groundwater and surface water contaminant in agricultural areas.

5.31 | BIOLOGICAL PROPERTIES OF PESTICIDES

Pesticides may gain access to groundwater and surface water supplies through direct application or through percolation and runoff from treated areas. Several recent surveys have shown that pesticides are present in many groundwater and surface water supplies. For example, one report indicated that 46 different pesticides were found in groundwaters in 26 states.²³ Concentrations are typically higher in surface waters than in groundwaters. Some pesticides are toxic to fish and other aquatic life at only a small fraction of a milligram per liter. They also tend to concentrate in aquatic plants and animals to values several thousand times that occurring in the water in which they live. Also, some pesticides are quite resistant to biological degradation and persist in soils and water for long periods of time. A major concern with all pesticides is the potential for incomplete transformation of the parent compound into metabolites that may be more or less toxic.

²³D. J. Munch et al., Methods Development and Implementation for the National Pesticide Survey. *Env. Sci. Tech.*, **24**: 1445–1451 (1990).

In general, the chlorinated pesticides are the most resistant to biological degradation and may persist for months or years following application. Many are also highly toxic to aquatic life or to birds that feed on aquatic life. This persistence and great potential for harm has led to restrictions on chlorinated pesticide usage. Several chlorinated pesticides (e.g., DDT, dieldrin, methoxychlor, toxaphene) are suspected endocrine disruptors. As a group, the organic phosphorus pesticides are not too toxic to fish life and have not caused much concern in this respect, except when large accidental spills have occurred. Also, they tend to hydrolyze rather quickly at pH values above neutral, thus losing their toxic properties. Under proper conditions such as dryness, however, some have been observed to persist for many months. Their main potential for harm is to farm workers who become exposed both from contact with previously sprayed foliage as well as from direct contact during organic phosphorus pesticide application. Some of these pesticides are readily absorbed through the skin and affect the nervous system by inhibiting the enzyme cholinesterase, which is important in the transmission of nerve impulses. The carbamates are noted for their low toxicity and high susceptibility to degradation. The s-triazines are in general quite resistant to environmental degradation and are known endocrine disruptors.

Because of the several potential health problems that have been associated with pesticides, drinking water MCLs have been established for several pesticides that are still in somewhat common usage. These are listed in Table 34.1.

5.32 | PHARMACEUTICALLY ACTIVE AND ENDOCRINE-DISRUPTING CHEMICALS

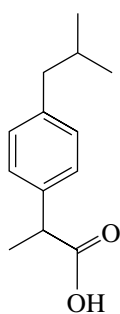
Two groups of chemicals of emerging concern are *pharmaceutically active chemicals* (PhACs) and *endocrine-disrupting chemicals* (EDCs). These compounds are being found in surface waters and groundwaters and in wastewater treatment plant effluents in the ng/L (parts per trillion) to $\mu\text{g/L}$ concentration range. Understanding the fate and effects of these chemicals in the environment and removing them from drinking water supplies and wastewaters present difficult challenges for environmental engineers and scientists.

Pharmaceutically Active Chemicals (PhACs)

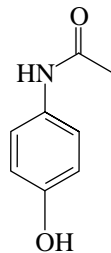
Pharmaceuticals are generally defined as chemicals used for the treatment or prevention of illness. As such, they can range from compounds used for cancer treatment (chemotherapy) and birth control to antibiotics used to combat infection to compounds used to relieve pain (e.g., aspirin and ibuprofen). They are found in personal care products such as fragrances, disinfectants and antiseptics, sunscreen agents, and preservatives. Pharmaceuticals are also used in veterinary health care (e.g., antibiotics and growth hormones). Very little is known with respect to the ef-

fect of PhAC on human and wildlife health. However, there is potential for adverse effects and the reasoning goes like this. Most of these compounds are lipophilic (“fat-loving”; synonymous with hydrophobic) and their activity is slow to decay (that is, they remain pharmaceutically active for an extended time). Thus, bioconcentration is possible. While the concentration of individual PhACs in water supplies is low (generally less than $0.5 \mu\text{g/L}$ with many in the ng/L range), the presence of numerous drugs with similar modes of action could lead to measurable effects. Finally, exposure can be chronic because PhACs are continually introduced into the environment via human wastewater treatment, livestock production, and similar activities. One special concern with antibiotics is the development of antibiotic-resistant strains of pathogenic bacteria due to overuse of these compounds. In general this is because a large portion of the administered antibiotic leaves the body (humans and animals) via urine and feces as a mixture of parent compound and metabolites.

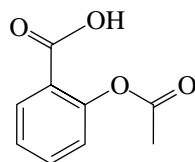
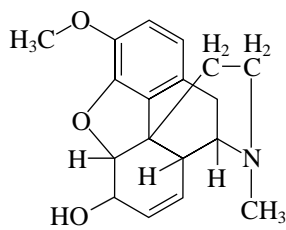
PhACs come from a wide variety of organic chemical classes. Examples of PhACs that have been found in surface waters and wastewater treatment effluents include pain killers such as ibuprofen (a chiral compound), acetaminophen, acetylsalicylic acid (aspirin), and codeine; antibiotics in the sulfonamide, tetracycline, fluoroquinolone, and macrolide classes; chlofibric acid [environmental metabolic of the lipid regulator clofibrate (helps lower cholesterol)], and caffeine. Some chemical structures are given here.



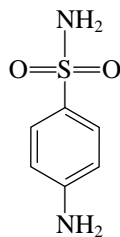
Ibuprofen



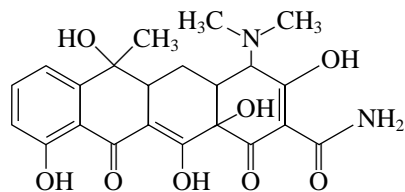
Acetaminophen

Acetylsalicylic acid
(aspirin)

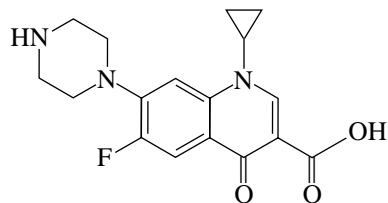
Codeine



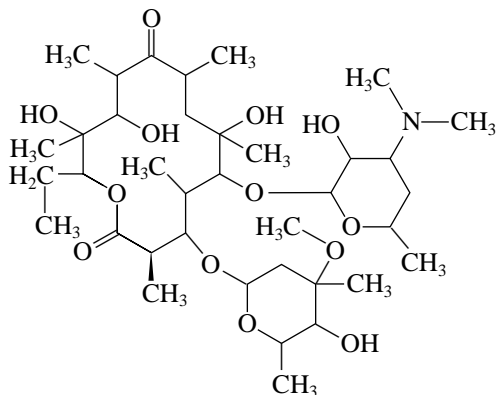
Sulfanilamide



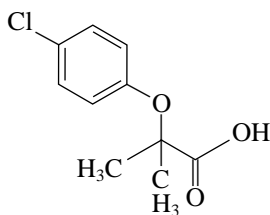
Tetracycline



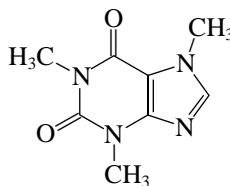
Fluoroquinolone



Erythromycin (a macrolide antibiotic)



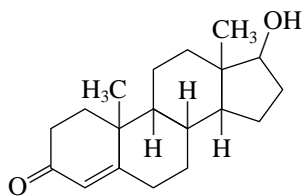
Clofibric acid



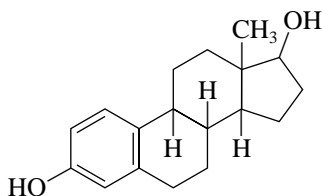
Caffeine

Endocrine-Disrupting Chemicals (EDCs)

The human endocrine system, which includes a variety of glands (e.g., thyroid, pituitary, pineal, ovaries, and testes) and the hormones they produce (e.g., adrenaline, estrogens, and testosterone), regulates growth, development, reproduction, and behavior. Chemical structures for testosterone and estradiol, an estrogen, are given here.



Testosterone



Estradiol (an estrogen)

There is concern that some synthetic organic chemicals released into the environment can interfere with or disrupt this system. In general, it is thought that such compounds mimic the body's natural hormones, binding with receptor molecules in the body, and thus interfering with the regulation of the endocrine system. An excellent review of how EDCs can interfere with the endocrine system is given by Trussell.²⁴ There is still some controversy as to whether observed effects of EDCs are due to their hormonal properties or some other toxicological mechanism.²⁵ For this and other reasons, a National Research Council committee recommends use of the term *hormonally active agent* (HAA) instead of EDC.²⁶ It should be noted that some naturally produced organic compounds (e.g., phytoestrogens produced by plants such as soybeans) and inorganic chemicals (e.g., lead, mercury) can also act as EDCs. Some PhACs are also EDCs (for example, growth hormones used in livestock production).

EDCs have been reported to have a variety of effects on humans and wildlife; most are developmental abnormalities, although some neurological and immunological effects have been reported. A widely reported example is the effect of diethylstilbestrol (DES), a synthetic estrogen used in the 1950s to prevent miscarriages. Children of mothers taking DES during pregnancy experienced a wide variety of problems including cancers of the vagina and cervix, malformed reproductive organs, undescended testicles, and abnormal sperm. These effects were associated with high exposure to DES. Recent reports indicate effects in wildlife associated with exposure to lower levels of EDCs. For example, developmental abnormalities in alligators in Florida and male fish living near outfalls from wastewater treatment plants, and declines in fish and bird populations in the Great Lakes have been associated with EDC exposure. It must be stressed that much more needs to be learned about the effects of EDCs on adverse health outcomes in humans and wildlife.

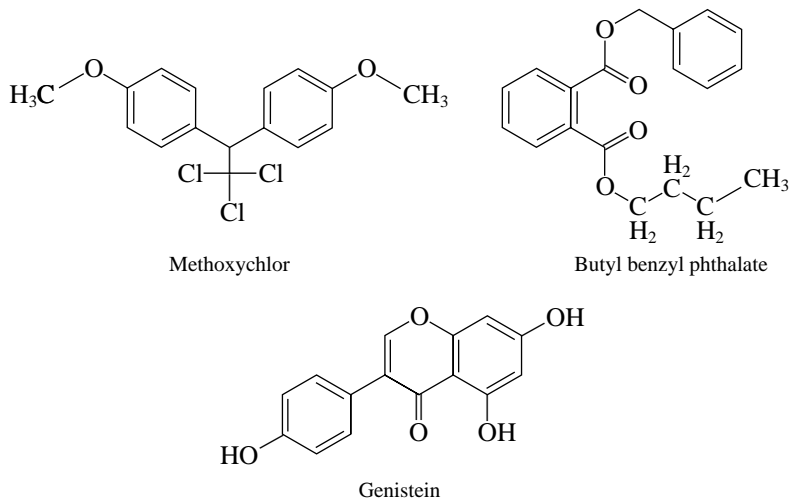
A wide variety of chemicals have been implicated as EDCs. These include several pesticides, organochlorine compounds including PCBs, phenolic compounds, phthalates, PAHs, synthetic steroids, and triazines. Specific examples include malathion, dieldrin, methoxychlor, DDT and its metabolites, dioxin (TCDD), pentachlorophenol, bisphenol A, nonylphenol, butyl benzyl phthalate, and atrazine. Phytoestrogens include a variety of flavones and isoflavones. Chemical structures for PCBs, malathion, dieldrin, DDT, dioxin, pentachlorophenol, bisphenol A, nonylphenol, and atrazine were given in Secs. 5.13 to 5.30. Structures

²⁴R. R. Trussell, Endocrine Disrupters and the Water Industry, *J. American Water Works Assoc.*, **93**(2): 58–65, 2001.

²⁵National Research Council, "Hormonally Active Agents in the Environment," National Academy Press, Washington, D.C., 1999.

²⁶Use of the acronym HAA for hormonally active agent may cause confusion. As noted in Sec. 5.8, HAA is also used by environmental engineers and scientists to describe the haloacetic acids produced as disinfection by-products and regulated as drinking water contaminants.

for methoxychlor, butyl benzyl phthalate, and genistein, an isoflavone in soybeans are given here.



BEHAVIOR OF ORGANICS IN THE ENVIRONMENT AND IN ENGINEERED SYSTEMS

5.33 | INTRODUCTION

It is important for the environmental engineer and scientist to have knowledge of the properties, both physicochemical and structural, of the different types and classes of organic compounds to aid in understanding and predicting the fate, effects, and potential of engineered processes for removal or control of these compounds. In the previous sections classes of organic compounds were described with respect to the functional group or groups characteristic of each class of compound. These characteristic functional groups also manifest themselves in other important properties that aid in understanding the behavior of organics in the environment and in engineered reactors. Physicochemical properties include, but are not limited to, solubility, hydrophobicity, polarity, volatility, density, and energy content. Solubility, hydrophobicity, and polarity are somewhat related and are useful in understanding the tendency of organics to partition between phases (i.e., solid-liquid or liquid-gas partitioning). Volatility, which can be quantified using Henry's constant or vapor pressure (Chap. 2), is useful in understanding partitioning between the gas and liquid phases. Density is useful in understanding physical separation potential and transport behavior. Energy content is useful in predicting bacterial yields (Chap. 6). Structural characteristics such as molecular connectivity and molecular surface area can be related through structure- and property-activity relationships (SARs and PARs) that can be used to predict compound behavior and fate. Detailed discussion of these and other properties is beyond the scope of this text; additional material can be found in the references listed at the end of the chapter.

5.34 | FATE OF ORGANICS

Important processes involved in the movement and fate of organics in the environment and in engineered systems are listed in Table 5.14. Processes especially important in understanding the fate and removal of organics found at contaminated sites and in industrial wastes and leachates are volatilization, sorption, and transformation reactions.

Volatilization

The concepts relevant to volatilization were introduced in Sec. 2.9 and are reviewed here. The equation for Henry's law constants (K_H) for chemical equilibrium between gaseous and aqueous phases is repeated here:

$$K_H = \frac{\text{concentration in gas}}{\text{concentration in water}} = \frac{P_{\text{gas}}}{C_{\text{equil}}} \quad (2.15)$$

K_H can be thought of as a partition coefficient between water and the atmosphere. It can take several forms. The most common units are partial pressure (atm)/molar concentration (mol/L) or atm/M. The so-called unitless Henry's constant H results when the concentrations in both water and gas are expressed in mol/vol. Conversion can be made using the following:

$$H = \frac{K_H}{RT} \quad (5.58)$$

where R is 0.08206 atm/M-K and T is the temperature (K). Henry's constant has a strong temperature dependence; organic compounds are less volatile at lower temperatures. Values of Henry's constant for some environmentally significant organic compounds are given in Table 5.15. The higher the value of K_H , the more likely the compound is to partition to the atmosphere.

Table 5.14 | Processes involved in the fate of organics

Process	Air	Water	Soil
Meteorological transport	X		
Condensation	X		
Settling	X	X	
Volatilization		X	X
Runoff (erosion)			X
Filtration			X
Sorption	X	X	X
Desorption	X	X	X
Precipitation	X	X	X
Chemical transformation			
Photolysis	X	X	
Hydrolysis	X	X	X
Oxidation	X	X	X
Reduction	X	X	X
Bio-uptake (bioconcentration)		X	X
Biodegradation (biotransformation)		X	X

Table 5.15 | Values of K_{ow} , water solubilities and Henry's law constants for selected organic compounds

Compound	$\log K_{ow}$	Water solubility, mg/L	K_H , atm/M
Data from Yaws for 25°C			
Halogenated aliphatic compounds			
Methanes			
Chloromethane	0.91	5,900	8.2
Dichloromethane	1.25	19,400	2.5
Chloroform	1.97	7,500	4.1
Bromoform	2.4	3,100	0.59
Carbon tetrachloride	2.83	790	29
Dichlorodifluoromethane	2.16	18,800	390
Ethanes			
Chloroethane	1.43	9,000	6.9
1,1-Dichloroethane	1.79	5,000	5.8
1,2-Dichloroethane	1.48	8,700	1.18
1,1,1-Trichloroethane	2.49	1,000	22
1,1,2-Trichloroethane	1.89	4,400	0.92
Hexachloroethane	3.91	8	25
Ethenes			
Vinyl chloride	1.62	2,700	22
1,1-Dichloroethene	2.13	3,400	23
1,2- <i>cis</i> -Dichloroethene	1.86	3,500	7.4
1,2- <i>trans</i> -Dichloroethene	2.09	6,300	6.7
Trichloroethene	2.42	1,100	11.6
Tetrachloroethene	3.4	150	26.9
Aromatic compounds			
Hydrocarbons			
Benzene	2.13	1,760	5.6
Toluene	2.73	540	6.4
Ethylbenzene	3.15	165	8.1
Styrene	2.95	322	2.6
<i>o</i> -Xylene	3.12	221	4.2
<i>m</i> -Xylene	3.2	174	6.8
<i>p</i> -Xylene	3.15	200	6.2
1,2,3-Trimethylbenzene	3.66	36	7.4
1,2,4-Trimethylbenzene	4.02	35	
Napthalene	3.3	32	0.46 (20°C)
Phenanthrene	4.46	1.18	
Anthracene	4.45	0.053	
Fluorene	4.18	1.89	
Other aromatic compounds			
Chlorobenzene	2.84	390	4.5
1,2-Dichlorobenzene	3.43	92	2.8
1,3-Dichlorobenzene	3.53	123	3.4
1,4-Dichlorobenzene	3.44	80	
1,2,4-Trichlorobenzene			3.0
Hexachlorobenzene	5.73	0.0047	

Table 5.15 | (continued)

Compound	log K_{ow}	Water solubility, mg/L	K_H , atm/M
Data from Yaws for 25°C			
Other aromatic compounds			
Nitrobenzene	1.85	1,940	0.021
3-Nitrotoluene	2.45	500	0.075
Phenol	1.46	80,000	0.00076
Diethyl phthalate	2.47	1,000	0.00014
2-Chlorophenol	2.15	25,000	0.037
3-Chlorophenol	2.5	25,000	0.00204
Dibenzofuran	4.12		
Other aliphatic compounds			
Methyl <i>t</i> -butyl ether	0.94	51,000	0.54
Methyl ethyl ketone	0.29	250,000	0.030
Data from Schnoor et al. for 20°C			
2-Nitrophenol	1.75	2,100	
Benzo(a)pyrene	6.06	0.0038	0.00049
Acrolein	0.01	210,000	0.0038
Alachlor	2.92	240	
Atrazine	2.69	33	
Pentachlorophenol	5.04	14	
DDT	6.91	0.0055	0.038
Lindane	3.72	7.52	0.0048
Dieldrin	3.54	0.2	0.0002
2,4-D	1.78	900	0.00000172

Sources: C. L. Yaws, "Chemical Properties Handbook." McGraw-Hill, New York, 1999. Schnoor et al., "Processes, Coefficients, and Models for Simulating Toxic Organics and Heavy Metals in Surface Waters," U.S. Environmental Protection Agency, EPA/600/3-87/015, June 1987.

In general, it is considered that if K_H is less than 0.2 atm/M or H is less than about 0.01, the compound will not be efficiently removed from water by air stripping in an engineered reactor (e.g., stripping tower, aeration pond). The larger the value of K_H (and H), the easier the compound can be removed by air stripping. It should be noted that values of K_H reported in the literature should be used with some caution, since methods and conditions used in determining K_H vary widely.

When designing an engineered system to remove organics by volatilization, the following relationship from Sec. 3.10 is often used:

$$\frac{dC}{dt} = K_L a (C_{\text{equil}} - C) \quad (3.52)$$

where C = concentration in water (mass/vol)

C_{equil} = concentration in water that would be in equilibrium with the concentration in air (mass/vol)

$K_L a$ = overall mass-transfer rate coefficient (time⁻¹)

Often the air concentration is near zero, so C_{equil} becomes zero. Different engineered systems will give different values for K_{La} , and this rate coefficient will be different for different organics as well. It is also a strong function of temperature, increasing with an increase in temperature.

EXAMPLE 5.1

Gossett²⁷ developed relationships describing the effect of temperature on Henry's constant for a variety of chlorinated aliphatic compounds. The relationship between K_H (atm-m³/mol) and T for trichloroethene (CHCl₂=CCl₂) is given here.

$$\ln K_H = 11.37 - \frac{4780}{T}$$

Calculate the value for K_H (atm/M) for temperatures of 10°C (283 K) and 25°C (298 K), which might represent the extremes in groundwater temperatures in the midwest.

$$\text{For } 10^\circ\text{C: } \ln K_H = 11.37 - \frac{4780}{283} = -5.52 \quad K_H = 0.0040 \text{ atm-m}^3/\text{mol or } 4 \text{ atm/M}$$

$$\text{For } 25^\circ\text{C: } \ln K_H = 11.37 - \frac{4780}{298} = -4.67 \quad K_H = 0.0094 \text{ atm-m}^3/\text{mol or } 9.4 \text{ atm/M}$$

For TCE, K_H more than doubled due to the 15°C temperature increase. This means it will be much easier to remove TCE from contaminated groundwater by air stripping in the summer months. It may be noted that the 25°C K_H value of 9.4 atm/M is somewhat less than the 11.6 atm/M value in Table 5.15, reflecting the different sources of the data.

EXAMPLE 5.2

Removing organics from water by volatilization can be thought of as forcing the organic to partition into the air. An important parameter is the air-to-water ratio, the volume of air exposed to a given volume of contaminated water. An easy way to view the importance of this ratio and of K_H is by using a simple equilibrium model in which a given volume of air is mixed with a given volume of water. A mass balance yields the following expression:

$$\frac{C}{C_0} = \frac{1}{1 + \left(\frac{V_a}{V_w}\right)\left(\frac{K_H}{RT}\right)}$$

where C = equilibrium concentration in water
 C_0 = initial concentration in water
 V_a/V_w = volume of air divided by volume of water (the air-to-water ratio)
 T = temperature (absolute)
 R = universal gas constant

²⁷J. J. Gossett, Measurements of Henry's Law Constants for C1 and C2 Chlorinated Hydrocarbons, *Env. Sci. Tech.*, **21**: 202–208, 1987.

Consider the two chlorinated solvents carbon tetrachloride and trichloroethene. What air-to-water ratio is required to remove 95 percent of each from water? For an air-to-water ratio of 100 (typical values for air stripping towers are 10 to 100), what is the percent removal of each compound? Assume a temperature of 25°C.

For 25°C, RT is 24.5 atm/M. From Table 5.15, K_H is 29 atm/M for carbon tetrachloride and 11.6 atm/M for trichloroethene.

For 95 percent removal, C/C_0 is 0.05. Solving the given expression for V_a/V_w yields

$$\frac{V_a}{V_w} = \left(\frac{C_0}{C} - 1 \right) \left(\frac{RT}{K_H} \right)$$

Substituting the proper K_H yields a V_a/V_w of 16 for carbon tetrachloride and 40 for trichloroethene.

A V_a/V_w of 100 yields a C/C_0 of 0.0084 (99.2 percent removal) for carbon tetrachloride and 0.0207 (97.9 percent removal) for trichloroethene.

Solubility

Water solubility of an organic compound is generally defined as the concentration (mass/vol or mol/vol) resulting when the water is in equilibrium with the pure compound [gas (1 atm), liquid, or solid]. There are many factors affecting compound solubility. They include, but are not limited to, size of the molecule; the nature, number, and location of functional groups in the molecule; temperature; pH; dissolved salt concentration; and the presence of other phases (i.e., organic liquids, solids, gases). In general, as molecular size increases, solubility decreases. Polar functional groups (e.g., —OH) tend to increase solubility. Addition of Cl atoms or NO_2 groups in general decreases solubility. As temperature increases, the solubility of solids generally increases as does volatility (vapor pressure and K_H). A detailed discussion of the thermodynamics of solubility is beyond the scope of this text. The interested reader is referred to the Schwarzenbach et al. text listed at the end of this chapter. Values of solubility for some environmentally significant compounds are given in Table 5.15. Caution should be exercised when using literature values for solubility, since methods and conditions used to determine them vary widely.

A word about the term *hydrophobicity* is warranted. The octanol-water partition coefficient (K_{ow} —described in Sorption/Partitioning) is often used to describe hydrophobicity. However, since the term hydrophobic refers to “water hating,” aqueous solubility is a truer measure of the hydrophobicity of a compound (how much it “hates” water). In general, compounds with high K_{ow} have low aqueous solubility. For example, DDT has a K_{ow} of $10^{6.91}$ and an aqueous solubility of 0.0055 mg/L (at 20°C). In some cases, however, compounds with low solubility do not have particularly high values of K_{ow} . For example, the explosive HMX (Sec. 5.17) has a solubility of 5 mg/L at 20°C and its K_{ow} is $10^{0.20}$.

Sorption/Partitioning

Adsorption was discussed in Sec. 3.12 with a primary emphasis on its use in engineered reactors. Adsorption of metals on surfaces was discussed in Sec. 4.9. Sorption is also an important process affecting the fate and transport of organic compounds in surface waters and groundwaters. The general term sorption is often used for the natural process rather than adsorption or absorption because the exact manner in which partitioning to solids occurs is often not known. Partitioning of an organic compound between solids and water (e.g., aquifer solids in groundwater, particulates and sediments in surface water systems) can be understood and predicted to some degree using physicochemical properties of organic compounds such as the relative partitioning between the liquid solvent *n*-octanol and water (octanol-water partition coefficient— K_{ow}) and water solubility. K_{ow} has long been used as a surrogate for living tissue and natural organic matter. For example, in the pharmaceutical industry, the K_{ow} of a drug is often correlated to its activity (higher K_{ow} , higher activity). Bioconcentration of organic compounds in fatty tissues of living organisms has been correlated to K_{ow} (Sec. 5.35). Values of K_{ow} for some environmentally significant compounds are given in Table 5.15. As with K_H and solubility, values of K_{ow} should be used with some caution, since methods and conditions used in determining them vary widely.

Sorption in most surface water and groundwater systems can be described by the Freundlich equation (Sec. 3.12). In some situations, concentration of the organic is low and the number of surface sites is quite high, so the value of *n* approaches 1 and a linear isotherm results (Fig. 5.2). In this case, *K* [Eq. (3.84)] is commonly called the partition coefficient K_p . The units of K_p are typically mg organic sorbed/kg of solid divided by mg organic/liter of water, or liter of water/kg of solid.

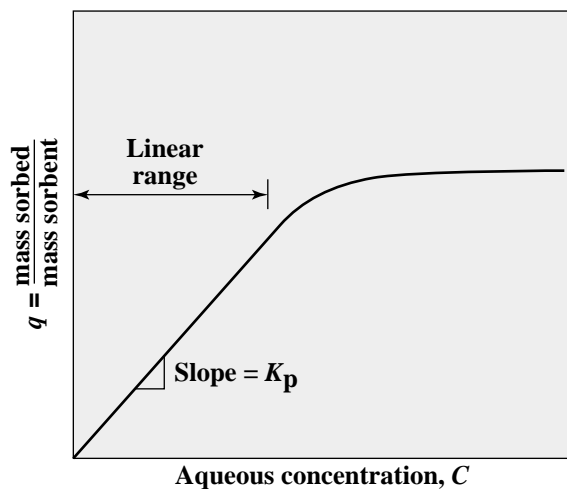


Figure 5.2
Linear isotherm for sorption of organics.

It has been found that sorption of hydrophobic organic compounds is often related to the organic content of the solids, indicating that the process is an organic-organic partitioning, or absorption, rather than true adsorption.²⁸ Thus, partitioning would be expected to be a function of the nature of the natural organic matter present. An organic-carbon-normalized partition coefficient K_{oc} is sometimes calculated by dividing K_p by the mass fraction of organic carbon in the solids. It should be noted that in some cases, equilibrium between solute and sorbent may take days, months, or even years, and may be more complicated than the linear isotherm given here.^{29,30} Desorption (partitioning back into the water) can be a very slow process. For hydrophobic compounds in contact with environmental solids for extended periods of time (sometimes called “aging”), sorption may be for all intents and purposes, irreversible. This behavior significantly affects our ability to remediate such soils.

Values for K_{oc} have been estimated from K_{ow} using the following relationship developed for a series of polycyclic aromatics and chlorinated hydrocarbons.³¹

$$K_{oc} = 0.63(K_{ow}) \quad (5.59)$$

where K_{oc} is the organic-carbon-normalized partition coefficient in liters per kilogram of organic carbon. Here K_{ow} serves as a surrogate for natural organic matter. Values for K_{oc} have also been related to water solubility.³²

$$\log K_{oc} = -0.54 \log S + 0.44 \quad (5.60)$$

where S is the water solubility of the compound expressed as mole fraction. For the compounds tested, use of K_{ow} provided a better estimate of K_{oc} than S .

One of the convenient uses of these concepts is in the understanding of retardation of groundwater contaminants (movement of compounds relative to movement of water) due to sorption. The following equation has been used.³³

$$t_r = 1 + \rho K_p / e \quad (5.61)$$

where t_r = retardation factor or ratio of water movement rate to chemical movement rate

p = bulk density of soil, kg/L

K_p = partition coefficient, L/kg

e = void fraction or porosity of soil

²⁸S. W. Karickhoff, D. S. Brown, and T. A. Scott, Sorption of Hydrophobic Pollutants on Natural Sediments, *Water Research*, **13**: 241–248 (1979).

²⁹W. J. Weber, Jr., P. M. McGinley, and L. E. Katz, A Distributed Reactivity Model for Sorption by Soils and Sediments. 1. Conceptual Basis and Equilibrium Assessments, *Env. Sci. Tech.*, **26**: 1955–1962 (1992).

³⁰R. P. Schwarzenbach, P. M. Gschwend, and D. M. Imboden, “Environmental Organic Chemistry,” Wiley-Interscience, New York, 1993.

³¹Karickhoff et al., Sorption of Hydrophobic Pollutants on Natural Sediments.

³²Ibid.

³³P. V. Roberts, M. Reinhard, and P. L. McCarty, Organic Contaminant Behavior During Groundwater Recharge, *J. Water Pollution Control Fed.*, **52**: 161–172 (1980).

EXAMPLE 5.3

Compare the retardation of chloroform, chlorobenzene, and DDT for the following groundwater conditions:

$$\rho = 2 \text{ kg/L}$$

$$f_{oc} = \text{fraction organic carbon} = 0.01 \text{ (soil contains 1 percent organic carbon)}$$

$$e = 0.20$$

The following equations are used to solve this problem:

$$K_p = K_{oc}f_{oc}$$

$$K_{oc} = 0.63(K_{ow})$$

$$t_r = 1 + \rho K_p / e$$

Using the data from Table 5.15:

Compound	$\log K_{ow}$	K_{ow}	K_{oc}	K_p	t_r
Chloroform	1.97	93.3	58.8	0.588	6.88
Chlorobenzene	2.84	692	436	4.36	44.6
DDT	6.91	8.13×10^6	5.12×10^6	5.12×10^4	5.12×10^5

These calculations indicate that chloroform will move slower than water by a factor of 7, chlorobenzene by a factor of 45, and DDT by a factor of about 500,000. Of these three compounds, chloroform is thus expected to move much more rapidly with groundwater flow whereas DDT is not likely to move far from its source.

Transformation Reactions

Transformation reactions important in the fate and removal of organics are listed in Table 5.14 and include photolysis, hydrolysis, oxidation, reduction, and biotransformation. Hydrolysis, oxidation, and reduction can be chemical (abiotic) or mediated by microorganisms (biotic). An additional transformation reaction important with halogenated organics is elimination (dehydrohalogenation). In many cases, microbially mediated transformation reactions are much more rapid than abiotic reactions. Photochemical transformations are sometimes quite rapid. Biotransformation reactions are discussed in more detail in Chap. 6.

Photochemical Transformations Photochemical transformations are important fate processes for organics in the near-surface aquatic environment as well as in the upper atmosphere. Enhanced photochemical processes are also being used for the treatment of some hazardous wastes. Inorganic pollutants can also be transformed by photochemical reactions; the best known such case is the production of photochemical smog. There are four major photochemical reactions of environmental significance: direct photolysis, indirect photolysis, oxidation, and free-radical oxidation.

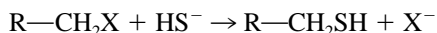
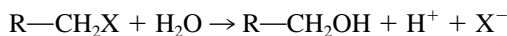
In direct photolysis, the organic absorbs light energy (photons) and is converted into an excited state which then releases this energy in conjunction with conversion into a product (different) compound. In indirect photolysis, a nontarget compound (for example, dissolved organic material such as humic substances) absorbs the

photons and becomes excited. This energized molecule then transmits its energy to the pollutant (target organic) causing it to be transformed.

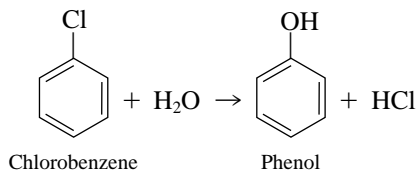
In oxidation and free-radical oxidation, light energy is typically absorbed by an intermediate compound such as dissolved organic matter, nitrate, or Fe(III), with the resultant production of oxidants such as H_2O_2 and O_3 , free radicals such as hydroxyl ($\cdot\text{OH}$) and peroxy ($\cdot\text{OOR}$), and/or other reactive species such as singlet oxygen $^1\text{O}_2$. These oxidants are then available to oxidize a wide variety of organics. Chlorinated compounds are particularly susceptible to oxidation by these species. Mixtures of ultraviolet light and ozone or hydrogen peroxide are used in engineered systems for treatment of trace levels of organics in gases and water, and rely on production of these activated chemical species. As described in Sec. 5.8, free-radical reactions are involved in the depletion of the ozone layer.

Hydrolysis and Other Nucleophilic Substitutions Hydrolysis reactions are nucleophilic substitution reactions where water acts as a nucleophile and attacks an organic bond. *Nucleophiles* are electron-rich ions (H_2O is an exception) that are often called “nucleus-liking, positive-charge-liking” species. They typically like to attack saturated bonds. Other common nucleophiles include OH^- , NO_3^- , SO_4^{2-} , HS^- , HCO_3^- , and HPO_4^{2-} . There is no change in oxidation state of the organic compound during these transformations. In aquatic systems, the most common reactions are those in which water is added, and these reactions may be abiotic or biotic. Abiotic reactions are a strong function of pH. Organic compounds susceptible to hydrolysis and nucleophilic substitution include alkyl halides (halogenated aliphatics), amides, amines, carbamates, epoxides, esters, nitriles, and phosphoric acid esters. A few examples, mostly with H_2O serving as the nucleophile, are given here.

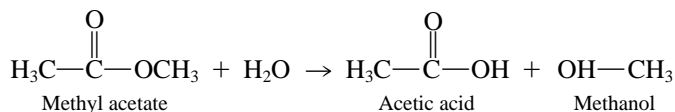
1. Alkyl halides (X = halogen)



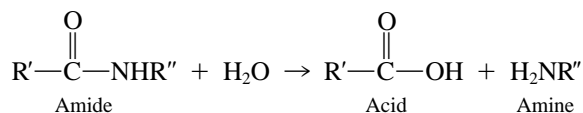
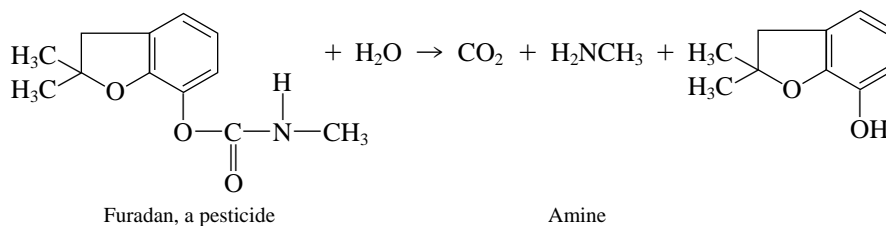
Iron sulfide minerals [e.g., mackinawite, typically abbreviated $\text{FeS}(s)$] can also facilitate nucleophilic substitution reactions for halogenated organic compounds. They can also bring about reductive dehalogenation and other electron-transferring processes. Halogenated aromatics (aryl halides) may also undergo hydrolysis. For example,



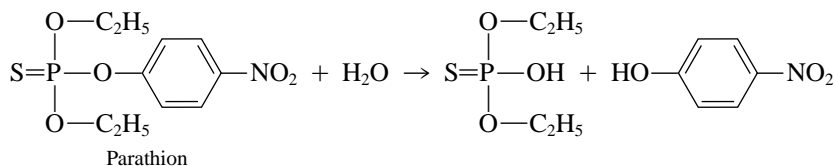
2. Esters



3. Amides

4. Carbamates are converted into CO₂, an amine, and other compounds (for example, alcohols).

5. Phosphoric esters



Nucleophilic substitution reactions are typically expressed as second-order or pseudo-first-order reactions:

$$\text{Rate} = -k_h[\text{C}][\text{N}] \quad (5.62)$$

where k_h = hydrolysis rate coefficient
 $[\text{C}]$ = concentration of organic
 $[\text{N}]$ = concentration of nucleophile

The minus sign represents the disappearance of the organic compound. When water is the nucleophile, or when the concentration of the nucleophile is constant or unknown, a pseudo-first-order expression may be used:

$$\text{Rate} = -k_h[\text{C}] \quad (5.63)$$

Hydrolysis reactions can be acid or base catalyzed, in which case the rate expressions can be a bit more complicated:

$$\text{Rate} = -(k_a[\text{H}^+] + k_n + k_b[\text{OH}^-])[\text{C}] \quad (5.64)$$

where k_a = acid-catalyzed rate coefficient
 k_n = neutral rate coefficient
 k_b = base-catalyzed rate coefficient

The overall hydrolysis rate coefficient can then be expressed as

$$k_h = k_a[\text{H}^+] + k_n + k_b[\text{OH}^-] \quad (5.65)$$

Care must be taken to ensure that the units used in these rate expressions are consistent.

The concept of half-life is often used to describe the persistence of an organic in the environment. Half-life ($t_{1/2}$) was defined in Sec. 3.10 as $0.693/k$, where k is a first-order rate coefficient. With hydrolysis, k is represented by k_h or $k_h[N]$. Hydrolysis reactions may be quite slow (half-lives of years) or quite rapid (half-lives of seconds) depending on the organic and the environmental conditions.

The following are hydrolysis rate coefficients reported by Jeffers and co-workers.³⁴

EXAMPLE 5.4

Compound	k_h, min^{-1}
Chloroform	7.13×10^{-10}
Carbon tetrachloride	3.26×10^{-8}
1,1,1-Trichloroethane	1.24×10^{-6}
Pentachloroethane	1.31×10^{-4}
Trichloroethene	1.07×10^{-12}
Tetrachloroethene	1.37×10^{-15}

From these data, calculate the half-lives, in years, of these compounds in the environment assuming that no other transformation reactions occur.

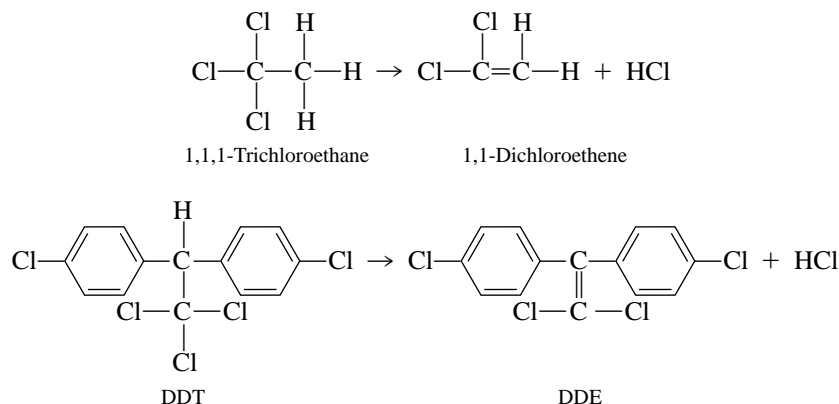
$$\text{Half-life} = t_{1/2} = \frac{\ln 2}{k_h} = \frac{0.693}{(k_h)(60)(24)(365)}$$

Compound	$t_{1/2}, \text{years}$
Chloroform	1849
Carbon tetrachloride	40
1,1,1-Trichloroethane	1.1
Pentachloroethane	0.010 (3.7 days)
Trichloroethene	1.23×10^6
Tetrachloroethene	9.62×10^8

These data indicate that chlorinated aliphatics are in general very slowly hydrolyzed. Other data indicate that the environmental half-lives of these compounds are sometimes much shorter, indicating that other transformation processes, perhaps biotic, are more important in controlling their fate.

³⁴P. Jeffers, L. Ward, L. Woytowitch, and L. Wolfe, Homogeneous Hydrolysis Rate Constants for Selected Chlorinated Methanes, Ethanes, Ethenes, and Propanes. *Env. Sci. Technol.*, **23**: 965–969 (1989).

Elimination (Dehydrohalogenation) Elimination reactions may occur abiotically or be microbially mediated. Although these reactions have been shown to occur with many organics, the ones of most importance to environmental engineers and scientists are those with halogenated organics. The most common of these reactions are characterized by the release of HX (dehydrohalogenation) and the formation of a double bond.



Oxidation Oxidation occurs when an organic loses (donates) one or more electrons to an oxidizing agent (electron acceptor). Abiotic oxidation reactions are typically very slow or nonexistent under environmental conditions. The most common natural oxidants are molecular oxygen, Fe(III), and Mn(III/IV). These are to be contrasted with the potentially rapid oxidations that occur with photochemically produced oxidants such as H_2O_2 , O_3 , the free radicals such as hydroxyl ($\cdot\text{OH}$) and peroxy ($\cdot\text{OOR}$), and other reactive species such as singlet oxygen $^1\text{O}_2$. Strong oxidizing agents such as H_2O_2 , O_3 , MnO_4^- (permanganate), and various chlorine species (e.g., Cl_2 , ClO_2) can oxidize organics during water and wastewater treatment. Biological oxidations will be covered in more detail in Chap. 6.

Rates of abiotic oxidation reactions are often described using a second-order rate expression:

$$\text{Rate} = -k_o[C][Ox] \quad (5.66)$$

where k_o = oxidation rate coefficient
 $[C]$ = concentration of organic
 $[Ox]$ = concentration of oxidant

Reduction Reduction occurs when an organic gains (accepts) one or more electrons from a reducing agent (electron donor). Highly oxidized organics (e.g., highly chlorinated organics and nitroaromatics) are susceptible to reduction. Abiotic reduction reactions are quite common, especially under reducing conditions (absence of oxygen). In many cases it is difficult to distinguish between truly abiotic reductions and those mediated by microorganisms. For example, HS^- can take part in nucleophilic substitution reactions (see Hydrolysis and Other Nucleophilic Substitutions) and can be involved in reduction reactions where it is oxidized to elemental sulfur

(S(s)) with the reduction of the organic. In anaerobic environments HS^- is present primarily due to microbial reduction of sulfate; without the microorganisms, the reduction would not take place. Reducing agents found in the environment include HS^- ; Fe(II) compounds such as iron sulfides, iron carbonates; iron oxides; iron and other porphyrins; and other reduced organic compounds (natural organic matter).

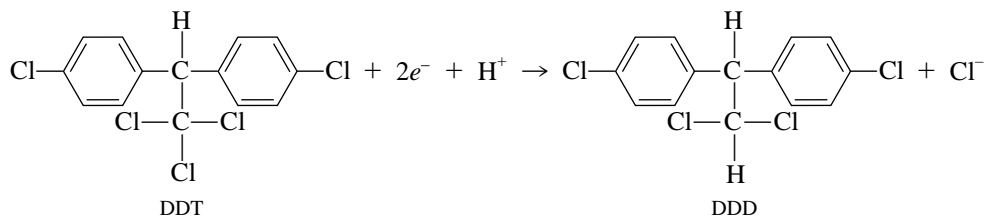
Rates of abiotic reduction reactions are often described using a second-order rate expression:

$$\text{Rate} = -k_r[C][\text{Red}] \quad (5.67)$$

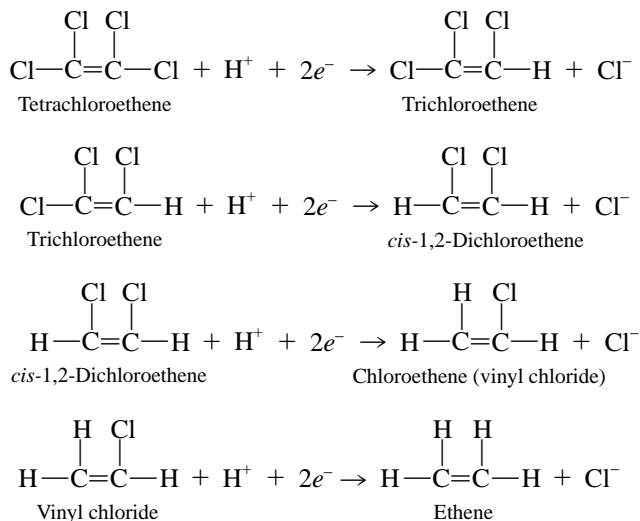
where k_r = reduction rate coefficient
 $[C]$ = concentration of organic
 $[\text{Red}]$ = concentration of reductant.

Many types of organics are susceptible to abiotic or biotic reduction. A few examples are given here.

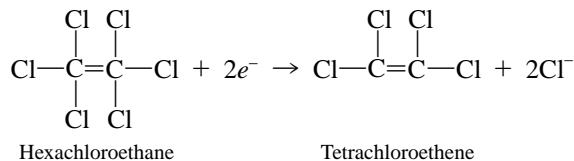
1. Reductive dehalogenation.



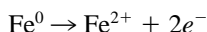
The biological reductive dehalogenation of tetrachloroethene (PCE) and trichloroethene (TCE) illustrate the potential for transformation reactions to result in more problematic products (vinyl chloride in this case). These reductions proceed with an overall transfer of $2e^-$ per molecule and replacement of one Cl atom with a H atom:



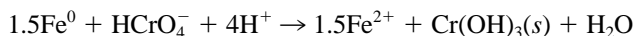
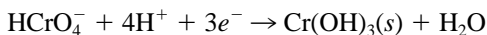
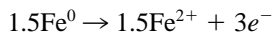
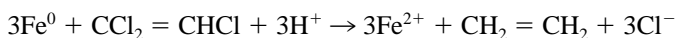
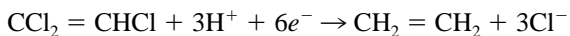
2. Reductive elimination



Treatment of contaminated groundwaters using *permeable reactive barriers* (PRB) containing iron metal (Fe(0)) is based on reduction. As Fe(0) is oxidized (corrodes), e^- are released which can be used to reduce highly oxidized pollutants:

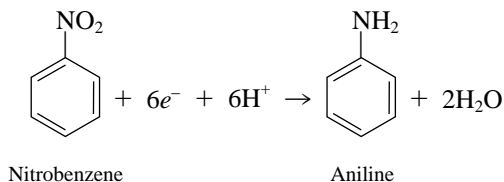


These Fe(0)-PRB have been used to treat groundwaters contaminated with chlorinated aliphatics such as perchloroethene and trichloroethene and highly oxidized metals such as Cr(VI). In the case of Cr(VI), the less mobile and less toxic trivalent form is produced. Example stoichiometries are given here for trichloroethene ($\text{CCl}_2 = \text{CHCl}$) reduction to ethene ($\text{CH}_2 = \text{CH}_2$) and chromate (HCrO_4^-) reduction to trivalent Cr ($\text{Cr}(\text{OH})_3(\text{s})$):



As discussed in Chap. 6, the electrons necessary for accomplishing reduction can also be provided by microbial oxidation of a wide variety of electron donors.

3. Reduction of nitro groups to the corresponding amino groups.



4. Reduction of disulfides to mercaptans.



5.35 | STRUCTURE- AND PROPERTY-ACTIVITY RELATIONSHIPS

There is considerable interest in developing methods for predicting the properties (e.g., solubility) and activities (e.g., fate, toxicity) of chemicals, especially organics, in the environment and in engineered systems. Physical, chemical, and structural (molecular) characteristics of organic compounds are used in this regard, and correlations have been developed for a wide variety of structures, properties, and activities. For the purposes of this discussion, *structure* refers to molecular characteristics. *Activity* refers to a biological effect such as toxicity, biotransformation, or bioconcentration (to be distinguished from the definition of activity given in Sec. 2.12). It may also refer to the potential for transformation of organic compounds via abiotic reactions. *Property* is a more all-encompassing term that includes such environmentally significant characteristics as solubility, volatility, and liquid-liquid or solid-liquid partitioning. It is the purpose of this section to introduce the student to the nature and usefulness of these relationships for understanding and predicting the behavior of organic compounds. The reader should be aware that the definition of the terms used herein may differ slightly with those used by others in this evolving field.

Relationships that have been developed include *structure-activity*, *property-activity*, *structure-property*, and *property-property* relationships. All are commonly referred to in the literature as *quantitative structure-activity relationships (QSAR)*. The general goal of any QSAR is to quantitatively relate, using a variety of statistical correlation techniques, a property or activity of a given set of chemicals to characteristics (structure or property), sometimes called descriptors, of these chemicals. QSARs were initially used in drug design and formulation of pesticides, and later were extended for use in environmental toxicology. QSARs are of current interest because they can help understand and predict the impact of organic chemicals for which there is very little environmental data. It has been estimated that there are about 70,000 synthetic chemicals currently being used, with 500–1000 new ones being added each year. Data about environmental fate and effects exist for only about 20% of these chemicals.³⁵ Although QSARs are empirical relationships, they do provide important information that can help interpret causes and mechanisms involved. Some caution must be exercised when attempting to use QSARs for compounds with properties (e.g., chemical structure) that are significantly different from the compounds used to develop the QSAR.

Relationships that are developed using basic structural (molecular) characteristics such as molecular connectivity, molar surface area, intrinsic molar volume, atomic charge, and others have some advantages in that they can be determined without need for experimental data. However, the environmental engineer or scientist must have access to the structural characteristics and calculation methods necessary to determine values for these parameters. Some of this infor-

³⁵S. Postel, in "State of the World 1987," L. R. Brown, et al., eds., Worldwatch Institute Report, W. W. Norton, New York, 1987.

mation is currently available in the literature, and more is becoming increasingly available in software packages that can be purchased.³⁶ Detailed discussion of these parameters and the methods used to determine them is beyond the scope of this text.

Prediction of Properties of Organic Chemicals

Relationships have been developed that allow for prediction of environmentally significant properties such as solubility, K_H , K_{ow} , and K_{oc} . An example of a structure-property relationship for solubility is³⁷

$$\log S = 1.543 + 1.638^{\circ}\chi - 1.374^{\circ}\chi^v + 1.003\bar{\Phi} \quad (5.68)$$

where S = aqueous solubility, mol/L
 $^{\circ}\chi$ = zero-order, simple molecular connectivity index
 $^{\circ}\chi^v$ = valence molecular connectivity index
 $\bar{\Phi}$ = modified polarizability parameter.

Values for $^{\circ}\chi$, $^{\circ}\chi^v$, and $\bar{\Phi}$ can be calculated from molecular structure without need for experimental data. Table 5.16 contains a sample of the type of data used to calculate solubility using this relationship. The relationship in Eq. (5.68) was developed from a data set of 145 different organic chemicals, including alcohols, halogenated aliphatics, and aromatics.

Many *property-property* relationships have been developed. Equation (5.59), relating K_{oc} to K_{ow} , and Eq. (5.60), relating K_{oc} to S , are examples. An additional example relates K_{ow} to S (mol/L) for a set of 36 different organic compounds.³⁸

$$\log K_{ow} = -0.862 \log S + 0.710 \quad (5.69)$$

Table 5.16 | $^{\circ}\chi$, $^{\circ}\chi^v$, and $\bar{\Phi}$ values for selected organic compounds

Compound	$^{\circ}\chi$	$^{\circ}\chi^v$	$\bar{\Phi}$
Phenol	4.38	3.83	-4.11
2-Chlorophenol	5.30	4.89	-4.71
Pentachlorophenol	9.00	9.46	-7.12
Naphthalene	5.61	5.61	-6.72
Benzo(a)pyrene	10.92	10.92	-12.00

Source: Data taken from N. N. Nirmalakhandan and R. E. Speece, Prediction of Aqueous Solubility of Organic Chemicals Based on Molecular Structure. 2. Application to PNAs, PCBs, PCDDs, etc., *Env. Sci. Tech.*, **23**: 708–713 (1989).

³⁶M. Reinhard and A. Drefahl, "Handbook for Estimating Physiochemical Properties of Organic Compounds," John Wiley & Sons, Inc., New York, 1999.

³⁷N. N. Nirmalakhandan and R. E. Speece, Prediction of Aqueous Solubility of Organic Chemicals Based on Molecular Structure. 2. Application to PNAs, PCBs, PCDDs, etc., *Env. Sci. Tech.*, **23**: 708–713 (1989).

³⁸C. T. Chiou, Partition Coefficient and Water Solubility in Environmental Chemistry, in "Assessment of Chemicals," vol. 1, Academic Press, pp. 117–153, 1981.

Prediction of Activities of Organic Chemicals

Activity in the context of QSARs usually refers to a biological effect such as toxicity, biotransformation, or bioconcentration. Many such relationships have been developed;³⁹ a few are described here.

It has long been recognized that bioaccumulation or bioconcentration (roughly defined as the ratio of the concentration of the organic compound in a target organism to the concentration of chemical in water) can be related to K_{ow} . This is expected since bioaccumulation is thought to be a partitioning process. An example of such a property-activity relationship is⁴⁰

$$\log \text{BF} = \log K_{ow} - 1.32 \quad (5.70)$$

where BF is the bioconcentration factor. Equation (5.70) was developed from a variety of aquatic organisms (fish, algae, and mussels) and a data set of 51 organic chemicals.

Attempts have been made to develop structure-activity relationships, such as biodegradability versus chemical structure. An example is⁴¹

$$\text{BOD} = 1015(|\Delta\delta|_{x-y}) + 1.193 \quad (5.71)$$

where BOD is the percentage of theoretical BOD achieved in 5 days and $|\Delta\delta|_{x-y}$ is the modulus of atomic charge differences across common bonds (e.g., C—O). This relationship was developed from 79 organic compounds, including amines, phenols, aldehydes, carboxylic acids, halogenated hydrocarbons, and amino acids.

One of the most promising uses of QSARs is in the understanding and prediction of toxicity of organic chemicals to organisms of environmental significance. Recent studies have related the toxicity of 50 to 130 organic chemicals to a variety of bacteria. Examples of *structure-activity* and *property-activity* relationships, respectively, for aerobic, heterotrophic bacteria are given here.⁴²

$$\log \text{IC}_{50} = 5.24 - 4.15(V_i/100) + 3.71\beta_m - 0.41\alpha_m \quad (5.72)$$

$$\log \text{IC}_{50} = 5.12 - 0.76 \log K_{ow} \quad (5.73)$$

where IC_{50} = concentration (mg/L) at which the biological reaction rate is reduced by 50 percent

V_i = intrinsic molar volume

β_m and α_m = measures of ability to participate in hydrogen bonding as a hydrogen donor or acceptor, respectively

V_i , β_m , and α_m are commonly termed linear solvation energy relationship (LSER) parameters. Table 5.17 contains a sample of values of these parameters needed to use Eq. (5.72).

³⁹Reinhard and Drefahl, "Handbook for Estimating Physicochemical Properties of Organic Compounds."

⁴⁰D. Mackay, Correlation of Bioconcentration Factors, *Env. Sci. Tech.*, **16**: 274–278 (1982).

⁴¹J. C. Dearden, and R. M. Nicholson, The Prediction of Biodegradability by the Use of Quantitative Structure-Activity Relationships: Correlation of Biological Oxygen Demand with Atomic Charge Difference, *Pesticide Science*, **17**: 305–310 (1986).

⁴²D. J. W. Blum and R. E. Speece, Determining Chemical Toxicity to Aquatic Species. *Env. Sci. Tech.*, **24**: 284–293 (1990).

Table 5.17 | Values of $V_i/100$, β_m , and α_m for selected organic compounds

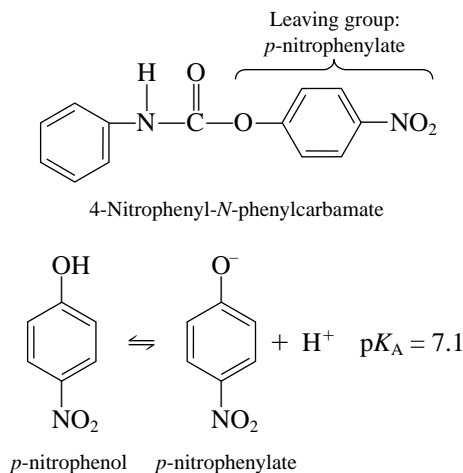
Compound	$V_i/100$	β_m	α_m
Dichloromethane	0.336	0.05	0.13
Chloroform	0.427	0	0.20
1,1,1-Trichloroethane	0.519	0	0
Trichloroethene	0.492	0.03	0.12
Benzene	0.491	0.14	0
Toluene	0.592	0.14	0
Chlorobenzene	0.581	0.09	0
Phenol	0.536	0.33	0.60

Source: Data taken from D. J. W. Blum, Chemical Toxicity to Environmental Bacteria: Quantitative Structure Activity Relationships and Interspecies Correlations and Comparisons, Ph.D. Dissertation, Drexel University, Philadelphia (1989).

One of the best-known property-activity relationships is commonly termed a linear free-energy relationship (LFER) and correlates reaction rates with equilibrium constants. This is an attempt to relate the kinetics of a chemical reaction to its thermodynamics. An example is given here for the base-catalyzed hydrolysis of a series of 16 *N*-phenylcarbamates.⁴³

$$\log k_b = -1.15\text{p}K_A + 13.6 \quad (5.74)$$

where k_b is the first-order hydrolysis rate ($\text{M}^{-1}\text{s}^{-1}$) and $\text{p}K_A$ is the $\text{p}K_A$ of the alcohol, or leaving group. Recall that hydrolysis of carbamates yields an amine, an alcohol, and CO_2 . Leaving groups included nitrophenolates, chlorophenolates, and halogenated aliphatic compounds, among others. An example is given here for 4-nitrophenyl-*N*-phenylcarbamate ($k_b = 2.7 \times 10^5 \text{M}^{-1}\text{s}^{-1}$):



⁴³R. P. Schwarzenbach and P. M. Gschwend, Chemical Transformations of Organic Pollutants in the Aquatic Environment, in "Aquatic Chemical Kinetics," W. Stumm, ed., Wiley-Interscience, New York, 1990.

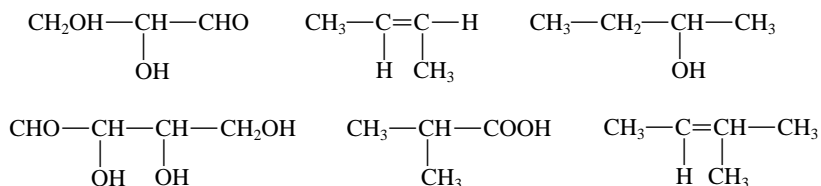
Another example of a LFER relates the surface-area normalized rate coefficient (k_{SA} , L/m²-h) for reduction of 48 chlorinated alkanes and alkenes by Fe(0) to calculated estimates of the lowest unoccupied molecular orbital energies (E_{LUMO} , eV) for these compounds.⁴⁴

$$\log k_{SA} = -5.603 - 1.49E_{LUMO} \quad (5.75)$$

For example, E_{LUMO} for tetrachloroethene is estimated to be -1.689 eV. Using Eq. (5.75) gives a rate coefficient of 8.2×10^{-4} L/m²-h. If the surface-area concentration in a Fe(0) permeable reactive barrier were 2 m²/mL (2000 m²/L), then the pseudo-first-order rate coefficient would be 1.64 h⁻¹.

PROBLEMS

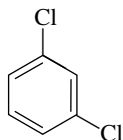
- 5.1 Why is it possible to have so many compounds of carbon?
- 5.2 Define homologous series, homolog, hydrocarbon, and alkyl radical.
- 5.3 Define isomerism and illustrate with structural formulas of compounds with the molecular formula C₆H₁₄.
- 5.4 In general, how do organic compounds differ from inorganic compounds?
- 5.5 How many grams of oxygen are required to furnish just enough oxygen for the complete oxidation of 20 g of butane?
- 5.6 What is the difference between an aliphatic and an aromatic compound?
- 5.7 Define with suitable illustrations the terms primary alcohol, secondary alcohol, and tertiary alcohol, and indicate their relative ease of biodegradation.
- 5.8 Show the structures and names of the intermediate compounds formed in the biological oxidation of *n*-butane to butyric acid.
- 5.9 Why are oxidation reactions of organic compounds important to environmental engineers and scientists?
- 5.10 What might be formed from CH₃—CH₂—CH=CH—CH₃ in the atmosphere in the presence of sunlight, oxides of nitrogen, and water droplets?
- 5.11 Which of the following compounds have optical isomers?



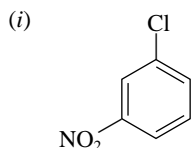
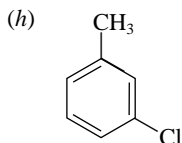
- 5.12 Show a general formula for fats and oils. What is the difference between a fat and an oil?
- 5.13 What is the difference between a fat and a wax?
- 5.14 How many asymmetric carbon atoms are there in glucose?

⁴⁴M. M. Scherer, B. A. Balko, D. A. Gallagher, and P. G. Tratnyek, Correlation Analysis of Rate Constants for Dechlorination by Zero-Valent Iron, *Env. Sci. Tech.*, **32**: 3026–3033 (1998).

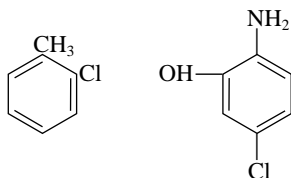
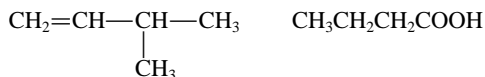
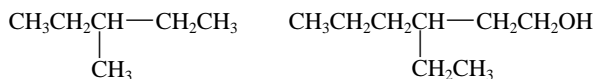
- 5.15** Write a possible structural formula for a ketopentose and for an aldopentose.
- 5.16** What is the major factor contributing to the difference in biodegradability between starch and cellulose?
- 5.17** Show a general formula for the building blocks of proteins and illustrate how these building blocks are connected to form proteins.
- 5.18** If a sample of food waste contains 2.5 percent of organic nitrogen, what approximate percentage of the sample is protein?
- 5.19** What functional group is characteristic of each of the following: alkenes, alcohols, aldehydes, ketones, acids, amines, amides, ethers, esters, and aromatic compounds?
- 5.20** What monosaccharides are formed upon hydrolysis of the following: cellulose, starch, and hemicellulose?
- 5.21** Name the three general classes of synthetic detergents, and give an example of each.
- 5.22** Name the four general classes of synthetic pesticides, and describe how the pesticides in each class differ in degree of biodegradability.
- 5.23** Explain why pharmaceutically active chemicals (PhACs) are of concern to environmental engineers and scientists. Give two examples of PhACs.
- 5.24** Explain why endocrine-disrupting chemicals (EDCs) are of concern to environmental engineers and scientists. Give two examples of EDCs.
- 5.25** Give the structural formula for each of the following:
- (a) 3-Nonene
 - (b) *n*-Octyl phenol
 - (c) Dimethyl ether
 - (d) 1,1,2-Trichloroethane
 - (e) Any PCB
 - (f) *n*-Pentanoic acid
 - (g) Isopropanol
 - (h) 2,4,6-Trinitrotoluene (TNT)
- 5.26** Give the structural formula for the following:
- (a) 1,2-Dichloroethene
 - (b) Diethyl ketone
 - (c) Pentachlorophenol
 - (d) Butyric acid
 - (e) *m*-Chlorophenol
 - (f) A poly-cyclic aromatic hydrocarbon (PAH)
 - (g) 3-Pentanol
 - (h) 1-Octene
- 5.27** Given the following structural formulas, name (IUPAC or common) the compound.
- (a) $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$
 - (b)



- (c) $\text{CHCl}_2\text{CH}_2\text{Br}$
 (d) $\text{CH}_3\text{OCH}_2\text{CH}_3$
 (e) CH_3CHO
 (f) CCl_2CHCl
 (g) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_3$



5.28 Name the following:



5.29 A contaminated groundwater contains $50 \mu\text{g/L}$ chlorobenzene, $25 \mu\text{g/L}$ dichloromethane, and $85 \mu\text{g/L}$ ethylbenzene. Using the simplified equilibrium model developed in Sec. 5.34, estimate the air-to-water ratio required to reduce the concentration of each of these compounds below $5 \mu\text{g/L}$. Assume a temperature of 25°C . If you were to design a stripping tower to remove these contaminants, would you expect your design air-to-water ratio to be larger, smaller, or the same? Why?

Answer: 48.9; 39.1; 48.3

5.30 Regarding air stripping for the removal of volatile organic compounds, what impact on removal efficiency would an increase in the following parameters have?

- (a) H
 (b) V_a/V_w
 (c) $K_L a$
 (d) Temperature

- 5.31** Rank the following compounds from most volatile (most likely to partition into the atmosphere) to least volatile. Include appropriate data and reference the data to substantiate your ranking.
- (a) Benzene
 - (b) Phenol
 - (c) Chloroform
 - (d) Bromoform
 - (e) Trichloroethene
 - (f) 1,1,1-Trichloroethane
 - (g) Tetrachloroethene (also called perchloroethene)
- 5.32** An industry has dumped a total of 100 pounds of trichloroethene (TCE) into a well-capped landfill (that is, assume the landfill is closed to the atmosphere). This chemical landfill is 100 feet long by 100 feet wide and 10 feet deep. The void volume is 30 percent and 70 percent of the voids are filled with water. Assuming that aqueous solubility is not exceeded and that there is no transformation or sorptive removal, estimate the concentration of TCE in the aqueous phase. Assume a temperature of 25°C. [Think about how complex this problem would be if biodegradation (vinyl chloride can be produced under anaerobic conditions!) and sorption occurred, and if the landfill were not capped and/or a substantial amount of methane were produced and vented to the atmosphere.]
- Answer:* 63 mg/L
- 5.33** A wastewater is saturated with trichloroethene giving a concentration of 1100 mg/L. One million liters of this waste is put into a *closed* holding tank (total tank volume = 2 million liters). What percent removal of TCE *from the liquid* would occur from this action? Assume a temperature of 25°C.
- Answer:* 32 percent
- 5.34** Using values from Table 5.15, estimate K_{oc} using octanol-water partition coefficients and water solubilities for the following compounds:
- (a) Chloroform
 - (b) 1,1,1-Trichloroethane
 - (c) Benzene
 - (d) Chlorobenzene
 - (e) Phenol
 - (f) Pentachlorophenol
 - (g) Benzo(a)pyrene
 - (h) Atrazine
- 5.35** Using data from Table 5.15, determine which of the following will move faster with groundwater. By what degree? Show all calculations necessary to justify your answer. Assume the aquifer has a void fraction of 0.20, a bulk density of 2 kg/L, and contains 1 percent organic carbon.
- (a) Benzene
 - (b) Toluene
 - (c) Trichloroethene
 - (d) 1,1,1-Trichloroethane

(e) Acrolein

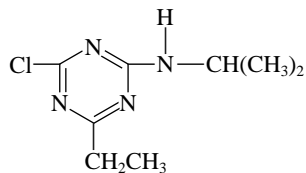
(f) Naphthalene

Answer: acrolein is fastest; naphthalene slowest

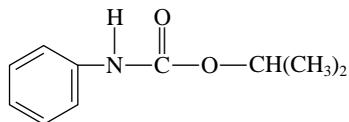
- 5.36** Assuming a temperature of 25°C, estimate the degree to which tetrachloroethene (PCE) will be retarded in a groundwater aquifer with
- (a) A void fraction of 0.30, a bulk density of 2000 kg/m³, and an organic carbon content of 0.25 percent.
- (b) A void fraction of 0.30, a bulk density of 2000 kg/m³, and an organic carbon content of 1.0 percent.
- 5.37** Which parameter, H , water solubility, or K_{ow} , would you expect to be a better predictor for whether a compound will sorb strongly to particulate material in soils and sediments? Why?
- 5.38** The organic compounds listed here are contained in a combined domestic-industrial wastewater. Rank the compounds in increasing order of susceptibility to removal by settling of wastewater suspended solids during primary sedimentation. Provide suitable justification for your rankings.
- (a) Alachlor
- (b) Phenol
- (c) Pentachlorophenol
- (d) Acrolein
- (e) Carbon tetrachloride
- (f) Nitrobenzene
- (g) Ethanol
- Answer:* pentachlorophenol most susceptible
- 5.39** Groundwater contamination problems have been caused because of underground storage tanks leaking gasoline. In most situations the compounds causing the most concern are MTBE and the BTEX compounds. Using data contained in Table 5.15, answer the following.
- (a) Which compound would you expect to move fastest in the groundwater? Why?
- (b) Which compound would be easiest to remove by air stripping? Why?
- (c) Which compound would be easiest to remove by adsorption? Why?
- 5.40** The following are types of transformation reactions. Give an adequate definition of each by writing an example reaction with a specific organic for each. Do *not* use the example reactions listed in the text, generate your own.
- (a) Hydrolysis
- (b) Elimination
- (c) Oxidation
- (d) Reduction
- (e) Nucleophilic substitution
- 5.41** Using example reactions, explain the difference between dehydrohalogenation, reductive dehalogenation, and reductive elimination.
- 5.42** The pesticides shown here are subject to transformation in the environment. Give the class of pesticide and suggest a transformation reaction that it may possibly undergo

in the environment. Balance the reaction as best you can and tell under what conditions it might occur (i.e., aerobic, anaerobic).

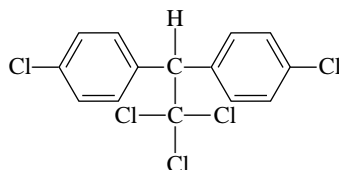
(a)



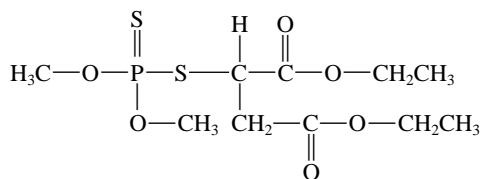
(b)



(c)



(d)



5.43 The following are pseudo-first-order rate coefficients for the pesticide parathion:

$$k_p = 0.10 \text{ day}^{-1} \quad \text{photolysis}$$

$$k_h = 0.028 \text{ day}^{-1} \quad \text{hydrolysis}$$

$$k_o = 0.005 \text{ day}^{-1} \quad \text{oxidation}$$

Calculate the environmental half-life for each of the transformation reaction types and the overall half-life of parathion. (*Note:* Rate coefficients for this problem were provided by Prof. J. L. Schnoor of the University of Iowa.)

Answer: 6.9 d; 24.8 d; 139 d; 5.2 d

5.44 A groundwater plume contains trichloroethene (TCE). TCE is reduced by iron metal (Fe(0)) following first-order kinetics with respect to TCE concentration. A permeable reactive barrier (PRB) containing Fe(0) is proposed to intercept and treat the contaminated groundwater. The following information is to be used to solve this problem.

$$\text{TCE concentration entering the PRB} = 100 \mu\text{g/L}$$

$$k_{\text{TCE}} = 0.002 \text{ h}^{-1}$$

For the PRB,

$$f_{\text{oc}} = 0.01 \quad \rho = 2.8 \text{ kg/L} \quad \text{porosity} = 0.45$$

$$\text{Linear groundwater velocity} = 0.3 \text{ ft/d}$$

Since the PRB contains organic carbon, TCE will be retarded as it passes through the PRB as well as reduced by the Fe(0). Will a 3-foot-wide PRB be adequate to reduce the concentration of TCE below its drinking water MCL ($5 \mu\text{g/L}$)? Assume a temperature of 25°C . *Hint: Calculate the "retarded" velocity of TCE and note that TCE removal by reduction is described by first-order kinetics.* (Note: This problem is courtesy of Prof. Michelle Scherer of the University of Iowa.)

- 5.45** Using Eq. (5.68), and assuming a temperature of 25°C , estimate the solubility of the compounds listed in Table 5.16. Compare these values with those given in Table 5.15.
- 5.46** Using Eq. (5.69) and K_{ow} data in Table 5.15, estimate the solubility of the compounds listed in Table 5.16. Compare these values with your answers for Prob. 5.45.
- 5.47** Using K_{ow} data from Table 5.15, rank the following compounds on the basis of lowest to highest degree of bioconcentration by estimating the bioconcentration factor for each.
- (a) Chloroform
 - (b) Trichloroethene
 - (c) Benzene
 - (d) Toluene
 - (e) Phenol
 - (f) Benzo(a)pyrene
 - (g) Acrolein
 - (h) DDT
- 5.48** Using K_{ow} data from Table 5.15, rank the following compounds on the basis of least to most toxic to aerobic heterotrophic bacteria by estimating the IC_{50} using Eqs. (5.72) and (5.73).
- (a) Dichloromethane
 - (b) Chloroform
 - (c) 1,1,1-Trichloroethane
 - (d) Trichloroethene
 - (e) Benzene
 - (f) Toluene
 - (g) Chlorobenzene
 - (h) Phenol
- Answer:* least, phenol or dichloromethane

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