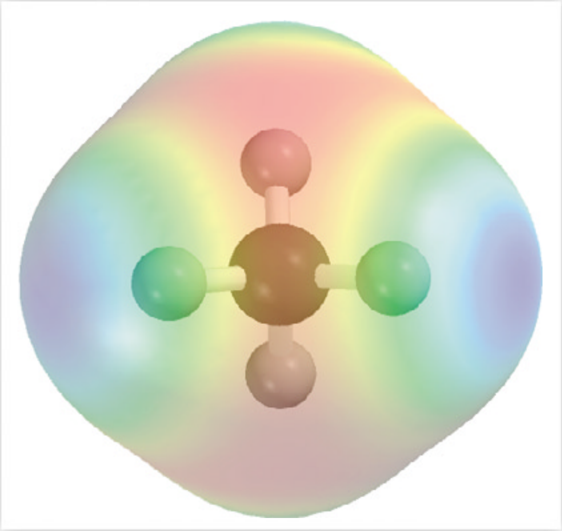

CHAPTER 1

CHEMICAL BONDING

Structure* is the key to everything in chemistry. The properties of a substance depend on the atoms it contains and the way the atoms are connected. What is less obvious, but very powerful, is the idea that someone who is trained in chemistry can look at a structural formula of a substance and tell you a lot about its properties. This chapter begins your training toward understanding the relationship between structure and properties in organic compounds. It reviews some fundamental principles of molecular structure and chemical **bonding.** By applying these principles you will learn to recognize the structural patterns that are more stable than others and develop skills in communicating chemical information by way of structural formulas that will be used throughout your study of organic chemistry.

1.1 ATOMS, ELECTRONS, AND ORBITALS

Before discussing bonding principles, let's first review some fundamental relationships between atoms and electrons. Each element is characterized by a unique **atomic number *Z*,** which is equal to the number of protons in its nucleus. A neutral atom has equal numbers of protons, which are positively charged, and electrons, which are negatively charged.

Electrons were believed to be particles from the time of their discovery in 1897 until 1924, when the French physicist Louis de Broglie suggested that they have wavelike properties as well. Two years later Erwin Schrödinger took the next step and calculated the energy of an electron in a hydrogen atom by using equations that treated the electron as if it were a wave. Instead of a single energy, Schrödinger obtained a series of **energy levels,** each of which corresponded to a different mathematical description of the electron wave. These mathematical descriptions are called **wave functions** and are symbolized by the Greek letter ψ (psi).

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*A glossary of important terms may be found immediately before the index at the back of the book.

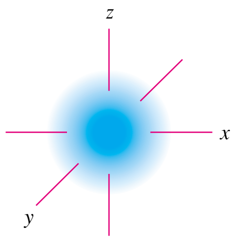


FIGURE 1.1 Probability distribution (ψ^2) for an electron in a 1*s* orbital.

According to the Heisenberg uncertainty principle, we can't tell exactly where an electron is, but we can tell where it is most likely to be. The probability of finding an electron at a particular spot relative to an atom's nucleus is given by the square of the wave function (ψ^2) at that point. Figure 1.1 illustrates the probability of finding an electron at various points in the lowest energy (most stable) state of a hydrogen atom. The darker the color in a region, the higher the probability. The probability of finding an electron at a particular point is greatest near the nucleus, and decreases with increasing distance from the nucleus but never becomes zero. We commonly describe Figure 1.1 as an "electron cloud" to call attention to the spread-out nature of the electron probability. Be careful, though. The "electron cloud" of a hydrogen atom, although drawn as a collection of many dots, represents only one electron.

Wave functions are also called **orbitals.** For convenience, chemists use the term "orbital" in several different ways. A drawing such as Figure 1.1 is often said to represent an orbital. We will see other kinds of drawings in this chapter, use the word "orbital" to describe them too, and accept some imprecision in language as the price to be paid for simplicity of expression.

Orbitals are described by specifying their size, shape, and directional properties. Spherically symmetrical ones such as shown in Figure 1.1 are called *s orbitals.* The letter *s* is preceded by the **principal quantum number** *n* (n = 1, 2, 3, etc.) which specifies the **shell** and is related to the energy of the orbital. An electron in a 1*s* orbital is likely to be found closer to the nucleus, is lower in energy, and is more strongly held than an electron in a 2*s* orbital.

Regions of a single orbital may be separated by **nodal surfaces** where the probability of finding an electron is zero. A 1*s* orbital has no nodes; a 2*s* orbital has one. A 1*s* and a 2*s* orbital are shown in cross section in Figure 1.2. The 2*s* wave function changes sign on passing through the nodal surface as indicated by the plus (+) and minus (−) signs in Figure 1.2. *Do not confuse these signs with electric charges—they have nothing to do with electron or nuclear charge.* Also, be aware that our "orbital" drawings are really representations of ψ^2 (which must be a positive number), whereas + and − refer to the sign of the wave function (ψ) itself. These customs may seem confusing at first but turn out not to complicate things in practice. Indeed, most of the time we won't

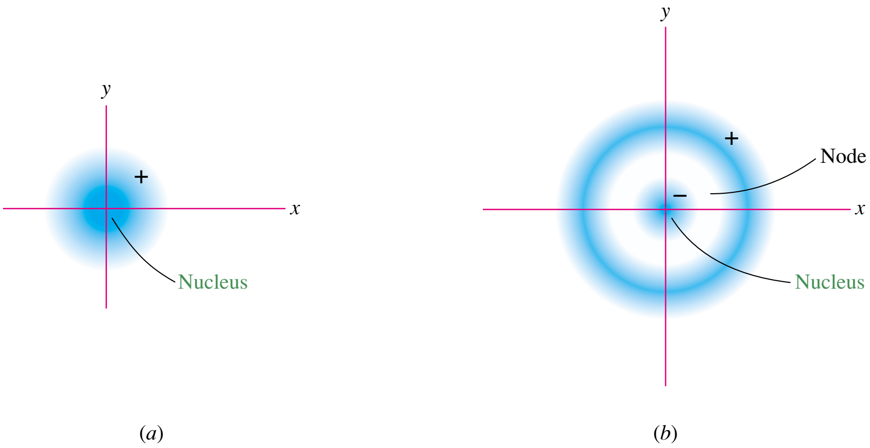


FIGURE 1.2 Cross sections of (*a*) a 1*s* orbital and (*b*) a 2*s* orbital. The wave function has the same sign over the entire 1*s* orbital. It is arbitrarily shown as +, but could just as well have been designated as −. The 2*s* orbital has a spherical node where the wave function changes sign.

even include + and − signs of wave functions in our drawings but only when they are necessary for understanding a particular concept.

Instead of probability distributions, it is more common to represent orbitals by their **boundary surfaces,** as shown in Figure 1.3 for the 1*s* and 2*s* orbitals. The boundary surface encloses the region where the probability of finding an electron is high—on the order of 90–95%. Like the probability distribution plot from which it is derived, a picture of a boundary surface is usually described as a drawing of an orbital.

A hydrogen atom ($Z = 1$) has one electron; a helium atom ($Z = 2$) has two. The single electron of hydrogen occupies a 1*s* orbital, as do the two electrons of helium. The respective electron configurations are described as:

$$\text{Hydrogen: } 1s^1 \qquad \text{Helium: } 1s^2$$

In addition to being negatively charged, electrons possess the property of **spin.** The **spin quantum number** of an electron can have a value of either $+\frac{1}{2}$ or $-\frac{1}{2}$. According to the **Pauli exclusion principle,** two electrons may occupy the same orbital only when they have opposite, or "paired," spins. For this reason, no orbital can contain more than two electrons. Since two electrons fill the 1*s* orbital, the third electron in lithium ($Z = 3$) must occupy an orbital of higher energy. After 1*s*, the next higher energy orbital is 2*s*. The third electron in lithium therefore occupies the 2*s* orbital, and the electron configuration of lithium is

$$\text{Lithium: } 1s^2 2s^1$$

A complete periodic table of the elements is presented on the inside back cover.

The **period** (or **row**) of the periodic table in which an element appears corresponds to the principal quantum number of the highest numbered occupied orbital ($n = 1$ in the case of hydrogen and helium). Hydrogen and helium are first-row elements; lithium ($n = 2$) is a second-row element.

With beryllium ($Z = 4$), the 2*s* level becomes filled, and the next orbitals to be occupied in it and the remaining second-row elements are the $2p_x$, $2p_y$, and $2p_z$ orbitals. These orbitals, portrayed in Figure 1.4, have a boundary surface that is usually described as "dumbbell-shaped." Each orbital consists of two "lobes," that is, slightly flattened spheres that touch each other along a nodal plane passing through the nucleus. The $2p_x$, $2p_y$, and $2p_z$ orbitals are equal in energy and mutually perpendicular.

The electron configurations of the first 12 elements, hydrogen through magnesium, are given in Table 1.1. In filling the 2*p* orbitals, notice that each is singly occupied before any one is doubly occupied. This is a general principle for orbitals of equal energy known

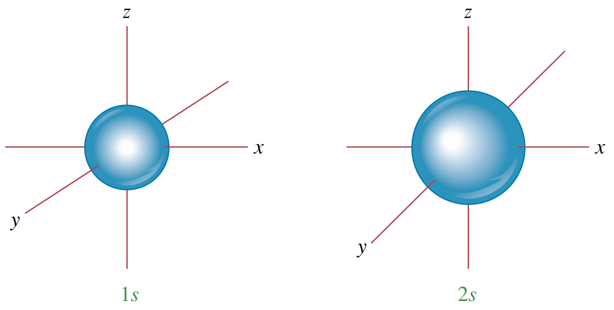


FIGURE 1.3 Boundary surfaces of a 1*s* orbital and a 2*s* orbital. The boundary surfaces enclose the volume where there is a 90–95% probability of finding an electron.

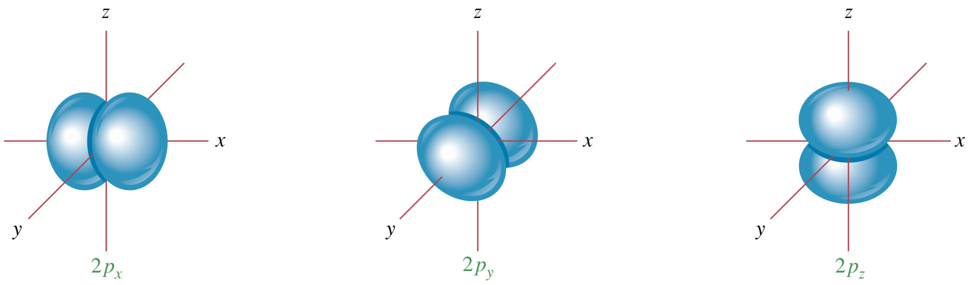


FIGURE 1.4 Boundary surfaces of the 2*p* orbitals. The wave function changes sign at the nucleus. The *yz*-plane is a nodal surface for the $2p_x$ orbital. The probability of finding a $2p_x$ electron in the *yz*-plane is zero. Analogously, the *xz*-plane is a nodal surface for the $2p_y$ orbital, and the *xy*-plane is a nodal surface for the $2p_z$ orbital.

as **Hund's rule.** *Of particular importance in Table 1.1 are hydrogen, carbon, nitrogen, and oxygen.* Countless organic compounds contain nitrogen, oxygen, or both in addition to carbon, the essential element of organic chemistry. Most of them also contain hydrogen.

It is often convenient to speak of the **valence electrons** of an atom. These are the outermost electrons, the ones most likely to be involved in chemical bonding and reactions. For second-row elements these are the 2*s* and 2*p* electrons. Because four orbitals (2*s*, $2p_x$, $2p_y$, $2p_z$) are involved, the maximum number of electrons in the **valence shell** of any second-row element is 8. Neon, with all its 2*s* and 2*p* orbitals doubly occupied, has eight valence electrons and completes the second row of the periodic table.

Answers to all problems that appear within the body of a chapter are found in Appendix 2. A brief discussion of the problem and advice on how to do problems of the same type are offered in the Study Guide.

PROBLEM 1.1 How many valence electrons does carbon have?

Once the 2*s* and 2*p* orbitals are filled, the next level is the 3*s*, followed by the $3p_x$, $3p_y$, and $3p_z$ orbitals. Electrons in these orbitals are farther from the nucleus than those in the 2*s* and 2*p* orbitals and are of higher energy.

TABLE 1.1 Electron Configurations of the First Twelve Elements of the Periodic Table

		Number of electrons in indicated orbital					
Element	**Atomic number *Z***	**1*s***	**2*s***	**$2p_x$**	**$2p_y$**	**$2p_z$**	**3*s***
Hydrogen	1	1					
Helium	2	2					
Lithium	3	2	1				
Beryllium	4	2	2				
Boron	5	2	2	1			
Carbon	6	2	2	1	1		
Nitrogen	7	2	2	1	1	1	
Oxygen	8	2	2	2	1	1	
Fluorine	9	2	2	2	2	1	
Neon	10	2	2	2	2	2	
Sodium	11	2	2	2	2	2	1
Magnesium	12	2	2	2	2	2	2

PROBLEM 1.2 Referring to the periodic table as needed, write electron configurations for all the elements in the third period.

SAMPLE SOLUTION The third period begins with sodium and ends with argon. The atomic number Z of sodium is 11, and so a sodium atom has 11 electrons. The maximum number of electrons in the 1s, 2s, and 2p orbitals is ten, and so the eleventh electron of sodium occupies a 3s orbital. The electron configuration of sodium is $1s^2 2s^2 2p_x^{\,2} 2p_y^{\,2} 2p_z^{\,2} 3s^1$.

In-chapter problems that contain multiple parts are accompanied by a sample solution to part (a). Answers to the other parts of the problem are found in Appendix 2, and detailed solutions are presented in the Study Guide.

Neon, in the second period, and argon, in the third, possess eight electrons in their valence shell; they are said to have a complete **octet** of electrons. Helium, neon, and argon belong to the class of elements known as **noble gases** or **rare gases.** The noble gases are characterized by an extremely stable "closed-shell" electron configuration and are very unreactive.

1.2 IONIC BONDS

Atoms combine with one another to give **compounds** having properties different from the atoms they contain. The attractive force between atoms in a compound is a **chemical bond.** One type of chemical bond, called an **ionic bond,** is the force of attraction between oppositely charged species (**ions**) (Figure 1.5). Ions that are positively charged are referred to as **cations;** those that are negatively charged are **anions.**

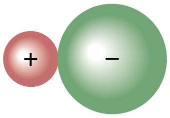


FIGURE 1.5 An ionic bond is the force of electrostatic attraction between oppositely charged ions, illustrated in this case by Na^+ (red) and Cl^- (green). In solid sodium chloride, each sodium ion is surrounded by six chloride ions and vice versa in a crystal lattice.

Whether an element is the source of the cation or anion in an ionic bond depends on several factors, for which the periodic table can serve as a guide. In forming ionic compounds, elements at the left of the periodic table typically lose electrons, forming a cation that has the same electron configuration as the nearest noble gas. Loss of an electron from sodium, for example, gives the species Na^+, which has the same electron configuration as neon.

$$\underset{\substack{\text{Sodium atom}\\ 1s^2 2s^2 2p^6 3s^1}}{Na(g)} \longrightarrow \underset{\substack{\text{Sodium ion}\\ 1s^2 2s^2 2p^6}}{Na^+(g)} + \underset{\text{Electron}}{e^-}$$

[The (g) indicates that the species is present in the gas phase.]

A large amount of energy, called the **ionization energy,** must be added to any atom in order to dislodge one of its electrons. The ionization energy of sodium, for example, is 496 kJ/mol (119 kcal/mol). Processes that absorb energy are said to be **endothermic.** Compared with other elements, sodium and its relatives in group IA have relatively low ionization energies. In general, ionization energy increases across a row in the periodic table.

The SI (*Système International d'Unites*) unit of energy is the *joule* (J). An older unit is the *calorie* (cal). Most organic chemists still express energy changes in units of kilocalories per mole (1 kcal/mol =4.184 kJ/mol).

Elements at the right of the periodic table tend to gain electrons to reach the electron configuration of the next higher noble gas. Adding an electron to chlorine, for example, gives the anion Cl^-, which has the same closed-shell electron configuration as the noble gas argon.

$$\underset{\substack{\text{Chlorine atom}\\ 1s^2 2s^2 2p^6 3s^2 3p^5}}{Cl(g)} + \underset{\text{Electron}}{e^-} \longrightarrow \underset{\substack{\text{Chloride ion}\\ 1s^2 2s^2 2p^6 3s^2 3p^6}}{Cl^-(g)}$$

Energy is released when a chlorine atom captures an electron. Energy-releasing reactions are described as **exothermic,** and the energy change for an exothermic process has a negative sign. The energy change for addition of an electron to an atom is referred to as its **electron affinity** and is −349 kJ/mol (−83.4 kcal/mol) for chlorine.

PROBLEM 1.3 Which of the following ions possess a noble gas electron configuration?

(a) K^+
(b) He^+
(c) H^-
(d) O^-
(e) F^-
(f) Ca^{2+}

SAMPLE SOLUTION (a) Potassium has atomic number 19, and so a potassium atom has 19 electrons. The ion K^+, therefore, has 18 electrons, the same as the noble gas argon. The electron configurations of K^+ and Ar are the same: $1s^22s^22p^63s^23p^6$.

Transfer of an electron from a sodium atom to a chlorine atom yields a sodium cation and a chloride anion, both of which have a noble gas electron configuration:

$$\underset{\text{Sodium atom}}{\mathrm{Na}(g)} \quad + \quad \underset{\text{Chlorine atom}}{\mathrm{Cl}(g)} \quad \longrightarrow \quad \underset{\text{Sodium chloride}}{\mathrm{Na}^+\mathrm{Cl}^-(g)}$$

Were we to simply add the ionization energy of sodium (496 kJ/mol) and the electron affinity of chlorine (−349 kJ/mol), we would conclude that the overall process is endothermic with $\Delta H° = +147$ kJ/mol. The energy liberated by adding an electron to chlorine is insufficient to override the energy required to remove an electron from sodium. This analysis, however, fails to consider the force of attraction between the oppositely charged ions Na^+ and Cl^-, which exceeds 500 kJ/mol and is more than sufficient to make the overall process exothermic. Attractive forces between oppositely charged particles are termed **electrostatic,** or **coulombic, attractions** and are what we mean by an **ionic bond** between two atoms.

Ionic bonding was proposed by the German physicist Walter Kossel in 1916, in order to explain the ability of substances such as sodium chloride to conduct an electric current.

PROBLEM 1.4 What is the electron configuration of C^+? Of C^-? Does either one of these ions have a noble gas (closed-shell) electron configuration?

Ionic bonds are very common in *inorganic* compounds, but rare in *organic* ones. The ionization energy of carbon is too large and the electron affinity too small for carbon to realistically form a C^{4+} or C^{4-} ion. What kinds of bonds, then, link carbon to other elements in millions of organic compounds? Instead of losing or gaining electrons, carbon *shares* electrons with other elements (including other carbon atoms) to give what are called covalent bonds.

1.3 COVALENT BONDS

The **covalent,** or **shared electron pair,** model of chemical bonding was first suggested by G. N. Lewis of the University of California in 1916. Lewis proposed that a *sharing* of two electrons by two hydrogen atoms permits each one to have a stable closed-shell electron configuration analogous to helium.

Gilbert Newton Lewis (born Weymouth, Massachusetts, 1875; died Berkeley, California, 1946) has been called the greatest American chemist. The January 1984 issue of the *Journal of Chemical Education* contains five articles describing Lewis' life and contributions to chemistry.

H· ·H

Two hydrogen atoms, each with a single electron

H:H

Hydrogen molecule: covalent bonding by way of a shared electron pair

Structural formulas of this type in which electrons are represented as dots are called **Lewis structures.**

The amount of energy required to dissociate a hydrogen molecule H_2 to two separate hydrogen atoms is called its **bond dissociation energy** (or **bond energy**). For H_2 it is quite large, being equal to 435 kJ/mol (104 kcal/mol). The main contributor to the strength of the covalent bond in H_2 is the increased binding force exerted on its two electrons. Each electron in H_2 "feels" the attractive force of two nuclei, rather than one as it would in an isolated hydrogen atom.

Covalent bonding in F_2 gives each fluorine 8 electrons in its valence shell and a stable electron configuration equivalent to that of the noble gas neon:

Two fluorine atoms, each with seven electrons in its valence shell

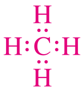
Fluorine molecule: covalent bonding by way of a shared electron pair

PROBLEM 1.5 Hydrogen is bonded to fluorine in hydrogen fluoride by a covalent bond. Write a Lewis formula for hydrogen fluoride.

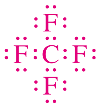
The Lewis model limits second-row elements (Li, Be, B, C, N, O, F, Ne) to a total of 8 electrons (shared plus unshared) in their valence shells. Hydrogen is limited to 2. Most of the elements that we'll encounter in this text obey the **octet rule:** *in forming compounds they gain, lose, or share electrons to give a stable electron configuration characterized by eight valence electrons.* When the octet rule is satisfied for carbon, nitrogen, oxygen, and fluorine, they have an electron configuration analogous to the noble gas neon.

Now let's apply the Lewis model to the organic compounds methane and carbon tetrafluoride.

Combine $\cdot\dot{\underset{\cdot}{C}}\cdot$ and four $H\cdot$ to write a Lewis structure for methane



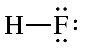
Combine $\cdot\dot{\underset{\cdot}{C}}\cdot$ and four $\cdot\ddot{\underset{\cdot\cdot}{F}}:$ to write a Lewis structure for carbon tetrafluoride



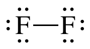
Carbon has 8 electrons in its valence shell in both methane and carbon tetrafluoride. By forming covalent bonds to four other atoms, carbon achieves a stable electron configuration analogous to neon. Each covalent bond in methane and carbon tetrafluoride is quite strong—comparable to the bond between hydrogens in H_2 in bond dissociation energy.

PROBLEM 1.6 Given the information that it has a carbon–carbon bond, write a satisfactory Lewis structure for C_2H_6 (ethane).

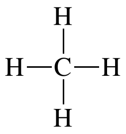
Representing a 2-electron covalent bond by a dash (—), the Lewis structures for hydrogen fluoride, fluorine, methane, and carbon tetrafluoride become:



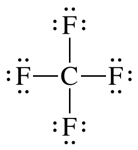
Hydrogen fluoride



Fluorine



Methane



Carbon tetrafluoride

1.4 DOUBLE BONDS AND TRIPLE BONDS

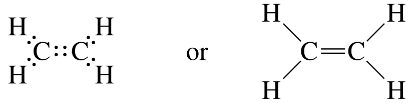
Lewis's concept of shared electron pair bonds allows for 4-electron **double bonds** and 6-electron **triple bonds.** Carbon dioxide (CO_2) has two carbon–oxygen double bonds, and the octet rule is satisfied for both carbon and oxygen. Similarly, the most stable Lewis structure for hydrogen cyanide (HCN) has a carbon–nitrogen triple bond.

Carbon dioxide: :Ö::C::Ö: or :Ö═C═Ö:

Hydrogen cyanide: H:C:::N: or H—C≡N:

Multiple bonds are very common in organic chemistry. Ethylene (C_2H_4) contains a carbon–carbon double bond in its most stable Lewis structure, and each carbon has a completed octet. The most stable Lewis structure for acetylene (C_2H_2) contains a carbon–carbon triple bond. Here again, the octet rule is satisfied.

Ethylene:



Acetylene: H:C:::C:H or H—C≡C—H

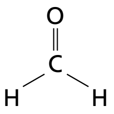
PROBLEM 1.7 Write the most stable Lewis structure for each of the following compounds:

(a) Formaldehyde, CH_2O. Both hydrogens are bonded to carbon. (A solution of formaldehyde in water is sometimes used to preserve biological specimens.)

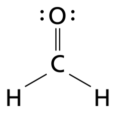
(b) Tetrafluoroethylene, C_2F_4. (The starting material for the preparation of Teflon.)

(c) Acrylonitrile, C_3H_3N. The atoms are connected in the order CCCN, and all hydrogens are bonded to carbon. (The starting material for the preparation of acrylic fibers such as Orlon and Acrilan.)

SAMPLE SOLUTION (a) Each hydrogen contributes 1 valence electron, carbon contributes 4, and oxygen 6 for a total of 12 valence electrons. We are told that both hydrogens are bonded to carbon. Since carbon forms four bonds in its stable compounds, join carbon and oxygen by a double bond. The partial structure so generated accounts for 8 of the 12 electrons. Add the remaining four electrons to oxygen as unshared pairs to complete the structure of formaldehyde.



Partial structure showing covalent bonds



Complete Lewis structure of formaldehyde

1.5 POLAR COVALENT BONDS AND ELECTRONEGATIVITY

Electrons in covalent bonds are not necessarily shared equally by the two atoms that they connect. If one atom has a greater tendency to attract electrons toward itself than the other, we say the electron distribution is *polarized,* and the bond is referred to as a **polar covalent bond.** Hydrogen fluoride, for example, has a polar covalent bond. Because fluorine attracts electrons more strongly than hydrogen, the electrons in the H—F bond are pulled toward fluorine, giving it a partial negative charge, and away from hydrogen giving it a partial positive charge. This polarization of electron density is represented in various ways.

$$^{\delta+}\mathrm{H{-}F}^{\delta-}$$

(The symbols $^{\delta+}$ and $^{\delta-}$ indicate partial positive and partial negative charge, respectively)

$$\overset{+\!\!\longrightarrow}{\mathrm{H{-}F}}$$

(The symbol $+\!\!\longrightarrow$ represents the direction of polarization of electrons in the H—F bond)

The tendency of an atom to draw the electrons in a covalent bond toward itself is referred to as its **electronegativity.** An **electronegative** element attracts electrons; an **electropositive** one donates them. Electronegativity increases across a row in the periodic table. The most electronegative of the second-row elements is fluorine; the most electropositive is lithium. Electronegativity decreases in going down a column. Fluorine is more electronegative than chlorine. The most commonly cited electronegativity scale was devised by Linus Pauling and is presented in Table 1.2.

Linus Pauling (1901–1994) was born in Portland, Oregon and was educated at Oregon State University and at the California Institute of Technology, where he earned a Ph.D. in chemistry in 1925. In addition to research in bonding theory, Pauling studied the structure of proteins and was awarded the Nobel Prize in chemistry for that work in 1954. Pauling won a second Nobel Prize (the Peace Prize) for his efforts to limit the testing of nuclear weapons. He was one of only four scientists to have won two Nobel Prizes. The first double winner was a woman. Can you name her?

PROBLEM 1.8 Examples of carbon-containing compounds include methane (CH_4), chloromethane (CH_3Cl), and methyllithium (CH_3Li). In which one does carbon bear the greatest partial positive charge? The greatest partial negative charge?

Centers of positive and negative charge that are separated from each other constitute a **dipole.** The **dipole moment μ** of a molecule is equal to the charge e (either the positive or the negative charge, since they must be equal) multiplied by the distance between the centers of charge:

$$\mu = e \times d$$

TABLE 1.2 Selected Values from the Pauling Electronegativity Scale

	Group number						
Period	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
1	H 2.1						
2	Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
3	Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4	K 0.8	Ca 1.0					Br 2.8
5							I 2.5

Because the charge on an electron is 4.80×10^{-10} electrostatic units (esu) and the distances within a molecule typically fall in the 10^{-8} cm range, molecular dipole moments are on the order of 10^{-18} esu·cm. In order to simplify the reporting of dipole moments this value of 10^{-18} esu·cm is defined as a **debye, D.** Thus the experimentally determined dipole moment of hydrogen fluoride, 1.7×10^{-18} esu·cm is stated as 1.7 D.

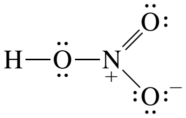
The debye unit is named in honor of Peter Debye, a Dutch scientist who did important work in many areas of chemistry and physics and was awarded the Nobel Prize in chemistry in 1936.

Table 1.3 lists the dipole moments of various bond types. For H—F, H—Cl, H—Br, and H—I these "bond dipoles" are really molecular dipole moments. A **polar** molecule has a dipole moment, a **nonpolar** one does not. Thus, all of the hydrogen halides are polar molecules. In order to be polar, a molecule must have polar bonds, but can't have a shape that causes all the individual bond dipoles to cancel. We will have more to say about this in Section 1.11 after we have developed a feeling for the three-dimensional shapes of molecules.

The bond dipoles in Table 1.3 depend on the difference in electronegativity of the bonded atoms and on the bond distance. The polarity of a C—H bond is relatively low; substantially less than a C—O bond, for example. Don't lose sight of an even more important difference between a C—H bond and a C—O bond, and that is the *direction* of the dipole moment. In a C—H bond the electrons are drawn away from H, toward C. In a C—O bond, electrons are drawn from C toward O. As we'll see in later chapters, the kinds of reactions that a substance undergoes can often be related to the size and direction of key bond dipoles.

1.6 FORMAL CHARGE

Lewis structures frequently contain atoms that bear a positive or negative charge. If the molecule as a whole is neutral, the sum of its positive charges must equal the sum of its negative charges. An example is nitric acid, HNO_3:



As written, the structural formula for nitric acid depicts different bonding patterns for its three oxygens. One oxygen is doubly bonded to nitrogen, another is singly bonded

TABLE 1.3 Selected Bond Dipole Moments

Bond*	Dipole moment, D	Bond*	Dipole moment, D
H—F	1.7	C—F	1.4
H—Cl	1.1	C—O	0.7
H—Br	0.8	C—N	0.4
H—I	0.4	C=O	2.4
H—C	0.3	C=N	1.4
H—N	1.3	C≡N	3.6
H—O	1.5		

*The direction of the dipole moment is toward the more electronegative atom. In the listed examples hydrogen and carbon are the positive ends of the dipoles. Carbon is the negative end of the dipole associated with the C—H bond.

to both nitrogen and hydrogen, and the third has a single bond to nitrogen and a negative charge. Nitrogen is positively charged. The positive and negative charges are called **formal charges,** and the Lewis structure of nitric acid would be incomplete were they to be omitted.

We calculate formal charges by counting the number of electrons "owned" by each atom in a Lewis structure and comparing this **electron count** with that of a neutral atom. Figure 1.6 illustrates how electrons are counted for each atom in nitric acid. Counting electrons for the purpose of computing the formal charge differs from counting electrons to see if the octet rule is satisfied. A second-row element has a filled valence shell if the sum of all the electrons, shared and unshared, is 8. Electrons that connect two atoms by a covalent bond count toward filling the valence shell of both atoms. When calculating the formal charge, however, only half the number of electrons in covalent bonds can be considered to be "owned" by an atom.

The number of valence electrons in an atom of a main-group element such as nitrogen is equal to its group number. In the case of nitrogen this is 5.

To illustrate, let's start with the hydrogen of nitric acid. As shown in Figure 1.6, hydrogen is associated with only two electrons—those in its covalent bond to oxygen. It shares those two electrons with oxygen, and so we say that the electron count of each hydrogen is $\frac{1}{2}(2) = 1$. Since this is the same as the number of electrons in a neutral hydrogen atom, the hydrogen in nitric acid has no formal charge.

It will always be true that a covalently bonded hydrogen has no formal charge (formal charge = 0).

Moving now to nitrogen, we see that it has four covalent bonds (two single bonds + one double bond), and so its electron count is $\frac{1}{2}(8) = 4$. A neutral nitrogen has five electrons in its valence shell. The electron count for nitrogen in nitric acid is 1 less than that of a neutral nitrogen atom, so its formal charge is $+1$.

It will always be true that a nitrogen with four covalent bonds has a formal charge of $+1$. (A nitrogen with four covalent bonds cannot have unshared pairs, because of the octet rule.)

Electrons in covalent bonds are counted as if they are shared equally by the atoms they connect, but unshared electrons belong to a single atom. Thus, the oxygen which is doubly bonded to nitrogen has an electron count of 6 (four electrons as two unshared pairs + two electrons from the double bond). Since this is the same as a neutral oxygen atom, its formal charge is 0. Similarly, the OH oxygen has two bonds plus two unshared electron pairs, giving it an electron count of 6 and no formal charge.

It will always be true that an oxygen with two covalent bonds and two unshared pairs has no formal charge.

The oxygen highlighted in yellow in Figure 1.6 owns three unshared pairs (six electrons) and shares two electrons with nitrogen to give it an electron count of 7. This is 1 more than the number of electrons in the valence shell of an oxygen atom, and so its formal charge is -1.

The method described for calculating formal charge has been one of reasoning through a series of logical steps. It can be reduced to the following equation:

$$\text{Formal charge} = \begin{matrix}\text{group number in}\\ \text{periodic table}\end{matrix} - \text{number of bonds} - \text{number of unshared electrons}$$

It will always be true that an oxygen with one covalent bond and three unshared pairs has a formal charge of -1.

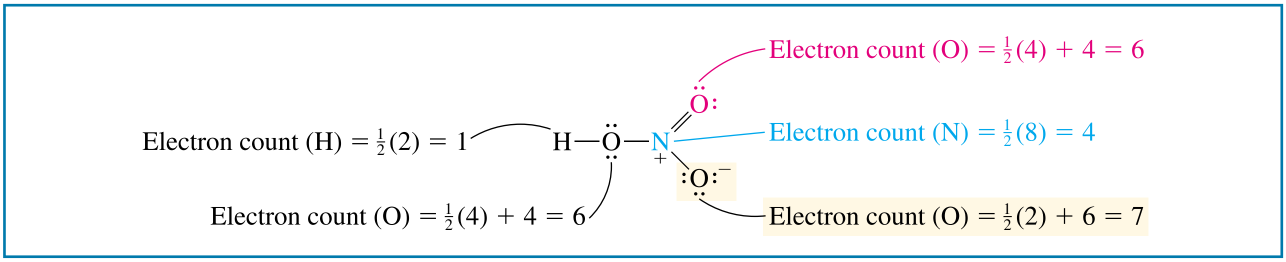
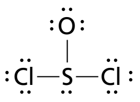
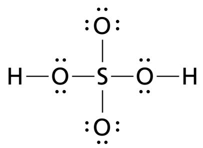


FIGURE 1.6 Counting electrons in nitric acid. The electron count of each atom is equal to half the number of electrons it shares in covalent bonds plus the number of electrons in its own unshared pairs.

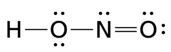
PROBLEM 1.9 Like nitric acid, each of the following inorganic compounds will be frequently encountered in this text. Calculate the formal charge on each of the atoms in the Lewis structures given.



(a) Thionyl chloride



(b) Sulfuric acid

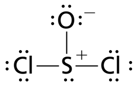


(c) Nitrous acid

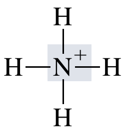
SAMPLE SOLUTION (a) The formal charge is the difference between the number of valence electrons in the neutral atom and the electron count in the Lewis structure. (The number of valence electrons is the same as the group number in the periodic table for the main-group elements.)

	Valence electrons of neutral atom	Electron count	Formal charge
Sulfur:	6	$\frac{1}{2}(6) + 2 = 5$	+1
Oxygen:	6	$\frac{1}{2}(2) + 6 = 7$	−1
Chlorine:	7	$\frac{1}{2}(2) + 6 = 7$	0

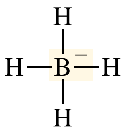
The formal charges are shown in the Lewis structure of thionyl chloride as



So far we've only considered neutral molecules—those in which the sums of the positive and negative formal charges were equal. With ions, of course, these sums will not be equal. Ammonium cation and borohydride anion, for example, are ions with net charges of +1 and −1, respectively. Nitrogen has a formal charge of +1 in ammonium ion, and boron has a formal charge of −1 in borohydride. None of the hydrogens in the Lewis structures shown for these ions bears a formal charge.



Ammonium ion



Borohydride ion

PROBLEM 1.10 Verify that the formal charges on nitrogen in ammonium ion and boron in borohydride ion are as shown.

Formal charges are based on Lewis structures in which electrons are considered to be shared equally between covalently bonded atoms. Actually, polarization of N—H bonds in ammonium ion and of B—H bonds in borohydride leads to some transfer of positive and negative charge, respectively, to the hydrogens.

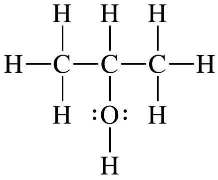
PROBLEM 1.11 Use $\delta+$ and $\delta-$ notation to show the dispersal of charge to the hydrogens in NH_4^+ and BH_4^-.

Determining formal charges on individual atoms of Lewis structures is an important element in good "electron bookkeeping." So much of organic chemistry can be made more understandable by keeping track of electrons that it is worth taking some time at the beginning to become proficient at the seemingly simple task of counting electrons.

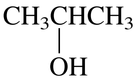
1.7 STRUCTURAL FORMULAS OF ORGANIC MOLECULES

Table 1.4 outlines a systematic procedure for writing Lewis structures. Notice that the process depends on knowing not only the molecular formula, but also the order in which the atoms are attached to one another. This order of attachment is called the **constitution,** or **connectivity,** of the molecule and is determined by experiment. Only rarely is it possible to deduce the constitution of a molecule from its molecular formula.

Organic chemists have devised a number of shortcuts to speed the writing of structural formulas. Sometimes we leave out unshared electron pairs, but only when we are sure enough in our ability to count electrons to know when they are present and when they're not. We've already mentioned representing covalent bonds by dashes. In **condensed structural formulas** we leave out some, many, or all of the covalent bonds and use subscripts to indicate the number of identical groups attached to a particular atom. These successive levels of simplification are illustrated as shown for isopropyl alcohol ("rubbing alcohol").



written as



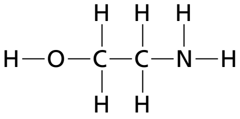
$CH_3\underset{\underset{OH}{|}}{C}HCH_3$

or condensed even further to $(CH_3)_2CHOH$

PROBLEM 1.12 Expand the following condensed formulas so as to show all the bonds and unshared electron pairs.

(a) $HOCH_2CH_2NH_2$
(b) $(CH_3)_3CH$
(c) $ClCH_2CH_2Cl$
(d) CH_3CHCl_2
(e) $CH_3NHCH_2CH_3$
(f) $(CH_3)_2CHCH{=}O$

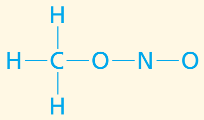
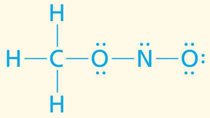
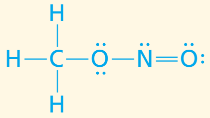
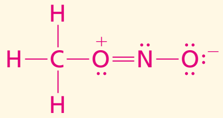
SAMPLE SOLUTION (a) The molecule contains two carbon atoms, which are bonded to each other. Both carbons bear two hydrogens. One carbon bears the group HO—; the other is attached to $—NH_2$.

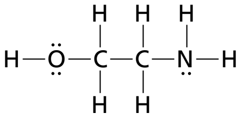


When writing the constitution of a molecule, it is not necessary to concern yourself with the spatial orientation of the atoms. There are many other correct ways to represent the constitution shown. What is important is to show the sequence OCCN (or its equivalent NCCO) and to have the correct number of hydrogens present on each atom.

In order to locate unshared electron pairs, first count the total number of valence electrons brought to the molecule by its component atoms. Each hydrogen contributes 1, each carbon 4, nitrogen 5, and oxygen 6, for a total of 26. There are ten bonds shown, accounting for 20 electrons; therefore 6 electrons must be contained in unshared pairs. Add pairs of electrons to oxygen and nitrogen so that their octets are complete, two unshared pairs to oxygen and one to nitrogen.

TABLE 1.4 How to Write Lewis Structures

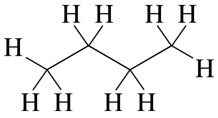
Step	Illustration
1. The molecular formula and the connectivity are determined experimentally and are included among the information given in the statement of the problem.	Methyl nitrite has the molecular formula CH_3NO_2. All hydrogens are bonded to carbon, and the order of atomic connections is CONO.
2. Count the number of valence electrons available. For a neutral molecule this is equal to the sum of the valence electrons of the constituent atoms.	Each hydrogen contributes 1 valence electron, carbon contributes 4, nitrogen contributes 5, and each oxygen contributes 6 for a total of 24 in CH_3NO_2.
3. Connect bonded atoms by a shared electron pair bond (:) represented by a dash (—).	For methyl nitrite we write the partial structure 
4. Count the number of electrons in shared electron pair bonds (twice the number of bonds), and subtract this from the total number of electrons to give the number of electrons to be added to complete the structure.	The partial structure in step 3 contains 6 bonds equivalent to 12 electrons. Since CH_3NO_2 contains 24 electrons, 12 more electrons need to be added.
5. Add electrons in pairs so that as many atoms as possible have 8 electrons. (Hydrogen is limited to 2 electrons.) When the number of electrons is insufficient to provide an octet for all atoms, assign electrons to atoms in order of decreasing electronegativity.	With 4 bonds, carbon already has 8 electrons. The remaining 12 electrons are added as indicated. Both oxygens have 8 electrons, but nitrogen (less electronegative than oxygen) has only 6. 
6. If one or more atoms have fewer than 8 electrons, use unshared pairs on an adjacent atom to form a double (or triple) bond to complete the octet.	An electron pair on the terminal oxygen is shared with nitrogen to give a double bond.  The structure shown is the best (most stable) Lewis structure for methyl nitrite. All atoms except hydrogen have 8 electrons (shared + unshared) in their valence shell.
7. Calculate formal charges.	None of the atoms in the Lewis structure shown in step 6 possesses a formal charge. An alternative Lewis structure for methyl nitrite,  although it satisfies the octet rule, is less stable than the one shown in step 6 because it has a separation of positive charge from negative charge.



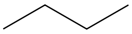
As you practice, you will begin to remember patterns of electron distribution. A neutral oxygen with two bonds has two unshared electron pairs. A neutral nitrogen with three bonds has one unshared pair.

With practice, writing structural formulas for organic molecules soon becomes routine and can be simplified even more. For example, a chain of carbon atoms can be represented by drawing all of the C—C bonds while omitting individual carbons. The resulting structural drawings can be simplified still more by stripping away the hydrogens.

$CH_3CH_2CH_2CH_3$ becomes

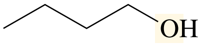


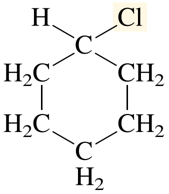
simplified to



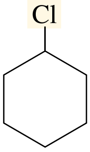
In these simplified representations, called **bond-line formulas** or **carbon skeleton diagrams,** the only atoms specifically written in are those that are neither carbon nor hydrogen bound to carbon. Hydrogens bound to these *heteroatoms* are shown, however.

$CH_3CH_2CH_2CH_2OH$ becomes



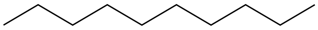


becomes

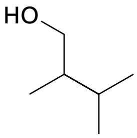


PROBLEM 1.13 Expand the following bond-line representations to show all the atoms including carbon and hydrogen.

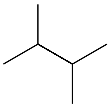
(a)



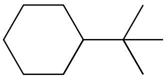
(c)



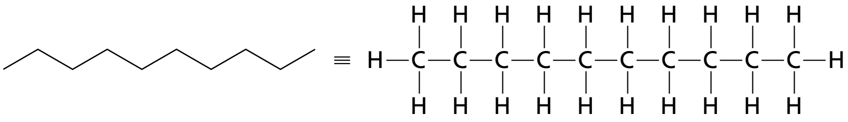
(b)



(d)



SAMPLE SOLUTION (a) There is a carbon at each bend in the chain and at the ends of the chain. Each of the ten carbon atoms bears the appropriate number of hydrogen substituents so that it has four bonds.



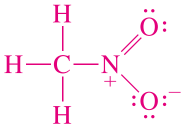
Alternatively, the structure could be written as $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ or in condensed form as $CH_3(CH_2)_8CH_3$.

1.8 CONSTITUTIONAL ISOMERS

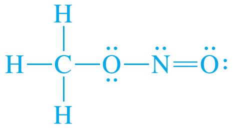
The suffix *-mer* in the word "isomer" is derived from the Greek word *meros,* meaning "part," "share," or "portion." The prefix *iso-* is also from Greek (*isos,* "the same"). Thus isomers are different molecules that have the same parts (elemental composition).

In the introduction we noted that both Berzelius and Wöhler were fascinated by the fact that two different compounds with different properties, ammonium cyanate and urea, possessed exactly the same molecular formula, CH_4N_2O. Berzelius had studied examples of similar phenomena earlier and invented the word **isomer** to describe *different compounds that have the same molecular formula.*

We can illustrate isomerism by referring to two different compounds, *nitromethane* and *methyl nitrite,* both of which have the molecular formula CH_3NO_2. Nitromethane, used to power race cars, is a liquid with a boiling point of 101°C. Methyl nitrite is a gas boiling at −12°C, which when inhaled causes dilation of blood vessels. Isomers that differ in the order in which their atoms are bonded are often referred to as **structural isomers.** A more modern term is **constitutional isomer.** As noted in the previous section, the order of atomic connections that defines a molecule is termed its *constitution*, and we say that two compounds are *constitutional isomers* if they have the same molecular formula but differ in the order in which their atoms are connected.



Nitromethane



Methyl nitrite

PROBLEM 1.14 There are many more isomers of CH_3NO_2 other than nitromethane and methyl nitrite. Some, such as *carbamic acid,* an intermediate in the commercial preparation of urea for use as a fertilizer, are too unstable to isolate. Given the information that the nitrogen and both oxygens of carbamic acid are bonded to carbon and that one of the carbon–oxygen bonds is a double bond, write a Lewis structure for carbamic acid.

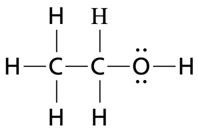
PROBLEM 1.15 Write structural formulas for all the constitutionally isomeric compounds having the given molecular formula.

(a) C_2H_6O

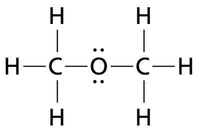
(b) C_3H_8O

(c) $C_4H_{10}O$

SAMPLE SOLUTION (a) Begin by considering the ways in which two carbons and one oxygen may be bonded. There are two possibilities: C—C—O and C—O—C. Add the six hydrogens so that each carbon has four bonds and each oxygen two. There are two constitutional isomers: ethyl alcohol and dimethyl ether.



Ethyl alcohol

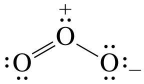


Dimethyl ether

In Chapter 3 another type of isomerism, called **stereoisomerism,** will be introduced. Stereoisomers have the same constitution but differ in the arrangement of atoms in space.

1.9 RESONANCE

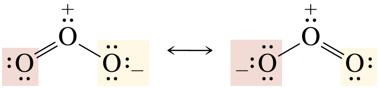
When writing a Lewis structure, we restrict a molecule's electrons to certain well-defined locations, either linking two atoms by a covalent bond or as unshared electrons on a single atom. Sometimes more than one Lewis structure can be written for a molecule, especially those that contain multiple bonds. An example often cited in introductory chemistry courses is ozone (O_3). Ozone occurs naturally in large quantities in the upper atmosphere, where it screens the surface of the earth from much of the sun's ultraviolet rays. Were it not for this ozone layer, most forms of surface life on earth would be damaged or even destroyed by the rays of the sun. The following Lewis structure for ozone satisfies the octet rule; all three oxygens have 8 electrons in their valence shell.



Bond distances in organic compounds are usually 1 to 2Å (1Å = 10^{-10}m). Since the angstrom (Å) is not an SI unit, we will express bond distances in picometers (1 pm = 10^{-12}m). Thus, 128 pm = 1.28 Å.

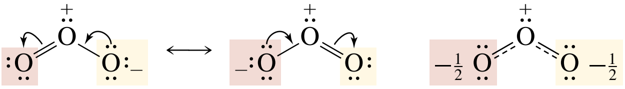
This Lewis structure, however, doesn't accurately portray the bonding in ozone, because the two terminal oxygens are bonded differently to the central oxygen. The central oxygen is depicted as doubly bonded to one and singly bonded to the other. Since it is generally true that double bonds are shorter than single bonds, we would expect ozone to exhibit two different O—O bond lengths, one of them characteristic of the O—O single bond distance (147 pm in hydrogen peroxide, H—O—O—H) and the other one characteristic of the O=O double bond distance (121 pm in O_2). Such is not the case. Both bond distances in ozone are exactly the same (128 pm)—somewhat shorter than the single bond distance and somewhat longer than the double bond distance. The structure of ozone requires that *the central oxygen must be identically bonded to both terminal oxygens.*

In order to deal with circumstances such as the bonding in ozone, the notion of **resonance** between Lewis structures was developed. According to the resonance concept, when more than one Lewis structure may be written for a molecule, a single structure is not sufficient to describe it. Rather, the true structure has an electron distribution that is a "hybrid" of all the possible Lewis structures that can be written for the molecule. In the case of ozone, two equivalent Lewis structures may be written. We use a double-headed arrow to represent resonance between these two Lewis structures.



It is important to remember that the double-headed resonance arrow does not indicate a *process* in which the two Lewis structures interconvert. Ozone, for example, has a *single* structure; it does not oscillate back and forth between two Lewis structures, rather its true structure is not adequately represented by any single Lewis structure.

Resonance attempts to correct a fundamental defect in Lewis formulas. Lewis formulas show electrons as being **localized;** they either are shared between two atoms in a covalent bond or are unshared electrons belonging to a single atom. In reality, electrons distribute themselves in the way that leads to their most stable arrangement. This sometimes means that a pair of electrons is **delocalized,** or shared by several nuclei. What we try to show by the resonance description of ozone is the delocalization of the lone-pair electrons of one oxygen and the electrons in the double bond over the three atoms of the molecule. Organic chemists often use curved arrows to show this electron delocalization. Alternatively, an average of two Lewis structures is sometimes drawn using a dashed line to represent a "partial" bond. In the dashed-line notation the central oxygen is linked to the other two by bonds that are halfway between a single bond and a double bond, and the terminal oxygens each bear one half of a unit negative charge.

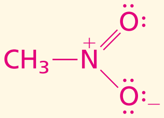
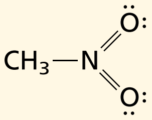


Curved arrow notation Dashed-line notation

Electron delocalization in ozone

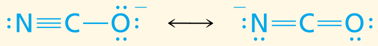
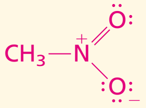
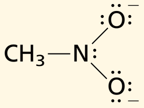
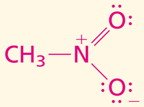
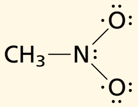
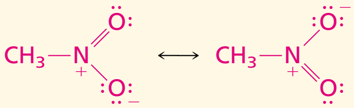
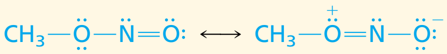
The rules to be followed when writing resonance structures are summarized in Table 1.5.

TABLE 1.5 Introduction to the Rules of Resonance*

Rule	Illustration
1. Atomic positions (connectivity) must be the same in all resonance structures; only the electron positions may vary among the various contributing structures.	The structural formulas  and $\mathrm{CH_3}-\ddot{\underset{..}{\mathrm{O}}}-\ddot{\mathrm{N}}=\ddot{\mathrm{O}}:$ A B represent different compounds, not different resonance forms of the same compound. A is a Lewis structure for *nitromethane;* B is *methyl nitrite.*
2. Lewis structures in which second-row elements own or share more than 8 valence electrons are especially unstable and make no contribution to the true structure. (The octet rule may be exceeded for elements beyond the second row.)	Structural formula C,  C has 10 electrons around nitrogen. It is not a permissible Lewis structure for nitromethane and so cannot be a valid resonance form.
3. When two or more structures satisfy the octet rule, the most stable one is the one with the smallest separation of oppositely charged atoms.	The two Lewis structures D and E of methyl nitrite satisfy the octet rule: $\mathrm{CH_3}-\ddot{\underset{..}{\mathrm{O}}}-\ddot{\mathrm{N}}=\ddot{\mathrm{O}}: \longleftrightarrow \mathrm{CH_3}-\overset{+}{\underset{..}{\mathrm{O}}}=\ddot{\mathrm{N}}-\ddot{\underset{..}{\mathrm{O}}}:^{-}$ D E Structure D has no separation of charge and is more stable than E, which does. The true structure of methyl nitrite is more like D than E.

(Continued)

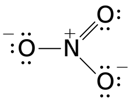
TABLE 1.5 Introduction to the Rules of Resonance* ***(Continued)***

Rule	Illustration
4. Among structural formulas in which the octet rule is satisfied for all atoms and one or more of these atoms bears a formal charge, the most stable resonance form is the one in which negative charge resides on the most electronegative atom (or positive charge on the most electropositive one).	The most stable Lewis structure for cyanate ion is F because the negative charge is on its oxygen.  $:N\equiv C-\underset{..}{\overset{..}{O}}:^{-} \longleftrightarrow {}^{-}:\underset{..}{N}=C=\underset{..}{O}:$ F G In G the negative charge is on nitrogen. Oxygen is more electronegative than nitrogen and can better support a negative charge.
5. Each contributing Lewis structure must have the same number of electrons and the same *net* charge, although the formal charges of individual atoms may vary among the various Lewis structures.	The Lewis structures  H and  I are *not* resonance forms of one another. Structure H has 24 valence electrons and a net charge of 0; I has 26 valence electrons and a net charge of −2.
6. Each contributing Lewis structure must have the same number of *unpaired* electrons.	Structural formula J is a Lewis structure of nitromethane; K is not, even though it has the same atomic positions and the same number of electrons.  J and  K Structure K has 2 unpaired electrons. Structure J has all its electrons paired and is a more stable structure.
7. Electron delocalization stabilizes a molecule. A molecule in which electrons are delocalized is more stable than implied by any of the individual Lewis structures that may be written for it. The degree of stabilization is greatest when the contributing Lewis structures are of equal stability.	Nitromethane is stabilized by electron delocalization more than methyl nitrite is. *The two most stable resonance forms of nitromethane are equivalent to each other.*  *The two most stable resonance forms of methyl nitrite are not equivalent.*  $CH_3-\underset{..}{\overset{..}{O}}-\overset{..}{N}=\overset{..}{O}: \longleftrightarrow CH_3-\overset{+}{\overset{..}{O}}=\overset{..}{N}-\underset{..}{\overset{..}{O}}:^{-}$

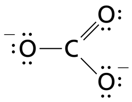
*These are the most important rules to be concerned with at present. Additional aspects of electron delocalization, as well as additional rules for its depiction by way of resonance structures, will be developed as needed in subsequent chapters.

PROBLEM 1.16 Electron delocalization can be important in ions as well as in neutral molecules. Using curved arrows, show how an equally stable resonance structure can be generated for each of the following anions:

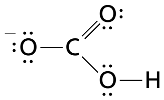
(a)



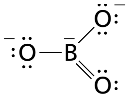
(c)



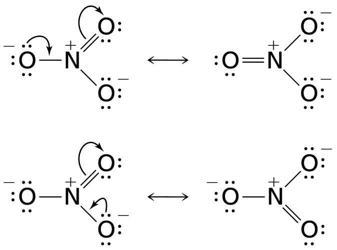
(b)



(d)



SAMPLE SOLUTION (a) When using curved arrows to represent the reorganization of electrons, begin at a site of high electron density, preferably an atom that is negatively charged. Move electron pairs until a proper Lewis structure results. For nitrate ion, this can be accomplished in two ways:



Three equally stable Lewis structures are possible for nitrate ion. The negative charge in nitrate is shared equally by all three oxygens.

It is good chemical practice to represent molecules by their most stable Lewis structure. The ability to write alternative resonance forms and to compare their relative stabilities, however, can provide insight into both molecular structure and chemical behavior. This will become particularly apparent in the last two thirds of this text, where the resonance concept will be used regularly.

1.10 THE SHAPES OF SOME SIMPLE MOLECULES

So far our concern has emphasized "electron bookkeeping." We now turn our attention to the shapes of molecules.

Methane, for example, is described as a tetrahedral molecule because its four hydrogens occupy the corners of a tetrahedron with carbon at its center as the various methane models in Figure 1.7 illustrate. We often show three-dimensionality in structural formulas by using a solid wedge (◀) to depict a bond projecting from the paper toward the reader and a dashed wedge (⦙⦙⦙⦙⦙) to depict one receding from the paper. A simple line (—) represents a bond that lies in the plane of the paper (Figure 1.8).

The tetrahedral geometry of methane is often explained in terms of the **valence shell electron-pair repulsion (VSEPR) model.** The VSEPR model rests on the idea that an electron pair, either a bonded pair or an unshared pair, associated with a particular atom will be as far away from the atom's other electron pairs as possible. Thus, a tetrahedral geometry permits the four bonds of methane to be maximally separated and is characterized by H—C—H angles of 109.5°, a value referred to as the **tetrahedral angle.**

Although reservations have been expressed concerning VSEPR as an *explanation* for molecular geometries, it remains a useful *tool* for predicting the shapes of organic compounds.

LEARNING BY MODELING

As early as the nineteenth century many chemists built scale models in order to better understand molecular structure. We can gain a clearer idea about the features that affect structure and reactivity when we examine the three-dimensional shape of a molecule. Several types of molecular models are shown for methane in Figure 1.7. Probably the most familiar are ball-and-stick models (Figure 1.7*b*), which direct approximately equal attention to the atoms and the bonds that connect them. Framework models (Figure 1.7*a*) and space-filling models (Figure 1.7*c*) represent opposite extremes. Framework models emphasize the pattern of bonds of a molecule while ignoring the sizes of the atoms. Space-filling models emphasize the volume occupied by individual atoms at the cost of a clear depiction of the bonds; they are most useful in cases in which one wishes to examine the overall molecular shape and to assess how closely two nonbonded atoms approach each other.

The earliest ball-and-stick models were exactly that: wooden balls in which holes were drilled to accommodate dowels that connected the atoms. Plastic versions, including relatively inexpensive student sets, became available in the 1960s and proved to be a valuable learning aid. Precisely scaled stainless steel framework and plastic space-filling models, although relatively expensive, were standard equipment in most research laboratories.

Computer graphics-based representations are rapidly replacing classical molecular models. Indeed, the term "molecular modeling" as now used in organic chemistry implies computer generation of models. The methane models shown in Figure 1.7 were all drawn on a personal computer using software that possesses the feature of displaying and printing the same molecule in framework, ball-and-stick, and space-filling formats. In addition to permitting models to be constructed rapidly, even the simplest software allows the model to be turned and viewed from a variety of perspectives.

More sophisticated programs not only draw molecular models, but also incorporate computational tools that provide useful insights into the electron distribution. Figure 1.7*d* illustrates this higher level approach to molecular modeling by using colors to display the electric charge distribution within the boundaries defined by the space-filling model. Figures such as 1.7*d* are called *electrostatic potential maps.* They show the transition from regions of highest to lowest electron density according to the colors of the rainbow. The most electron-rich regions are red; the most electron-poor are blue. For methane, the overall shape of the electrostatic potential map is similar to the volume occupied by the space-filling model. The most electron-rich regions are closer to carbon and the most electron-poor regions closer to the hydrogen atoms.

—Cont.

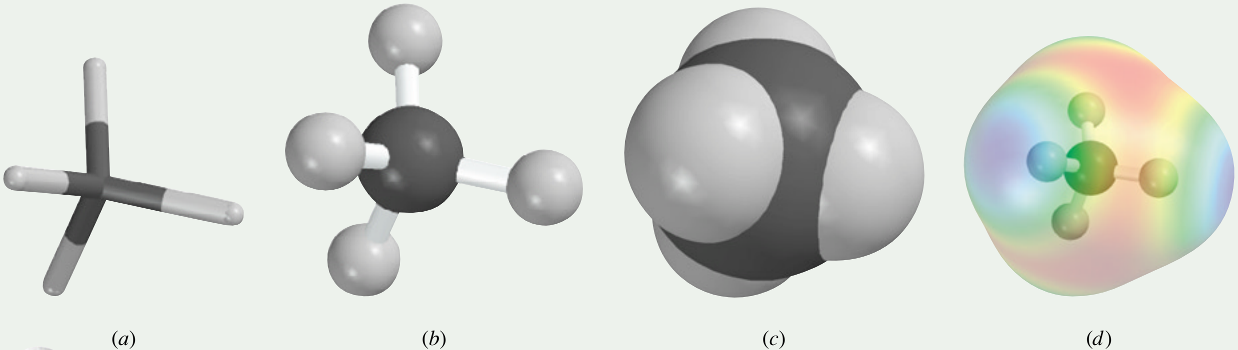


FIGURE 1.7 (*a*) A framework (tube) molecular model of methane (CH_4). A framework model shows the bonds connecting the atoms of a molecule, but not the atoms themselves. (*b*) A ball-and-stick (ball-and-spoke) model of methane. (*c*) A space-filling model of methane. (*d*) An electrostatic potential map superimposed on a ball-and-stick model of methane. The electrostatic potential map corresponds to the space-filling model, but with an added feature. The colors identify regions according to their electric charge, with red being the most negative and blue the most positive.

Organic chemistry is a very visual science and computer modeling is making it even more so. Accompanying this text is a CD-ROM entitled *Learning By Modeling.* As its name implies, it is a learning tool, designed to help you better understand molecular structure and properties, and contains two major components:

- *SpartanBuild* software that you can use to build molecular models of various types include tube, ball-and-spoke, and space-filling. This text includes a number of modeling exercises for you to do, but don't limit yourself to them. You can learn a lot by simply experimenting with *SpartanBuild* to see what you can make.
- *SpartanView* software with which you can browse through an archive of already-prepared models on the *Learning By Modeling* CD. These models include many of the same substances that appear in this text. *SpartanView* is the tool you will use to view electrostatic potential maps as well as animations of many organic chemical transformations.

All of the models, those you make yourself and those already provided on *Learning By Modeling,* can be viewed in different formats and rotated in three dimensions.

Immediately preceding the Glossary at the back of this text is a tutorial showing you how to use *SpartanBuild* and *SpartanView,* and describing some additional features.

As you go through this text, you will see two different modeling icons. The *SpartanBuild* icon alerts you to a model-building opportunity, the *SpartanView* icon indicates that the *Learning By Modeling* CD includes a related model or animation.

SpartanBuild icon *SpartanView* icon

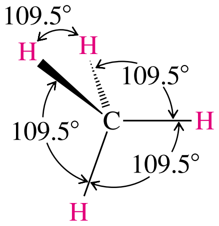


FIGURE 1.8 A wedge-and-dash drawing of the structure of methane. A solid wedge projects from the plane of the paper toward you; a dashed wedge projects away from you. A bond represented by a line drawn in the customary way lies in the plane of the paper.

Water, ammonia, and methane share the common feature of an approximately tetrahedral arrangement of four electron pairs. Because we describe the shape of a molecule according to the positions of its atoms rather than the disposition of its electron pairs, however, water is said to be *bent,* and ammonia is *trigonal pyramidal* (Figure 1.9). The H—O—H angle in water (105°) and the H—N—H angle in ammonia (107°) are slightly less than the tetrahedral angle.

Boron trifluoride (BF_3; Figure 1.10) is a *trigonal planar* molecule. There are 6 electrons, 2 for each B—F bond, associated with the valence shell of boron. These three bonded pairs are farthest apart when they are coplanar, with F—B—F bond angles of 120°.

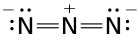
PROBLEM 1.17 The salt sodium borohydride, $NaBH_4$, has an ionic bond between Na^+ and the anion BH_4^-. What are the H—B—H angles in the borohydride anion?

Multiple bonds are treated as a single unit in the VSEPR model. Formaldehyde (Figure 1.11) is a trigonal planar molecule in which the electrons of the double bond and those of the two single bonds are maximally separated. A linear arrangement of atoms in carbon dioxide (Figure 1.12) allows the electrons in one double bond to be as far away as possible from the electrons in the other double bond.

PROBLEM 1.18 Specify the shape of the following:

(a) $H{-}C{\equiv}N\colon$ (Hydrogen cyanide)

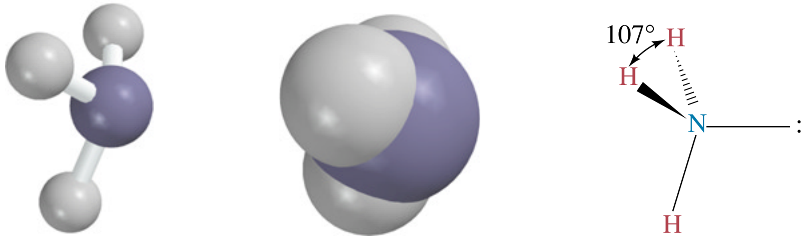
(b) H_4N^+ (Ammonium ion)

(c)  $\colon\overset{-\,\cdot\cdot}{N}{=}\overset{+}{N}{=}\overset{\cdot\cdot\,-}{N}\colon$ (Azide ion)

(d) CO_3^{2-} (Carbonate ion)

SAMPLE SOLUTION (a) The structure shown accounts for all the electrons in hydrogen cyanide. There are no unshared electron pairs associated with carbon, and so the structure is determined by maximizing the separation between its single bond to hydrogen and the triple bond to nitrogen. Hydrogen cyanide is a *linear* molecule.

(*a*) Water (H_2O) has a bent structure.



(*b*) Ammonia (NH_3) has a trigonal pyramidal structure.

FIGURE 1.9 Ball-and-spoke and space-filling models and wedge-and-dash drawings of (*a*) water and (*b*) ammonia. The shape of a molecule is described in terms of its atoms. An approximately tetrahedral arrangement of electron pairs translates into a bent geometry for water and a trigonal pyramidal geometry for ammonia.

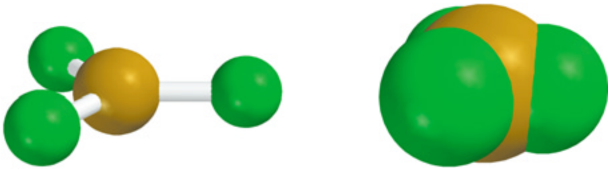


FIGURE 1.10 Representations of the trigonal planar geometry of boron trifluoride (BF_3). There are 6 electrons in the valence shell of boron, a pair for each covalent bond to fluorine. The three pairs of electrons are farthest apart when the F—B—F angle is 120°.

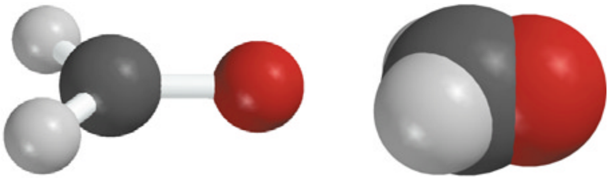


FIGURE 1.11 Models of formaldehyde ($H_2C{=}O$) showing the trigonal planar geometry of the bonds to carbon. Many molecular models, including those shown here, show only the connections between the atoms without differentiating among single bonds, double bonds, and triple bonds.

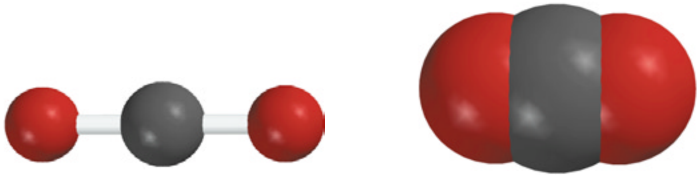
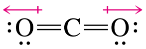


FIGURE 1.12 Ball-and-spoke and space-filling models showing the linear geometry of carbon dioxide (O═C═O).

1.11 MOLECULAR DIPOLE MOMENTS

We can combine our knowledge of molecular geometry with a feel for the polarity of chemical bonds to predict whether a molecule has a dipole moment or not. The molecular dipole moment is the resultant of all of the individual bond dipole moments of a substance. Some molecules, such as carbon dioxide, have polar bonds, but lack a dipole moment because their shape (see Figure 1.12) causes the individual C═O bond dipoles to cancel.

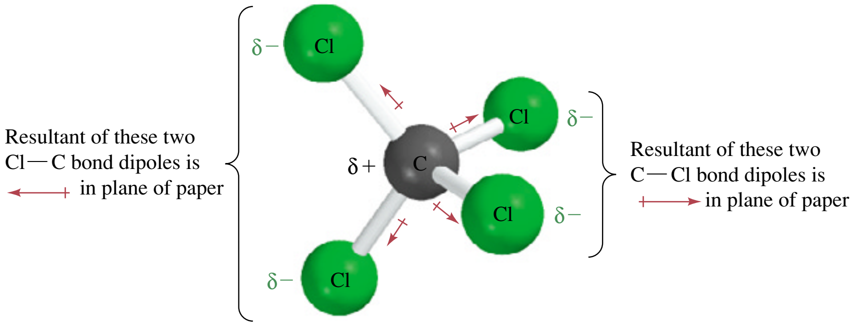


$$\overset{\longleftarrow\!\!+}{:\ddot{O}}=C=\overset{+\!\!\longrightarrow}{\ddot{O}:}$$

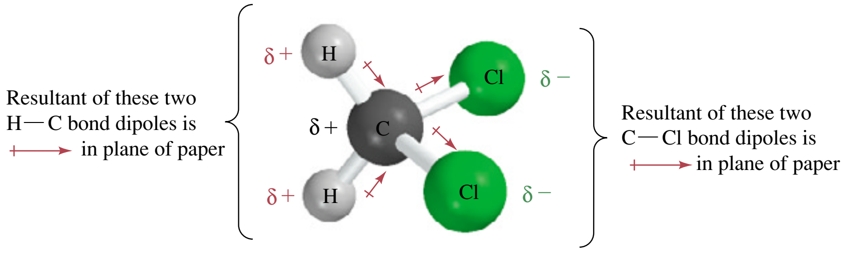
Dipole moment = 0 D

Carbon dioxide

Carbon tetrachloride, with four polar C—Cl bonds and a tetrahedral shape, has no net dipole moment, because the resultant of the four bond dipoles, as shown in Figure 1.13, is zero. Dichloromethane, on the other hand, has a dipole moment of 1.62 D. The C—H bond dipoles reinforce the C—Cl bond dipoles.



(*a*) There is a mutual cancellation of individual bond dipoles in carbon tetrachloride. It has no dipole moment.



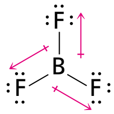
(*b*) The H—C bond dipoles reinforce the C—Cl bond moment in dichloromethane. The molecule has a dipole moment of 1.62 D.

FIGURE 1.13 Contribution of individual bond dipole moments to the molecular dipole moments of (*a*) carbon tetrachloride (CCl_4) and (*b*) dichloromethane (CH_2Cl_2).

PROBLEM 1.19 Which of the following compounds would you expect to have a dipole moment? If the molecule has a dipole moment, specify its direction.

(a) BF_3
(b) H_2O
(c) CH_4
(d) CH_3Cl
(e) CH_2O
(f) HCN

SAMPLE SOLUTION (a) Boron trifluoride is planar with 120° bond angles. Although each boron–fluorine bond is polar, their combined effects cancel and the molecule has no dipole moment.



$\mu = 0$ D

1.12 ELECTRON WAVES AND CHEMICAL BONDS

Lewis proposed his shared electron-pair model of bonding in 1916, almost a decade before de Broglie's theory of wave–particle duality. De Broglie's radically different view of an electron, and Schrödinger's success in using wave equations to calculate the energy of an electron in a hydrogen *atom,* encouraged the belief that bonding in *molecules* could be explained on the basis of interactions between electron waves. This thinking produced two widely used theories of chemical bonding: one is called the **valence bond model,** the other the **molecular orbital model.**

Before we describe these theories, let's first think about bonding between two hydrogen atoms in the most fundamental terms. We'll begin with two hydrogen atoms that are far apart and see what happens as the distance between them decreases. The forces involved are electron–electron (− −) repulsions, nucleus–nucleus (+ +) repulsions, and electron–nucleus (− +) attractions. All of these forces increase as the distance between the two hydrogens decreases. Because the electrons are so mobile, however, they can choreograph their motions so as to minimize their mutual repulsion while maximizing their attractive forces with the protons. Thus, as shown in Figure 1.14, there is a net, albeit weak, attractive force between the two hydrogens even when the atoms are far apart. This interaction becomes stronger as the two atoms approach each other—the electron of each hydrogen increasingly feels the attractive force of two protons rather than one, the total energy decreases, and the system becomes more stable. A potential energy minimum is reached when the separation between the nuclei reaches 74 pm, which corresponds to the H—H bond length in H_2. At distances shorter than this, the nucleus–nucleus and electron–electron repulsions dominate, and the system becomes less stable.

The valence bond and molecular orbital theories differ in how they use the orbitals of two hydrogen atoms to describe the orbital that contains the electron pair in H_2. Both theories assume that electron waves behave much like more familiar waves, such as sound and light waves. One property of waves that is important here is called "interference" in physics. *Constructive interference* occurs when two waves combine so as to reinforce each other ("in phase"); *destructive interference* occurs when they oppose each other ("out of phase") (Figure 1.15). In the valence bond model constructive interference between two electron waves is seen as the basis for the shared electron-pair bond. In the molecular orbital model, the wave functions of molecules are derived by combining wave functions of atoms.

All of the forces in chemistry, except for nuclear chemistry, are electrical. Opposite charges attract; like charges repel. This simple fact can take you a long way.

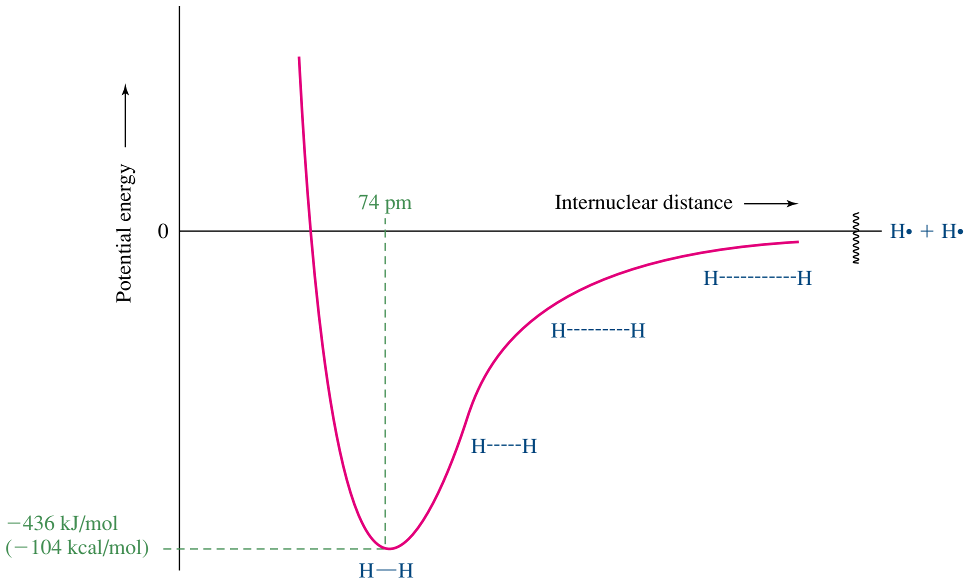
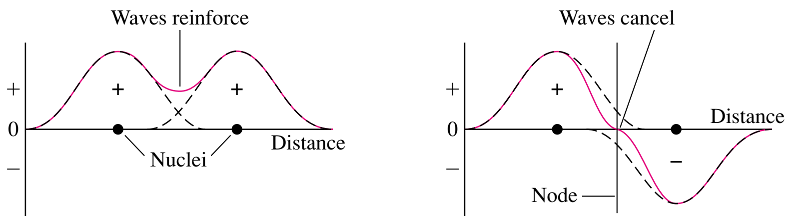


FIGURE 1.14 Plot of potential energy versus distance for two hydrogen atoms. At long distances, there is a weak attractive force. As the distance decreases, the potential energy decreases, and the system becomes more stable because each electron now feels the attractive force of two protons rather than one. The optimum distance of separation (74 pm) corresponds to the normal bond distance of an H_2 molecule. At shorter distances, nucleus–nucleus and electron–electron repulsions are greater than electron–nucleus attractions, and the system becomes less stable.



(*a*) Amplitudes of wave functions added (*b*) Amplitudes of wave functions subtracted

FIGURE 1.15 Interference between waves. (*a*) Constructive interference occurs when two waves combine in phase with each other. The amplitude of the resulting wave at each point is the sum of the amplitudes of the original waves. (*b*) Destructive interference in the case of two phases out of phase with each other causes a mutual cancellation.

1.13 BONDING IN H_2: THE VALENCE BOND MODEL

The characteristic feature of valence bond theory is that it describes a covalent bond between two atoms in terms of an in-phase overlap of a half-filled orbital of one atom with a half-filled orbital of the other, illustrated for the case of H_2 in Figure 1.16. Two hydrogen atoms, each containing an electron in a 1*s* orbital, combine so that their orbitals overlap to give a new orbital associated with both of them. In-phase orbital overlap (constructive interference) increases the probability of finding an electron in the region of overlap.

Figure 1.17 uses electrostatic potential maps to show the buildup of electron density in the region between the atoms as two hydrogen atoms approach each other closely enough for their orbitals to overlap.

Were we to slice through the H_2 molecule perpendicular to the internuclear axis, its cross section would appear as a circle. We describe the electron distribution in such a bond as having rotational symmetry and refer to it as a **sigma (σ) bond.**

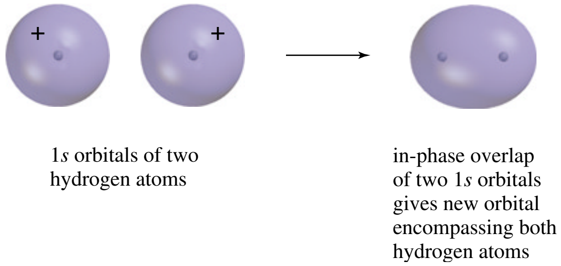
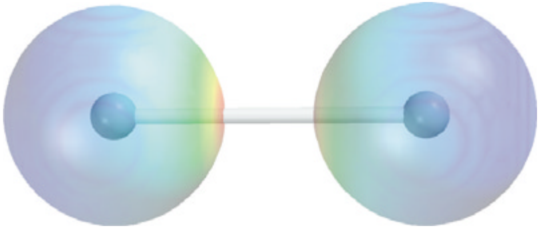
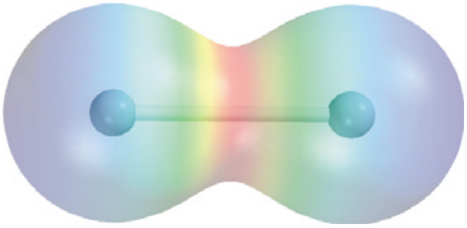


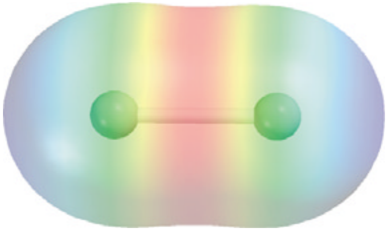
FIGURE 1.16 Valence bond picture of bonding in H_2. Overlap of half-filled 1*s* orbitals of two hydrogen atoms gives a new orbital encompassing both atoms. This new orbital contains the two original electrons. The electron density (electron probability) is highest in the region between the two atoms. The black dots correspond to the nuclei, and the + signs to the signs of the wave functions. When the wave functions are of the same sign, constructive interference leads to an increase in the probability of finding an electron in the region where the two orbitals overlap.



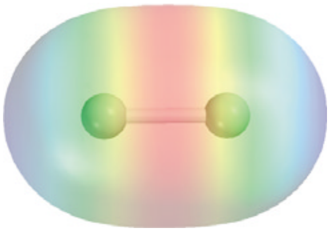
(*a*) The 1*s* orbitals of two separated hydrogen atoms, sufficiently far apart so that essentially no interaction takes place between them. Each electron is associated with only a single proton.



(*b*) As the hydrogen atoms approach each other, their 1*s* orbitals begin to overlap and each electron begins to feel the attractive force of both protons.



(*c*) The hydrogen atoms are close enough so that appreciable overlap of the two 1*s* orbitals occurs. The concentration of electron density in the region between the two protons is more readily apparent.



(*d*) A molecule of H_2. The center-to-center distance between the hydrogen atoms is 74 pm. The two individual 1*s* orbitals have been replaced by a new orbital that encompasses both hydrogens and contains both electrons. The electron density is greatest in the region between the two hydrogens.

FIGURE 1.17 Valence bond picture of bonding in H_2. The drawings illustrate how the 1*s* orbitals of two hydrogen atoms overlap to give the orbital that contains both electrons of a hydrogen molecule. The colors of the rainbow, red through violet, are used to depict highest to lowest electrostatic potential, respectively.

We will use the valence bond approach extensively in our discussion of organic molecules and expand on it later in this chapter. First though, let's introduce the molecular orbital method to see how it uses the 1*s* orbitals of two hydrogen atoms to generate the orbitals of an H_2 molecule.

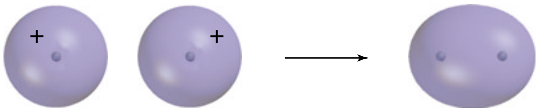
1.14 BONDING IN H_2: THE MOLECULAR ORBITAL MODEL

The molecular orbital approach to chemical bonding is based on the notion that, as electrons in atoms occupy *atomic orbitals,* electrons in molecules occupy *molecular orbitals.* Just as the first task in writing the electron configuration of an atom is to identify the atomic orbitals that are available to it, so too must we first describe the orbitals available to a molecule. In the molecular orbital method this is accomplished by representing molecular orbitals as combinations of atomic orbitals, the *linear combination of atomic orbitals-molecular orbital* (LCAO-MO) method.

Take H_2 for example. Two molecular orbitals (MOs) are generated by combining the 1*s* atomic orbitals (AOs) of two hydrogen atoms. In one combination, the two wave functions are added; in the other they are subtracted. The two new orbitals that are produced are portrayed in Figure 1.18. The additive combination generates a **bonding orbital;** the subtractive combination generates an **antibonding orbital.** Both the bonding and antibonding orbitals have rotational symmetry around the line connecting the two atoms; they have σ symmetry. The two are differentiated by calling the bonding orbital σ and the antibonding orbital σ* ("sigma star"). The bonding orbital is characterized by a region of high electron probability between the two atoms, and the antibonding orbital has a nodal surface between them.

A molecular orbital diagram for H_2 is shown in Figure 1.19. The customary format shows the starting AOs at the left and right sides and the MOs in the middle. It must always be true that *the number of MOs is the same as the number of AOs that combine to produce them.* Thus, when the 1*s* AOs of two hydrogen atoms combine, two MOs result. The bonding MO (σ) is lower in energy and the antibonding MO (σ*) higher in energy than either of the original 1*s* orbitals.

(*a*) Add the 1*s* wave functions of two hydrogen atoms to generate a bonding molecular orbital (σ) of H_2. There is a high probability of finding both electrons in the region between the two nuclei.



(*b*) Subtract the 1*s* wave function of one hydrogen atom from the other to generate an antibonding molecular orbital (σ*) of H_2. There is a nodal surface where there is a zero probability of finding the electrons in the region between the two nuclei.

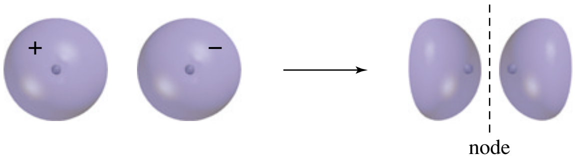


FIGURE 1.18 Generation of σ and σ* molecular orbitals of H_2 by combining 1*s* orbitals of two hydrogen atoms.

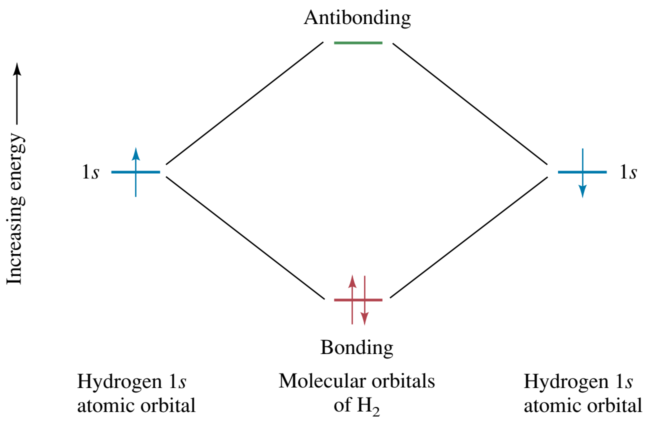


FIGURE 1.19 Two molecular orbitals are generated by combining two hydrogen 1*s* orbitals. One molecular orbital is a bonding molecular orbital and is lower in energy than either of the atomic orbitals that combine to produce it. The other molecular orbital is antibonding and is of higher energy than either atomic orbital. Each arrow indicates one electron; the electron spins are opposite in sign. The bonding orbital contains both electrons of H_2.

When assigning electrons to MOs, the same rules apply as for writing electron configurations of atoms. Electrons fill the MOs in order of increasing orbital energy, and the maximum number of electrons in any orbital is 2. The 2 electrons of H_2 occupy the bonding orbital, have opposite spins, and both are held more strongly than they would be in separated hydrogen atoms. There are no electrons in the antibonding orbital.

For a molecule as simple as H_2, it is hard to see much difference between the valence bond and molecular orbital methods. The most important differences appear in molecules with more than two atoms—a very common situation indeed. In those cases, the valence bond method continues to view a molecule as a collection of bonds between connected atoms. The molecular orbital method, however, leads to a picture in which the same electron can be associated with many, or even all, of the atoms in a molecule.

In the remaining sections of this chapter we will use a modification of valence bond theory to describe CH and CC bonds in some fundamental types of organic compounds.

1.15 BONDING IN METHANE AND ORBITAL HYBRIDIZATION

A vexing puzzle in the early days of valence bond theory concerned the bonding in methane (CH_4). Since covalent bonding requires the overlap of half-filled orbitals of the connected atoms, carbon with an electron configuration of $1s^22s^22p_x^{\,1}2p_y^{\,1}$ has only two half-filled orbitals (Figure 1.20*a*), so how can it have bonds to four hydrogens?

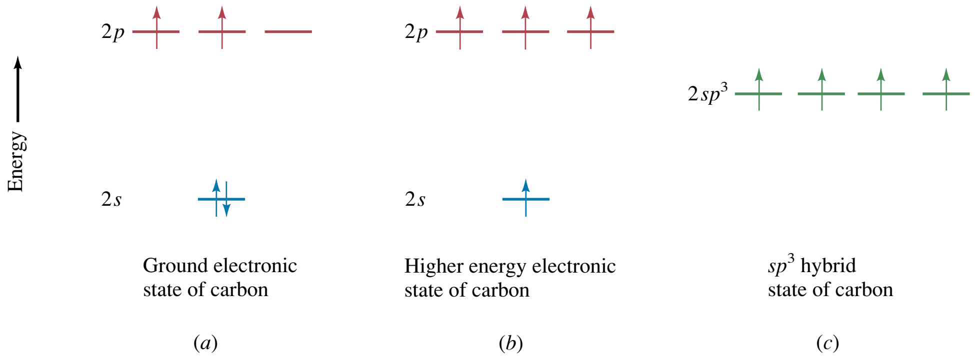


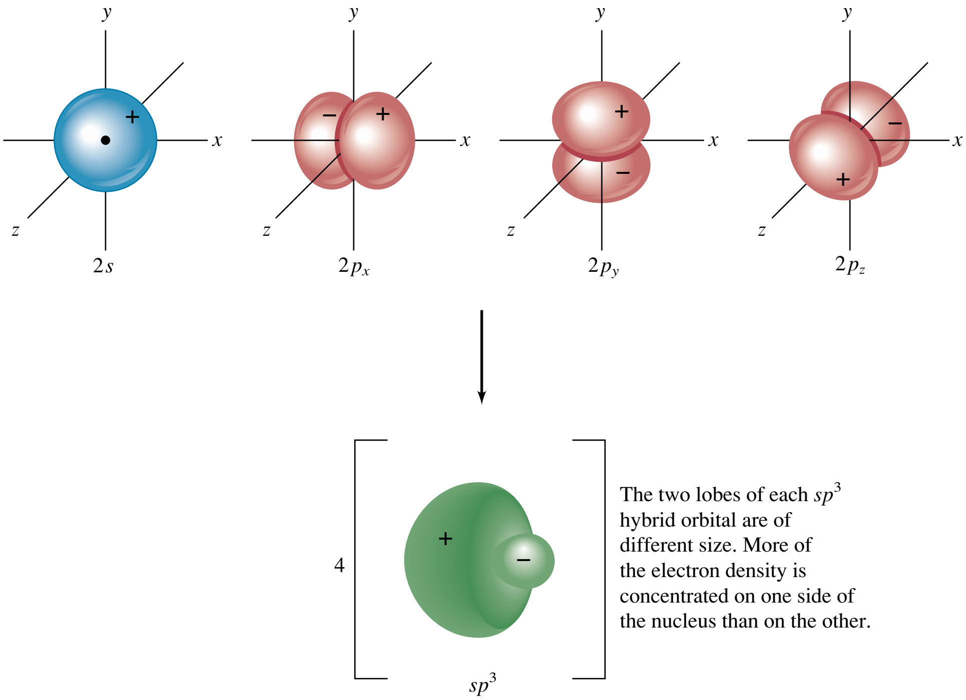
FIGURE 1.20 (*a*) Electron configuration of carbon in its most stable state. (*b*) An electron is "promoted" from the 2*s* orbital to the vacant 2*p* orbital. (*c*) The 2*s* orbital and the three 2*p* orbitals are combined to give a set of four equal-energy sp^3-hybridized orbitals, each of which contains one electron.

In the 1930s Linus Pauling offered an ingenious solution to the puzzle. He began with a simple idea: "promoting" one of the 2*s* electrons to the empty $2p_z$ orbital gives four half-filled orbitals and allows for four C—H bonds (Figure 1.20*b*). The electron configuration that results ($1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$), however, is inconsistent with the fact that all of these bonds are equivalent and directed toward the corners of a tetrahedron. The second part of Pauling's idea was novel: mix together **(hybridize)** the four valence orbitals of carbon (2*s*, $2p_x$, $2p_y$, and $2p_z$) to give four half-filled orbitals of equal energy (Figure 1.20*c*). The four new orbitals in Pauling's scheme are called **sp^3 hybrid orbitals** because they come from one *s* orbital and three *p* orbitals.

Figure 1.21 depicts some of the spatial aspects of orbital hybridization. Each sp^3 hybrid orbital has two lobes of unequal size, making the electron density greater on one side of the nucleus than the other. In a bond to hydrogen, it is the larger lobe of a carbon sp^3 orbital that overlaps with a hydrogen 1*s* orbital. The orbital overlaps corresponding to the four C—H bonds of methane are portrayed in Figure 1.22. Orbital overlap along the internuclear axis generates a bond with rotational symmetry—in this case a C($2sp^3$)—H(1*s*) σ bond. *A tetrahedral arrangement of four σ bonds is characteristic of sp^3-hybridized carbon.*

The peculiar shape of sp^3 hybrid orbitals turn out to have an important consequence. Since most of the electron density in an sp^3 hybrid orbital lies to one side of a carbon atom, overlap with a half-filled 1*s* orbital of hydrogen, for example, on that side produces a stronger bond than would result otherwise. If the electron probabilities were equal on both sides of the nucleus, as it would be in a *p* orbital, half of the time the electron would be remote from the region between the bonded atoms, and the bond would be weaker. Thus, not only does Pauling's orbital hybridization proposal account for carbon forming four bonds rather than two, these bonds are also stronger than they would be otherwise.

Combine one 2*s* and three 2*p* orbitals to give four equivalent sp^3 hybrid orbitals:



The two lobes of each sp^3 hybrid orbital are of different size. More of the electron density is concentrated on one side of the nucleus than on the other.

FIGURE 1.21 Representation of orbital mixing in sp^3 hybridization. Mixing of one *s* orbital with three *p* orbitals generates four sp^3 hybrid orbitals. Each sp^3 hybrid orbital has 25% *s* character and 75% *p* character. The four sp^3 hybrid orbitals have their major lobes directed toward the corners of a tetrahedron, which has the carbon atom at its center.

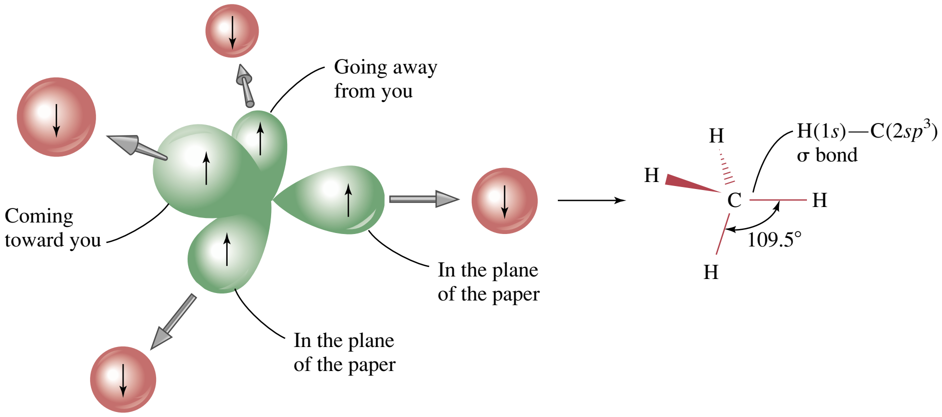


FIGURE 1.22 The sp^3 hybrid orbitals are arranged in a tetrahedral fashion around carbon. Each orbital contains one electron and can form a bond with a hydrogen atom to give a tetrahedral methane molecule. (*Note:* Only the major lobe of each sp^3 orbital is shown. As indicated in Figure 1.21, each orbital contains a smaller back lobe, which has been omitted for the sake of clarity.)

PROBLEM 1.20 Construct an orbital diagram like that of Figure 1.20 for nitrogen in ammonia, assuming sp^3 hybridization. In what kind of orbital is the unshared pair? What orbital overlaps are involved in the N—H bonds?

1.16 *sp*³ HYBRIDIZATION AND BONDING IN ETHANE

The orbital hybridization model of covalent bonding is readily extended to carbon–carbon bonds. As Figure 1.23 illustrates, ethane is described in terms of a carbon–carbon σ bond joining two CH_3 **(methyl)** groups. Each methyl group consists of an sp^3-hybridized carbon attached to three hydrogens by sp^3–$1s$ σ bonds. Overlap of the remaining half-filled orbital of one carbon with that of the other generates a σ bond between them. Here is a third kind of σ bond, one that has as its basis the overlap of two sp^3-hybridized orbitals. *In general, you can expect that carbon will be sp^3-hybridized when it is directly bonded to four atoms.*

The C—H and C—C bond distances in ethane are 111 and 153 pm, respectively, and the bond angles are close to tetrahedral.

PROBLEM 1.21 Describe the bonding in methylsilane (H_3CSiH_3), assuming that it is analogous to that of ethane. What is the principal quantum number of the orbitals of silicon that are hybridized?

The orbital hybridization model of bonding is not limited to compounds in which all the bonds are single, but can be adapted to compounds with double and triple bonds, as described in the following two sections.

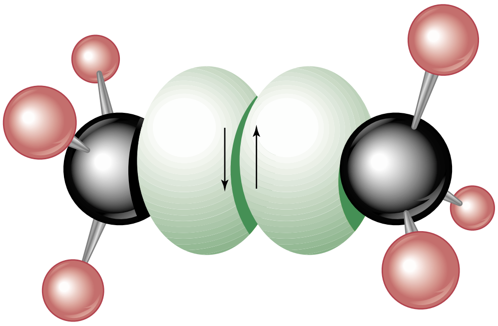


FIGURE 1.23 Orbital overlap description of the sp^3–sp^3 σ bond between the two carbon atoms of ethane.

1.17 *sp*^{2} HYBRIDIZATION AND BONDING IN ETHYLENE

Another name for ethylene is *ethene.*

Ethylene is a planar molecule, as the structural representations of Figure 1.24 indicate. Because *sp*^{3} hybridization is associated with a tetrahedral geometry at carbon, it is not appropriate for ethylene, which has a trigonal planar geometry at both of its carbons. The hybridization scheme is determined by the number of atoms to which the carbon is directly attached. In ethane, four atoms are attached to carbon by σ bonds, and so four equivalent *sp*^{3} hybrid orbitals are required. In ethylene, three atoms are attached to each carbon, so three equivalent hybrid orbitals are required. As shown in Figure 1.25, these three orbitals are generated by mixing the carbon 2*s* orbital with two of the 2*p* orbitals and are called ***sp*^{2} hybrid orbitals.** One of the 2*p* orbitals is left unhybridized.

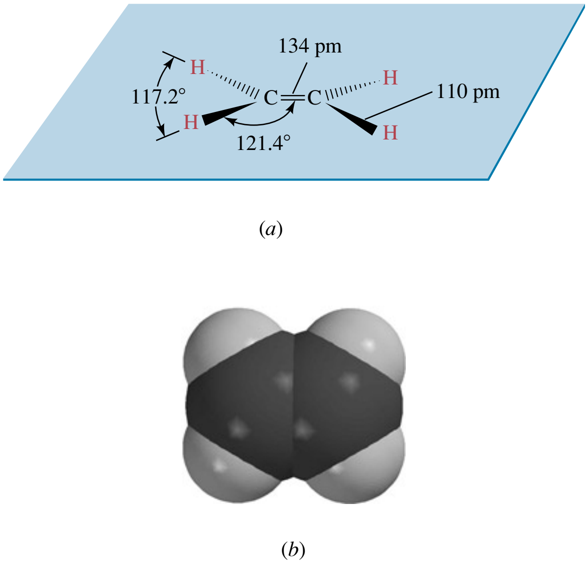


FIGURE 1.24 (*a*) All the atoms of ethylene lie in the same plane. All the bond angles are close to 120°, and the carbon–carbon bond distance is significantly shorter than that of ethane. (*b*) A space-filling model of ethylene.

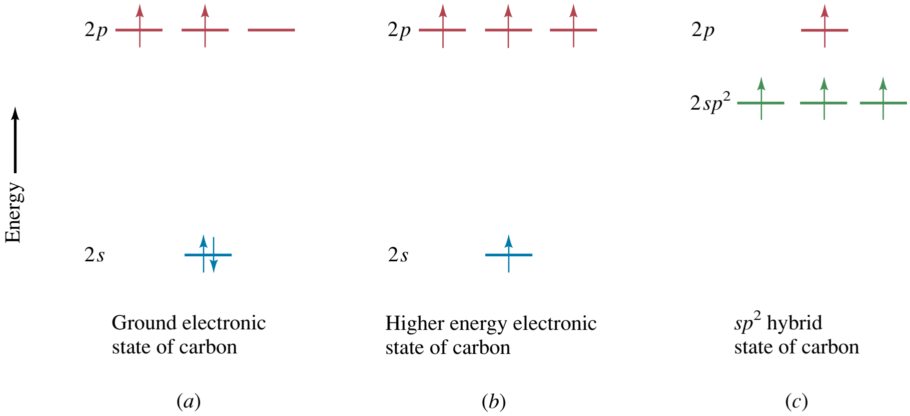


FIGURE 1.25 (*a*) Electron configuration of carbon in its most stable state. (*b*) An electron is "promoted" from the 2*s* orbital to the vacant 2*p* orbital. (*c*) The 2*s* orbital and two of the three 2*p* orbitals are combined to give a set of three equal-energy *sp*^{2}-hybridized orbitals. One of the 2*p* orbitals remains unchanged.

Figure 1.26 illustrates the mixing of orbitals in sp^2 hybridization. The three sp^2 orbitals are of equal energy; each has one-third *s* character and two-thirds *p* character. Their axes are coplanar, and each has a shape much like that of an sp^3 orbital.

Each carbon of ethylene uses two of its sp^2 hybrid orbitals to form σ bonds to two hydrogen atoms, as illustrated in the first part of Figure 1.27. The remaining sp^2 orbitals, one on each carbon, overlap along the internuclear axis to give a σ bond connecting the two carbons.

As Figure 1.27 shows, each carbon atom still has, at this point, an unhybridized 2*p* orbital available for bonding. These two half-filled 2*p* orbitals have their axes perpendicular to the framework of σ bonds of the molecule and overlap in a side-by-side manner to give what is called a **pi (π) bond.** According to this analysis, the carbon–carbon double bond of ethylene is viewed as a combination of a σ bond plus a π bond. The additional increment of bonding makes a carbon–carbon double bond both stronger and shorter than a carbon–carbon single bond.

One measure of the strength of a bond is its *bond dissociation energy.* This topic will be introduced in Section 4.17 and applied to ethylene in Section 5.2.

Electrons in a π bond are called **π electrons.** The probability of finding a π electron is highest in the region above and below the plane of the molecule. The plane of the molecule corresponds to a nodal plane, where the probability of finding a π electron is zero.

In general, you can expect that carbon will be sp^2-hybridized when it is directly bonded to three atoms.

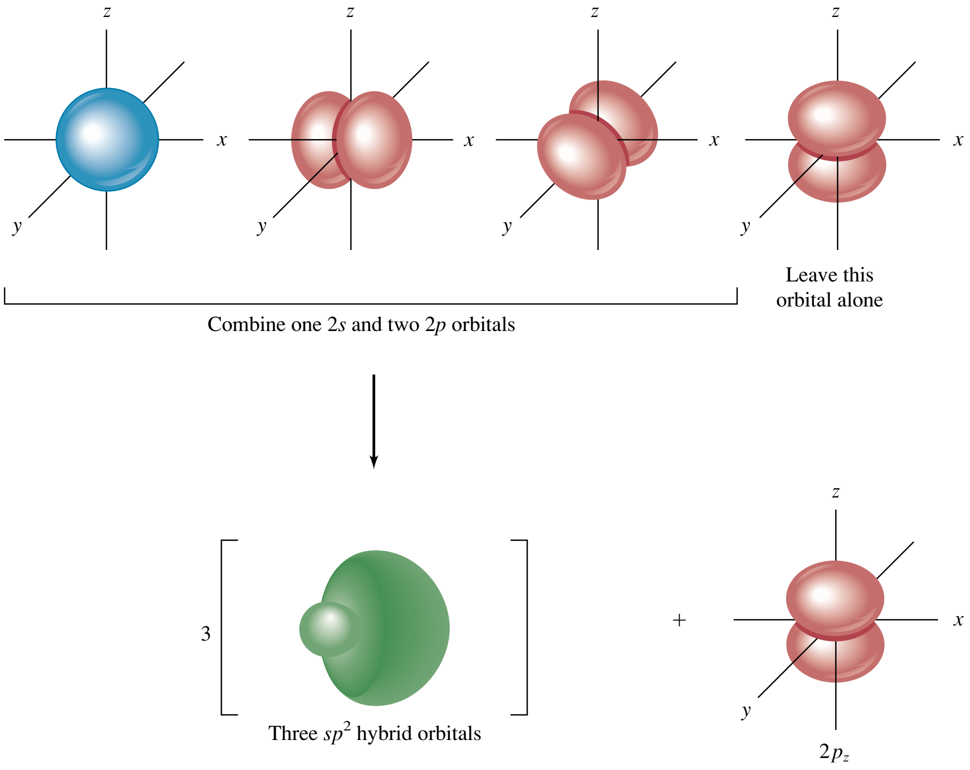


FIGURE 1.26 Representation of orbital mixing in sp^2 hybridization. Mixing of one *s* orbital with two *p* orbitals generates three sp^2 hybrid orbitals. Each sp^2 hybrid orbital has one-third *s* character and two-thirds *p* character. The axes of the three sp^2 hybrid orbitals are coplanar. One 2*p* orbital remains unhybridized, and its axis is perpendicular to the plane defined by the axes of the sp^2 orbitals.

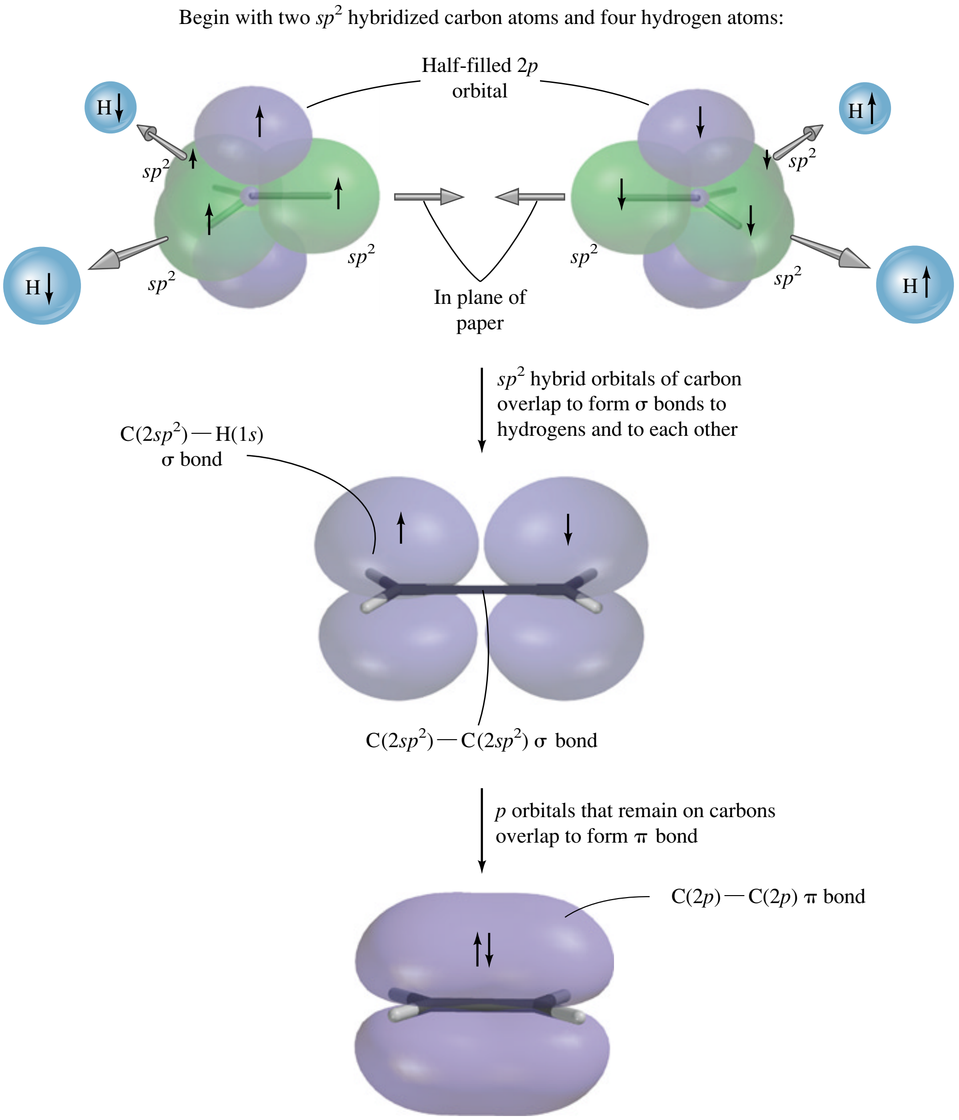


FIGURE 1.27 The carbon–carbon double bond in ethylene has a σ component and a π component. The σ component arises from overlap of sp^2-hybridized orbitals along the internuclear axis. The π component results from a side-by-side overlap of 2p orbitals.

1.18 *sp* HYBRIDIZATION AND BONDING IN ACETYLENE

One more hybridization scheme is important in organic chemistry. It is called ***sp* hybridization** and applies when carbon is directly bonded to two atoms, as it is in acetylene. The structure of acetylene is shown in Figure 1.28 along with its bond distances and bond angles.

Another name for acetylene is *ethyne.*

Since each carbon in acetylene is bonded to two other atoms, the orbital hybridization model requires each carbon to have two equivalent orbitals available for the formation of σ bonds as outlined in Figures 1.29 and 1.30. According to this model the carbon 2s orbital and one of the 2p orbitals combine to generate a pair of two equivalent sp hybrid orbitals. Each sp hybrid orbital has 50% s character and 50% p character. These two sp orbitals share a common axis, but their major lobes are oriented at an angle of 180° to each other. Two of the original 2p orbitals remain unhybridized. Their axes are perpendicular to each other and to the common axis of the pair of sp hybrid orbitals.

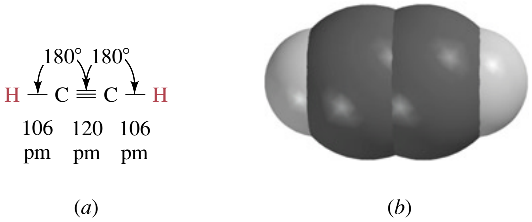


FIGURE 1.28 Acetylene is a linear molecule as indicated in the (*a*) structural formula and a (*b*) space-filling model.

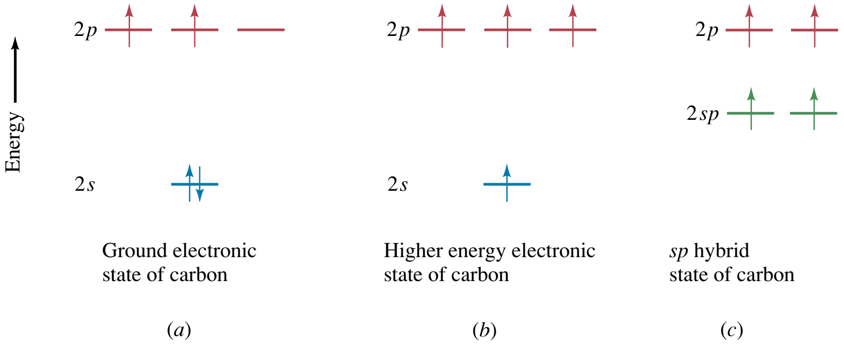


FIGURE 1.29 (*a*) Electron configuration of carbon in its most stable state. (*b*) An electron is "promoted" from the 2*s* orbital to the vacant 2*p* orbital. (*c*) The 2*s* orbital and one of the three 2*p* orbitals are combined to give a set of two equal-energy *sp*-hybridized orbitals. Two of the 2*p* orbitals remain unchanged.

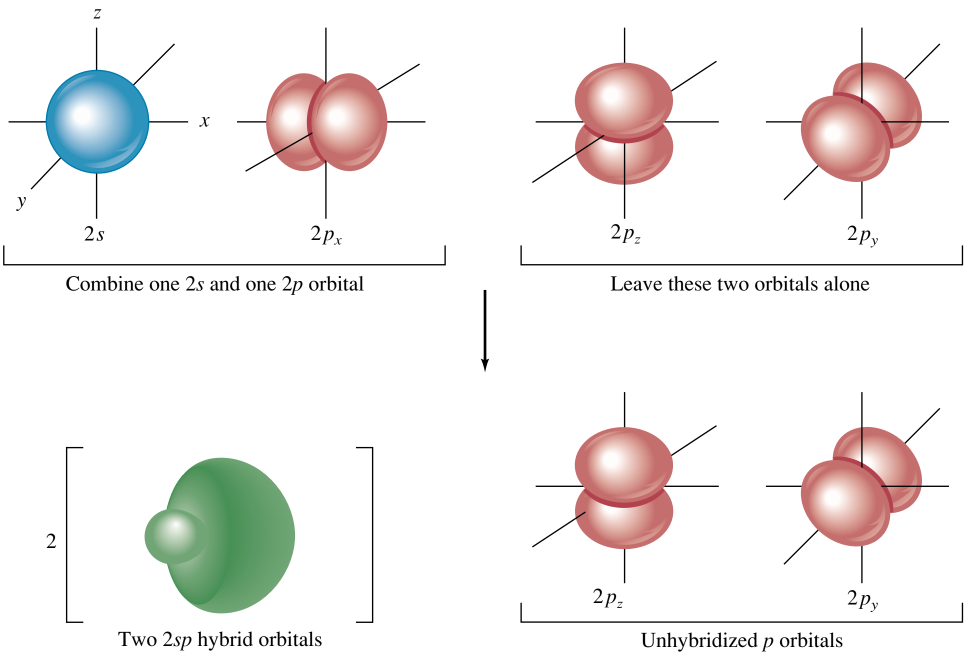


FIGURE 1.30 Representation of orbital mixing in *sp* hybridization. Mixing of the 2*s* orbital with one of the *p* orbitals generates two *sp* hybrid orbitals. Each *sp* hybrid orbital has 50% *s* character and 50% *p* character. The axes of the two *sp* hybrid orbitals are colinear. Two 2*p* orbitals remain unhybridized, and their axes are perpendicular to each other and to the long axis of the molecule.

As portrayed in Figure 1.31, the two carbons of acetylene are connected to each other by a 2*sp*–2*sp* σ bond, and each is attached to a hydrogen substituent by a 2*sp*–1*s* σ bond. The unhybridized 2*p* orbitals on one carbon overlap with their counterparts on the other to form two π bonds. The carbon–carbon triple bond in acetylene is viewed as a multiple bond of the $\sigma + \pi + \pi$ type.

In general, you can expect that carbon will be sp-hybridized when it is directly bonded to two atoms.

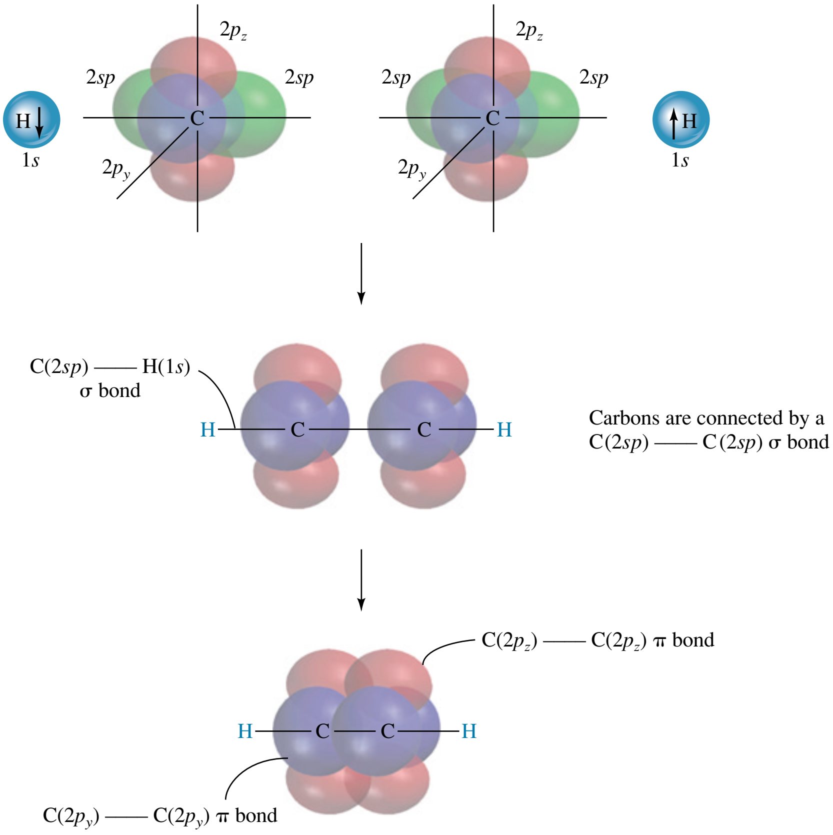


FIGURE 1.31 A description of bonding in acetylene based on *sp* hybridization of carbon. The carbon–carbon triple bond is viewed as consisting of one σ bond and two π bonds.

PROBLEM 1.22 Give the hybridization state of each carbon in the following compounds:

(a) Carbon dioxide (O═C═O)

(b) Formaldehyde ($H_2C{=}O$)

(c) Ketene ($H_2C{=}C{=}O$)

(d) Propene ($CH_3CH{=}CH_2$)

(e) Acetone [$(CH_3)_2C{=}O$]

(f) Acrylonitrile ($CH_2{=}CHC{\equiv}N$)

SAMPLE SOLUTION (a) Carbon in CO_2 is directly bonded to two other atoms. It is *sp*-hybridized.

1.19 WHICH THEORY OF CHEMICAL BONDING IS BEST?

We have introduced three approaches to chemical bonding in this chapter:

1. The Lewis model
2. The orbital hybridization model (which is a type of valence bond model)
3. The molecular orbital model

Which one should you learn?

Generally speaking, the three models offer complementary information. Organic chemists use all three, emphasizing whichever one best suits a particular feature of structure or reactivity. Until recently, the Lewis and orbital hybridization models were used far more than the molecular orbital model. But that is changing.

The Lewis rules are relatively straightforward, easiest to master, and the most familiar. You will find that your ability to write Lewis formulas increases rapidly with experience. *Get as much practice as you can early in the course. Success in organic chemistry depends on writing correct Lewis structures.*

Orbital hybridization descriptions, since they too are based on the shared electron-pair bond, enhance the information content of Lewis formulas by distinguishing among various types of atoms, electrons, and bonds. As you become more familiar with a variety of structural types, you will find that the term "sp^3-hybridized carbon" triggers a group of associations in your mind that are different from those of some other term, such as "sp^2-hybridized carbon," for example.

Molecular orbital theory can provide insights into structure and reactivity that the Lewis and orbital hybridization models can't. It is the least intuitive of the three methods, however, and requires the most training, background, and chemical knowledge to apply. We have *discussed* molecular orbital theory so far only in the context of the bonding in H_2. We have *used* the results of molecular orbital theory, however, several times without acknowledging it until now. The electrostatic potential map of methane that opened this chapter and was repeated as Figure 1.7*d* was obtained by a molecular orbital calculation. Four molecular orbital calculations provided the drawings that illustrated how electron density builds up between the atoms in the valence bond (!) treatment of H_2 (see Figure 1.17). Molecular orbital theory is well suited to quantitative applications and is becoming increasingly available for routine use via software that runs on personal computers. You will see the results of molecular orbital theory often in this text, but the theory itself will be developed only at an introductory level.

1.20 SUMMARY

The first half of this chapter reviews the Lewis model of chemical bonding and the procedures for writing structural formulas of chemical compounds, especially organic ones. The second half discusses bonding in terms of the wave nature of electrons and concludes with its application to compounds that contain carbon–carbon single bonds, double bonds, and triple bonds.

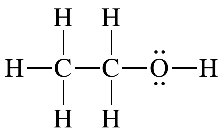
Section 1.1 A review of some fundamental knowledge about atoms and electrons leads to a discussion of **wave functions, orbitals,** and the **electron configurations** of atoms. Neutral atoms have as many electrons as the number of protons in the nucleus. These electrons occupy orbitals in order of increasing energy, with no more than two electrons in any one orbital. The most frequently encountered atomic orbitals in this text are *s* orbitals (spherically symmetrical) and *p* orbitals ("dumbbell"-shaped).

Boundary surface of an *s* orbital with carbon at its center

Boundary surface of a *p* orbital with carbon at its center

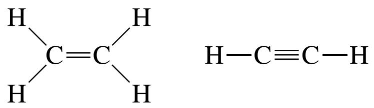
Section 1.2 An **ionic bond** is the force of electrostatic attraction between two oppositely charged ions. Atoms at the upper right of the periodic table, especially fluorine and oxygen, tend to gain electrons to form anions. Elements toward the left of the periodic table, especially metals such as sodium, tend to lose electrons to form cations. Ionic bonds in which carbon is the cation or anion are rare.

Section 1.3 The most common kind of bonding involving carbon is **covalent bonding.** A covalent bond is the sharing of a pair of electrons between two atoms. **Lewis structures** are written on the basis of the **octet rule,** which limits second-row elements to no more than 8 electrons in their valence shells. In most of its compounds, carbon has four bonds.



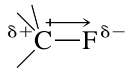
Each carbon has four bonds in ethyl alcohol;
oxygen and each carbon are surrounded by eight electrons.

Section 1.4 Many organic compounds have **double** or **triple bonds** to carbon. Four electrons are involved in a double bond; six in a triple bond.



Ethylene has a carbon–carbon double bond;
acetylene has a carbon–carbon triple bond.

Section 1.5 When two atoms that differ in **electronegativity** are covalently bonded, the electrons in the bond are drawn toward the more electronegative element.

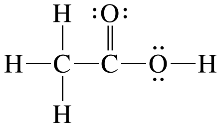


The electrons in a carbon–fluorine bond are
drawn away from carbon, toward fluorine.

Section 1.6 Counting electrons and assessing charge distribution in molecules is essential to understanding how structure affects properties. A particular atom in a Lewis structure may be neutral, positively charged, or negatively charged. The **formal charge** of an atom in the Lewis structure of a molecule can be calculated by comparing its electron count with that of the neutral atom itself.

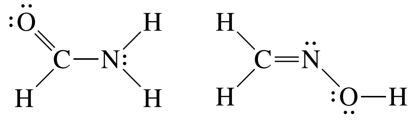
$$\begin{aligned}\text{Formal charge} = {} & \text{(number of electrons in neutral atom)} \\ & - \text{(number of electrons in unshared pairs)} \\ & - \tfrac{1}{2}\,\text{(number of electrons in covalent bonds)}\end{aligned}$$

Section 1.7 Table 1.4 in this section sets forth the procedure to be followed in writing Lewis structures for organic molecules. It begins with experimentally determined information: the **molecular formula** and the **constitution** (order in which the atoms are connected).



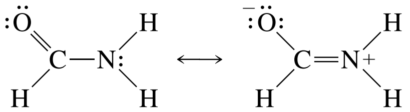
The Lewis structure of acetic acid

Section 1.8 Different compounds that have the same molecular formula are called **isomers.** If they are different because their atoms are connected in a different order, they are called **constitutional isomers.**



Formamide (*left*) and formaldoxime (*right*) are constitutional isomers; both have the same molecular formula (CH_3NO), but the atoms are connected in a different order.

Section 1.9 Many molecules can be represented by two or more Lewis structures that differ only in the placement of electrons. In such cases the electrons are delocalized, and the real electron distribution is a composite of the contributing Lewis structures, each of which is called a **resonance** form. The rules for resonance are summarized in Table 1.5.



Two Lewis structures (resonance forms) of formamide; the atoms are connected in the same order, but the arrangment of the electrons is different.

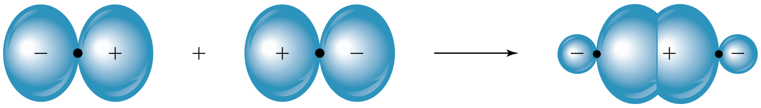
Section 1.10 The shapes of molecules can often be predicted on the basis of **valence shell electron-pair repulsions.** A tetrahedral arrangement gives the maximum separation of four electron pairs (*left*); a trigonal planar arrangement is best for three electron pairs (*center*), and a linear arrangement for two electron pairs (*right*).

Section 1.11 Knowing the shape of a molecule and the polarity of its various bonds allows the presence or absence of a **molecular dipole moment** and its direction to be predicted.

Both water and carbon dioxide have polar bonds,
but water is a polar molecule and carbon dioxide is not.

Section 1.12 Both modern theories of bonding, **valence bond** and **molecular orbital theory,** are based on the wave nature of an electron. Constructive interference between the electron wave of one atom and that of another gives a region between the two atoms in which the probability of sharing an electron is high—a bond.

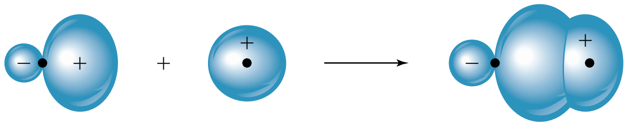
Section 1.13 In valence bond theory a covalent bond is described in terms of in-phase overlap of a half-filled orbital of one atom with a half-filled orbital of another.



Overlap of two *p* orbitals along internuclear axis
gives a σ bond.

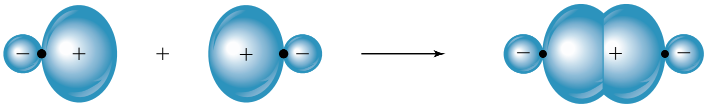
Section 1.14 In molecular orbital theory, molecular wave functions (MOs) are approximated by combining the wave functions of the molecule's atoms (AOs). The number of MOs must equal the number of AOs in the molecule's atoms.

Section 1.15 Bonding in methane is most often described by an **orbital hybridization** model, which is a modified form of valence bond theory. Four equivalent sp^3 hybrid orbitals of carbon are generated by mixing the $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals. The C—H σ bonds are formed by overlap of each half-filled ***sp*³ hybrid** orbital with a half-filled hydrogen $1s$ orbital.



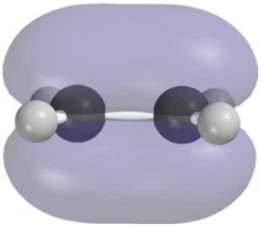
Overlap of an sp^3-hybridized orbital of carbon with
the $2s$ orbital of hydrogen to give a C—H σ bond.

Section 1.16 The carbon–carbon bond in ethane (CH_3CH_3) is a σ bond generated by overlap of an sp^3 orbital of one carbon with an sp^3 orbital of the other.



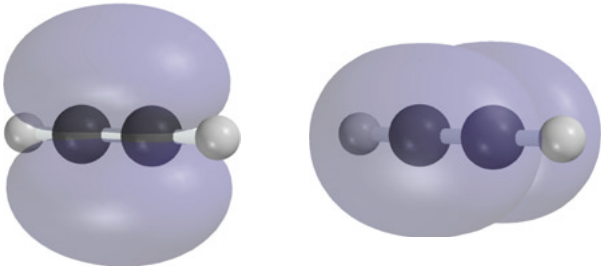
Overlap of an sp^3-hybridized orbital of each
of two carbon atoms to give a C—C σ bond.

Section 1.17 Carbon is ***sp*^{2}-hybridized** in ethylene, and the double bond is considered to have a σ component and a π component. The *sp*^{2} hybridization state of carbon is derived by mixing the 2*s* and two of the three 2*p* orbitals. Three equivalent *sp*^{2} orbitals result, and the axes of these orbitals are coplanar. Overlap of an *sp*^{2} orbital of one carbon with an *sp*^{2} orbital of another produces a σ bond between them. Each carbon still has one unhybridized *p* orbital available for bonding, and "side-by-side" overlap of the *p* orbitals of adjacent carbons gives a π bond between them.



The π bond in ethylene generated by overlap of *p* orbitals of adjacent carbons

Section 1.18 Carbon is ***sp*-hybridized** in acetylene, and the triple bond is of the σ + π + π type. The 2*s* orbital and one of the 2*p* orbitals combine to give two equivalent *sp* orbitals that have their axes in a straight line. A σ bond between the two carbons is supplemented by two π bonds formed by overlap of the remaining half-filled *p* orbitals.



The triple bond of acetylene has a σ bond component and two π bonds; the two π bonds are shown here and are perpendicular to each other.

Section 1.19 Lewis structures, orbital hybridization, and molecular orbital descriptions of bonding are all used in organic chemistry. Lewis structures are used the most, MO descriptions the least. All will be used in this text.

PROBLEMS

1.23 Each of the following species will be encountered at some point in this text. They all have the same number of electrons binding the same number of atoms and the same arrangement of bonds; they are *isoelectronic*. Specify which atoms, if any, bear a formal charge in the Lewis structure given and the net charge for each species.

(a) $:N{\equiv}N:$

(b) $:C{\equiv}N:$

(c) $:C{\equiv}C:$

(d) $:N{\equiv}O:$

(e) $:C{\equiv}O:$

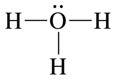
1.24 You will meet all the following isoelectronic species in this text. Repeat the previous problem for these three structures.

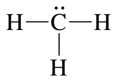
(a) $:\ddot{O}=C=\ddot{O}:$ (b) $:\ddot{N}=N=\ddot{N}:$ (c) $:\ddot{O}=N=\underset{\cdot\cdot}{O}:$

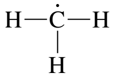
1.25 All the following compounds are characterized by ionic bonding between a group I metal cation and a tetrahedral anion. Write an appropriate Lewis structure for each anion, remembering to specify formal charges where they exist.

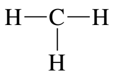
(a) $NaBF_4$
(b) $LiAlH_4$
(c) K_2SO_4
(d) Na_3PO_4

1.26 Determine the formal charge at all the atoms in each of the following species and the net charge on the species as a whole.

(a) 
$H-\underset{\underset{H}{|}}{\ddot{O}}-H$

(b) 
$H-\underset{\underset{H}{|}}{\ddot{C}}-H$

(c) 
$H-\underset{\underset{H}{|}}{\dot{C}}-H$

(d) 
$H-\underset{\underset{H}{|}}{C}-H$

(e) $H-\ddot{C}-H$

1.27 What is the formal charge of oxygen in each of the following Lewis structures?

(a) $CH_3\underset{\cdot\cdot}{\ddot{O}}:$ (b) $(CH_3)_2\ddot{O}:$ (c) $(CH_3)_3O:$

1.28 Write a Lewis structure for each of the following organic molecules:

(a) C_2H_5Cl (ethyl chloride: sprayed from aerosol cans onto skin to relieve pain)

(b) C_2H_3Cl [vinyl chloride: starting material for the preparation of poly(vinyl chloride), or PVC, plastics]

(c) $C_2HBrClF_3$(halothane: a nonflammable inhalation anesthetic; all three fluorines are bonded to the same carbon)

(d) $C_2Cl_2F_4$(Freon 114: formerly used as a refrigerant and as an aerosol propellant; each carbon bears one chlorine)

1.29 Write a structural formula for the CH_3NO isomer characterized by the structural unit indicated. None of the atoms in the final structure should have a formal charge.

(a) $C-N=O$
(b) $C=N-O$
(c) $O-C=N$
(d) $O=C-N$

1.30 Consider structural formulas A, B, and C:

$H_2\ddot{C}-N\equiv N:$ $H_2C=N=\ddot{N}:$ $H_2C-\ddot{N}=\ddot{N}:$

A B C

(a) Are A, B, and C constitutional isomers, or are they resonance forms?

(b) Which structures have a negatively charged carbon?

(c) Which structures have a positively charged carbon?

(d) Which structures have a positively charged nitrogen?

(e) Which structures have a negatively charged nitrogen?

(f) What is the net charge on each structure?

(g) Which is a more stable structure, A or B? Why?

(h) Which is a more stable structure, B or C? Why?

(i) What is the CNN geometry in each structure according to VSEPR?

1.31 Consider structural formulas A, B, C, and D:

$\mathrm{H{-}\underset{\cdot\cdot}{C}{=}N{=}\underset{\cdot\cdot}{O}\colon}$ A

$\mathrm{H{-}C{\equiv}N{-}\underset{\cdot\cdot}{\ddot{O}}\colon}$ B

$\mathrm{H{-}C{\equiv}N{=}\underset{\cdot\cdot}{O}\colon}$ C

$\mathrm{H{-}C{=}\ddot{N}{-}\underset{\cdot\cdot}{\ddot{O}}\colon}$ D

(a) Which structures contain a positively charged carbon?

(b) Which structures contain a positively charged nitrogen?

(c) Which structures contain a positively charged oxygen?

(d) Which structures contain a negatively charged carbon?

(e) Which structures contain a negatively charged nitrogen?

(f) Which structures contain a negatively charged oxygen?

(g) Which structures are electrically neutral (contain equal numbers of positive and negative charges)? Are any of them cations? Anions?

(h) Which structure is the most stable?

(i) Which structure is the least stable?

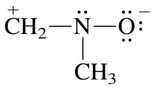
1.32 In each of the following pairs, determine whether the two represent resonance forms of a single species or depict different substances. If two structures are not resonance forms, explain why.

(a) $\mathrm{\colon\underset{\cdot\cdot}{\ddot{N}}{-}N{\equiv}N\colon}$ and $\mathrm{\colon\underset{\cdot\cdot}{N}{=}N{=}\underset{\cdot\cdot}{N}\colon}$

(b) $\mathrm{\colon\underset{\cdot\cdot}{\ddot{N}}{-}N{\equiv}N\colon}$ and $\mathrm{\colon\ddot{N}{-}N{=}\ddot{N}\colon}$

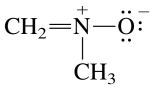
(c) $\mathrm{\colon\underset{\cdot\cdot}{\ddot{N}}{-}N{\equiv}N\colon}$ and $\mathrm{\colon\underset{\cdot\cdot}{\ddot{N}}{-}\underset{\cdot\cdot}{\ddot{N}}{-}\underset{\cdot\cdot}{\ddot{N}}\colon}$

1.33 Among the following four structures, one is *not* a permissible resonance form. Identify the wrong structure. Why is it incorrect?



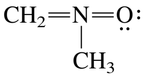
$\overset{+}{\mathrm{C}}\mathrm{H_2{-}\underset{CH_3}{\underset{|}{\ddot{N}}}{-}\underset{\cdot\cdot}{\ddot{O}}\colon^{-}}$

A



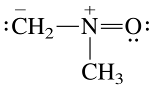
$\mathrm{CH_2{=}\underset{CH_3}{\underset{|}{\overset{+}{N}}}{-}\underset{\cdot\cdot}{\ddot{O}}\colon^{-}}$

B



$\mathrm{CH_2{=}\underset{CH_3}{\underset{|}{N}}{=}\underset{\cdot\cdot}{O}\colon}$

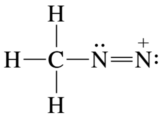
C

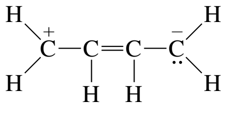


$\mathrm{\colon\overset{-}{C}H_2{-}\underset{CH_3}{\underset{|}{\overset{+}{N}}}{=}\underset{\cdot\cdot}{O}\colon}$

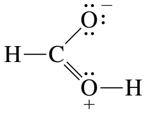
D

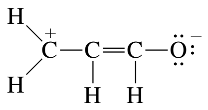
1.34 Keeping the same atomic connections and moving only electrons, write a more stable Lewis structure for each of the following. Be sure to specify formal charges, if any, in the new structure.

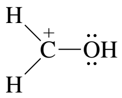
(a)


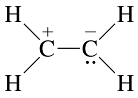
(d)


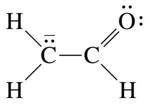
(g) $\mathrm{H{-}\overset{+}{C}{=}\ddot{O}\colon}$

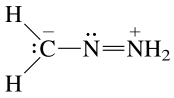
(b)


(e)


(h)


(c)


(f)


(i)


1.35 (a) Write a Lewis structure for sulfur dioxide in which the octet rule is satisfied for all three atoms. Show all electron pairs and include any formal charges. The atoms are connected in the order OSO.

(b) The octet rule may be violated for elements beyond the second period of the periodic table. Write a Lewis structure for sulfur dioxide in which each oxygen is connected to sulfur by a double bond. Show all electron pairs and formal charges.

1.36 Write structural formulas for all the constitutionally isomeric compounds having the given molecular formula.

(a) C_4H_{10}
(b) C_5H_{12}
(c) $C_2H_4Cl_2$
(d) C_4H_9Br
(e) C_3H_9N

1.37 Write structural formulas for all the constitutional isomers of

(a) C_3H_8
(b) C_3H_6
(c) C_3H_4

1.38 Write structural formulas for all the constitutional isomers of molecular formula C_3H_6O that contain

(a) Only single bonds
(b) One double bond

1.39 For each of the following molecules that contain polar covalent bonds, indicate the positive and negative ends of the dipole, using the symbol $\leftrightarrow$. Refer to Table 1.2 as needed.

(a) HCl
(b) ICl
(c) HI
(d) H_2O
(e) HOCl

1.40 The compounds FCl and ICl have dipole moments μ that are similar in magnitude (0.9 and 0.7 D, respectively) but opposite in direction. In one compound, chlorine is the positive end of the dipole; in the other it is the negative end. Specify the direction of the dipole moment in each compound, and explain your reasoning.

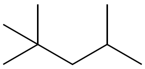
1.41 Which compound in each of the following pairs would you expect to have the greater dipole moment μ? Why?

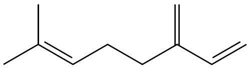
(a) NaCl or HCl
(b) HF or HCl
(c) HF or BF_3
(d) $(CH_3)_3CH$ or $(CH_3)_3CCl$
(e) $CHCl_3$ or CCl_3F
(f) CH_3NH_2 or CH_3OH
(g) CH_3NH_2 or CH_3NO_2

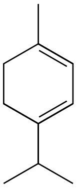
1.42 Apply the VSEPR method to deduce the geometry around carbon in each of the following species:

(a) $:\overset{-}{C}H_3$
(b) $\overset{+}{C}H_3$
(c) $:CH_2$

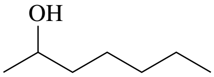
1.43 Expand the following structural representations so as to more clearly show all the atoms and any unshared electron pairs.

(a)  A component of high-octane gasoline

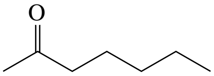
(b)  Occurs in bay and verbena oil

(c) 

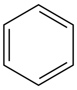
Pleasant-smelling substance found in marjoram oil

(d) 

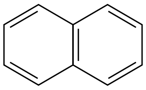
Present in oil of cloves

(e) 

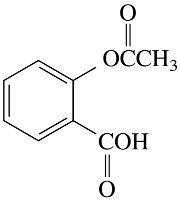
Found in Roquefort cheese

(f) 

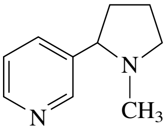
Benzene: parent compound of a large family of organic substances

(g) 

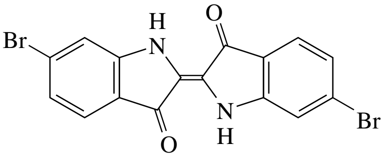
Naphthalene: sometimes used as a moth repellent

(h) 

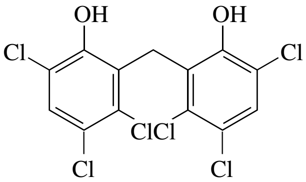
Aspirin

(i) 

Nicotine: a toxic substance present in tobacco

(j) 

Tyrian purple: a purple dye extracted from a species of Mediterranean sea snail

(k) 

Hexachlorophene: an antiseptic

1.44 Molecular formulas of organic compounds are customarily presented in the fashion $C_2H_5BrO_2$. The number of carbon and hydrogen atoms are presented first, followed by the other atoms in alphabetical order. Give the molecular formulas corresponding to each of the compounds in the preceding problem. Are any of them isomers?

1.45 Select the compounds in Problem 1.43 in which all the carbons are

(a) sp^3-hybridized (b) sp^2-hybridized

Do any of the compounds in Problem 1.43 contain an *sp*-hybridized carbon?

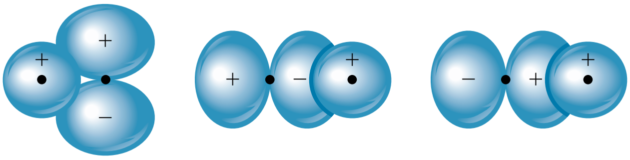
1.46 Account for all the electrons in each of the following species, assuming sp^3 hybridization of the second-row element in each case. Which electrons are found in sp^3-hybridized orbitals? Which are found in σ bonds?

(a) Ammonia (NH_3)
(b) Water (H_2O)
(c) Hydrogen fluoride (HF)
(d) Ammonium ion (NH_4^+)
(e) Borohydride anion (BH_4^-)
(f) Amide anion ($:\underset{..}{\overline{N}}H_2$)
(g) Methyl anion ($:\overline{C}H_3$)

1.47 Imagine describing the bonding in ammonia as arising by overlap of the half-filled *unhybridized* $2p_x$, $2p_y$, and $2p_z$ orbitals of nitrogen with the half-filled 1*s* orbitals of three hydrogen atoms.

(a) What kind of orbital would the unshared pair occupy?
(b) What would you expect the bond angles to be?

1.48 Of the orbital overlaps shown in the illustration, one is bonding, one is antibonding, and the third is nonbonding (neither bonding nor antibonding). Which orbital overlap corresponds to which interaction? Why?



(*a*) (*b*) (*c*)

1.49 Practice working with your *Learning By Modeling* software. Construct molecular models of ethane, ethylene, and acetylene, and compare them with respect to their geometry, bond angles, and C—H and C—C bond distances.

1.50 How many different structures (isomers) can you make that have the formula (a) CH_2Cl_2; (b) $Cl_2C{=}CH_2$; and (c) $ClCH{=}CHCl$?

1.51 Examine the molecular models of H_2, HF, CH_4, CH_3F, and CF_4. Find the calculated dipole moment of each compound, and examine their electrostatic potential maps.

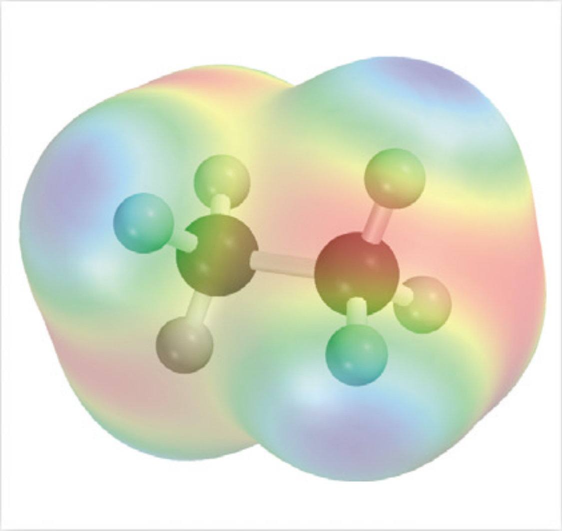
1.52 Examine the electrostatic potential map of ethylene. Where is the most negative region? What kinds of electrons are most responsible for the high electron density in this region? Are they electrons in σ bonds or in the π bond?

1.53 (a) Find the models of I—Br and Cl—F, and compare their calculated dipole moments. Which is more important, the difference in electronegativity between the bonded halogens or the length of the bond between them? [Remember that the dipole moment depends on both charge and distance ($\mu = e \times d$).]

(b) Compare the electrostatic potential maps of IBr and ClF. How do they correspond to the information provided by the dipole moment calculations?

1.54 Compare the dipole moments of cyanogen bromide ($BrC{\equiv}N$) and cyanogen chloride ($ClC{\equiv}N$). Which is larger? Why? What does this tell you about the electronegativity of the CN group?

1.55 Problem 1.8 concerned the charge distribution in methane (CH_4), chloromethane (CH_3Cl), and methyllithium (CH_3Li). Inspect molecular models of each of these compounds, and compare them with respect to how charge is distributed among the various atoms (carbon, hydrogen, chlorine, and lithium). Compare their electrostatic potential maps.



CHAPTER 2

ALKANES

Now that we've reviewed the various bonding models, we are ready to examine organic compounds in respect to their *structure, reactions, properties,* and *applications.* Were we to list the physical and chemical properties of each of the more than 8 million organic compounds separately, it would tax the capacity of even a powerful computer. Yet someone who is trained in organic chemistry can simply look at the structure of a substance and make reasonably confident predictions about its properties, including how it will behave in a chemical reaction.

Organic chemists associate particular structural units, called **functional groups,** with characteristic patterns of reactivity; they look at large molecules as collections of functional groups attached to nonreactive frameworks. Not only does this "functional group approach" have predictive power, but time and experience have shown that it organizes the material in a way that makes learning organic chemistry easier for most students.

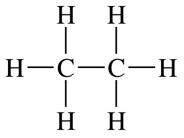
We'll begin the chapter with a brief survey of various kinds of *hydrocarbons*—compounds that contain only carbon and hydrogen—introduce some functional groups, then return to hydrocarbons to discuss *alkanes* in some detail. The names of alkanes may seem strange at first, but they form the foundation for the most widely accepted system of *organic nomenclature*. The fundamentals of this nomenclature system, the **IUPAC rules,** constitute one of the main topics of this chapter.

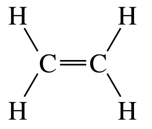
2.1 CLASSES OF HYDROCARBONS

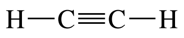
Hydrocarbons are compounds that contain only carbon and hydrogen and are divided into two main classes: **aliphatic** hydrocarbons and **aromatic** hydrocarbons. This classification dates from the nineteenth century, when organic chemistry was almost exclusively devoted to the study of materials from natural sources, and terms were coined that reflected a substance's origin. Two sources were fats and oils, and the word *aliphatic* was derived from the Greek word *aleiphar* ("fat"). Aromatic hydrocarbons, irrespective of their own odor, were typically obtained by chemical treatment of pleasant-smelling plant extracts.

Aliphatic hydrocarbons include three major groups: *alkanes, alkenes,* and *alkynes.* **Alkanes** are hydrocarbons in which all the bonds are single bonds, **alkenes** contain a carbon–carbon double bond, and **alkynes** contain a carbon–carbon triple bond. Examples of the three classes of aliphatic hydrocarbons are the two-carbon compounds *ethane, ethylene,* and *acetylene.*

Bonding in ethane, ethylene, and acetylene was discussed in Sections 1.16–1.18.

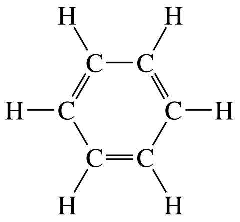

Ethane
(alkane)


Ethylene
(alkene)


Acetylene
(alkyne)

Another name for aromatic hydrocarbons is **arenes.** Arenes have properties that are much different from alkanes, alkenes, and alkynes. The most important aromatic hydrocarbon is *benzene.*

Bonding in benzene will be discussed in Section 11.5.


Benzene
(arene)

Many of the principles of organic chemistry can be developed by examining the series of hydrocarbons in the order: alkanes, alkenes, alkynes, and arenes. Alkanes are introduced in this chapter, alkenes in Chapters 5 and 6, alkynes in Chapter 9, and arenes in Chapters 11 and 12.

2.2 REACTIVE SITES IN HYDROCARBONS

A functional group is the structural unit responsible for a given molecule's reactivity under a particular set of conditions. It can be as small as a single hydrogen atom, or it can encompass several atoms. The functional group of an alkane is any one of its hydrogen substituents. A reaction that we shall discuss in Chapter 4 is one in which an alkane reacts with chlorine. For example:

$$\underset{\text{Ethane}}{CH_3CH_3} + \underset{\text{Chlorine}}{Cl_2} \longrightarrow \underset{\text{Chloroethane}}{CH_3CH_2Cl} + \underset{\text{Hydrogen chloride}}{HCl}$$

One of the hydrogen atoms of ethane is replaced by chlorine. This replacement of hydrogen by chlorine is a characteristic reaction of all alkanes and can be represented for the general case by the equation:

$$\underset{\text{Alkane}}{R{-}H} + \underset{\text{Chlorine}}{Cl_2} \longrightarrow \underset{\text{Alkyl chloride}}{R{-}Cl} + \underset{\text{Hydrogen chloride}}{HCl}$$

In the general equation the functional group (—H) is shown explicitly while the remainder of the alkane molecule is abbreviated as R. This is a commonly used notation which helps focus our attention on the functional group transformation without being distracted by the parts of the molecule that remain unaffected. A hydrogen atom in one alkane is very much like the hydrogen of any other alkane in its reactivity toward chlorine. Our ability to write general equations such as the one shown illustrates why the functional group approach is so useful in organic chemistry.

A hydrogen atom is a functional unit in alkenes and alkynes as well as in alkanes. These hydrocarbons, however, contain a second functional group as well. The carbon–carbon double bond is a functional group in alkenes, and the carbon–carbon triple bond is a functional group in alkynes.

A hydrogen atom is a functional group in arenes, and we represent arenes as ArH to reflect this. What will become apparent when we discuss the reactions of arenes, however, is that their chemistry is much richer than that of alkanes, and it is therefore more appropriate to consider the ring in its entirety as the functional group.

2.3 THE KEY FUNCTIONAL GROUPS

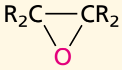
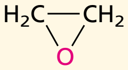
As a class, alkanes are not particularly reactive compounds, and the H in RH is not a particularly reactive functional group. Indeed, when a group other than hydrogen is present on an alkane framework, that group is almost always the functional group. Table 2.1 lists examples of some compounds of this type. All will be discussed in later chapters.

Some of the most important families of organic compounds, those that contain the carbonyl group (C═O), deserve separate mention and are listed in Table 2.2 Carbonyl-containing compounds rank among the most abundant and biologically significant classes of naturally occurring substances.

Carbonyl group chemistry is discussed in a block of five chapters (Chapters 17–21).

PROBLEM 2.1 Many compounds contain more than one functional group. The structure of *prostaglandin E_1*, a hormone that regulates the relaxation of smooth muscles, contains two different kinds of carbonyl groups. Classify each one (aldehyde, ketone, carboxylic acid, ester, amide, acyl chloride, or carboxylic acid anhydride).

TABLE 2.1 Functional Groups in Some Important Classes of Organic Compounds

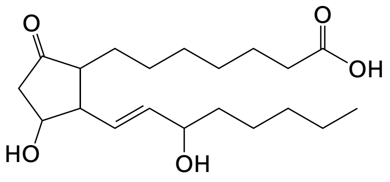
Class	Generalized abbreviation	Representative example	Name of example*
Alcohol	ROH	CH_3CH_2OH	Ethanol
Alkyl halide	RCl	CH_3CH_2Cl	Chloroethane
Amine[†]	RNH_2	$CH_3CH_2NH_2$	Ethanamine
Epoxide			Oxirane
Ether	ROR	$CH_3CH_2OCH_2CH_3$	Diethyl ether
Nitrile	$RC\equiv N$	$CH_3CH_2C\equiv N$	Propanenitrile
Nitroalkane	RNO_2	$CH_3CH_2NO_2$	Nitroethane
Thiol	RSH	CH_3CH_2SH	Ethanethiol

*Most compounds have more than one acceptable name.

[†] The example given is a *primary* amine (RNH_2). *Secondary* amines have the general structure R_2NH; *tertiary* amines are R_3N.

TABLE 2.2 Classes of Compounds That Contain a Carbonyl Group

Class	Generalized abbreviation	Representative example	Name of example
Aldehyde	$\mathrm{R\overset{O}{\overset{\|}{C}}H}$	$\mathrm{CH_3\overset{O}{\overset{\|}{C}}H}$	Ethanal
Ketone	$\mathrm{R\overset{O}{\overset{\|}{C}}R}$	$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_3}$	2-Propanone
Carboxylic acid	$\mathrm{R\overset{O}{\overset{\|}{C}}OH}$	$\mathrm{CH_3\overset{O}{\overset{\|}{C}}OH}$	Ethanoic acid
Carboxylic acid derivatives:			
Acyl halide	$\mathrm{R\overset{O}{\overset{\|}{C}}X}$	$\mathrm{CH_3\overset{O}{\overset{\|}{C}}Cl}$	Ethanoyl chloride
Acid anhydride	$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}R}$	$\mathrm{CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3}$	Ethanoic anhydride
Ester	$\mathrm{R\overset{O}{\overset{\|}{C}}OR}$	$\mathrm{CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3}$	Ethyl ethanoate
Amide	$\mathrm{R\overset{O}{\overset{\|}{C}}NR_2}$	$\mathrm{CH_3\overset{O}{\overset{\|}{C}}NH_2}$	Ethanamide



Prostaglandin E_1

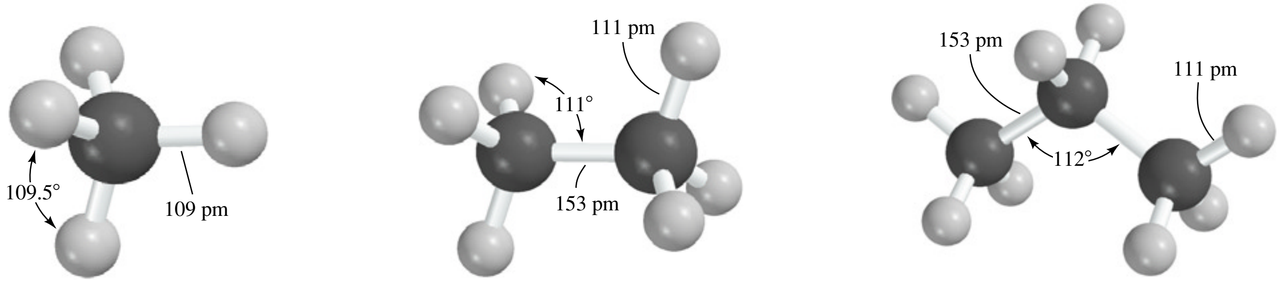
The reactions of the carbonyl group feature prominently in *organic synthesis*—the branch of organic chemistry that plans and carries out the preparation of compounds of prescribed structure.

2.4 INTRODUCTION TO ALKANES: METHANE, ETHANE, AND PROPANE

See the boxed essay: *"Methane and the Biosphere"* that accompanies this section.

Alkanes have the general molecular formula C_nH_{2n+2}. The simplest one, **methane** (CH_4), is also the most abundant. Large amounts are present in our atmosphere, in the ground, and in the oceans. Methane has been found on Jupiter, Saturn, Uranus, Neptune, and Pluto, and even on Halley's Comet.

Ethane (C_2H_6: CH_3CH_3) and **propane** (C_3H_8: $CH_3CH_2CH_3$) are second and third, respectively, to methane in many ways. Ethane is the alkane next to methane in structural simplicity, followed by propane. Ethane ($\approx$ 10%) is the second and propane ($\approx$ 5%) the third most abundant component of natural gas, which is $\approx$ 75% methane. The characteristic odor of natural gas we use for heating our homes and cooking comes from



Methane Ethane Propane

FIGURE 2.1 Structures of methane, ethane, and propane showing bond distances and bond angles.

trace amounts of unpleasant-smelling sulfur-containing compounds such as ethanethiol (see Table 2.1) that are deliberately added to it in order to warn us of potentially dangerous leaks. Natural gas is colorless and nearly odorless, as are methane, ethane, and propane.

Methane is the lowest boiling alkane, followed by ethane, then propane.

	CH_4	CH_3CH_3	$CH_3CH_2CH_3$
	Methane	Ethane	Propane
Boiling point:	−160°C	−89°C	−42°C

Boiling points cited in this text are at 1 atm (760 mm of mercury) unless otherwise stated.

This will generally be true as we proceed to look at other alkanes; as the number of carbon atoms increases, so does the boiling point. All the alkanes with four carbons or less are gases at room temperature and atmospheric pressure. With the highest boiling point of the three, propane is the easiest one to liquefy. We are all familiar with "propane tanks." These are steel containers in which a propane-rich mixture of hydrocarbons called *liquefied petroleum gas* (LPG) is maintained in a liquid state under high pressure as a convenient clean-burning fuel.

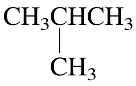
The structural features of methane, ethane, and propane are summarized in Figure 2.1. All of the carbon atoms are *sp*^{3}-hybridized, all of the bonds are σ bonds, and the bond angles at carbon are close to tetrahedral.

Use your *Learning By Modeling* software to reproduce the models shown in Figure 2.1 so that you can better view their three-dimensional shapes.

2.5 ISOMERIC ALKANES: THE BUTANES

Methane is the only alkane of molecular formula CH_4, ethane the only one that is C_2H_6, and propane the only one that is C_3H_8. Beginning with C_4H_{10}, however, constitutional isomers (Section 1.8) are possible; two alkanes have this particular molecular formula. In one, called ***n*-butane,** four carbons are joined in a continuous chain. The *n* in *n*-butane stands for "normal" and means that the carbon chain is unbranched. The second isomer has a branched carbon chain and is called **isobutane.**

$CH_3CH_2CH_2CH_3$



$$\underset{\displaystyle CH_3}{CH_3\underset{|}{C}HCH_3}$$

or $(CH_3)_3CH$

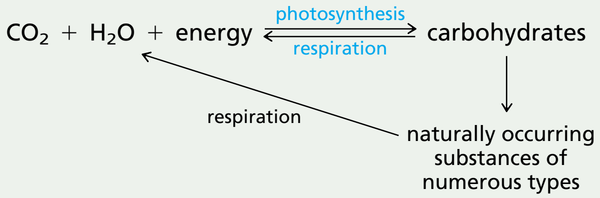
	n-Butane	Isobutane
Boiling point:	−0.4°C	−10.2°C
Melting point:	−139°C	−160.9°C

Make molecular models of the two isomers of C_4H_{10}.

As noted earlier (Section 1.16), CH_3 is called a *methyl* group. In addition to having methyl groups at both ends, *n*-butane contains two CH_2, or **methylene** groups. Isobutane contains three methyl groups bonded to a CH unit. The CH unit is called a **methine** group.

METHANE AND THE BIOSPHERE*

One of the things that environmental scientists do is to keep track of important elements in the biosphere—in what form do these elements normally occur, to what are they transformed, and how are they returned to their normal state? Careful studies have given clear, although complicated, pictures of the "nitrogen cycle," the "sulfur cycle," and the "phosphorus cycle," for example. The "carbon cycle," begins and ends with atmospheric carbon dioxide. It can be represented in an abbreviated form as:



Methane is one of literally millions of compounds in the carbon cycle, but one of the most abundant. It is formed when carbon-containing compounds decompose in the absence of air (*anaerobic* conditions). The organisms that bring this about are called *methanoarchaea.* Cells can be divided into three types: *archaea, bacteria,* and *eukarya.* Methanoarchaea are one kind of archaea and may rank among the oldest living things on earth. They can convert a number of carbon-containing compounds, including carbon dioxide and acetic acid, to methane.

Virtually anywhere water contacts organic matter in the absence of air is a suitable place for methanoarchaea to thrive—at the bottom of ponds, bogs, and rice fields, for example. *Marsh gas (swamp gas)* is mostly methane. Methanoarchaea live inside termites and grass-eating animals. One source quotes 20 L/day as the methane output of a large cow.

The scale on which methanoarchaea churn out methane, estimated to be 10^{11}–10^{12} lb/year, is enormous. About 10% of this amount makes its way into the atmosphere, but most of the rest simply ends up completing the carbon cycle. It exits the anaerobic environment where it was formed and enters the aerobic world where it is eventually converted to carbon dioxide by a variety of processes.

When we consider sources of methane we have to add "old" methane, methane that was formed millions of years ago but became trapped beneath the earth's surface, to the "new" methane just described. *Firedamp,* an explosion hazard to miners, occurs in layers of coal and is mostly methane. Petroleum deposits, formed by microbial decomposition of plant material under anaerobic conditions, are always accompanied by pockets of natural gas, which is mostly methane.

An interesting thing happens when trapped methane leaks from sites under the deep ocean floor. If the pressure is high enough (50 atm) and the water cold enough (4°C), the methane doesn't simply bubble to the surface. Individual methane molecules become trapped inside clusters of 6–18 water molecules forming *methane clathrates* or *methane hydrates.* Aggregates of these clathrates stay at the bottom of the ocean in what looks like a lump of dirty ice. Ice that burns. Far from being mere curiosities, methane clathrates are potential sources of energy on a scale greater than that of all known oil reserves combined. At present, it is not economically practical to extract the methane, however.

Methane clathrates have received recent attention from a different segment of the scientific community. While diving in the Gulf of Mexico in 1997, a research team of biologists and environmental scientists were surprised to find a new species of worm grazing on the mound of a methane clathrate. What were these worms feeding on? Methane? Bacteria that live on the methane? A host of questions having to do with deep-ocean ecosystems suddenly emerged. Stay tuned.

*The biosphere is the part of the earth where life is; it includes the surface, the oceans, and the lower atmosphere.

n-Butane and isobutane have the same molecular formula but differ in the order in which their atoms are connected. They are *constitutional isomers* of each other (Section 1.8). Because they are different in structure, they can have different properties. Both are gases at room temperature, but *n*-butane boils almost 10°C higher than isobutane and has a melting point that is over 20°C higher.

The bonding in *n*-butane and isobutane continues the theme begun with methane, ethane, and propane. All of the carbon atoms are sp^3-hybridized, all of the bonds are σ bonds, and the bond angles at carbon are close to tetrahedral. This generalization holds for all alkanes regardless of the number of carbons they have.

"Butane" lighters contain about 5% *n*-butane and 95% isobutane in a sealed container. The pressure produced by the two compounds (about 3 atm) is enough to keep them in the liquid state until opening a small valve emits a fine stream of the vaporized mixture across a spark which ignites it.

2.6 HIGHER *n*-ALKANES

n-Alkanes are alkanes that have an unbranched carbon chain. ***n*-Pentane** and ***n*-hexane** are *n*-alkanes possessing five and six carbon atoms, respectively.

$CH_3CH_2CH_2CH_2CH_3$ $\quad$ $CH_3CH_2CH_2CH_2CH_2CH_3$

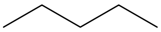
n-Pentane $\quad$ *n*-Hexane

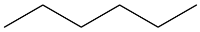
Their condensed structural formulas can be abbreviated even more by indicating within parentheses the number of methylene groups in the chain. Thus, *n*-pentane may be written as $CH_3(CH_2)_3CH_3$ and *n*-hexane as $CH_3(CH_2)_4CH_3$. This shortcut is especially convenient with longer-chain alkanes. The laboratory synthesis of the "ultralong" alkane $CH_3(CH_2)_{388}CH_3$ was achieved in 1985; imagine trying to write a structural formula for this compound in anything other than an abbreviated way!

PROBLEM 2.2 An *n*-alkane of molecular formula $C_{28}H_{58}$ has been isolated from a certain fossil plant. Write a condensed structural formula for this alkane.

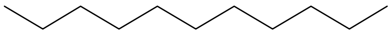
n-Alkanes have the general formula $CH_3(CH_2)_xCH_3$ and are said to belong to a **homologous series** of compounds. A homologous series is one in which successive members differ by a $—CH_2—$ group.

Unbranched alkanes are sometimes referred to as "straight-chain alkanes," but, as we'll see in Chapter 3, their chains are not straight but instead tend to adopt the "zigzag" shape portrayed in the bond-line formulas introduced in Section 1.7.


Bond-line formula of *n*-pentane


Bond-line formula of *n*-hexane

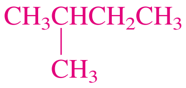
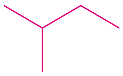
PROBLEM 2.3 Much of the communication between insects involves chemical messengers called *pheromones.* A species of cockroach secretes a substance from its mandibular glands that alerts other cockroaches to its presence and causes them to congregate. One of the principal components of this *aggregation pheromone* is the alkane shown in the bond-line formula that follows. Give the molecular formula of this substance, and represent it by a condensed formula.



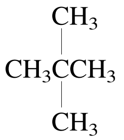
2.7 THE C_5H_{12} ISOMERS

Three isomeric alkanes have the molecular formula C_5H_{12}. The unbranched isomer is, as we have seen, *n*-pentane. The isomer with a single methyl branch is called **isopentane.** The third isomer has a three-carbon chain with two methyl branches. It is called **neopentane.**

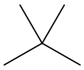
n-Pentane: $CH_3CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_3CH_3$ or 

Isopentane:  $\underset{\displaystyle CH_3}{CH_3\overset{}{C}HCH_2CH_3}$ or $(CH_3)_2CHCH_2CH_3$ or 

Make molecular models of the three isomers of C_5H_{12}.

Neopentane: 

$$\begin{array}{c} CH_3 \\ | \\ CH_3CCH_3 \\ | \\ CH_3 \end{array}$$

or $(CH_3)_4C$ or 

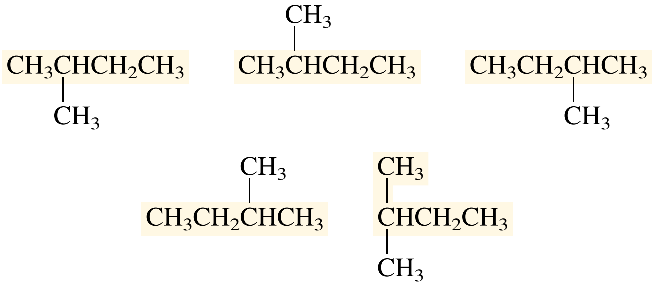
The number of C_nH_{2n+2} isomers has been calculated for values of *n* from 1 to 400 and the comment made that the number of isomers of $C_{167}H_{336}$ exceeds the number of particles in the known universe (10^{80}). These observations and the historical background of isomer calculation are described in a paper in the April 1989 issue of the *Journal of Chemical Education* (pp. 278–281).

Table 2.3 presents the number of possible alkane isomers as a function of the number of carbon atoms they contain. As the table shows, the number of isomers increases enormously with the number of carbon atoms and raises two important questions:

1. How can we tell when we have written all the possible isomers corresponding to a particular molecular formula?
2. How can we name alkanes so that each one has a unique name?

The answer to the first question is that you cannot easily calculate the number of isomers. The data in Table 2.3 were determined by a mathematician who concluded that there was no simple expression from which to calculate the number of isomers. The best way to ensure that you have written all the isomers of a particular molecular formula is to work systematically, beginning with the unbranched chain and then shortening it while adding branches one by one. It is essential that you be able to recognize when two different-looking structural formulas are actually the same molecule written in different ways. The key point is the *connectivity* of the carbon chain. For example, the following group of structural formulas do *not* represent different compounds; they are just a portion of the many ways we could write a structural formula for isopentane. Each one has a continuous chain of four carbons with a methyl branch located one carbon from the end of the chain.

The fact that all of these structural formulas represent the same substance can be clearly seen by making molecular models.



$$CH_3\underset{\substack{|\\ CH_3}}{CH}CH_2CH_3 \qquad CH_3\overset{\substack{CH_3\\ |}}{CH}CH_2CH_3 \qquad CH_3CH_2\underset{\substack{|\\ CH_3}}{CH}CH_3$$

$$CH_3CH_2\overset{\substack{CH_3\\ |}}{CH}CH_3 \qquad \begin{array}{l} CH_3 \\ | \\ CHCH_2CH_3 \\ | \\ CH_3 \end{array}$$

TABLE 2.3 The Number of Constitutionally Isomeric Alkanes of Particular Molecular Formulas

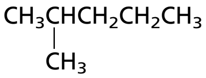
Molecular formula	Number of constitutional isomers
CH_4	1
C_2H_6	1
C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{40}H_{82}$	62,491,178,805,831

PROBLEM 2.4 Write condensed and bond-line formulas for the five isomeric C_6H_{14} alkanes.

SAMPLE SOLUTION When writing isomeric alkanes, it is best to begin with the unbranched isomer.

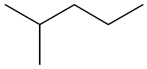
$CH_3CH_2CH_2CH_2CH_2CH_3$ or

Next, remove a carbon from the chain and use it as a one-carbon (methyl) branch at the carbon atom next to the end of the chain.



$$\begin{array}{l}CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3\end{array}$$

or



Now, write structural formulas for the remaining three isomers. Be sure that each one is a unique compound and not simply a different representation of one written previously.

The answer to the second question—how to provide a name that is unique to a particular structure—is presented in the following section. It is worth noting, however, that being able to name compounds in a *systematic* way is a great help in deciding whether two structural formulas represent isomeric substances or are the same compound represented in two different ways. By following a precise set of rules, one will always get the same systematic name for a compound, regardless of how it is written. Conversely, two different compounds will always have different names.

2.8 IUPAC NOMENCLATURE OF UNBRANCHED ALKANES

Nomenclature in organic chemistry is of two types: **common** (or "trivial") and **systematic.** Some common names existed long before organic chemistry became an organized branch of chemical science. Methane, ethane, propane, *n*-butane, isobutane, *n*-pentane, isopentane, and neopentane are common names. One simply memorizes the name that goes with a compound in just the same way that one matches names with faces. So long as there are only a few names and a few compounds, the task is manageable. But there are millions of organic compounds already known, and the list continues to grow! A system built on common names is not adequate to the task of communicating structural information. Beginning in 1892, chemists developed a set of rules for naming organic compounds based on their structures, which we now call the **IUPAC rules,** in which *IUPAC* stands for the "International Union of Pure and Applied Chemistry." (See the accompanying box, "A Brief History of Systematic Organic Nomenclature.")

The IUPAC rules assign names to unbranched alkanes as shown in Table 2.4. Methane, ethane, propane, and butane are retained for CH_4, CH_3CH_3, $CH_3CH_2CH_3$, and $CH_3CH_2CH_2CH_3$, respectively. Thereafter, the number of carbon atoms in the chain is specified by a Latin or Greek prefix preceding the suffix *-ane,* which identifies the compound as a member of the alkane family. Notice that the prefix *n-* is not part of the IUPAC system. The IUPAC name for $CH_3CH_2CH_2CH_3$ is butane, not *n*-butane.

A more detailed account of the history of organic nomenclature may be found in the article "The Centennial of Systematic Organic Nomenclature" in the November 1992 issue of the *Journal of Chemical Education* (pp. 863–865).

PROBLEM 2.5 Refer to Table 2.4 as needed to answer the following questions:

(a) Beeswax contains 8–9% hentriacontane. Write a condensed structural formula for hentriacontane.

(b) Octacosane has been found to be present in a certain fossil plant. Write a condensed structural formula for octacosane.

TABLE 2.4 IUPAC Names of Unbranched Alkanes

Number of carbon atoms	Name	Number of carbon atoms	Name	Number of carbon atoms	Name
1	Methane	11	Undecane	21	Henicosane
2	Ethane	12	Dodecane	22	Docosane
3	Propane	13	Tridecane	23	Tricosane
4	Butane	14	Tetradecane	24	Tetracosane
5	Pentane	15	Pentadecane	30	Triacontane
6	Hexane	16	Hexadecane	31	Hentriacontane
7	Heptane	17	Heptadecane	32	Dotriacontane
8	Octane	18	Octadecane	40	Tetracontane
9	Nonane	19	Nonadecane	50	Pentacontane
10	Decane	20	Icosane*	100	Hectane

*Spelled "eicosane" prior to 1979 version of IUPAC rules.

(c) What is the IUPAC name of the alkane described in Problem 2.3 as a component of the cockroach aggregation pheromone?

SAMPLE SOLUTION (a) Note in Table 2.4 that hentriacontane has 31 carbon atoms. All the alkanes in Table 2.4 have unbranched carbon chains. Hentriacontane has the condensed structural formula $CH_3(CH_2)_{29}CH_3$.

In Problem 2.4 you were asked to write structural formulas for the five isomeric alkanes of molecular formula C_6H_{14}. In the next section you will see how the IUPAC rules generate a unique name for each isomer.

2.9 APPLYING THE IUPAC RULES: THE NAMES OF THE C_6H_{14} ISOMERS

You might find it helpful to make molecular models of all the C_6H_{14} isomers.

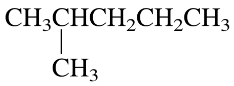
We can present and illustrate the most important of the IUPAC rules for alkane nomenclature by naming the five C_6H_{14} isomers. By definition (Table 2.4), the unbranched C_6H_{14} isomer is hexane.

$$CH_3CH_2CH_2CH_2CH_2CH_3$$

IUPAC name: hexane

(common name: *n*-hexane)

The IUPAC rules name branched alkanes as *substituted derivatives* of the unbranched alkanes listed in Table 2.4. Consider the C_6H_{14} isomer represented by the structure



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$$

Step 1

Pick out the *longest continuous carbon chain,* and find the IUPAC name in Table 2.4 that corresponds to the unbranched alkane having that number of carbons. This is the parent alkane from which the IUPAC name is to be derived.

A BRIEF HISTORY OF SYSTEMATIC ORGANIC NOMENCLATURE

The first successful formal system of chemical nomenclature was advanced in France in 1787 to replace the babel of common names which then plagued the science. Hydrogen (instead of "inflammable air") and oxygen (instead of "vital air") are just two of the substances that owe their modern names to the proposals described in the *Méthode de nomenclature chimique.* It was then that important compounds such as sulfuric, phosphoric, and carbonic acid and their salts were named. The guidelines were more appropriate to inorganic compounds; it was not until the 1830s that names reflecting chemical composition began to appear in organic chemistry.

In 1889, a group with the imposing title of the International Commission for the Reform of Chemical Nomenclature was organized, and this group, in turn, sponsored a meeting of 34 prominent European chemists in Switzerland in 1892. Out of this meeting arose a system of organic nomenclature known as the **Geneva rules.** The principles on which the Geneva rules were based are the forerunners of our present system.

A second international conference was held in 1911, but the intrusion of World War I prevented any substantive revisions of the Geneva rules. The International Union of Chemistry was established in 1930 and undertook the necessary revision leading to publication in 1930 of what came to be known as the **Liège rules.**

After World War II, the International Union of Chemistry became the International Union of Pure and Applied Chemistry (known in the chemical community as the *IUPAC*). Since 1949, the IUPAC has issued reports on chemical nomenclature on a regular basis. The most recent **IUPAC rules** for organic chemistry were published in 1993. The IUPAC rules often offer several different ways to name a single compound. Thus although it is true that no two compounds can have the same name, it is incorrect to believe that there is only a single IUPAC name for a particular compound.

The 1993 IUPAC recommendations and their more widely used 1979 predecessors may both be accessed at the same web site:

www.acdlabs.com/iupac/nomenclature

The IUPAC rules are not the only nomenclature system in use today. Chemical Abstracts Service surveys all the world's leading scientific journals that publish papers relating to chemistry and publishes brief abstracts of those papers. The publication *Chemical Abstracts* and its indexes are absolutely essential to the practice of chemistry. For many years *Chemical Abstracts* nomenclature was very similar to IUPAC nomenclature, but the tremendous explosion of chemical knowledge in recent years has required *Chemical Abstracts* to modify its nomenclature so that its indexes are better adapted to computerized searching. This means that whenever feasible, a compound has a single *Chemical Abstracts* name. Unfortunately, this *Chemical Abstracts* name may be different from any of the several IUPAC names. In general, it is easier to make the mental connection between a chemical structure and its IUPAC name than its *Chemical Abstracts* name.

It is worth noting that the **generic name** of a drug is not directly derived from systematic nomenclature. Furthermore, different pharmaceutical companies will call the same drug by their own trade name, which is different from its generic name. Generic names are invented on request (for a fee) by the U.S. Adopted Names Council, a private organization founded by the American Medical Association, the American Pharmaceutical Association, and the U.S. Pharmacopeial Convention.

In this case, the longest continuous chain has *five* carbon atoms; the compound is named as a derivative of pentane. The key word here is *continuous.* It does not matter whether the carbon skeleton is drawn in an extended straight-chain form or in one with many bends and turns. All that matters is the number of carbons linked together in an uninterrupted sequence.

Step 2

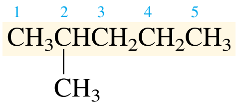
Identify the substituent groups attached to the parent chain.

The parent pentane chain bears a methyl (CH_3) group as a substituent.

Step 3

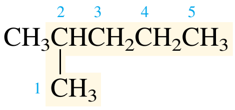
Number the longest continuous chain in the direction that gives the lowest number to the substituent group at the first point of branching.

The numbering scheme



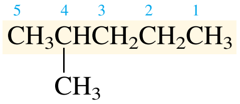
$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$

is equivalent to



$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$

Both schemes count five carbon atoms in their longest continuous chain and bear a methyl group as a substituent at the second carbon. An alternative numbering sequence that begins at the other end of the chain is incorrect:

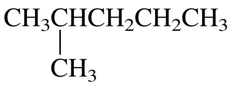


$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$

(methyl group attached to C-4)

Step 4

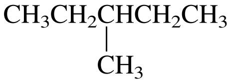
Write the name of the compound. The parent alkane is the last part of the name and is preceded by the names of the substituent groups and their numerical locations **(locants).** Hyphens separate the locants from the words.



$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$

IUPAC name: 2-methylpentane

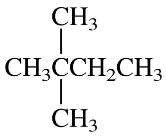
The same sequence of four steps gives the IUPAC name for the isomer that has its methyl group attached to the middle carbon of the five-carbon chain.



$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_3$

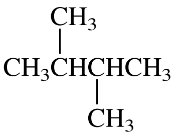
IUPAC name: 3-methylpentane

Both remaining C_6H_{14} isomers have two methyl groups as substituents on a four-carbon chain. Thus the parent chain is butane. When the same substituent appears more than once, use the multiplying prefixes *di-, tri-, tetra-,* and so on. A separate locant is used for each substituent, and the locants are separated from each other by commas and from the words by hyphens.



$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}CH_2CH_3$

IUPAC name: 2,2-dimethylbutane



$CH_3\overset{\displaystyle CH_3}{\overset{|}{C}}H\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$

IUPAC name: 2,3-dimethylbutane

PROBLEM 2.6 Phytane is a naturally occurring alkane produced by the alga *Spirogyra* and is a constituent of petroleum. The IUPAC name for phytane is 2,6,10,14-tetramethylhexadecane. Write a structural formula for phytane.

PROBLEM 2.7 Derive the IUPAC names for

(a) The isomers of C_4H_{10}

(b) The isomers of C_5H_{12}

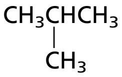
(c) $(CH_3)_3CCH_2CH(CH_3)_2$

(d) $(CH_3)_3CC(CH_3)_3$

SAMPLE SOLUTION (a) There are two C_4H_{10} isomers. Butane (see Table 2.4) is the IUPAC name for the isomer that has an unbranched carbon chain. The other isomer has three carbons in its longest continuous chain with a methyl branch at the central carbon; its IUPAC name is 2-methylpropane.

$CH_3CH_2CH_2CH_3$

IUPAC name: butane
(common name: *n*-butane)



$$\begin{array}{c} CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3 \end{array}$$

IUPAC name: 2-methylpropane
(common name: isobutane)

So far, the only branched alkanes that we've named have methyl groups attached to the main chain. What about groups other than CH_3? What do we call these groups, and how do we name alkanes that contain them?

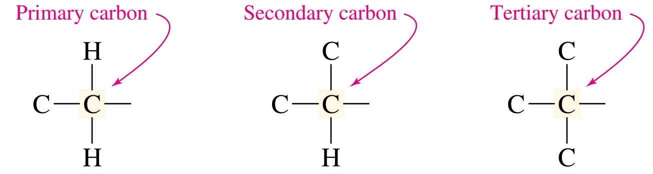
2.10 ALKYL GROUPS

An alkyl group lacks one of the hydrogen substituents of an alkane. A methyl group (CH_3—) is an alkyl group derived from methane (CH_4). Unbranched alkyl groups in which the point of attachment is at the end of the chain are named in IUPAC nomenclature by replacing the *-ane* endings of Table 2.4 by *-yl.*

CH_3CH_2—	$CH_3(CH_2)_5CH_2$—	$CH_3(CH_2)_{16}CH_2$—
Ethyl group	**Heptyl** group	**Octadecyl** group

The dash at the end of the chain represents a potential point of attachment for some other atom or group.

Carbon atoms are classified according to their degree of substitution by other carbons. A **primary** carbon is one that is *directly* attached to one other carbon. Similarly, a **secondary** carbon is directly attached to two other carbons, a **tertiary** carbon to three, and a **quaternary** carbon to four. Alkyl groups are designated as primary, secondary, or tertiary according to the degree of substitution of the carbon at the potential point of attachment.



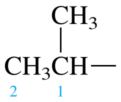
Primary alkyl group Secondary alkyl group Tertiary alkyl group

Ethyl (CH_3CH_2—), heptyl [$CH_3(CH_2)_5CH_2$—], and octadecyl [$CH_3(CH_2)_{16}CH_2$—] are examples of primary alkyl groups.

Branched alkyl groups are named by using the longest continuous chain that begins at the point of attachment as the base name. Thus, the systematic names of the two C_3H_7 alkyl groups are propyl and 1-methylethyl. Both are better known by their common names, *n*-propyl and isopropyl, respectively.

$CH_3CH_2CH_2$—

Propyl group
(common name: *n*-propyl)



$$\underset{2}{CH_3}\underset{1}{\overset{\displaystyle CH_3}{\overset{|}{C}}H}— \quad \text{or} \quad (CH_3)_2CH—$$

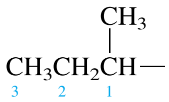
1-Methylethyl group
(common name: isopropyl)

An isopropyl group is a *secondary* alkyl group. Its point of attachment is to a secondary carbon atom, one that is directly bonded to two other carbons.

The C_4H_9 alkyl groups may be derived either from the unbranched carbon skeleton of butane or from the branched carbon skeleton of isobutane. Those derived from butane are the butyl (*n*-butyl) group and the 1-methylpropyl (*sec*-butyl) group.

$CH_3CH_2CH_2CH_2—$

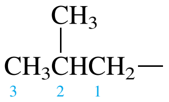
Butyl group
(common name: *n*-butyl)



$$\underset{3}{CH_3}\underset{2}{CH_2}\underset{1}{\overset{\overset{\displaystyle CH_3}{|}}{CH}}—$$

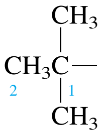
1-Methylpropyl group
(common name: *sec*-butyl)

Those derived from isobutane are the 2-methylpropyl (isobutyl) group and the 1,1-dimethylethyl (*tert*-butyl) group. Isobutyl is a primary alkyl group because its potential point of attachment is to a primary carbon. *tert*-Butyl is a tertiary alkyl group because its potential point of attachment is to a tertiary carbon.



$$\underset{3}{CH_3}\underset{2}{\overset{\overset{\displaystyle CH_3}{|}}{CH}}\underset{1}{CH_2}— \quad \text{or} \quad (CH_3)_2CHCH_2—$$

2-Methylpropyl group
(common name: isobutyl)

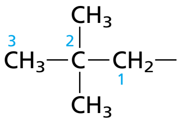


$$\underset{2}{CH_3}\underset{1}{\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}— \quad \text{or} \quad (CH_3)_3C—$$

1,1-Dimethylethyl group
(common name: *tert*-butyl)

PROBLEM 2.8 Give the structures and IUPAC names of all the C_5H_{11} alkyl groups, and identify them as primary, secondary, or tertiary alkyl groups, as appropriate.

SAMPLE SOLUTION Consider the alkyl group having the same carbon skeleton as $(CH_3)_4C$. All the hydrogens are equivalent, so that replacing any one of them by a potential point of attachment is the same as replacing any of the others.



$$\overset{3}{CH_3}—\overset{\overset{\displaystyle CH_3}{|\,2}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—\underset{1}{CH_2}— \quad \text{or} \quad (CH_3)_3CCH_2—$$

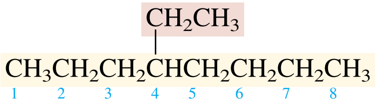
Numbering always begins at the point of attachment and continues through the longest continuous chain. In this case the chain is three carbons and there are two methyl groups at C-2. The IUPAC name of this alkyl group is **2,2-dimethylpropyl.** (The common name for this group is *neopentyl.*) It is a *primary* alkyl group because the carbon that bears the potential point of attachment (C-1) is itself directly bonded to one other carbon.

The names and structures of the most frequently encountered alkyl groups are given on the inside back cover.

In addition to methyl and ethyl groups, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, *tert*-butyl, and neopentyl groups will appear often throughout this text. Although these are common names, they have been integrated into the IUPAC system and are an acceptable adjunct to systematic nomenclature. You should be able to recognize these groups on sight and to give their structures when needed.

2.11 IUPAC NAMES OF HIGHLY BRANCHED ALKANES

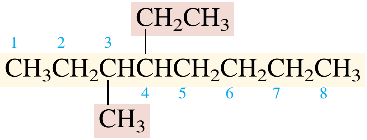
By combining the basic principles of IUPAC notation with the names of the various alkyl groups, we can develop systematic names for highly branched alkanes. We'll start with the following alkane, name it, then increase its complexity by successively adding methyl groups at various positions.



$$CH_3CH_2CH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2CH_2CH_3$$

As numbered on the structural formula, the longest continuous chain contains eight carbons, and so the compound is named as a derivative of octane. Numbering begins at the end nearest the branch, and so the ethyl substituent is located at C-4, and the name of the alkane is **4-ethyloctane.**

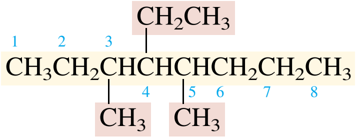
What happens to the IUPAC name when a methyl replaces one of the hydrogens at C-3?



$$CH_3CH_2\underset{CH_3}{\underset{|}{C}}H\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2CH_2CH_3$$

The compound becomes an octane derivative that bears a C-3 methyl group and a C-4 ethyl group. *When two or more different substituents are present, they are listed in alphabetical order in the name.* The IUPAC name for this compound is **4-ethyl-3-methyloctane.**

Replicating prefixes such as *di-*, *tri-*, and *tetra-* (see Section 2.9) are used as needed but are ignored when alphabetizing. Adding a second methyl group to the original structure, at C-5, for example, converts it to **4-ethyl-3,5-dimethyloctane.**

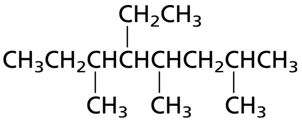


$$CH_3CH_2\underset{CH_3}{\underset{|}{C}}H\overset{CH_2CH_3}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$$

Italicized prefixes such as *sec-* and *tert-* are ignored when alphabetizing except when they are compared with each other. *tert*-Butyl precedes isobutyl, and *sec*-butyl precedes *tert*-butyl.

PROBLEM 2.9 Give an acceptable IUPAC name for each of the following alkanes:

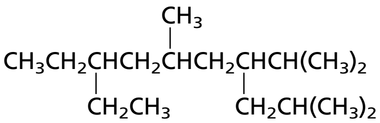
(a)



$$CH_3CH_2\underset{CH_3}{\underset{|}{C}}H\overset{CH_2CH_3}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}HCH_2\underset{CH_3}{\underset{|}{C}}HCH_3$$

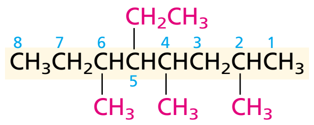
(b) $(CH_3CH_2)_2CHCH_2CH(CH_3)_2$

(c)



$$CH_3CH_2\underset{CH_2CH_3}{\underset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}HCH_2\underset{CH_2CH(CH_3)_2}{\underset{|}{C}}HCH(CH_3)_2$$

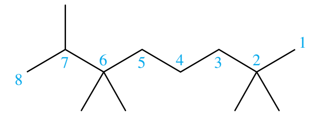
SAMPLE SOLUTION (a) This problem extends the preceding discussion by adding a third methyl group to 4-ethyl-3,5-dimethyloctane, the compound just described. It is, therefore, an *ethyltrimethyloctane.* Notice, however, that the numbering sequence needs to be changed in order to adhere to the rule of numbering from the end of the chain nearest the first branch. When numbered properly, this compound has a methyl group at C-2 as its first-appearing substituent.



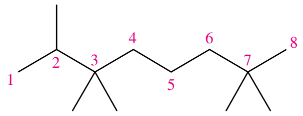
$$\overset{8}{C}H_3\overset{7}{C}H_2\underset{CH_3}{\overset{6}{C}H}\overset{CH_2CH_3}{\underset{5}{C}H}\underset{CH_3}{\overset{4}{C}H}\overset{3}{C}H_2\underset{CH_3}{\overset{2}{C}H}\overset{1}{C}H_3$$

5-Ethyl-2,4,6-trimethyloctane

An additional feature of IUPAC nomenclature that concerns the direction of numbering is called the "first point of difference" rule. Consider the two directions in which the following alkane may be numbered:



2,2,6,6,7-Pentamethyloctane
(correct)



2,3,3,7,7-Pentamethyloctane
(incorrect!)

When deciding on the proper direction, a point of difference occurs when one order gives a lower locant than another. Thus, while 2 is the first locant in both numbering schemes, the tie is broken at the second locant, and the rule favors 2,2,6,6,7, which has 2 as its second locant, whereas 3 is the second locant in 2,3,3,7,7. Notice that locants are *not* added together, but examined one by one.

Finally, when equal locants are generated from two different numbering directions, the direction is chosen which gives the lower number to the substituent that appears first in the name. (Remember, substituents are listed alphabetically.)

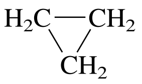
Tabular summaries of the IUPAC rules for alkane and alkyl group nomenclature appear on pages 81–83.

The IUPAC nomenclature system is inherently logical and incorporates healthy elements of common sense into its rules. Granted, some long, funny-looking, hard-to-pronounce names are generated. Once one knows the code (rules of grammar) though, it becomes a simple matter to convert those long names to unique structural formulas.

2.12 CYCLOALKANE NOMENCLATURE

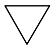
Cycloalkanes are one class of *alicyclic* (*ali*phatic *cyclic*) hydrocarbons.

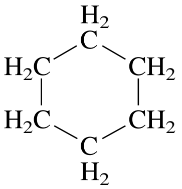
Cycloalkanes are alkanes that contain a ring of three or more carbons. They are frequently encountered in organic chemistry and are characterized by the molecular formula C_nH_{2n}. Some examples include:



Cyclopropane

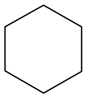
usually represented as





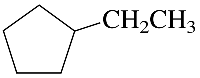
Cyclohexane

usually represented as

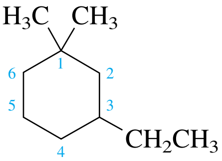


If you make a molecular model of cyclohexane, you will find its shape to be very different from a planar hexagon. We'll discuss the reasons why in Chapter 3.

As you can see, cycloalkanes are named, under the IUPAC system, by adding the prefix *cyclo-* to the name of the unbranched alkane with the same number of carbons as the ring. Substituent groups are identified in the usual way. Their positions are specified by numbering the carbon atoms of the ring in the direction that gives the lowest number to the substituents at the first point of difference.

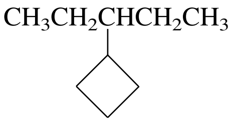


Ethylcyclopentane



3-Ethyl-1,1-dimethylcyclohexane
(not 1-ethyl-3,3-dimethylcyclohexane, because first point of difference rule requires 1,1,3 substitution pattern rather than 1,3,3)

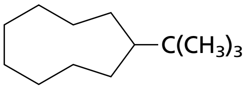
When the ring contains fewer carbon atoms than an alkyl group attached to it, the compound is named as an alkane, and the ring is treated as a cycloalkyl substituent:



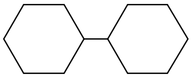
3-Cyclobutylpentane

PROBLEM 2.10 Name each of the following compounds:

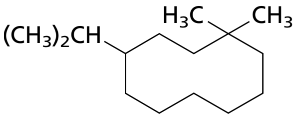
(a)



(c)



(b)



SAMPLE SOLUTION (a) The molecule has a *tert*-butyl group bonded to a nine-membered cycloalkane. It is *tert*-butylcyclononane. Alternatively, the *tert*-butyl group could be named systematically as a 1,1-dimethylethyl group, and the compound would then be named (1,1-dimethylethyl)cyclononane. (Parentheses are used when necessary to avoid ambiguity. In this case the parentheses alert the reader that the locants 1,1 refer to substituents on the alkyl group and not to ring positions.)

2.13 SOURCES OF ALKANES AND CYCLOALKANES

As noted earlier, natural gas is especially rich in methane and also contains ethane and propane, along with smaller amounts of other low-molecular-weight alkanes. Natural gas is often found associated with petroleum deposits. Petroleum is a liquid mixture containing hundreds of substances, including approximately 150 hydrocarbons, roughly half of which are alkanes or cycloalkanes. Distillation of crude oil gives a number of fractions, which by custom are described by the names given in Figure 2.2. High-boiling fractions such as kerosene and gas oil find wide use as fuels for diesel engines and furnaces, and the nonvolatile residue can be processed to give lubricating oil, greases, petroleum jelly, paraffin wax, and asphalt.

The word *petroleum* is derived from the Latin words for "rock" *(petra)* and "oil" *(oleum)*.

Although both are closely linked in our minds and by our own experience, the petroleum industry predated the automobile industry by half a century. The first oil well, drilled in Titusville, Pennsylvania, by Edwin Drake in 1859, provided "rock oil," as it was then called, on a large scale. This was quickly followed by the development of a process to "refine" it so as to produce kerosene. As a fuel for oil lamps, kerosene burned with a bright, clean flame and soon replaced the more expensive whale oil then in use. Other oil fields were discovered, and uses for other petroleum products were found—illuminating gas lit city streets, and oil heated homes and powered locomotives. There were oil refineries long before there were automobiles. By the time the first Model T rolled off Henry Ford's assembly line in 1908, John D. Rockefeller's Standard Oil holdings had already made him one of the half-dozen wealthiest people in the world.

Modern petroleum refining involves more than distillation, however, and includes two major additional operations:

1. **Cracking.** It is the more volatile, lower-molecular-weight hydrocarbons that are useful as automotive fuels and as a source of petrochemicals. Cracking increases the proportion of these hydrocarbons at the expense of higher molecular-weight ones by processes that involve the cleavage of carbon–carbon bonds induced by heat *(thermal cracking)* or with the aid of certain catalysts *(catalytic cracking)*.
2. **Reforming.** The physical properties of the crude oil fractions known as *light gasoline* and *naphtha* (Figure 2.2) are appropriate for use as a motor fuel, but their ignition characteristics in high-compression automobile engines are poor and give rise to preignition, or "knocking." Reforming converts the hydrocarbons in petroleum to aromatic hydrocarbons and highly branched alkanes, both of which show less tendency for knocking than unbranched alkanes and cycloalkanes.

The tendency of a gasoline to cause "knocking" in an engine is given by its octane number. The lower the octane number, the greater the tendency. The two standards are heptane (assigned a value of 0) and 2,2,4-trimethylpentane (assigned a value of 100). The octane number of a gasoline is equal to the percentage of 2,2,4-trimethylpentane in a mixture of 2,2,4-trimethylpentane and heptane that has the same tendency to cause knocking as that sample of gasoline.

The leaves and fruit of many plants bear a waxy coating made up of alkanes that prevents loss of water. In addition to being present in beeswax (see Problem 2.5), hentriacontane, $CH_3(CH_2)_{29}CH_3$, is a component of the wax of tobacco leaves.

Cyclopentane and cyclohexane are present in petroleum, but as a rule, unsubsti-

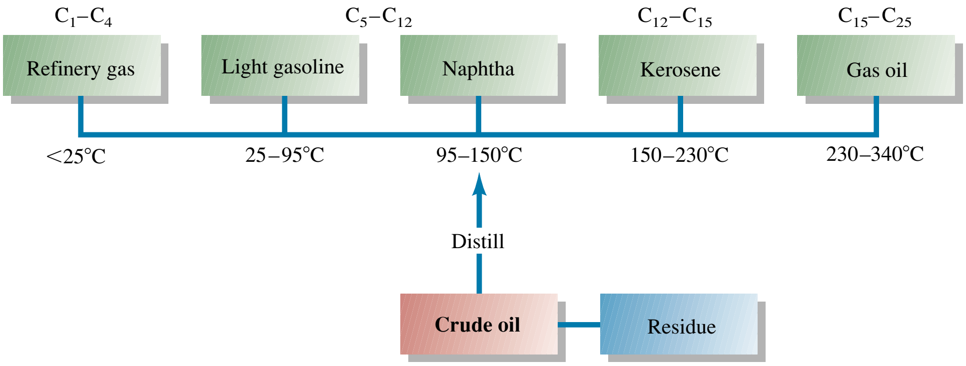
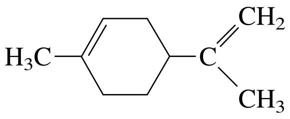
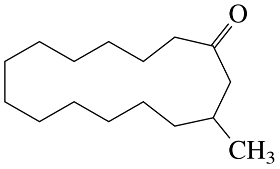


FIGURE 2.2 Distillation of crude oil yields a series of volatile fractions having the names indicated, along wih a nonvolatile residue. The number of carbon atoms that characterize the hydrocarbons in each fraction is approximate.

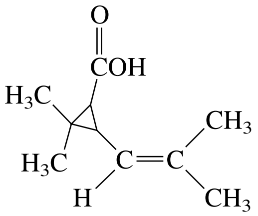
tuted cycloalkanes are rarely found in natural sources. Compounds that contain rings of various types, however, are quite abundant.



Limonene
(present in lemons and oranges)



Muscone
(responsible for odor of musk; used in perfumery)



Chrysanthemic acid
(obtained from chrysanthemum flowers)

2.14 PHYSICAL PROPERTIES OF ALKANES AND CYCLOALKANES

Boiling Point. As we have seen earlier in this chapter, methane, ethane, propane, and butane are gases at room temperature. The unbranched alkanes pentane (C_5H_{12}) through heptadecane ($C_{17}H_{36}$) are liquids, whereas higher homologs are solids. As shown in Figure 2.3, the boiling points of unbranched alkanes increase with the number of carbon atoms. Figure 2.3 also shows that the boiling points for 2-methyl-branched alkanes are lower than those of the unbranched isomer. By exploring at the molecular level the reasons for the increase in boiling point with the number of carbons and the difference in boiling point between branched and unbranched alkanes, we can begin to connect structure with properties.

Appendix 1 lists selected physical properties for representative alkanes as well as members of other families of organic compounds.

A substance exists as a liquid rather than a gas because attractive forces between

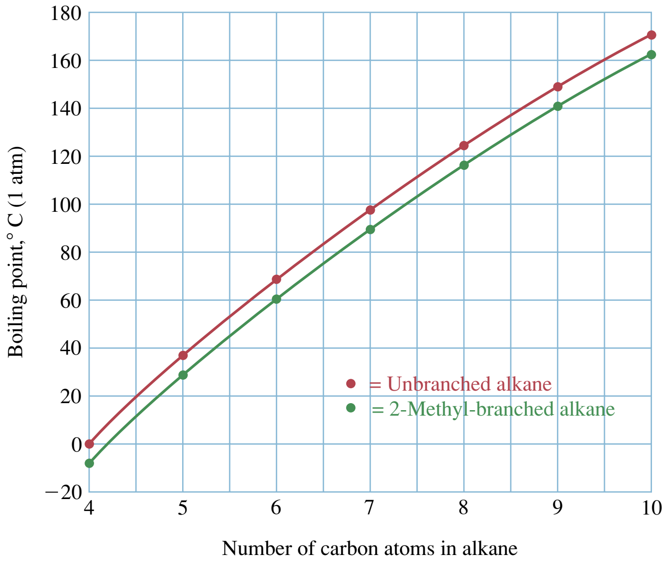


FIGURE 2.3 Boiling points of unbranched alkanes and their 2-methyl-branched isomers. (Temperatures in this text are expressed in degrees Celsius, °C. The SI unit of temperature is the kelvin, K. To convert degrees Celsius to kelvins add 273.15.)

molecules **(intermolecular attractive forces)** are greater in the liquid than in the gas phase. Attractive forces between neutral species (atoms or molecules, but not ions) are referred to as **van der Waals forces** and may be of three types:

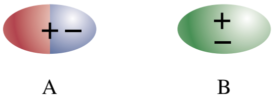
1. dipole–dipole
2. dipole/induced-dipole
3. induced-dipole/induced-dipole

Van der Waals forces involving induced dipoles are often called *London forces,* or *dispersion forces.*

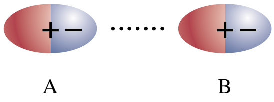
These forces are electrical in nature, and in order to vaporize a substance, enough energy must be added to overcome them. Most alkanes have no measurable dipole moment, and therefore the only van der Waals force to be considered is the induced- dipole/induced-dipole attractive force.

It might seem that two nearby molecules A and B of the same nonpolar substance would be unaffected by each other.

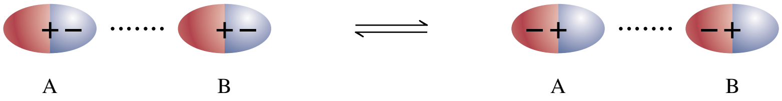
The electric field of a molecule, however, is not static, but fluctuates rapidly. Although, on average, the centers of positive and negative charge of an alkane nearly coincide, at any instant they may not, and molecule A can be considered to have a temporary dipole moment.



The neighboring molecule B "feels" the dipolar electric field of A and undergoes a spontaneous adjustment in its electron positions, giving it a temporary dipole moment that is complementary to that of A.



The electric fields of both A and B fluctuate, but always in a way that results in a weak attraction between them.

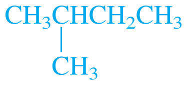


Extended assemblies of induced-dipole/induced-dipole attractions can accumulate to give substantial intermolecular attractive forces. An alkane with a higher molecular weight has more atoms and electrons and, therefore, more opportunities for intermolecular attractions and a higher boiling point than one with a lower molecular weight.

As noted earlier in this section, branched alkanes have lower boiling points than their unbranched isomers. Isomers have, of course, the same number of atoms and electrons, but a molecule of a branched alkane has a smaller surface area than an unbranched one. The extended shape of an unbranched alkane permits more points of contact for intermolecular associations. Compare the boiling points of pentane and its isomers:

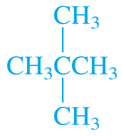
$CH_3CH_2CH_2CH_2CH_3$

Pentane
(bp 36°C)



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}CH_2CH_3$$

2-Methylbutane
(bp 28°C)



$$CH_3\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_3$$

2,2-Dimethylpropane
(bp 9°C)

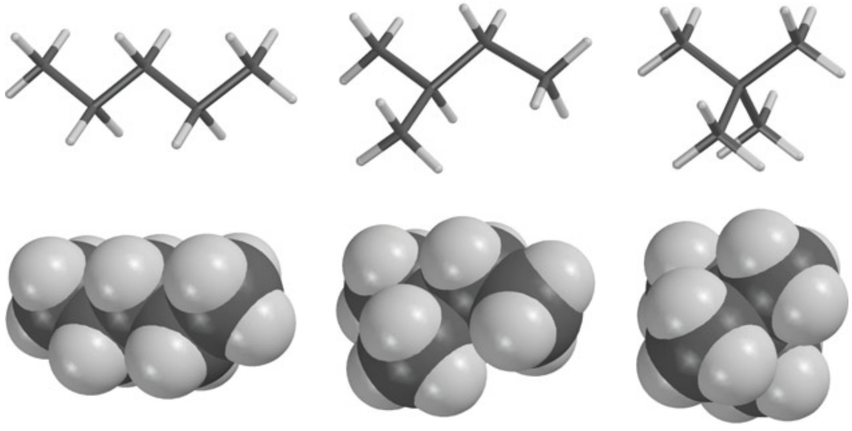
If you haven't already made models of the C_5H_{12} isomers, this would be a good time to do so.

The shapes of these isomers are clearly evident in the space-filling models depicted in Figure 2.4. Pentane has the most extended structure and the largest surface area available for "sticking" to other molecules by way of induced-dipole/induced-dipole attractive forces; it has the highest boiling point. 2,2-Dimethylpropane has the most compact structure, engages in the fewest induced-dipole/induced-dipole attractions, and has the lowest boiling point.

Induced-dipole/induced-dipole attractions are very weak forces individually, but a typical organic substance can participate in so many of them that they are collectively the most important of all the contributors to intermolecular attraction in the liquid state. They are the only forces of attraction possible between nonpolar molecules such as alkanes.

PROBLEM 2.11 Match the boiling points with the appropriate alkanes.
Alkanes: octane, 2-methylheptane, 2,2,3,3-tetramethylbutane, nonane
Boiling points (°C, 1 atm): 106, 116, 126, 151

Melting Point. Solid alkanes are soft, generally low-melting materials. The forces responsible for holding the crystal together are the same induced-dipole/induced-dipole interactions that operate between molecules in the liquid, but the degree of organization



(*a*) Pentane: $CH_3CH_2CH_2CH_2CH_3$

(*b*) 2-Methylbutane: $(CH_3)_2CHCH_2CH_3$

(*c*) 2,2-Dimethylpropane: $(CH_3)_4C$

FIGURE 2.4 Space-filling models of (*a*) pentane, (*b*) 2-methylbutane, and (c) 2,2-dimethylpropane. The most branched isomer, 2,2-dimethylpropane, has the most compact, most spherical, three-dimensional shape.

is greater in the solid phase. By measuring the distances between the atoms of one molecule and its neighbor in the crystal, it is possible to specify a distance of closest approach characteristic of an atom called its **van der Waals radius.** In space-filling molecular models, such as those of pentane, 2-methylbutane, and 2,2-dimethylpropane shown in Figure 2.4, the radius of each sphere corresponds to the van der Waals radius of the atom it represents. The van der Waals radius for hydrogen is 120 pm. When two alkane molecules are brought together so that a hydrogen of one molecule is within 240 pm of a hydrogen of the other, the balance between electron–nucleus attractions versus electron–electron and nucleus–nucleus repulsions is most favorable. Closer approach is resisted by a strong increase in repulsive forces.

Solubility in Water. A familiar physical property of alkanes is contained in the adage "oil and water don't mix." Alkanes—indeed all hydrocarbons—are virtually insoluble in water. When a hydrocarbon dissolves in water, the framework of hydrogen bonds between water molecules becomes more ordered in the region around each molecule of the dissolved hydrocarbon. This increase in order, which corresponds to a decrease in entropy, signals a process that can be favorable only if it is reasonably exothermic. Such is not the case here. Being insoluble, and with densities in the 0.6–0.8 g/mL range, alkanes float on the surface of water (as the Alaskan oil spill of 1989 and the even larger Persian Gulf spill of 1991 remind us). The exclusion of nonpolar molecules, such as alkanes, from water is called the **hydrophobic effect.** We will encounter it again at several points later in the text.

2.15 CHEMICAL PROPERTIES. COMBUSTION OF ALKANES

Alkanes are so unreactive that George A. Olah of the University of Southern California was awarded the 1994 Nobel Prize in chemistry in part for developing novel substances that do react with alkanes.

An older name for alkanes is **paraffin hydrocarbons.** *Paraffin* is derived from the Latin words *parum affinis* ("with little affinity") and testifies to the low level of reactivity of alkanes. Like most other organic compounds, however, alkanes burn readily in air. This combination with oxygen is known as **combustion** and is quite exothermic. All hydrocarbons yield carbon dioxide and water as the products of their combustion.

$$\underset{\text{Methane}}{CH_4} + \underset{\text{Oxygen}}{2O_2} \longrightarrow \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Water}}{2H_2O} \qquad \Delta H^\circ = -890\text{ kJ } (-212.8\text{ kcal})$$

$$\underset{\text{2-Methylbutane}}{(CH_3)_2CHCH_2CH_3} + \underset{\text{Oxygen}}{8O_2} \longrightarrow \underset{\text{Carbon dioxide}}{5CO_2} + \underset{\text{Water}}{6H_2O} \qquad \Delta H^\circ = -3529\text{ kJ } (-843.4\text{ kcal})$$

PROBLEM 2.12 Write a balanced chemical equation for the combustion of cyclohexane.

The heat released on combustion of a substance is called its **heat of combustion.** The heat of combustion is equal to $-\Delta H^\circ$ for the reaction written in the direction shown. By convention

$$\Delta H^\circ = H^\circ_{\text{products}} - H^\circ_{\text{reactants}}$$

where H° is the heat content, or **enthalpy,** of a compound in its standard state, that is, the gas, pure liquid, or crystalline solid at a pressure of 1 atm. In an exothermic process the enthalpy of the products is less than that of the starting materials, and ΔH° is a negative number.

Table 2.5 lists the heats of combustion of several alkanes. Unbranched alkanes have slightly higher heats of combustion than their 2-methyl-branched isomers, but the most important factor is the number of carbons. The unbranched alkanes and the 2-methyl-branched alkanes constitute two separate *homologous series* (see Section 2.6) in which there is a regular increase of about 653 kJ/mol (156 kcal/mol) in the heat of combustion for each additional CH_2 group.

PROBLEM 2.13 Using the data in Table 2.5, estimate the heat of combustion of
(a) 2-Methylnonane (in kcal/mol) (b) Icosane (in kJ/mol)

SAMPLE SOLUTION (a) The last entry for the group of 2-methylalkanes in the table is 2-methylheptane. Its heat of combustion is 1306 kcal/mol. Since 2-methylnonane has two more methylene groups than 2-methylheptane, its heat of combustion is 2 × 156 kcal/mol higher.

$$\text{Heat of combustion of 2-methylnonane} = 1306 + 2(156) = 1618 \text{ kcal/mol}$$

Heats of combustion can be used to measure the relative stability of isomeric hydrocarbons. They tell us not only which isomer is more stable than another, but by how much. Consider a group of C_8H_{18} alkanes:

$CH_3(CH_2)_6CH_3$ Octane

$(CH_3)_2CHCH_2CH_2CH_2CH_2CH_3$ 2-Methylheptane

$(CH_3)_3CCH_2CH_2CH_2CH_3$ 2,2-Dimethylhexane

$(CH_3)_3CC(CH_3)_3$ 2,2,3,3-Tetramethylbutane

Figure 2.5 compares the heats of combustion of these C_8H_{18} isomers on a *potential energy diagram*. **Potential energy** is comparable with enthalpy; it is the energy a molecule has exclusive of its kinetic energy. A molecule with more potential energy is less

TABLE 2.5 Heats of Combustion ($-\Delta H°$) of Representative Alkanes

		$-\Delta H°$	
Compound	**Formula**	**kJ/mol**	**kcal/mol**
Unbranched alkanes			
Hexane	$CH_3(CH_2)_4CH_3$	4,163	995.0
Heptane	$CH_3(CH_2)_5CH_3$	4,817	1151.3
Octane	$CH_3(CH_2)_6CH_3$	5,471	1307.5
Nonane	$CH_3(CH_2)_7CH_3$	6,125	1463.9
Decane	$CH_3(CH_2)_8CH_3$	6,778	1620.1
Undecane	$CH_3(CH_2)_9CH_3$	7,431	1776.1
Dodecane	$CH_3(CH_2)_{10}CH_3$	8,086	1932.7
Hexadecane	$CH_3(CH_2)_{14}CH_3$	10,701	2557.6
2-Methyl-branched alkanes			
2-Methylpentane	$(CH_3)_2CHCH_2CH_2CH_3$	4,157	993.6
2-Methylhexane	$(CH_3)_2CH(CH_2)_3CH_3$	4,812	1150.0
2-Methylheptane	$(CH_3)_2CH(CH_2)_4CH_3$	5,466	1306.3

stable than an isomer with less potential energy. Since these C_8H_{18} isomers all undergo combustion to the same final state according to the equation

$$C_8H_{18} + \tfrac{25}{2}O_2 \longrightarrow 8CO_2 + 9H_2O$$

the differences in their heats of combustion translate directly to differences in their potential energies. *When comparing isomers, the one with the lowest potential energy (in this case, the lowest heat of combustion) is the most stable.* Among the C_8H_{18} alkanes, the most highly branched isomer, 2,2,3,3-tetramethylbutane, is the most stable, and the unbranched isomer octane is the least stable. It is generally true for alkanes that a more branched isomer is more stable than a less branched one.

The small differences in stability between branched and unbranched alkanes result from an interplay between attractive and repulsive forces within a molecule **(intramolecular forces).** These forces are nucleus–nucleus repulsions, electron–electron repulsions, and nucleus–electron attractions, the same set of fundamental forces we met when talking about chemical bonding (see Section 1.12) and van der Waals forces between molecules (see Section 2.14). When the energy associated with these interactions is calculated for all of the nuclei and electrons within a molecule, it is found that the attractive forces increase more than the repulsive forces as the structure becomes more compact. Sometimes, though, two atoms in a molecule are held too closely together. We'll explore the consequences of that in Chapter 3.

PROBLEM 2.14 Without consulting Table 2.5, arrange the following compounds in order of decreasing heat of combustion: pentane, isopentane, neopentane, hexane.

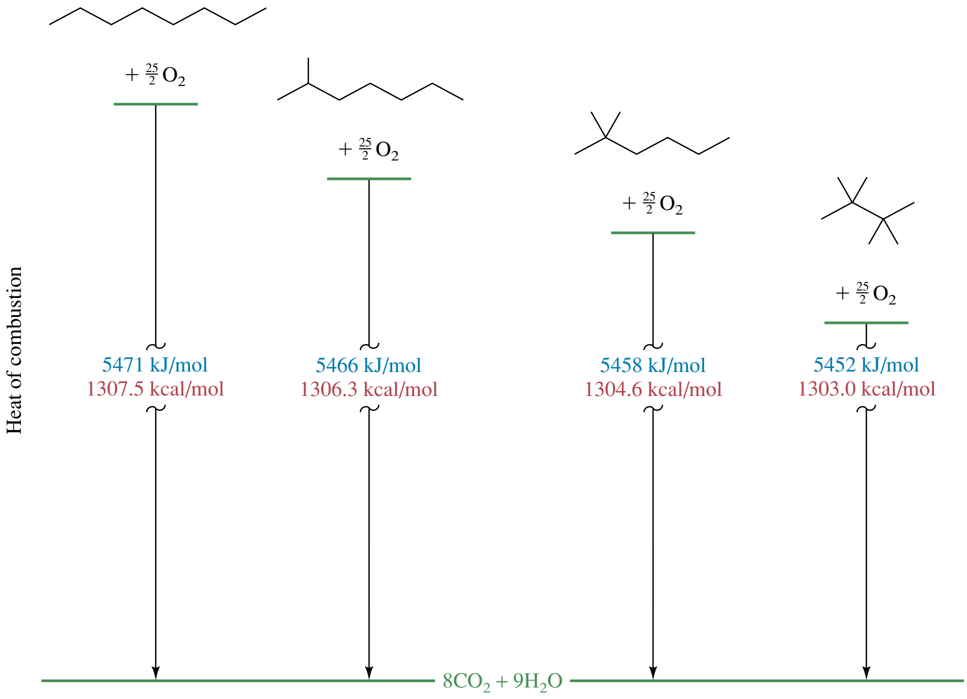


FIGURE 2.5 Energy diagram comparing heats of combustion of isomeric C_8H_{18} alkanes.

THERMOCHEMISTRY

Thermochemistry is the study of the heat changes that accompany chemical processes. It has a long history dating back to the work of the French chemist Antoine Laurent Lavoisier in the late eighteenth century. Thermochemistry provides quantitative information that complements the qualitative description of a chemical reaction and can help us understand why some reactions occur and others do not. It is of obvious importance when assessing the relative value of various materials as fuels, when comparing the stability of isomers, or when determining the practicality of a particular reaction. In the field of bioenergetics, thermochemical information is applied to the task of sorting out how living systems use chemical reactions to store and use the energy that originates in the sun.

By allowing compounds to react in a calorimeter, it is possible to measure the heat evolved in an exothermic reaction or the heat absorbed in an endothermic reaction. Thousands of reactions have been studied to produce a rich library of thermochemical data. These data take the form of **heats of reaction** and correspond to the value of the enthalpy change $\Delta H°$ for a particular reaction of a particular substance.

In this section you have seen how heats of combustion can be used to determine relative stabilities of isomeric alkanes. In later sections we shall expand our scope to include the experimentally determined heats of certain other reactions, such as *bond dissociation energies* (Section 4.17) and *heats of hydrogenation* (Section 6.2), to see how $\Delta H°$ values from various sources can aid our understanding of structure and reactivity.

Heat of formation ($\Delta H_f°$), the enthalpy change for formation of a compound directly from the elements, is one type of heat of reaction. In cases such as the formation of CO_2 or H_2O from the combustion of carbon or hydrogen, respectively, the heat of formation of a substance can be measured directly. In most other cases, heats of formation are not measured experimentally but are calculated from the measured heats of other reactions. Consider, for example, the heat of formation of methane. The reaction that defines the formation of methane from the elements,

$$\underset{\text{Carbon}}{\text{C (graphite)}} + \underset{\text{Hydrogen}}{2H_2(g)} \longrightarrow \underset{\text{Methane}}{CH_4(g)}$$

can be expressed as the sum of three reactions:

$$\begin{array}{ll}
(1)\ \text{C (graphite)} + O_2(g) \longrightarrow CO_2(g) & \Delta H° = -393\text{ kJ} \\
(2)\ 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) & \Delta H° = -572\text{ kJ} \\
(3)\ CO_2(g) + 2H_2O(l) \longrightarrow CH_4(g) + 2O_2(g) & \\
 & \Delta H° = +890\text{ kJ} \\
\hline
\quad \text{C (graphite)} + 2H_2 \longrightarrow CH_4 & \Delta H° = -75\text{ kJ}
\end{array}$$

Equations (1) and (2) are the heats of formation of carbon dioxide and water, respectively. Equation (3) is the reverse of the combustion of methane, and so the heat of reaction is equal to the heat of combustion but opposite in sign. The **molar heat of formation** of a substance is the enthalpy change for formation of one mole of the substance from the elements. For methane $\Delta H_f° = -75$ kJ/mol.

The heats of formation of most organic compounds are derived from heats of reaction by arithmetic manipulations similar to that shown. Chemists find a table of $\Delta H_f°$ values to be convenient because it replaces many separate tables of $\Delta H°$ values for individual reaction types and permits $\Delta H°$ to be calculated for any reaction, real or imaginary, for which the heats of formation of reactants and products are available. It is more appropriate for our purposes, however, to connect thermochemical data to chemical processes as directly as possible, and therefore we will cite heats of particular reactions, such as heats of combustion and heats of hydrogenation, rather than heats of formation.

2.16 OXIDATION–REDUCTION IN ORGANIC CHEMISTRY

As we have just seen, the reaction of alkanes with oxygen to give carbon dioxide and water is called *combustion.* A more fundamental classification of reaction types places it in the *oxidation–reduction* category. To understand why, let's review some principles of oxidation–reduction, beginning with the **oxidation number** (also known as **oxidation state**).

There are a variety of methods for calculating oxidation numbers. In compounds that contain a single carbon, such as methane (CH_4) and carbon dioxide (CO_2), the oxidation number of carbon can be calculated from the molecular formula. Both molecules are neutral, and so the algebraic sum of all the oxidation numbers must equal zero. Assuming, as is customary, that the oxidation state of hydrogen is $+1$, the oxidation state of carbon in CH_4 is calculated to be -4. Similarly, assuming an oxidation state of -2 for oxygen, carbon is $+4$ in CO_2. This kind of calculation provides an easy way to develop a list of one-carbon compounds in order of increasing oxidation state, as shown in Table 2.6.

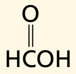
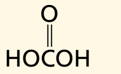
The carbon in methane has the lowest oxidation number (-4) of any of the compounds in Table 2.6. Methane contains carbon in its most *reduced* form. Carbon dioxide and carbonic acid have the highest oxidation numbers ($+4$) for carbon, corresponding to its most *oxidized* state. When methane or any alkane undergoes combustion to form carbon dioxide, carbon is oxidized and oxygen is reduced.

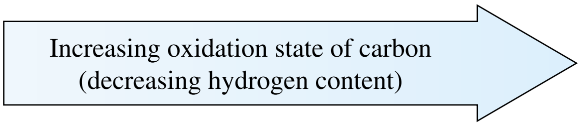
A useful generalization from Table 2.6 is the following:

> *Oxidation of carbon corresponds to an increase in the number of bonds between carbon and oxygen or to a decrease in the number of carbon–hydrogen bonds.* Conversely, *reduction corresponds to an increase in the number of carbon–hydrogen bonds or to a decrease in the number of carbon–oxygen bonds.* From Table 2.6 it can be seen that each successive increase in oxidation state increases the number of bonds between carbon and oxygen and decreases the number of carbon–hydrogen bonds. Methane has four C—H bonds and no C—O bonds; carbon dioxide has four C—O bonds and no C—H bonds.

Among the various classes of hydrocarbons, alkanes contain carbon in its most reduced state, and alkynes contain carbon in its most oxidized state.

TABLE 2.6 Oxidation Number of Carbon in One-Carbon Compounds

Compound	Structural formula	Molecular formula	Oxidation number
Methane	CH_4	CH_4	-4
Methanol	CH_3OH	CH_4O	-2
Formaldehyde	$H_2C{=}O$	CH_2O	0
Formic acid	 $H\overset{\overset{O}{\|}}{C}OH$	CH_2O_2	$+2$
Carbonic acid	 $HO\overset{\overset{O}{\|}}{C}OH$	H_2CO_3	$+4$
Carbon dioxide	$O{=}C{=}O$	CO_2	$+4$



CH_3CH_3	$CH_2{=}CH_2$	$HC{\equiv}CH$
Ethane	Ethylene	Acetylene
(6 C—H bonds)	(4 C—H bonds)	(2 C—H bonds)

We can extend the generalization by recognizing that the pattern is not limited to increasing hydrogen or oxygen content. Any element *more electronegative* than carbon will have the same effect on oxidation number as oxygen. Thus, the oxidation numbers of carbon in CH_3Cl and in CH_3OH are the same (-2), and the reaction of methane with chlorine (to be discussed in Section 4.16) involves *oxidation* of carbon.

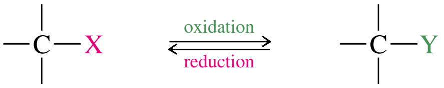
$$\underset{\text{Methane}}{CH_4} + \underset{\text{Chlorine}}{Cl_2} \longrightarrow \underset{\text{Chloromethane}}{CH_3Cl} + \underset{\text{Hydrogen chloride}}{HCl}$$

Any element *less electronegative* than carbon will have the same effect on oxidation number as hydrogen. Thus, the oxidation numbers of carbon in CH_3Li and in CH_4 are the same (-4), and the reaction of CH_3Cl with lithium (to be discussed in Section 14.3) involves *reduction* of carbon.

$$\underset{\text{Chloromethane}}{CH_3Cl} + \underset{\text{Lithium}}{2Li} \longrightarrow \underset{\text{Methyllithium}}{CH_3Li} + \underset{\text{Lithium chloride}}{LiCl}$$

The oxidation number of carbon *decreases* from -2 in CH_3Cl to -4 in CH_3Li.

The generalization can be expressed in terms broad enough to cover both the preceding reactions and many others as well, as follows: *Oxidation of carbon occurs when a bond between carbon and an atom which is less electronegative than carbon is replaced by a bond to an atom that is more electronegative than carbon. The reverse process is reduction.*



X is less electronegative than carbon

Y is more electronegative than carbon

Organic chemists are much more concerned with whether a particular reaction is an oxidation or a reduction of carbon than with determining the precise change in oxidation number. The generalizations described permit reactions to be examined in this way and eliminate the need for calculating oxidation numbers themselves.

Methods for calculating oxidation numbers in complex molecules are available. They are time-consuming to apply, however, and are rarely used in organic chemistry.

PROBLEM 2.15 The reactions shown will all be encountered in Chapter 6. Classify each according to whether it proceeds by oxidation of carbon, by reduction of carbon, or by a process other than oxidation–reduction.

(a) $CH_2{=}CH_2 + H_2O \longrightarrow CH_3CH_2OH$

(b) $CH_2{=}CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$

(c) $6CH_2{=}CH_2 + B_2H_6 \longrightarrow 2(CH_3CH_2)_3B$

SAMPLE SOLUTION (a) In this reaction one new C—H bond and one new C—O bond are formed. One carbon is reduced, the other is oxidized. Overall, there is no net change in oxidation state, and the reaction is not classified as an oxidation–reduction.

The ability to recognize when oxidation or reduction occurs is of value when deciding on the kind of reactant with which an organic molecule must be treated in order to convert it into some desired product. Many of the reactions to be discussed in subsequent chapters involve oxidation–reduction.

2.17 SUMMARY

Section 2.1 The classes of hydrocarbons are **alkanes, alkenes, alkynes,** and **arenes.** Alkanes are hydrocarbons in which all of the bonds are *single* bonds and are characterized by the molecular formula C_nH_{2n+2}.

Section 2.2 **Functional groups** are the structural units responsible for the characteristic reactions of a molecule. The functional groups in an alkane are its hydrogen atoms.

Section 2.3 The families of organic compounds listed on the inside front cover and in Tables 2.1 and 2.2 bear functional groups that are more reactive than H, and the hydrocarbon chain to which they are attached can often be considered as simply a supporting framework. For example, ethanolamine ($H_2NCH_2CH_2OH$) contains both amine (RNH_2) and alcohol (ROH) functional groups.

Section 2.4 The first three alkanes are **methane** (CH_4), **ethane** (CH_3CH_3), and **propane** ($CH_3CH_2CH_3$). All can be described according to the orbital hybridization model of bonding based on sp^3 hybridization of carbon.

Section 2.5 Two constitutionally isomeric alkanes have the molecular formula C_4H_{10}. One has an unbranched chain ($CH_3CH_2CH_2CH_3$) and is called ***n*-butane;** the other has a branched chain [$(CH_3)_3CH$] and is called **isobutane.** Both *n*-butane and isobutane are **common names.**

Section 2.6 Unbranched alkanes of the type $CH_3(CH_2)_nCH_3$ are often referred to as *n*-alkanes.

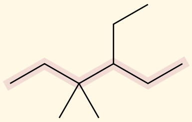
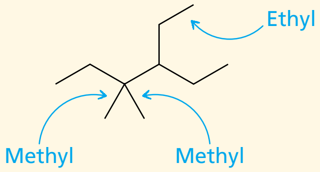
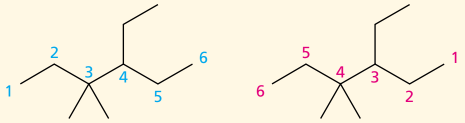
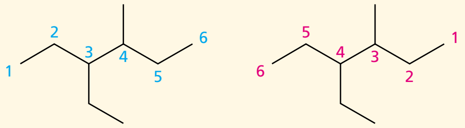
Section 2.7 There are three constitutional isomers of C_5H_{12}: ***n*-pentane** ($CH_3CH_2CH_2CH_2CH_3$), **isopentane** [$(CH_3)_2CHCH_2CH_3$], and **neopentane** [$(CH_3)_4C$].

Sections 2.8–2.12 A single alkane may have several different names; a name may be a common name, or it may be a *systematic name* developed by a well-defined set of rules. The most widely used system is **IUPAC nomenclature.** Table 2.7 summarizes the rules for alkanes and cycloalkanes. Table 2.8 gives the rules for naming alkyl groups.

Section 2.13 Natural gas is an abundant source of methane, ethane, and propane. Petroleum is a liquid mixture of many hydrocarbons, including alkanes. Alkanes also occur naturally in the waxy coating of leaves and fruits.

Section 2.14 Alkanes and cycloalkanes are nonpolar and insoluble in water. The forces of attraction between alkane molecules are **induced-dipole/induced-dipole** attractive forces. The boiling points of alkanes increase as the

TABLE 2.7 Summary of IUPAC Nomenclature of Alkanes and Cycloalkanes

Rule	Example
A. Alkanes	
1. Find the longest continuous chain of carbon atoms, and assign a basis name to the compound corresponding to the IUPAC name of the unbranched alkane having the same number of carbons.	The longest continuous chain in the alkane shown is six carbons.  This alkane is named as a derivative of *hexane.*
2. List the substituents attached to the longest continuous chain in alphabetical order. Use the prefixes *di-, tri-, tetra-,* and so on, when the same substituent appears more than once. Ignore these prefixes when alphabetizing.	The alkane bears two methyl groups and an ethyl group. It is an *ethyldimethylhexane.* 
3. Number the chain in the direction that gives the lower locant to a substituent at the first point of difference.	When numbering from left to right, the substituents appear at carbons 3, 3, and 4. When numbering from right to left the locants are 3, 4, and 4; therefore, number from left to right.  Correct Incorrect The correct name is *4-ethyl-3,3-dimethylhexane.*
4. When two different numbering schemes give equivalent sets of locants, choose the direction that gives the lower locant to the group that appears first in the name.	In the following example, the substituents are located at carbons 3 and 4 regardless of the direction in which the chain is numbered.  Correct Incorrect Ethyl precedes methyl in the name; therefore *3-ethyl-4-methylhexane* is correct.

(Continued)

TABLE 2.7 Summary of IUPAC Nomenclature of Alkanes and Cycloalkanes ***(Continued)***

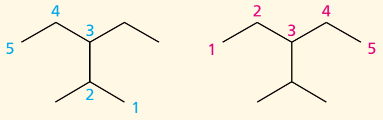
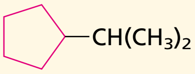
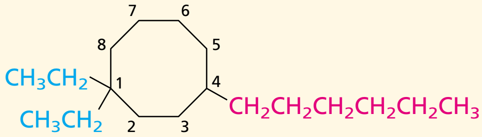
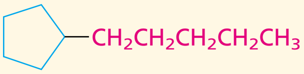
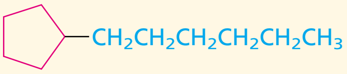
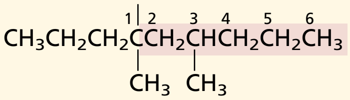
Rule	Example
5. When two chains are of equal length, choose the one with the greater number of substituents as the parent. (Although this requires naming more substituents, the substituents have simpler names.)	Two different chains contain five carbons in the alkane:  Correct Incorrect The correct name is *3-ethyl-2-methylpentane* (disubstituted chain), rather than 3-isopropylpentane (monosubstituted chain).
B. Cycloalkanes	
1. Count the number of carbons in the ring, and assign a basis name to the cycloalkane corresponding to the IUPAC name of the unbranched alkane having the same number of carbons.	The compound shown contains five carbons in its ring.  It is named as a derivative of *cyclopentane.*
2. Name the alkyl group, and append it as a prefix to the cycloalkane. No locant is needed if the compound is a monosubstituted cycloalkane. It is understood that the alkyl group is attached to C-1.	The previous compound is *isopropylcyclopentane.* Alternatively, the alkyl group can be named according to the rules summarized in Table 2.8, whereupon the name becomes (*1-methylethyl*)*cyclopentane.* Parentheses are used to set off the name of the alkyl group as needed to avoid ambiguity.
3. When two or more different substituents are present, list them in alphabetical order, and number the ring in the direction that gives the lower number at the first point of difference.	The compound shown is *1,1-diethyl-4-hexylcyclooctane.* 
4. Name the compound as a cycloalkyl-substituted alkane if the substituent has more carbons than the ring.	 is *pentylcyclopentane* but  is *1-cyclopentylhexane*

TABLE 2.8 Summary of IUPAC Nomenclature of Alkyl Groups

Rule	Example
1. Number the carbon atoms beginning at the point of attachment, proceeding in the direction that follows the longest continuous chain.	The longest continuous chain that begins at the point of attachment in the group shown contains six carbons.  $\mathrm{CH_3CH_2CH_2\underset{CH_3}{\overset{1\,|\,2}{C}}CH_2\underset{CH_3}{\overset{3}{C}}\overset{4}{H}\overset{5}{CH_2}CH_2\overset{6}{CH_3}}$
2. Assign a basis name according to the number of carbons in the corresponding unbranched alkane. Drop the ending *-ane* and replace it by *-yl.*	The alkyl group shown in step 1 is named as a substituent *hexyl* group.
3. List the substituents on the basis group in alphabetical order using replicating prefixes when necessary.	The alkyl group in step 1 is a *dimethylpropylhexyl* group.
4. Locate the substituents according to the numbering of the main chain described in step 1.	The alkyl group is a *1,3-dimethyl-1-propylhexyl* group.

number of carbon atoms increases. Branched alkanes have lower boiling points than their unbranched isomers. There is a limit to how closely two molecules can approach each other, which is given by the sum of their **van der Waals radii.**

Section 2.15 Alkanes and cycloalkanes burn in air to give carbon dioxide, water, and heat. This process is called **combustion.**

$$(CH_3)_2CHCH_2CH_3 + 8O_2 \longrightarrow 5CO_2 + 6H_2O$$

2-Methylbutane Oxygen Carbon dioxide Water

$$\Delta H° = -3529 \text{ kJ } (-843.4 \text{ kcal})$$

The heat evolved on burning an alkane increases with the number of carbon atoms. The relative stability of isomers may be determined by comparing their respective **heats of combustion.** The more stable of two isomers has the lower heat of combustion.

Section 2.16 Combustion of alkanes is an example of **oxidation–reduction.** Although it is possible to calculate oxidation numbers of carbon in organic molecules, it is more convenient to regard oxidation of an organic substance as an increase in its oxygen content or a decrease in its hydrogen content.

PROBLEMS

2.16 Write structural formulas, and give the IUPAC names for the nine alkanes that have the molecular formula C_7H_{16}.

2.17 From among the 18 constitutional isomers of C_8H_{18}, write structural formulas, and give the IUPAC names for those that are named as derivatives of

(a) Heptane
(b) Hexane
(c) Pentane
(d) Butane

2.18 Write a structural formula for each of the following compounds:

(a) 6-Isopropyl-2,3-dimethylnonane
(b) 4-*tert*-Butyl-3-methylheptane
(c) 4-Isobutyl-1,1-dimethylcyclohexane
(d) *sec*-Butylcycloheptane
(e) Cyclobutylcyclopentane
(f) (2,2-Dimethylpropyl)cyclohexane
(g) Pentacosane
(h) 10-(1-methylpentyl)pentacosane

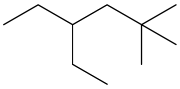
2.19 Give the IUPAC name for each of the following compounds:

(a) $CH_3(CH_2)_{25}CH_3$

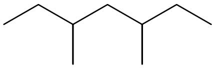
(b) $(CH_3)_2CHCH_2(CH_2)_{14}CH_3$

(c) $(CH_3CH_2)_3CCH(CH_2CH_3)_2$

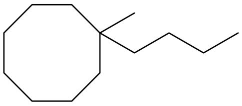
(d)



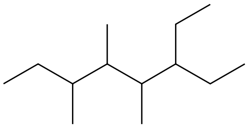
(e)



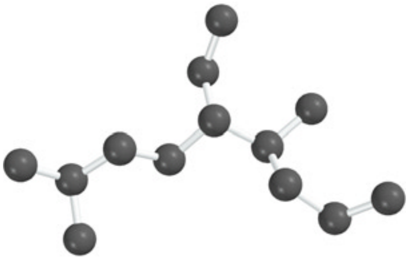
(f)



(g)



2.20 All the parts of this problem refer to the alkane having the carbon skeleton shown.

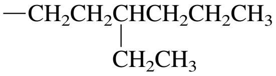


(a) What is the molecular formula of this alkane?
(b) What is its IUPAC name?
(c) How many methyl groups are present in this alkane? Methylene groups? Methine groups?
(d) How many carbon atoms are primary? Secondary? Tertiary? Quaternary?

2.21 Give the IUPAC name for each of the following alkyl groups, and classify each one as primary, secondary, or tertiary:

(a) $CH_3(CH_2)_{10}CH_2—$

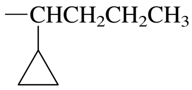
(b)



$$—CH_2CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$$

(c) $—C(CH_2CH_3)_3$

(d)



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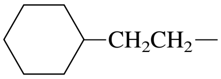
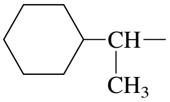


(f)



2.22 *Pristane* is an alkane that is present to the extent of about 14% in shark liver oil. Its IUPAC name is 2,6,10,14-tetramethylpentadecane. Write its structural formula.

2.23 Hectane is the IUPAC name for the unbranched alkane that contains 100 carbon atoms.

(a) How many σ bonds are there in hectane?

(b) How many alkanes have names of the type x-methylhectane?

(c) How many alkanes have names of the type 2,x-dimethylhectane?

2.24 Which of the compounds in each of the following groups are isomers?

(a) Butane, cyclobutane, isobutane, 2-methylbutane

(b) Cyclopentane, neopentane, 2,2-dimethylpentane, 2,2,3-trimethylbutane

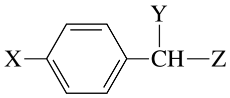
(c) Cyclohexane, hexane, methylcyclopentane, 1,1,2-trimethylcyclopropane

(d) Ethylcyclopropane, 1,1-dimethylcyclopropane, 1-cyclopropylpropane, cyclopentane

(e) 4-Methyltetradecane, 2,3,4,5-tetramethyldecane, pentadecane, 4-cyclobutyldecane

2.25 *Epichlorohydrin* is the common name of an industrial chemical used as a component in epoxy cement. The molecular formula of epichlorohydrin is C_3H_5ClO. Epichlorohydrin has an epoxide functional group; it does not have a methyl group. Write a structural formula for epichlorohydrin.

2.26 (a) Complete the structure of the pain-relieving drug *ibuprofen* on the basis of the fact that ibuprofen is a carboxylic acid that has the molecular formula $C_{13}H_{18}O_2$, X is an isobutyl group, and Y is a methyl group.

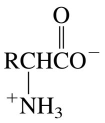


(b) *Mandelonitrile* may be obtained from peach flowers. Derive its structure from the template in part (a) given that X is hydrogen, Y is the functional group that characterizes alcohols, and Z characterizes nitriles.

2.27 *Isoamyl acetate* is the common name of the substance most responsible for the characteristic odor of bananas. Write a structural formula for isoamyl acetate, given the information that it is an ester in which the carbonyl group bears a methyl substituent and there is a 3-methylbutyl group attached to one of the oxygens.

2.28 *n-Butyl mercaptan* is the common name of a foul-smelling substance obtained from skunk fluid. It is a thiol of the type RX, where R is an n-butyl group and X is the functional group that characterizes a thiol. Write a structural formula for this substance.

2.29 Some of the most important organic compounds in biochemistry are the α-*amino acids,* represented by the general formula shown.



$$R\underset{\displaystyle {}^{+}NH_3}{\underset{|}{C}}H\overset{\displaystyle O}{\overset{\|}{C}}O^-$$

Write structural formulas for the following α-amino acids.

(a) Alanine (R = methyl)

(b) Valine (R = isopropyl)

(c) Leucine (R = isobutyl)

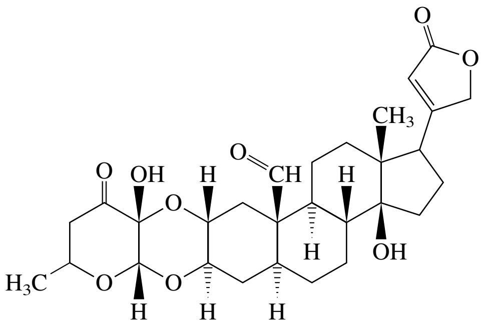
(d) Isoleucine (R = *sec*-butyl)

(e) Serine (R = XCH_2, where X is the functional group that characterizes alcohols)

(f) Cysteine (R = XCH_2, where X is the functional group that characterizes thiols)

(g) Aspartic acid (R = XCH_2, where X is the functional group that characterizes carboxylic acids)

2.30 Uscharidin is the common name of a poisonous natural product having the structure shown. Locate all of the following in uscharidin:



(a) Alcohol, aldehyde, ketone, and ester functional groups

(b) Methylene groups

(c) Primary carbons

2.31 Write the structural formula of a compound of molecular formula $C_4H_8Cl_2$ in which

(a) All the carbons belong to methylene groups

(b) None of the carbons belong to methylene groups

2.32 Female tiger moths signify their presence to male moths by giving off a sex attractant. The sex attractant has been isolated and found to be a 2-methyl-branched alkane having a molecular weight of 254. What is this material?

2.33 Write a balanced chemical equation for the combustion of each of the following compounds:

(a) Decane

(b) Cyclodecane

(c) Methylcyclononane

(d) Cyclopentylcyclopentane

2.34 The heats of combustion of methane and butane are 890 kJ/mol (212.8 kcal/mol) and 2876 kJ/mol (687.4 kcal/mol), respectively. When used as a fuel, would methane or butane generate more heat for the same mass of gas? Which would generate more heat for the same volume of gas?

2.35 In each of the following groups of compounds, identify the one with the largest heat of combustion and the one with the smallest. (Try to do this problem without consulting Table 2.5.)

(a) Hexane, heptane, octane

(b) Isobutane, pentane, isopentane

(c) Isopentane, 2-methylpentane, neopentane

(d) Pentane, 3-methylpentane, 3,3-dimethylpentane

(e) Ethylcyclopentane, ethylcyclohexane, ethylcycloheptane

2.36 (a) Given $\Delta H°$ for the reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H° = -286 \text{ kJ}$$

along with the information that the heat of combustion of ethane is 1560 kJ/mol and that of ethylene is 1410 kJ/mol, calculate $\Delta H°$ for the hydrogenation of ethylene:

$$CH_2{=}CH_2(g) + H_2(g) \longrightarrow CH_3CH_3(g)$$

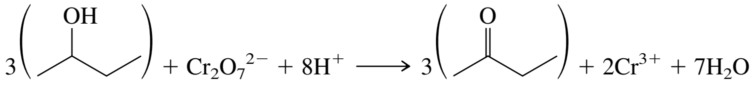
(b) If the heat of combustion of acetylene is 1300 kJ/mol, what is the value of $\Delta H°$ for its hydrogenation to ethylene? To ethane?

(c) What is the value of $\Delta H°$ for the hypothetical reaction

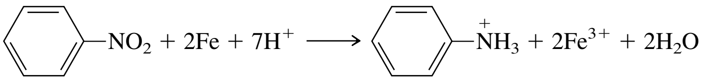
$$2CH_2{=}CH_2(g) \longrightarrow CH_3CH_3(g) + HC{\equiv}CH(g)$$

2.37 Each of the following reactions will be encountered at some point in this text. Classify each one according to whether the organic substrate is oxidized or reduced in the process.

(a) $CH_3C{\equiv}CH + 2Na + 2NH_3 \longrightarrow CH_3CH{=}CH_2 + 2NaNH_2$

(b) 

(c) $HOCH_2CH_2OH + HIO_4 \longrightarrow 2CH_2{=}O + HIO_3 + H_2O$

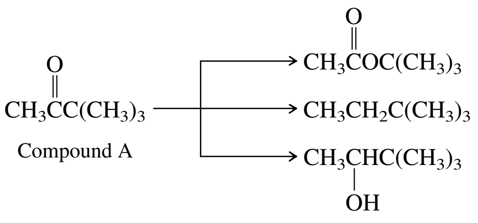
(d) 

2.38 The reaction shown is important in the industrial preparation of dichlorodimethylsilane for eventual conversion to silicone polymers.

$$2CH_3Cl + Si \longrightarrow (CH_3)_2SiCl_2$$

Is carbon oxidized, or is it reduced in this reaction?

2.39 Compound A undergoes the following reactions:



$$\underset{\text{Compound A}}{CH_3\overset{\overset{\Large O}{\|}}{C}C(CH_3)_3} \longrightarrow \begin{cases} CH_3\overset{\overset{O}{\|}}{C}OC(CH_3)_3 \\ CH_3CH_2C(CH_3)_3 \\ CH_3\underset{\underset{OH}{|}}{C}HC(CH_3)_3 \end{cases}$$

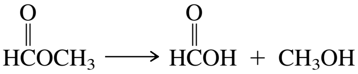
(a) To what class of compounds does compound A belong?

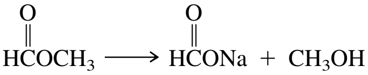
(b) Which of the reactions shown require(s) an oxidizing agent?

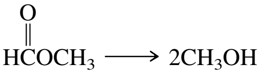
(c) Which of the reactions shown require(s) a reducing agent?

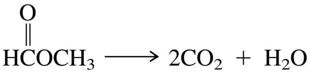
(d) Identify the class to which each of the reaction products belongs.

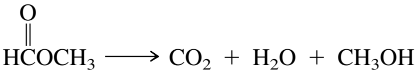
2.40 Each of the following equations describes a reaction of a compound called *methyl formate.* To what class of compounds does methyl formate belong? Which reactions require a reducing agent? Which require an oxidizing agent? Which reactions are not oxidation–reduction?

(a) 
$$\mathrm{H\overset{\overset{O}{\|}}{C}OCH_3 \longrightarrow H\overset{\overset{O}{\|}}{C}OH + CH_3OH}$$

(b) 
$$\mathrm{H\overset{\overset{O}{\|}}{C}OCH_3 \longrightarrow H\overset{\overset{O}{\|}}{C}ONa + CH_3OH}$$

(c) 
$$\mathrm{H\overset{\overset{O}{\|}}{C}OCH_3 \longrightarrow 2CH_3OH}$$

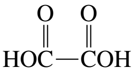
(d) 
$$\mathrm{H\overset{\overset{O}{\|}}{C}OCH_3 \longrightarrow 2CO_2 + H_2O}$$

(e) 
$$\mathrm{H\overset{\overset{O}{\|}}{C}OCH_3 \longrightarrow CO_2 + H_2O + CH_3OH}$$

2.41 Which atoms in the following reaction undergo changes in their oxidation state? Which atom is oxidized? Which one is reduced?

$$\mathrm{2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2}$$

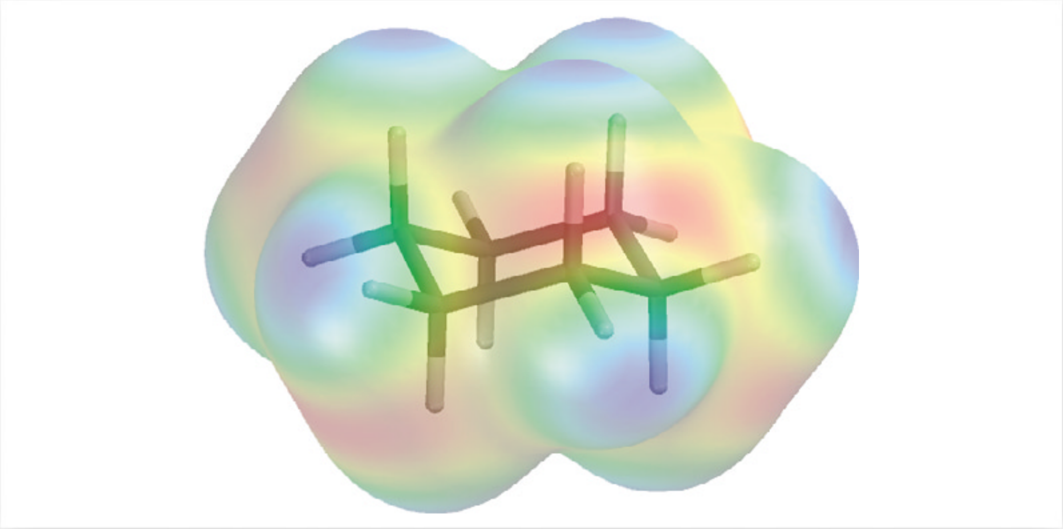
2.42 We have not talked about heats of combustion of compounds other than hydrocarbons. Nevertheless, from among the compounds shown here, you should be able to deduce which one gives off the most heat on combustion (to give CO_2 and H_2O) and which one the least.

$\mathrm{CH_3CH_2OH}$ $\mathrm{HOCH_2CH_2OH}$ 
$$\mathrm{HO\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}OH}$$

2.43 Make a molecular model of each of the compounds given as a representative example of the various functional group classes in Table 2.1.

2.44 The compound identified as "ethanoic acid" in Table 2.2 is better known as acetic acid. Make a molecular model of acetic acid, and compare the two C—O bond distances. Compare these with the C—O bond distance in ethanol (Problem 2.43).

2.45 You have seen that a continuous chain of *sp*^{3}-hybridized carbons, as in an alkane, is not "straight," but rather adopts a zigzag geometry. What would the hybridization state of carbon have to be in order for the chain to be truly straight?

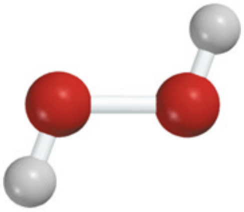


CHAPTER 3

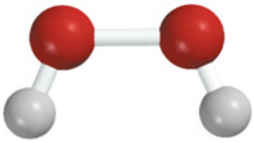
CONFORMATIONS OF ALKANES AND CYCLOALKANES

Hydrogen peroxide is formed in the cells of plants and animals but is toxic to them. Consequently, living systems have developed mechanisms to rid themselves of hydrogen peroxide, usually by enzyme-catalyzed reduction to water. An understanding of how reactions take place, be they reactions in living systems or reactions in test tubes, begins with a thorough knowledge of the structure of the reactants, products, and catalysts. Even a simple molecule such as hydrogen peroxide may be structurally more complicated than you think. Suppose we wanted to write the structural formula for H_2O_2 in enough detail to show the positions of the atoms relative to one another. We could write two different planar geometries A and B that differ by a 180° rotation about the O—O bond. We could also write an infinite number of nonplanar structures, of which C is but one example, that differ from one another by tiny increments of rotation about the O—O bond.

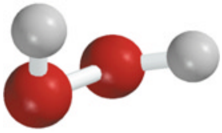
Structures A, B, and C represent different **conformations** of hydrogen peroxide. *Conformations are different spatial arrangements of a molecule that are generated by rotation about single bonds.* Although we can't tell from simply looking at these structures, we now know from experimental studies that C is the most stable conformation.



A



B



C

Learning By Modeling contains an animation showing the rotation about the O—O bond in hydrogen peroxide.

In this chapter we'll examine the conformations of various alkanes and cycloalkanes, focusing most of our attention on three of them: *ethane, butane,* and *cyclohexane.* A detailed study of even these three will take us a long way toward understanding the main ideas of **conformational analysis.**

The conformation of a molecule affects many of its properties. Conformational analysis is a tool used not only by chemists but also by researchers in the life sciences as they attempt to develop a clearer picture of how molecules—as simple as hydrogen peroxide or as complicated as DNA—behave in biological processes.

3.1 CONFORMATIONAL ANALYSIS OF ETHANE

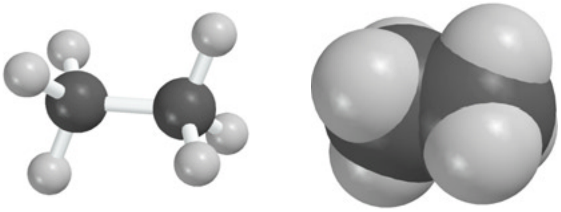
Ethane is the simplest hydrocarbon that can have distinct conformations. Two, the **staggered conformation** and the **eclipsed conformation,** deserve special attention and are illustrated in Figure 3.1. The C—H bonds in the staggered conformation are arranged so that each one bisects the angle made by a pair of C—H bonds on the adjacent carbon. In the eclipsed conformation each C—H bond is aligned with a C—H bond on the adjacent carbon. The staggered and eclipsed conformations interconvert by rotation around the carbon–carbon bond. Different conformations of the same molecule are sometimes called **conformers** or **rotamers.**

Among the various ways in which the staggered and eclipsed forms are portrayed, wedge-and-dash, sawhorse, and Newman projection drawings are especially useful. These are shown for the staggered conformation of ethane in Figure 3.2 and for the eclipsed conformation in Figure 3.3.

Newman projections were devised by Professor Melvin S. Newman of Ohio State University in the 1950s.

We used *wedge-and-dash* drawings in earlier chapters, and so Figures 3.2*a* and 3.3*a* are familiar to us. A *sawhorse* drawing (Figures 3.2*b* and 3.3*b*) shows the conformation of a molecule without having to resort to different styles of bonds. In a *Newman projection* (Figures 3.2*c* and 3.3*c*), we sight down the C—C bond, and represent the front carbon by a point and the back carbon by a circle. Each carbon has three substituents that are placed symmetrically around it.

Staggered conformation of ethane



Eclipsed conformation of ethane

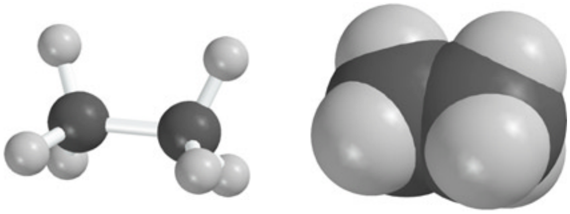
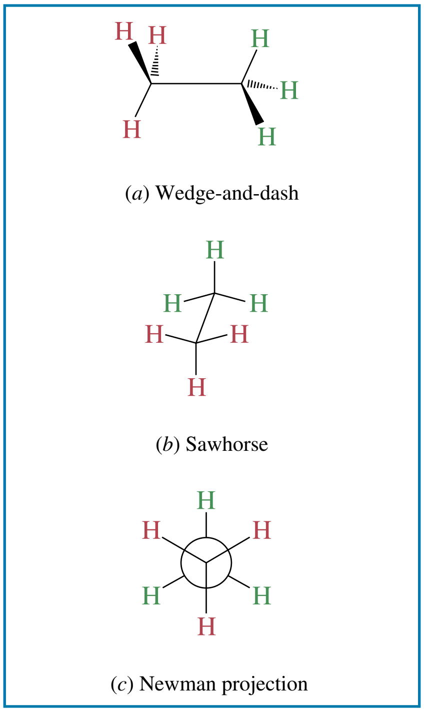


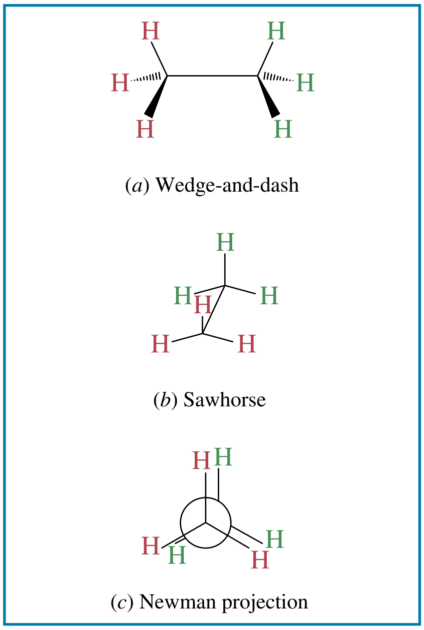
FIGURE 3.1 The staggered and eclipsed conformations of ethane shown as ball-and-spoke models *(left)* and as space-filling models *(right)*.


(*a*) Wedge-and-dash

(*b*) Sawhorse

(*c*) Newman projection

FIGURE 3.2 Some commonly used representations of the staggered conformation of ethane.


(*a*) Wedge-and-dash

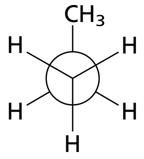
(*b*) Sawhorse

(*c*) Newman projection

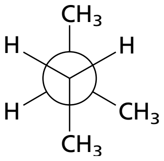
FIGURE 3.3 Some commonly used representations of the eclipsed conformation of ethane.

PROBLEM 3.1 Identify the alkanes corresponding to each of the drawings shown.

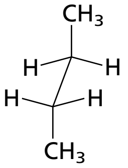
(a)



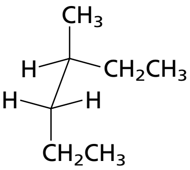
(c)



(b)

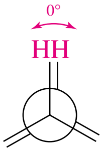


(d)

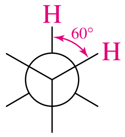


SAMPLE SOLUTION (a) The Newman projection of this alkane resembles that of ethane except one of the hydrogens has been replaced by a methyl group. The drawing is a Newman projection of propane, $CH_3CH_2CH_3$.

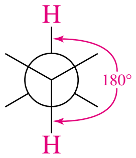
The structural feature that Figures 3.2 and 3.3 illustrate is the spatial relationship between atoms on adjacent carbon atoms. Each H—C—C—H unit in ethane is characterized by a *torsion angle* or *dihedral angle,* which is the angle between the H—C—C plane and the C—C—H plane. The torsion angle is easily seen in a Newman projection of ethane as the angle between C—H bonds of adjacent carbons.



Torsion angle = 0°
Eclipsed



Torsion angle = 60°
Gauche



Torsion angle = 180°
Anti

Eclipsed bonds are characterized by a torsion angle of 0°. When the torsion angle is approximately 60°, we say that the spatial relationship is **gauche;** and when it is 180° we say that it is **anti.** Staggered conformations have only gauche or anti relationships between bonds on adjacent atoms.

Of the two conformations of ethane, the staggered is more stable than the eclipsed. The measured difference in potential energy between them is 12 kJ/mol (2.9 kcal/mol). A simple explanation has echoes of VSEPR (Section 1.10). The staggered conformation allows the electron pairs in the C—H bonds of one carbon to be farther away from the electron pairs in the C—H bonds of the other than the eclipsed conformation allows. Electron-pair repulsions on adjacent carbons govern the relative stability of staggered and eclipsed conformations in much the same way that electron-pair repulsions influence the bond angles at a central atom.

The destabilization that comes from eclipsed bonds on adjacent atoms is called **torsional strain.** Torsional strain is one of several structural features resulting from its three-dimensional makeup that destabilize a molecule. The total strain of all of the spatially dependent features is often called **steric strain.** Because three pairs of eclipsed bonds produce 12 kJ/mol (2.9 kcal/mol) of torsional strain in ethane, it is reasonable to assign an "energy cost" of 4 kJ/mol (1 kcal/mol) to each pair of eclipsed bonds.

Steric is derived from the Greek word *stereos* for "solid" and refers to the three-dimensional or spatial aspects of chemistry.

In principle there are an infinite number of conformations of ethane, differing by only tiny increments in their torsion angles. Not only is the staggered conformation more stable than the eclipsed, it is the most stable of all of the conformations; the eclipsed is the least stable. Figure 3.4 shows how the potential energy of ethane changes for a 360° rotation about the carbon–carbon bond. Three equivalent eclipsed conformations and three equivalent staggered conformations occur during the 360° rotation; the eclipsed conformations appear at the highest points on the curve (*potential energy maxima*), the staggered ones at the lowest (*potential energy minima*).

The animation on the *Learning By Modeling* CD shows rotation about the C—C bond in ethane.

PROBLEM 3.2 Find the conformations in Figure 3.4 in which the red circles are (a) gauche and (b) anti.

Diagrams such as Figure 3.4 can be quite helpful for understanding how the potential energy of a system changes during a process. The process can be a simple one such as the one described here—rotation around a carbon–carbon bond. Or it might be more complicated—a chemical reaction, for example. We will see applications of potential energy diagrams to a variety of processes throughout the text.

Let's focus our attention on a portion of Figure 3.4. The region that lies between a torsion angle of 60° and 180° tracks the conversion of one staggered conformation of

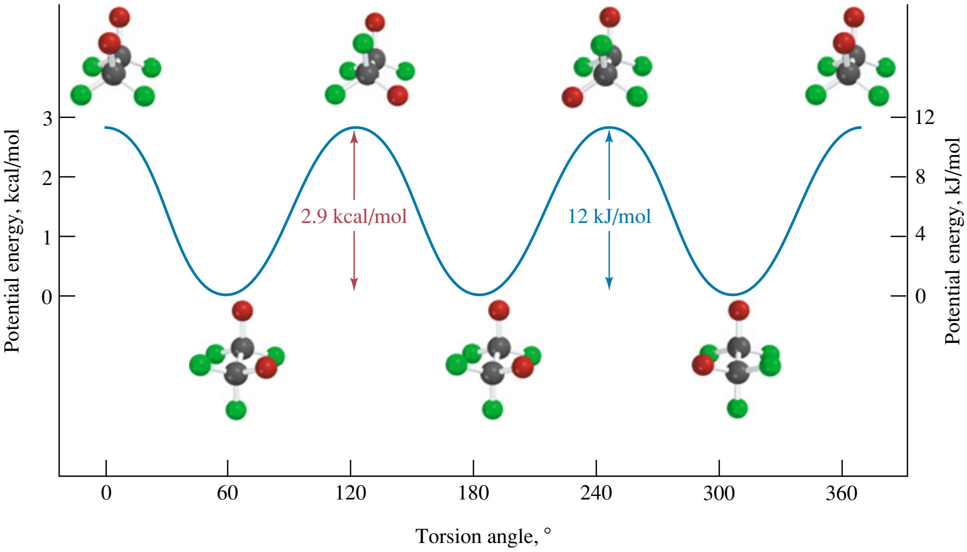


FIGURE 3.4 Potential energy diagram for rotation about the carbon–carbon bond in ethane. Two of the hydrogens are shown in red and four in green so as to indicate more clearly the bond rotation.

ethane to the next one. Both staggered conformations are equivalent and equal in energy, but for one staggered conformation to get to the next, it must first pass through an eclipsed conformation and needs to gain 12 kJ/mol (2.9 kcal/mol) of energy to reach it. This amount of energy is the **activation energy** (E_{act}) for the process. Molecules must become energized in order to undergo a chemical reaction or, as in this case, to undergo rotation around a carbon–carbon bond. Kinetic (thermal) energy is absorbed by a molecule from collisions with other molecules and is transformed into potential energy. When the potential energy exceeds E_{act}, the unstable arrangement of atoms that exists at that instant can relax to a more stable structure, giving off its excess potential energy in collisions with other molecules or with the walls of a container. The point of maximum potential energy encountered by the reactants as they proceed to products is called the **transition state.** The eclipsed conformation is the transition state for the conversion of one staggered conformation of ethane to another.

The structure that exists at the transition state is sometimes referred to as the *transition structure* or the *activated complex.*

Rotation around carbon–carbon bonds is one of the fastest processes in chemistry. Among the ways that we can describe the rate of a process is by its *half-life,* which is the length of time it takes for one half of the molecules to react. It takes less than 10^{-6} seconds for half of the molecules in a sample of ethane to go from one staggered conformation to another at 25°C. At any instant, almost all of the molecules are in staggered conformations; hardly any are in eclipsed conformations.

As with all chemical processes, the rate of rotation about the carbon–carbon bond increases with temperature. The reason for this can be seen by inspecting Figure 3.5, where it can be seen that most of the molecules in a sample have energies that are clustered around some average value; some have less energy, a few have more. Only molecules with a potential energy greater than E_{act}, however, are able to go over the transition state and proceed on to products. The number of these molecules is given by the shaded areas under the curve in Figure 3.5. The energy distribution curve flattens out at higher temperatures, and a greater proportion of molecules have energies in excess of E_{act} at T_2 (higher) than at T_1 (lower). The effect of temperature is quite pronounced; an increase of only 10°C produces a two- to threefold increase in the rate of a typical chemical process.

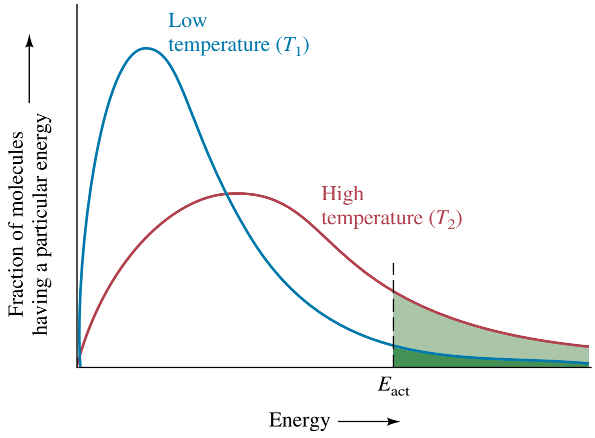


FIGURE 3.5 Distribution of molecular energies. (*a*) The number of molecules with energy greater than E_{act} at temperature T_1 is shown as the darker-green shaded area. (*b*) At some higher temperature T_2, the shape of the energy distribution curve is different, and more molecules have energies in excess of E_{act}.

3.2 CONFORMATIONAL ANALYSIS OF BUTANE

The next alkane that we examine is butane. In particular, we consider conformations related by rotation about the bond between the middle two carbons ($CH_3CH_2—CH_2CH_3$). Unlike ethane, in which the staggered conformations are equivalent, two different staggered conformations occur in butane, shown in Figure 3.6. The methyl groups are gauche to each other in one, anti in the other. Both conformations are staggered, so are free of torsional strain, but two of the methyl hydrogens of the gauche conformation lie within 210 pm of each other. This distance is less than the sum of their van der Waals radii (240 pm), and there is a repulsive force between them. The destabilization of a molecule that results when two of its atoms are too close to each other is

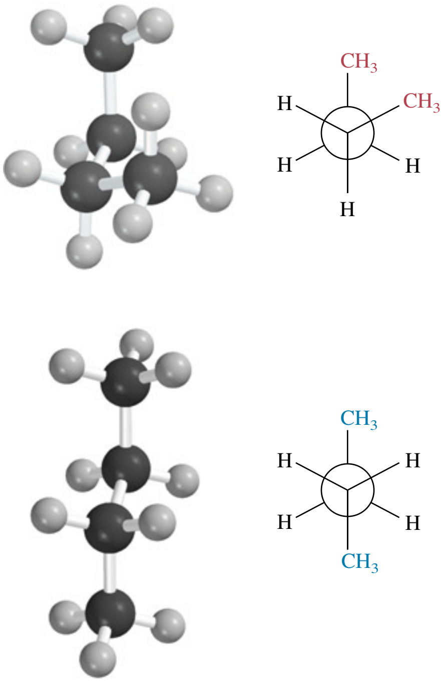


FIGURE 3.6 The gauche and anti conformations of butane shown as ball-and-spoke models *(left)* and as Newman projections *(right)*. The gauche conformation is less stable than the anti because of the van der Waals strain between the methyl groups.

called **van der Waals strain,** or **steric hindrance** and contributes to the total steric strain. In the case of butane, van der Waals strain makes the gauche conformation approximately 3.2 kJ/mol (0.8 kcal/mol) less stable than the anti.

Figure 3.7 illustrates the potential energy relationships among the various conformations of butane. The staggered conformations are more stable than the eclipsed. At any instant, almost all the molecules exist in staggered conformations, and more are present in the anti conformation than in the gauche. The point of maximum potential energy lies some 25 kJ/mol (6.1 kcal/mol) above the anti conformation. The total strain in this structure is approximately equally divided between the torsional strain associated with three pairs of eclipsed bonds (12 kJ/mol; 2.9 kcal/mol) and the van der Waals strain between the methyl groups.

PROBLEM 3.3 Sketch a potential energy diagram for rotation around a carbon–carbon bond in propane. Clearly identify each potential energy maximum and minimum with a structural formula that shows the conformation of propane at that point. Does your diagram more closely resemble that of ethane or of butane? Would you expect the activation energy for bond rotation in propane to be more than or less than that of ethane? Of butane?

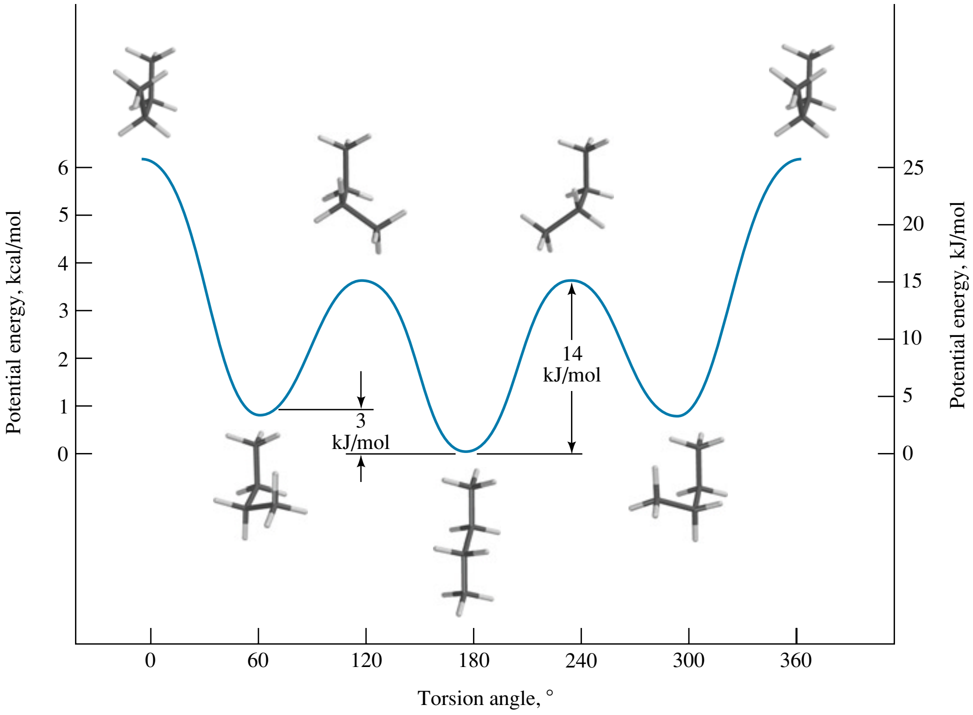


FIGURE 3.7 Potential energy diagram for rotation around the central carbon–carbon bond in butane.

MOLECULAR MECHANICS APPLIED TO ALKANES AND CYCLOALKANES

Of the numerous applications of computer technology to chemistry, one that has been enthusiastically embraced by organic chemists examines molecular structure from a perspective similar to that gained by manipulating molecular models but with an additional quantitative dimension. *Molecular mechanics* is a computational method that allows us to assess the stability of a molecule by comparing selected features of its structure with those of ideal "unstrained" standards. Molecular mechanics makes no attempt to explain why the van der Waals radius of hydrogen is 120 pm, why the bond angles in methane are 109.5°, why the C—C bond distance in ethane is 153 pm, or why the staggered conformation of ethane is 12 kJ/mol more stable than the eclipsed, but instead uses these and other experimental observations as benchmarks to which the corresponding features of other substances are compared.

If we assume that there are certain "ideal" values for bond angles, bond distances, and so on, it follows that deviations from these ideal values will destabilize a particular structure and increase its potential energy. This increase in potential energy is referred to as the **strain energy** of the structure. Other terms include **steric energy** and **steric strain.** Arithmetically, the total strain energy (E_s) of an alkane or cycloalkane can be considered as

$$E_s = E_{\text{bond stretching}} + E_{\text{angle bending}} + E_{\text{torsional}} + E_{\text{van der Waals}}$$

where

$E_{\text{bond stretching}}$ is the strain that results when C—C and C—H bond distances are distorted from their ideal values of 153 pm and 111 pm, respectively.

$E_{\text{angle bending}}$ is the strain that results from the expansion or contraction of bond angles from the normal values of 109.5° for sp^3 hybridized carbon.

$E_{\text{torsional}}$ is the strain that results from deviation of torsion angles from their stable staggered relationship.

$E_{\text{van der Waals}}$ is the strain that results from "nonbonded interactions."

Nonbonded interactions are the forces between atoms that aren't bonded to one another; they may be either attractive or repulsive. It often happens that the shape of a molecule may cause two atoms to be close in space even though they are separated from each other by many bonds. Induced-dipole/induced-dipole interactions make van der Waals forces in alkanes weakly attractive at most distances, but when two atoms are closer to each other than the sum of their van der Waals radii, nuclear–nuclear and electron–electron repulsive forces between them dominate the $E_{\text{van der Waals}}$ term. The resulting destabilization is called van der Waals strain.

At its most basic level, separating the total strain of a structure into its components is a qualitative exercise. For example, a computer-drawn model of the eclipsed conformation of butane using ideal bond angles and bond distances (Figure 3.8) reveals that two pairs of hydrogens are separated by a distance of only 175 pm, a value considerably smaller than the sum of their van der Waals radii (2 × 120 pm = 240 pm). Thus, this conformation is destabilized not only by the torsional strain associated with its eclipsed bonds, but also by van der Waals strain.

At a higher level, molecular mechanics is applied quantitatively to strain energy calculations. Each component of strain is separately described by a mathematical expression developed and refined so that it gives solutions that match experimental observations for reference molecules. These empirically derived and tested expressions are then used to calculate the most stable structure of a substance. The various structural features are interdependent; van der Waals strain, for example, might be decreased at the expense of introducing some angle strain, torsional strain, or both. The computer program searches for the combination of bond angles, distances, torsion angles, and nonbonded interactions that gives the molecule the lowest total strain. This procedure is called *strain energy minimization* and is based on the commonsense notion that the most stable structure is the one that has the least strain.

—Cont.

The first widely used molecular mechanics program was developed by Professor N. L. Allinger of the University of Georgia and was known in its various versions as *MM2, MM3,* and so on. They have been refined to the extent that many structural features can be calculated more easily and more accurately than they can be measured experimentally.

Once requiring minicomputers and workstations, many molecular mechanics programs are available for personal computers. The information that strain energy calculations can provide is so helpful that molecular mechanics is no longer considered a novelty but rather as one more tool to be used by the practicing organic chemist. They have been joined by programs that calculate the energies of conformations by molecular orbital methods. The *Learning By Modeling* CD that accompanies this text contains molecular mechanics software that lets you seek out the most stable conformation of the structures you assemble. It also contains the most stable conformations of some molecules as determined by molecular orbital calculations.

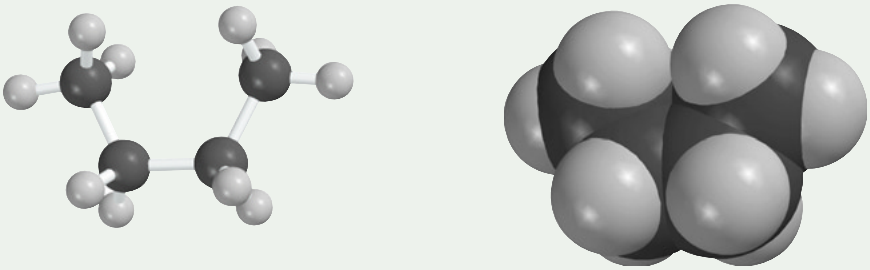
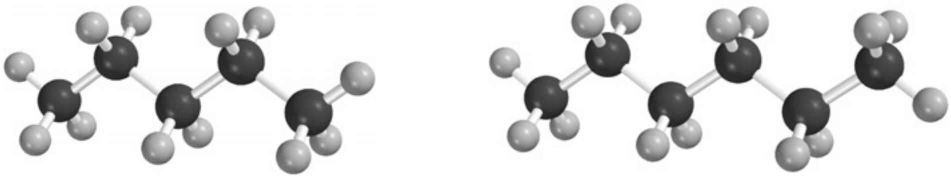


FIGURE 3.8 Ball-and-spoke and space-filling models of methyl-methyl eclipsed conformation of butane.

3.3 CONFORMATIONS OF HIGHER ALKANES

Higher alkanes having unbranched carbon chains are, like butane, most stable in their all-anti conformations. The energy difference between gauche and anti conformations is similar to that of butane, and appreciable quantities of the gauche conformation are present in liquid alkanes at 25°C. In depicting the conformations of higher alkanes it is often more helpful to look at them from the side rather than end-on as in a Newman projection. Viewed from this perspective, the most stable conformations of pentane and hexane have their carbon "backbones" arranged in a zigzag fashion, as shown in Figure 3.9. All the bonds are staggered, and the chains are characterized by anti arrangements of C—C—C—C units.



Pentane

Hexane

FIGURE 3.9 Ball-and-spoke models of pentane and hexane in their all-anti (zigzag) conformations.

3.4 THE SHAPES OF CYCLOALKANES: PLANAR OR NONPLANAR?

During the nineteenth century it was widely believed—incorrectly, as we'll soon see—that cycloalkane rings are planar. A leading advocate of this view was the German chemist Adolf von Baeyer. He noted that compounds containing rings other than those based on cyclopentane and cyclohexane were rarely encountered naturally and were difficult to synthesize. Baeyer connected both observations with cycloalkane stability, which he suggested was related to how closely the angles of planar rings match the tetrahedral value of 109.5°. For example, the 60° bond angle of cyclopropane and the 90° bond angles of a planar cyclobutane ring are much smaller than the tetrahedral angle of 109.5°. Baeyer suggested that three- and four-membered rings suffer from what we now call **angle strain.** *Angle strain* is the strain a molecule has because one or more of its bond angles deviate from the ideal value; in the case of alkanes the ideal value is 109.5°.

Although better known now for his incorrect theory that cycloalkanes were planar, Baeyer was responsible for notable advances in the chemistry of organic dyes such as indigo and was awarded the 1905 Nobel Prize in chemistry for his work in that area.

According to Baeyer, cyclopentane should be the most stable of all the cycloalkanes because the ring angles of a planar pentagon, 108°, are closer to the tetrahedral angle than those of any other cycloalkane. A prediction of the *Baeyer strain theory* is that the cycloalkanes beyond cyclopentane should become increasingly strained and correspondingly less stable. The angles of a regular hexagon are 120°, and the angles of larger polygons deviate more and more from the ideal tetrahedral angle.

Some of the inconsistencies in the Baeyer strain theory will become evident as we use heats of combustion (Table 3.1) to probe the relative energies of cycloalkanes. The most important column in the table is the heat of combustion per methylene (CH_2) group. Since all of the cycloalkanes have molecular formulas of the type C_nH_{2n}, dividing the heat of combustion by *n* allows direct comparison of ring size and potential energy. Cyclopropane has the highest heat of combustion per methylene group, which is consistent with the idea that its potential energy is raised by angle strain. Cyclobutane has less angle strain at each of its carbon atoms and a lower heat of combustion per methylene group. Cyclopentane, as expected, has a lower value still. Notice, however, that contrary to the prediction of the Baeyer strain theory, cyclohexane has a smaller heat of combustion per methylene group than cyclopentane. If bond angle distortion were greater in cyclohexane than in cyclopentane, the opposite would have been observed.

TABLE 3.1 Heats of Combustion ($-\Delta H°$) of Cycloalkanes

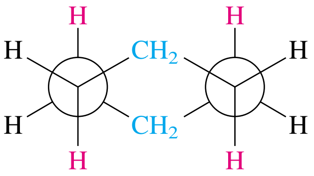
Cycloalkane	Number of CH_2 groups	Heat of combustion kJ/mol	Heat of combustion (kcal/mol)	Heat of combustion per CH_2 group kJ/mol	Heat of combustion per CH_2 group (kcal/mol)
Cyclopropane	3	2,091	(499.8)	697	(166.6)
Cyclobutane	4	2,721	(650.3)	681	(162.7)
Cyclopentane	5	3,291	(786.6)	658	(157.3)
Cyclohexane	6	3,920	(936.8)	653	(156.0)
Cycloheptane	7	4,599	(1099.2)	657	(157.0)
Cyclooctane	8	5,267	(1258.8)	658	(157.3)
Cyclononane	9	5,933	(1418.0)	659	(157.5)
Cyclodecane	10	6,587	(1574.3)	659	(157.5)
Cycloundecane	11	7,237	(1729.8)	658	(157.3)
Cyclododecane	12	7,845	(1875.1)	654	(156.3)
Cyclotetradecane	14	9,139	(2184.2)	653	(156.0)
Cyclohexadecane	16	10,466	(2501.4)	654	(156.3)

Furthermore, the heats of combustion per methylene group of the very large rings are all about the same and similar to that of cyclohexane. Rather than rising because of increasing angle strain in large rings, the heat of combustion per methylene group remains constant at approximately 653 kJ/mol (156 kcal/mol), the value cited in Section 2.15 as the difference between successive members of a homologous series of alkanes. We conclude, therefore, that the bond angles of large cycloalkanes are not much different from the bond angles of alkanes themselves. The prediction of the Baeyer strain theory that angle strain increases steadily with ring size is contradicted by experimental fact.

The Baeyer strain theory is useful to us in identifying angle strain as a destabilizing effect. Its fundamental flaw is its assumption that the rings of cycloalkanes are planar. *With the exception of cyclopropane, cycloalkanes are nonplanar.* Sections 3.5–3.11 describe the shapes of cycloalkanes. Six-membered rings rank as the most important ring size among organic compounds; thus let us begin with cyclohexane to examine the forces that determine the shapes of cycloalkanes.

3.5 CONFORMATIONS OF CYCLOHEXANE

Experimental evidence indicating that six-membered rings are nonplanar began to accumulate in the 1920s. Eventually, Odd Hassel of the University of Oslo established that the most stable conformation of cyclohexane has the shape shown in Figure 3.10. This is called the **chair** conformation. With C—C—C bond angles of 111°, the chair conformation is nearly free of angle strain. All its bonds are staggered, making it free of torsional strain as well. The staggered arrangement of bonds in the chair conformation of cyclohexane is apparent in a Newman-style projection.



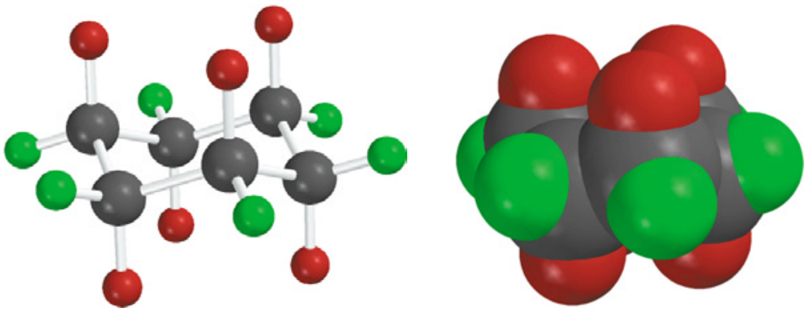
Staggered arrangement of bonds in chair conformation of cyclohexane

Hassel shared the 1969 Nobel Prize in chemistry with Sir Derek Barton of Imperial College (London), now at Texas A&M University. Barton demonstrated how Hassel's structural results could be extended to an analysis of conformational effects on chemical reactivity.

Make a molecular model of the chair conformation of cyclohexane, and turn it so that you can look down one of the C—C bonds.

A second, but much less stable, nonplanar conformation called the **boat** is shown in Figure 3.11. Like the chair, the boat conformation has bond angles that are approximately tetrahedral and is relatively free of angle strain. As noted in Figure 3.11, however, the boat is destabilized by van der Waals strain involving its two "flagpole" hydrogens, which are within 180 pm of each other. An even greater contribution to the

Recall from Section 3.2 that the sum of the van der Waals radii of two hydrogen atoms is 240 pm.



(*a*) (*b*)

FIGURE 3.10 (*a*) A ball-and-spoke model and (*b*) a space-filling model of the chair conformation of cyclohexane.

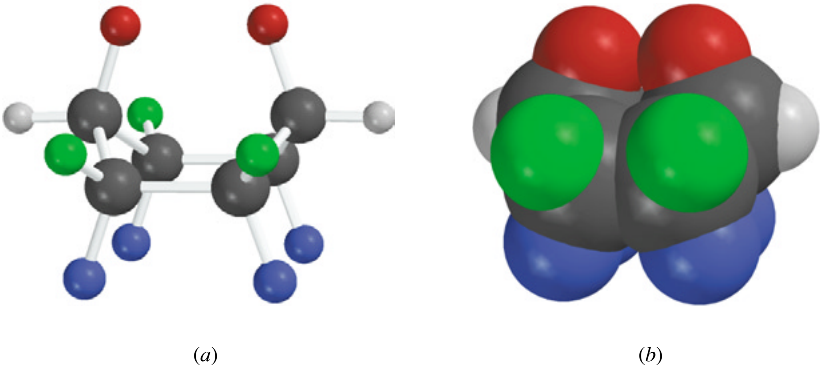


FIGURE 3.11 (*a*) A ball-and-spoke model and (*b*) a space-filling model of the boat conformation of cyclohexane. The close approach of the two uppermost hydrogen substituents is clearly evident in the space-filling model.

estimated 27 kJ/mol (6.4 kcal/mol) energy difference between the chair and the boat is the torsional strain associated with eclipsed bonds on four of the carbons in the boat. Figure 3.12 depicts the eclipsed bonds and demonstrates how the associated torsional strain may be reduced by rotation about the carbon–carbon bonds to give the slightly more stable **twist boat,** or **skew boat,** conformation. The same bond rotations that reduce the torsional strain also reduce the van der Waals strain by increasing the distance between the two flagpole hydrogens.

The various conformations of cyclohexane are in rapid equilibrium with one another, but at any moment almost all of the molecules exist in the chair conformation. Not more than one or two molecules per thousand are present in the higher energy skew boat and boat conformations. Thus, the discussion of cyclohexane conformational analysis that follows focuses exclusively on the chair conformation.

3.6 AXIAL AND EQUATORIAL BONDS IN CYCLOHEXANE

One of the most important findings to come from conformational studies of cyclohexane is that its 12 hydrogen atoms are not all identical but are divided into two groups, as shown in Figure 3.13. Six of the hydrogens, called **axial** hydrogens, have their bonds parallel to a vertical axis that passes through the ring's center. These axial bonds alter-

FIGURE 3.12 (*a*) The boat and (*b*) skew boat conformations of cyclohexane. A portion of the torsional strain in the boat is relieved by rotation about C—C bonds in the skew boat. Bond rotation is accompanied by movement of flagpole hydrogens away from each other, which reduces the van der Waals strain between them.

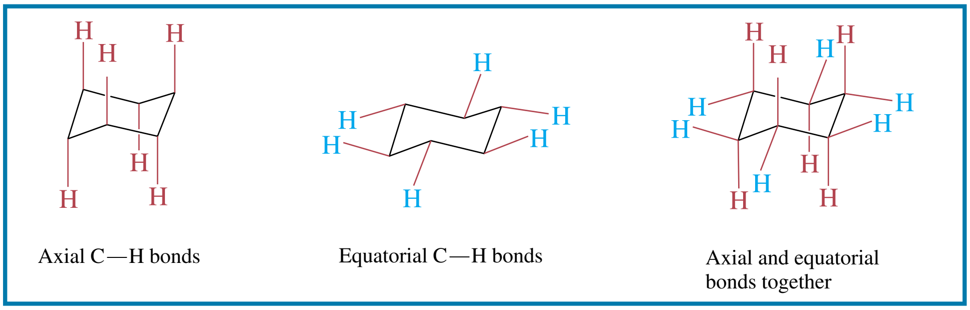
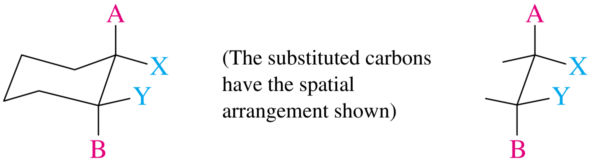


FIGURE 3.13 Axial and equatorial bonds in cyclohexane.

nately are directed up and down on adjacent carbons. The second set of six hydrogens, called **equatorial** hydrogens, are located approximately along the equator of the molecule. Notice that the four bonds to each carbon are arranged tetrahedrally, consistent with an sp^3 hybridization of carbon.

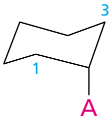
The conformational features of six-membered rings are fundamental to organic chemistry, so it is essential that you have a clear understanding of the directional properties of axial and equatorial bonds and be able to represent them accurately. Figure 3.14 offers some guidance on the drawing of chair cyclohexane rings.

It is no accident that sections of our chair cyclohexane drawings resemble sawhorse projections of staggered conformations of alkanes. The same spatial relationships seen in alkanes carry over to substituents on a six-membered ring. In the structure



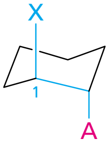
substituents A and B are anti to each other, and the other relationships—A and Y, X and Y, and X and B—are gauche.

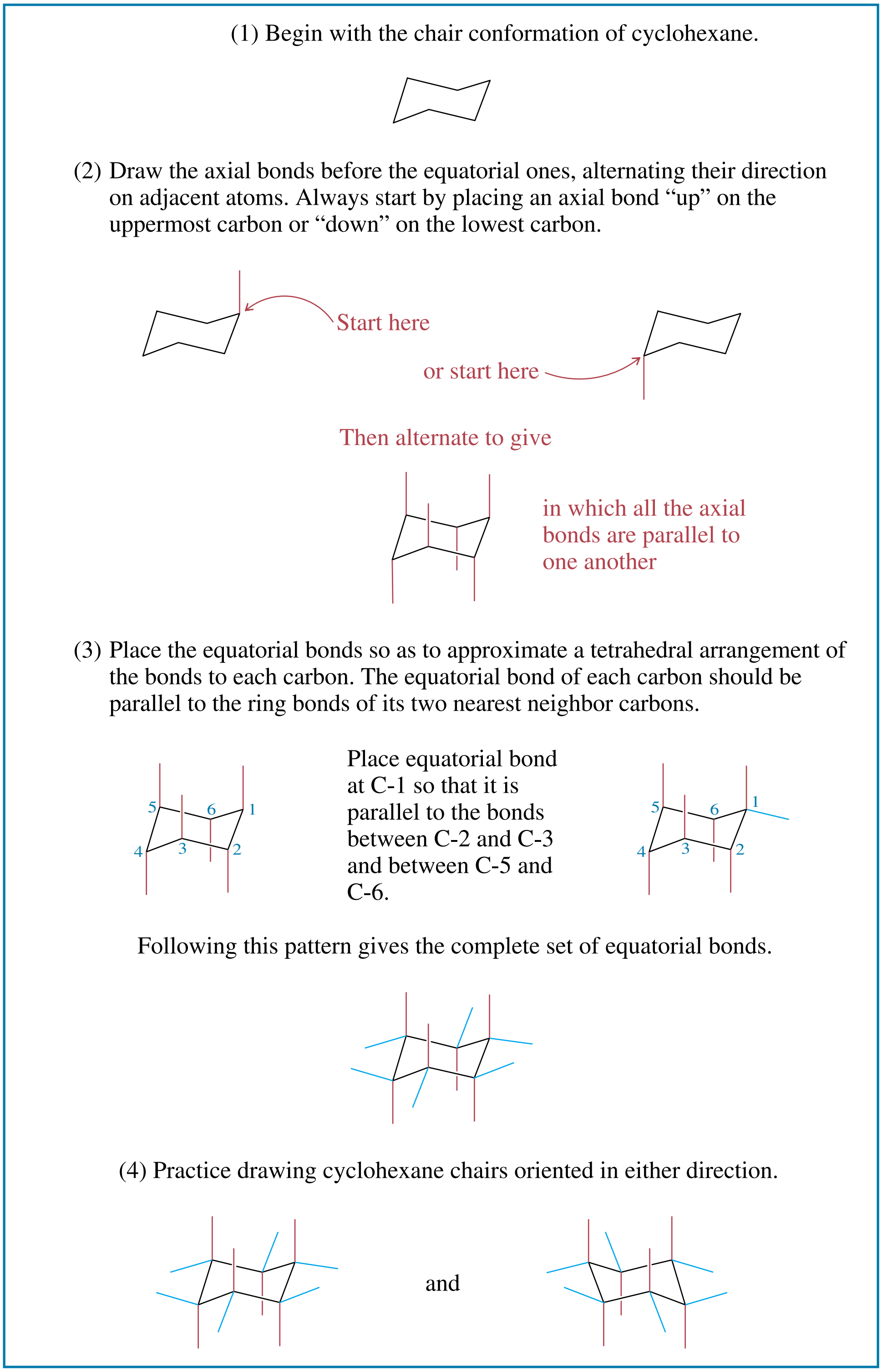
PROBLEM 3.4 Given the following partial structure, add a substituent X to C-1 so that it satisfies the indicated stereochemical requirement. You may find it helpful to build a molecular model for reference.



(a) Anti to A
(b) Gauche to A
(c) Anti to C-3
(d) Gauche to C-3

SAMPLE SOLUTION (a) In order to be anti to A, substituent X must be axial. The blue lines in the drawing show the A—C—C—X torsion angle to be 180°.





(1) Begin with the chair conformation of cyclohexane.

(2) Draw the axial bonds before the equatorial ones, alternating their direction on adjacent atoms. Always start by placing an axial bond "up" on the uppermost carbon or "down" on the lowest carbon.

(3) Place the equatorial bonds so as to approximate a tetrahedral arrangement of the bonds to each carbon. The equatorial bond of each carbon should be parallel to the ring bonds of its two nearest neighbor carbons.

Place equatorial bond at C-1 so that it is parallel to the bonds between C-2 and C-3 and between C-5 and C-6.

Following this pattern gives the complete set of equatorial bonds.

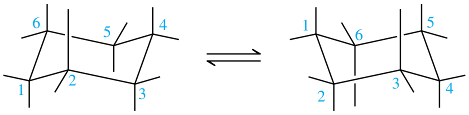
(4) Practice drawing cyclohexane chairs oriented in either direction.

FIGURE 3.14 A guide to representing the orientations of the bonds in the chair conformation of cyclohexane.

3.7 CONFORMATIONAL INVERSION (RING FLIPPING) IN CYCLOHEXANE

We have seen that alkanes are not locked into a single conformation. Rotation around the central carbon–carbon bond in butane occurs rapidly, interconverting anti and gauche conformations. Cyclohexane, too, is conformationally mobile. Through a process known as **ring inversion, chair–chair interconversion,** or, more simply, **ring flipping,** one chair conformation is converted to another chair.

A more detailed discussion of cyclohexane ring inversion can be found in the July 1997 issue of the *Journal of Chemical Education,* pp. 813–814.

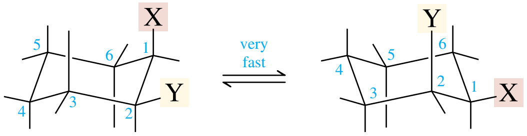


The activation energy for cyclohexane ring inversion is 45 kJ/mol (10.8 kcal/mol). It is a very rapid process with a half-life of about 10^{-5} *s* at 25°C.

A potential energy diagram for ring inversion in cyclohexane is shown in Figure 3.15. In the first step the chair conformation is converted to a skew boat, which then proceeds to the inverted chair in the second step. The skew boat conformation is an *intermediate* in the process of ring inversion. Unlike a transition state, an **intermediate** is not a potential energy maximum but is a local minimum on the potential energy profile.

The best way to understand ring flipping in cyclohexane is to view the animation of Figure 3.15 in *Learning By Modeling.*

The most important result of ring inversion is that any substituent that is axial in the original chair conformation becomes equatorial in the ring-flipped form and vice versa.



X axial; Y equatorial

X equatorial; Y axial

The consequences of this point are developed for a number of monosubstituted cyclohexane derivatives in the following section, beginning with methylcyclohexane.

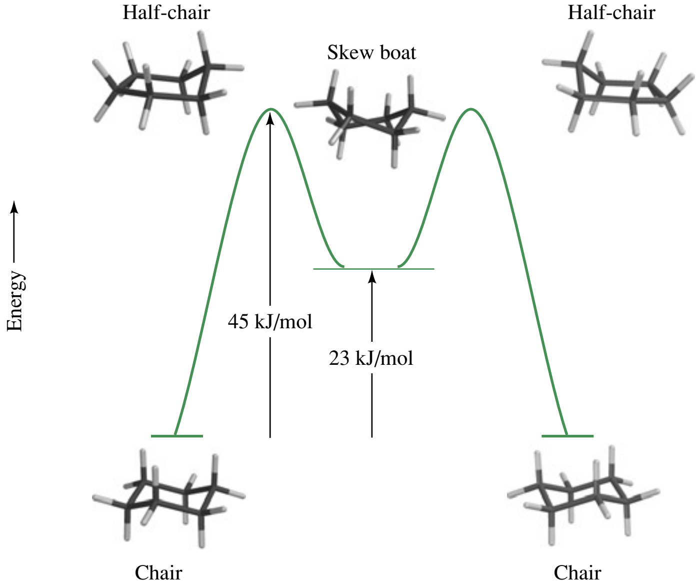
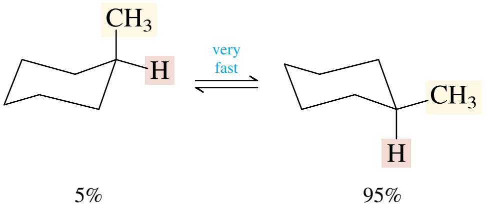


FIGURE 3.15 Energy diagram showing interconversion of various conformations of cyclohexane. In order to simplify the diagram, the boat conformation has been omitted. The boat is a transition state for the interconversion of skew boat conformations.

3.8 CONFORMATIONAL ANALYSIS OF MONOSUBSTITUTED CYCLOHEXANES

Ring inversion in methylcyclohexane differs from that of cyclohexane in that the two chair conformations are not equivalent. In one chair the methyl group is axial; in the other it is equatorial. At room temperature approximately 95% of the molecules of methylcyclohexane are in the chair conformation that has an equatorial methyl group whereas only 5% of the molecules have an axial methyl group.

See *Learning By Modeling* for an animation of this process.

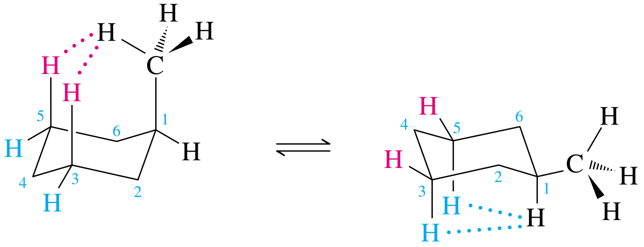


See the box entitled "Enthalpy, Free Energy, and Equilibrium Constant" accompanying this section for a discussion of these relationships.

When two conformations of a molecule are in equilibrium with each other, the one with the lower free energy predominates. Why is equatorial methylcyclohexane more stable than axial methylcyclohexane?

A methyl group is less crowded when it is equatorial than when it is axial. One of the hydrogens of an axial methyl group is within 190–200 pm of the axial hydrogens at C-3 and C-5. This distance is less than the sum of the van der Waals radii of two hydrogens (240 pm) and causes van der Waals strain in the axial conformation. When the methyl group is equatorial, it experiences no significant crowding.

Make a molecular model of each chair conformation of methylcyclohexane, and compare their energies.

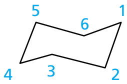


Van der Waals strain between hydrogen of axial CH_3 and axial hydrogens at C-3 and C-5

Smaller van der Waals strain between hydrogen at C-1 and axial hydrogens at C-3 and C-5

The greater stability of an equatorial methyl group, compared with an axial one, is another example of a *steric effect* (Section 3.2). An axial substituent is said to be crowded because of **1,3-diaxial repulsions** between itself and the other two axial substituents located on the same side of the ring.

PROBLEM 3.5 The following questions relate to a cyclohexane ring depicted in the chair conformation shown.

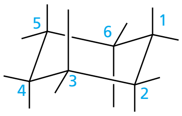


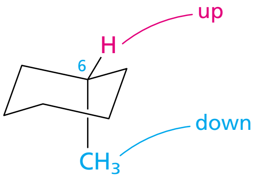
(a) Is a methyl group at C-6 that is "down" axial or equatorial?

(b) Is a methyl group that is "up" at C-1 more or less stable than a methyl group that is up at C-4?

(c) Place a methyl group at C-3 in its most stable orientation. Is it up or down?

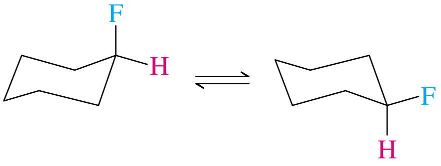
SAMPLE SOLUTION (a) First indicate the directional properties of the bonds to the ring carbons. A substituent is down if it is below the other substituent on the same carbon atom. A methyl group that is down at C-6 is therefore axial.





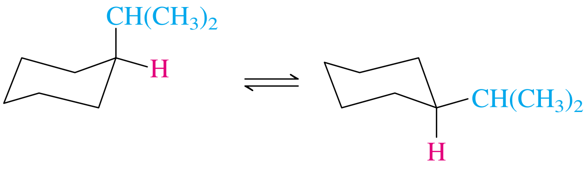
Other substituted cyclohexanes are similar to methylcyclohexane. Two chair conformations exist in rapid equilibrium, and the one in which the substituent is equatorial is more stable. The relative amounts of the two conformations depend on the effective size of the substituent. The size of a substituent, in the context of cyclohexane conformations, is related to the degree of branching at its point of connection to the ring. A single atom, such as a halogen substituent, does not take up much space, and its preference for an equatorial orientation is less pronounced than that of a methyl group.

The halogens F, Cl, Br, and I do not differ much in their preference for the equatorial position. As the atomic radius increases in the order F < Cl < Br < I, so does the carbon–halogen bond distance, and the two effects tend to cancel.



40% 60%

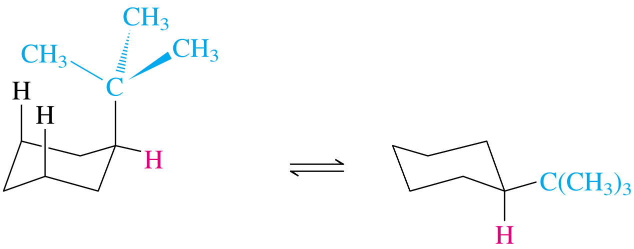
A branched alkyl group such as isopropyl exhibits a greater preference for the equatorial orientation than does methyl.



3% 97%

A *tert*-butyl group is so large that *tert*-butylcyclohexane exists almost entirely in the conformation in which the *tert*-butyl group is equatorial. The amount of axial *tert*-butylcyclohexane present is too small to measure.

Highly branched groups such as *tert*-butyl are commonly described as "bulky."



Less than 0.01%
(Serious 1,3-diaxial repulsions involving *tert*-butyl group)

Greater than 99.99%
(Decreased van der Waals strain)

PROBLEM 3.6 Draw or construct a molecular model of the most stable conformation of 1-*tert*-butyl-1-methylcyclohexane.

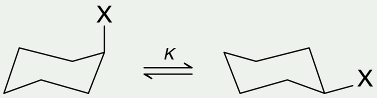
ENTHALPY, FREE ENERGY, AND EQUILIBRIUM CONSTANT

One of the fundamental equations of thermodynamics concerns systems at equilibrium and relates the equilibrium constant K to the difference in **free energy** ($\Delta G°$) between the products and the reactants.

$$\Delta G° = G°_{\text{products}} - G°_{\text{reactants}} = -RT\ln K$$

where T is the absolute temperature in kelvins and the constant R equals 8.314 J/mol · K (1.99 cal/mol · K).

For the equilibrium between the axial and equatorial conformations of a monosubstituted cyclohexane,



the equilibrium constant is given by the expression

$$K = \frac{[\text{products}]}{[\text{reactants}]}$$

Inserting the appropriate values for R, T (298 K), and K gives the values of $\Delta G°$ listed in the table (page 107) for the various substituents discussed in Section 3.8.

The relationship between $\Delta G°$ and K is plotted in Figure 3.17. A larger value of K is associated with a more negative $\Delta G°$.

Free energy and enthalpy are related by the expression

$$\Delta G° = \Delta H° - T\Delta S°$$

where $\Delta S°$ is the difference in *entropy* between the products and reactants. A positive $\Delta S°$ is accompanied by an increase in the disorder of a system. A positive $T\Delta S°$ term leads to a $\Delta G°$ that is more negative than $\Delta H°$ and a larger K than expected on the basis of enthalpy considerations alone. Conversely, a negative $\Delta S°$ gives a smaller K than expected. In the case of conformational equilibration between the chair forms of a substituted cyclohexane, $\Delta S°$ is close to zero and $\Delta G°$ and $\Delta H°$ are approximately equal.

—Cont.

3.9 SMALL RINGS: CYCLOPROPANE AND CYCLOBUTANE

Conformational analysis is far simpler in cyclopropane than in any other cycloalkane. Cyclopropane's three carbon atoms are, of geometric necessity, coplanar, and rotation about its carbon–carbon bonds is impossible. You saw in Section 3.4 how angle strain in cyclopropane leads to an abnormally large heat of combustion. Let's now look at cyclopropane in more detail to see how our orbital hybridization bonding model may be adapted to molecules of unusual geometry.

Strong sp^3–sp^3 σ bonds are not possible for cyclopropane, because the 60° bond angles of the ring do not permit the orbitals to be properly aligned for effective overlap (Figure 3.16). The less effective overlap that does occur leads to what chemists refer to

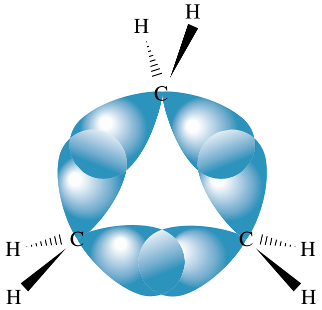


FIGURE 3.16 "Bent bonds" in cyclopropane. The orbitals involved in carbon–carbon bond formation overlap in a region that is displaced from the internuclear axis. Orbital overlap is less effective than in a normal carbon–carbon σ bond, and the carbon–carbon bond is weaker.

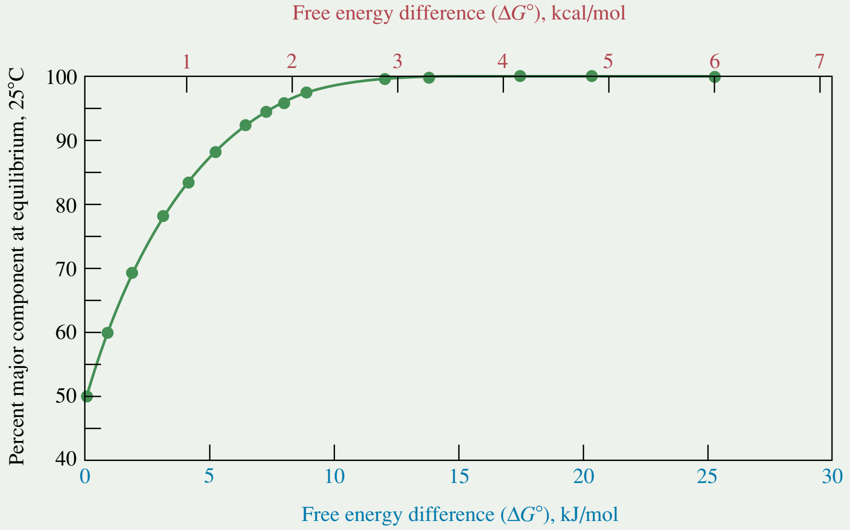


FIGURE 3.17 Distribution of two products at equilibrium plotted as a function of the difference in free energy ($\Delta G°$) at 25°C between them.

				$\Delta G°_{298\ K}$	
Substituent X	**Percent axial**	**Percent equatorial**	***K***	**kJ/mol**	**(kcal/mol)**
—F	40	60	1.5	−1.0	(−0.24)
$—CH_3$	5	95	19	−7.3	(−1.7)
$—CH(CH_3)_2$	3	97	32.3	−8.6	(−2.1)
$—C(CH_3)_3$	<0.01	>99.99	>9999	−22.8	(−5.5)

as "bent" bonds. The electron density in the carbon–carbon bonds of cyclopropane does not lie along the internuclear axis but is distributed along an arc between the two carbon atoms. The ring bonds of cyclopropane are weaker than other carbon–carbon σ bonds.

In addition to angle strain, cyclopropane is destabilized by torsional strain. Each C—H bond of cyclopropane is eclipsed with two others.

In keeping with the "bent-bond" description of Figure 3.16, the carbon–carbon bond distance in cyclopropane (151 pm) is slightly shorter than that of ethane (153 pm) and cyclohexane (154 pm). The calculated values from molecular models (see *Learning By Modeling*) reproduce these experimental values.

All adjacent pairs
of bonds are eclipsed

Cyclobutane has less angle strain than cyclopropane and can reduce the torsional strain that goes with a planar geometry by adopting the nonplanar "puckered" conformation shown in Figure 3.18.

PROBLEM 3.7 The heats of combustion of ethylcyclopropane and methylcyclobutane have been measured as 3352 and 3384 kJ/mol (801.2 and 808.8 kcal/mol), respectively. Assign the correct heat of combustion to each isomer.

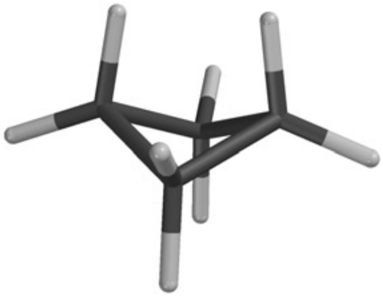


FIGURE 3.18 Nonplanar ("puckered") conformation of cyclobutane. The nonplanar conformation is more stable because it avoids the eclipsing of bonds on adjacent carbons that characterizes the planar conformation.

3.10 CYCLOPENTANE

Neighboring C—H bonds are eclipsed in any planar cycloalkane. Thus all planar conformations are destabilized by torsional strain.

Angle strain in the planar conformation of cyclopentane is relatively small because the 108° angles of a regular pentagon are not much different from the normal 109.5° bond angles of sp^3 hybridized carbon. The torsional strain, however, is substantial, since five bonds are eclipsed on the top face of the ring, and another set of five are eclipsed on the bottom face (Figure 3.19*a*). Some, but not all, of this torsional strain is relieved in nonplanar conformations. Two nonplanar conformations of cyclopentane, the **envelope** (Figure 3.19*b*) and the **half-chair** (Figure 3.19*c*) are of similar energy.

In the envelope conformation four of the carbon atoms are coplanar. The fifth carbon is out of the plane of the other four. There are three coplanar carbons in the half-chair conformation, with one carbon atom displaced above that plane and another below it. In both the envelope and the half-chair conformations, in-plane and out-of-plane carbons exchange positions rapidly. Equilibration between conformations of cyclopentane occurs at rates that are comparable with the rate of rotation about the carbon–carbon bond of ethane.

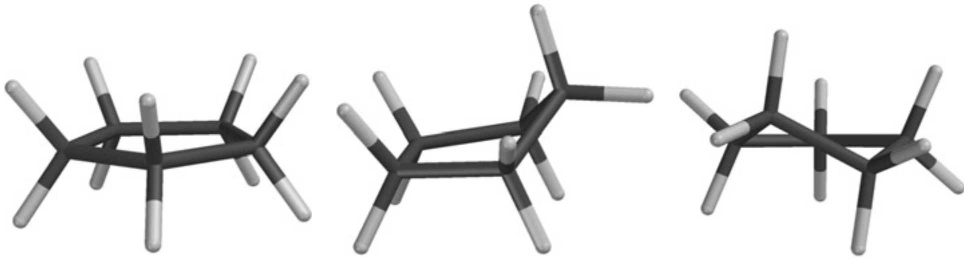
3.11 MEDIUM AND LARGE RINGS

In 1978, a German-Swiss team of organic chemists reported the synthesis of a cycloalkane with 96 carbons in its ring (cyclo-$C_{96}H_{192}$).

Beginning with cycloheptane, which has four conformations of similar energy, conformational analysis of cycloalkanes becomes more complicated. The same fundamental principles apply to medium and large rings as apply to smaller ones—there are simply more atoms and more bonds to consider and more conformational possibilities.

3.12 DISUBSTITUTED CYCLOALKANES: STEREOISOMERS

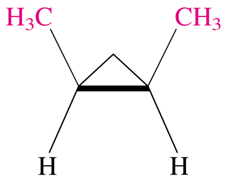
When a cycloalkane bears two substituents on different carbons—methyl groups, for example—these substituents may be on the same or on opposite sides of the ring. When substituents are on the same side, we say they are ***cis*** to each other; if they are on oppo-



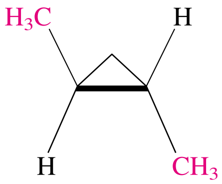
(*a*) Planar (*b*) Envelope (*c*) Half-Chair

FIGURE 3.19 The (*a*) planar, (*b*) envelope, and (*c*) half-chair conformations of cyclopentane.

site sides, they are ***trans*** to each other. Both terms come from the Latin, in which *cis* means "on this side" and trans means "across."



cis-1,2-Dimethylcyclopropane



trans-1,2-Dimethylcyclopropane

PROBLEM 3.8 Exclusive of compounds with double bonds, four hydrocarbons are *constitutional* isomers of *cis*- and *trans*-1,2-dimethylcyclopropane. Identify these compounds.

The cis and trans forms of 1,2-dimethylcyclopropane are *stereoisomers*. **Stereoisomers** are isomers that have their atoms bonded in the same order—that is, they have the same constitution, but they differ in the arrangement of atoms in space. Stereoisomers of the cis–trans type are sometimes referred to as *geometric isomers*. You learned in Section 2.15 that constitutional isomers could differ in stability. What about stereoisomers?

The prefix *stereo*- is derived from the Greek word *stereos*, meaning "solid." *Stereochemistry* is the term applied to the three-dimensional aspects of molecular structure and reactivity.

We can measure the energy difference between *cis*- and *trans*-1,2-dimethylcyclopropane by comparing their heats of combustion. As illustrated in Figure 3.20, the two compounds are isomers, and so the difference in their heats of combustion is a direct measure of the difference in their energies. Because the heat of combustion of *trans*-1,2-dimethylcyclopropane is 5 kJ/mol (1.2 kcal/mol) less than that of its *cis* stereoisomer, it follows that *trans*-1,2-dimethylcyclopropane is 5 kJ/mol (1.2 kcal/mol) more stable than *cis*-1,2-dimethylcyclopropane.

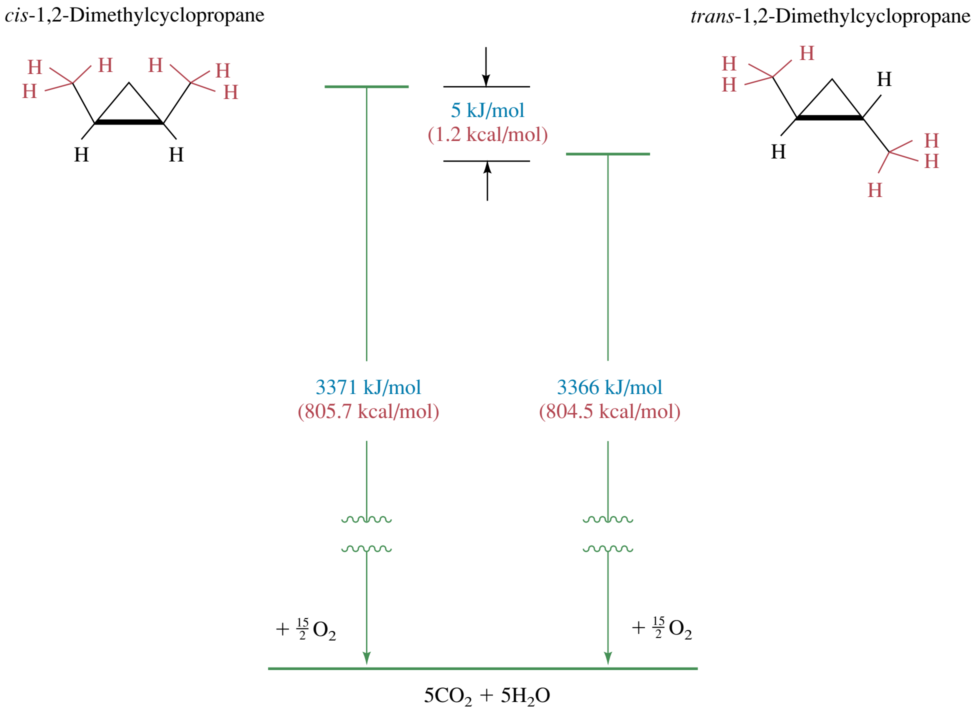


FIGURE 3.20 The enthalpy difference between *cis*- and *trans*-1,2-dimethylcyclopropane can be determined from their heats of combustion. Van der Waals strain between methyl groups on the same side of the ring makes the cis isomer less stable than the trans.

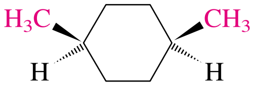
Make molecular models of *cis*- and *trans*-1,2-dimethylcyclopropane, and compare their strain energies.

In this case, the relationship between stability and stereochemistry is easily explained on the basis of van der Waals strain. The methyl groups on the same side of the ring in *cis*-1,2-dimethylcyclopropane crowd each other and increase the potential energy of this stereoisomer. Steric hindrance between methyl groups is absent in *trans*-1,2-dimethylcyclopropane.

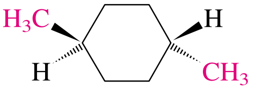
Disubstituted cyclopropanes exemplify one of the simplest cases involving stability differences between stereoisomers. A three-membered ring has no conformational mobility, and there is no way the ring can adjust to reduce the van der Waals strain between cis substituents on adjacent carbons. The situation is different in disubstituted derivatives of cyclohexane.

3.13 CONFORMATIONAL ANALYSIS OF DISUBSTITUTED CYCLOHEXANES

We'll begin with *cis*- and *trans*-1,4-dimethylcyclohexane. A conventional method to represent cis and trans stereoisomers in cyclic systems uses wedge-and-dash descriptions as shown.



cis-1,4-Dimethylcyclohexane



trans-1,4-Dimethylcyclohexane

Wedge-and-dash drawings fail to show conformation, and it's important to remember that the rings of *cis*- and *trans*-1,2-dimethylcyclohexane exist in a chair conformation. This fact must be taken into consideration when evaluating the relative stabilities of the stereoisomers.

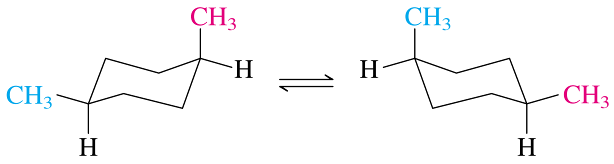
Their heats of combustion (Table 3.2) reveal that *trans*-1,4-dimethylcyclohexane is 7 kJ/mol (1.6 kcal/mol) more stable than the cis stereoisomer. It is unrealistic to believe that van der Waals strain between cis substituents is responsible, because the methyl groups are too far away from each other. To understand why *trans*-1,4-dimethylcyclohexane is more stable than *cis*-1,4-dimethylcyclohexane, we need to examine each stereoisomer in its most stable conformation.

cis-1,4-Dimethylcyclohexane can adopt either of two equivalent chair conformations, *each having one axial methyl group and one equatorial methyl group.* The two are

TABLE 3.2 Heats of Combustion of Isomeric Dimethylcyclohexanes

Compound	Orientation of methyl groups in most stable conformation	Heat of combustion		Difference in heat of combustion		More stable stereoisomer
		kJ/mol	(kcal/mol)	kJ/mol	(kcal/mol)	
cis-1,2-Dimethylcyclohexane	Axial–equatorial	5223	(1248.3)	6	(1.5)	trans
trans-1,2-Dimethylcyclohexane	Diequatorial	5217	(1246.8)			
cis-1,3-Dimethylcyclohexane	Diequatorial	5212	(1245.7)	7	(1.7)	cis
trans-1,3-Dimethylcyclohexane	Axial–equatorial	5219	(1247.4)			
cis-1,4-Dimethylcyclohexane	Axial–equatorial	5219	(1247.4)	7	(1.7)	trans
trans-1,4-Dimethylcyclohexane	Diequatorial	5212	(1245.7)			

in rapid equilibrium with each other by ring flipping. The equatorial methyl group becomes axial and the axial methyl group becomes equatorial.



(One methyl group is axial, the other equatorial)

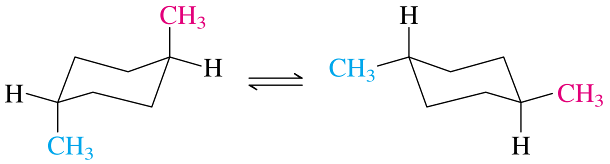
(One methyl group is axial, the other equatorial)

(Both methyl groups are up)

cis-1,4-Dimethylcyclohexane

The methyl groups are described as cis because both are up relative to the hydrogen present at each carbon. If both methyl groups were down, they would still be cis to each other. Notice that ring flipping does not alter the cis relationship between the methyl groups. Nor does it alter their up-versus-down quality; substituents that are up in one conformation remain up in the ring-flipped form.

The most stable conformation of trans-*1,4-dimethylcyclohexane has both methyl groups in equatorial orientations.* The two chair conformations of *trans*-1,4-dimethylcyclohexane are not equivalent to each other. One has two equatorial methyl groups; the other, two axial methyl groups.



(Both methyl groups are axial: less stable chair conformation)

(Both methyl groups are equatorial: more stable chair conformation)

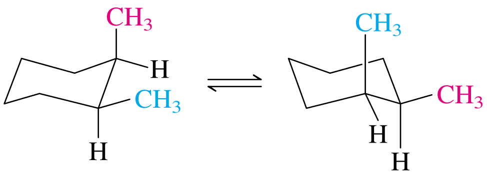
(One methyl group is up, the other down)

trans-1,4-Dimethylcyclohexane

The more stable chair—the one with both methyl groups equatorial—is the conformation adopted by most of the *trans*-1,4-dimethylcyclohexane molecules.

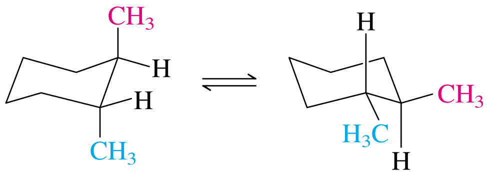
trans-1,4-Dimethylcyclohexane is more stable than *cis*-1,4-dimethylcyclohexane because both methyl groups are equatorial in its most stable conformation. One methyl group must be axial in the cis stereoisomer. Remember, it is a general rule that any substituent is more stable in an equatorial orientation than in an axial one. It is worth pointing out that the 7 kJ/mol (1.7 kcal/mol) energy difference between *cis*- and *trans*-1,4-dimethylcyclohexane is the same as the energy difference between the axial and equatorial conformations of methylcyclohexane. There is a simple reason for this: in both instances the less stable structure has one axial methyl group, and the 7 kJ/mol (1.6 kcal/mol) energy difference can be considered the "energy cost" of having a methyl group in an axial rather than an equatorial orientation.

Like the 1,4-dimethyl derivatives, *trans*-1,2-dimethylcyclohexane has a lower heat of combustion (see Table 3.2) and is more stable than *cis*-1,2-dimethylcyclohexane. The cis stereoisomer has two chair conformations of equal energy, each containing one axial and one equatorial methyl group.



cis-1,2-Dimethylcyclohexane

Both methyl groups are equatorial in the most stable conformation of *trans*-1,2-dimethylcyclohexane.



(Both methyl groups are axial: less stable chair conformation)

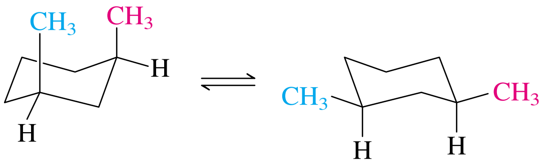
(Both methyl groups are equatorial: more stable chair conformation)

trans-1,2-Dimethylcyclohexane

As in the 1,4-dimethylcyclohexanes, the 6 kJ/mol (1.5 kcal/mol) energy difference between the more stable (trans) and the less stable (cis) stereoisomer is attributed to the strain associated with the presence of an axial methyl group in the cis isomer.

Probably the most interesting observation in Table 3.2 concerns the 1,3-dimethylcyclohexanes. Unlike the 1,2- and 1,4-dimethylcyclohexanes, in which the trans stereoisomer is more stable than the cis, we find that *cis*-1,3-dimethylcyclohexane is 7 kJ/mol (1.7 kcal/mol) more stable than *trans*-1,3-dimethylcyclohexane. Why?

The most stable conformation of *cis*-1,3-dimethylcyclohexane has both methyl groups equatorial.

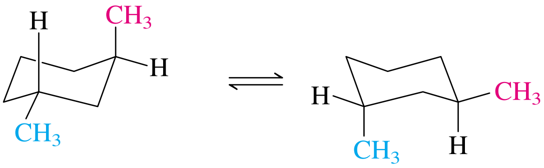


(Both methyl groups are axial: less stable chair conformation)

(Both methyl groups are equatorial: more stable chair conformation)

cis-1,3-Dimethylcyclohexane

The two chair conformations of *trans*-1,3-dimethylcyclohexane are equivalent to each other. Both contain one axial and one equatorial methyl group.



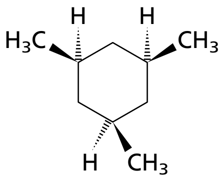
(One methyl group is axial, the other equatorial)

(One methyl group is axial, the other equatorial)

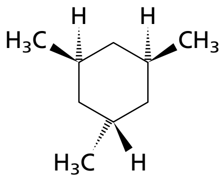
trans-1,3-Dimethylcyclohexane

Thus the trans stereoisomer, with one axial methyl group, is less stable than *cis*-1,3-dimethylcyclohexane where both methyl groups are equatorial.

PROBLEM 3.9 Based on what you know about disubstituted cyclohexanes, which of the following two stereoisomeric 1,3,5-trimethylcyclohexanes would you expect to be more stable?

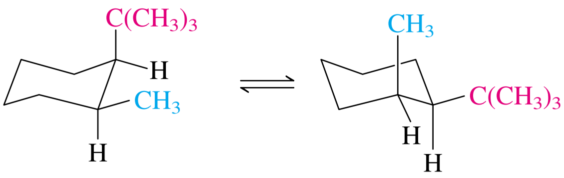


cis-1,3,5-Trimethylcyclohexane



trans-1,3,5-Trimethylcyclohexane

If a disubstituted cyclohexane has two different substituents, then the most stable conformation is the chair that has the larger substituent in an equatorial orientation. This is most apparent when one of the substituents is a bulky group such as *tert*-butyl. Thus, the most stable conformation of *cis*-1-*tert*-butyl-2-methylcyclohexane has an equatorial *tert*-butyl group and an axial methyl group.



(Less stable conformation: larger group is axial)

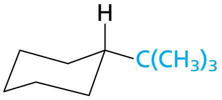
(More stable conformation: larger group is equatorial)

cis-1-*tert*-Butyl-2-methylcyclohexane

PROBLEM 3.10 Write structural formulas or make molecular models for the most stable conformation of each of the following compounds:

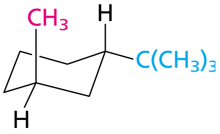
(a) *trans*-1-*tert*-Butyl-3-methylcyclohexane
(b) *cis*-1-*tert*-Butyl-3-methylcyclohexane
(c) *trans*-1-*tert*-Butyl-4-methylcyclohexane
(d) *cis*-1-*tert*-Butyl-4-methylcyclohexane

SAMPLE SOLUTION (a) The most stable conformation is the one that has the larger substituent, the *tert*-butyl group, equatorial. Draw a chair conformation of cyclohexane, and place an equatorial *tert*-butyl group at one of its carbons. Add a methyl group at C-3 so that it is trans to the *tert*-butyl group.



tert-Butyl group equatorial on six-membered ring

Add methyl group to axial position at C-3 so that it is trans to *tert*-butyl group



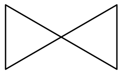
trans-1-*tert*-Butyl-3-methylcyclohexane

Cyclohexane rings that bear *tert*-butyl substituents are examples of conformationally biased molecules. A *tert*-butyl group has such a pronounced preference for the equatorial orientation that it will strongly bias the equilibrium to favor such conformations. This does not mean that ring inversion does not occur, however. Ring inversion does occur, but at any instant only a tiny fraction of the molecules exist in conformations having axial *tert*-butyl groups. It is not strictly correct to say that *tert*-butylcyclohexane and its derivatives are "locked" into a single conformation; conformations related by ring flipping are in rapid equilibrium with one another, but the distribution between them strongly favors those in which the *tert*-butyl group is equatorial.

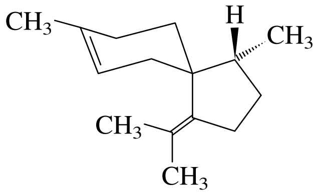
3.14 POLYCYCLIC RING SYSTEMS

Organic molecules in which *one* carbon atom is common to two rings are called **spirocyclic** compounds. The simplest spirocyclic hydrocarbon is *spiropentane,* a product of laboratory synthesis. More complicated spirocyclic hydrocarbons not only have been synthesized but also have been isolated from natural sources. α-*Alaskene,* for example, occurs in the fragrant oil given off by the needles of the Alaskan yellow cedar; one of its carbon atoms is common to both the six-membered ring and the five-membered ring.

Make a molecular model of spiropentane. What feature of its geometry is more apparent from a model than from its structural formula?

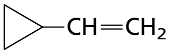


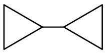
Spiropentane

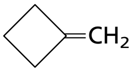


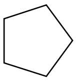
α-Alaskene

PROBLEM 3.11 Which of the following compounds are isomers of spiropentane?

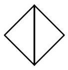




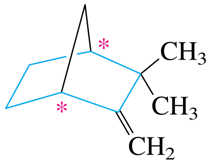




When *two* or more atoms are common to more than one ring, the compounds are called **polycyclic** ring systems. They are classified as *bicyclic, tricyclic, tetracyclic* etc., according to the minimum number of bond cleavages required to generate a noncyclic structure. *Bicyclobutane* is the simplest bicyclic hydrocarbon; its four carbons form 2 three-membered rings that share a common side. *Camphene* is a naturally occurring bicyclic hydrocarbon obtained from pine oil. It is best regarded as a six-membered ring (indicated by blue bonds in the structure shown here) in which two of the carbons (designated by asterisks) are bridged by a CH$_2$ group.



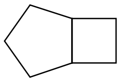
Bicyclobutane



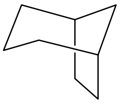
Camphene

PROBLEM 3.12 Use the bond-cleavage criterion to verify that bicyclobutane and camphene are bicyclic.

Bicyclic compounds are named in the IUPAC system by counting the number of carbons in the ring system, assigning to the structure the base name of the unbranched alkane having the same number of carbon atoms, and attaching the prefix “bicyclo-.” The number of atoms in each of the bridges connecting the common atoms is then placed, in descending order, within brackets.



Bicyclo[3.2.0]heptane



Bicyclo[3.2.1]octane

PROBLEM 3.13 Write structural formulas for each of the following bicyclic hydrocarbons:

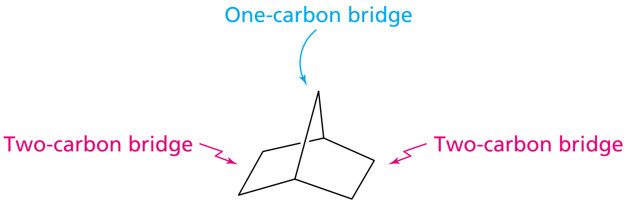
(a) Bicyclo[2.2.1]heptane

(b) Bicyclo[5.2.0]nonane

(c) Bicyclo[3.1.1]heptane

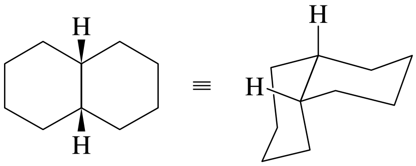
(d) Bicyclo[3.3.0]octane

SAMPLE SOLUTION (a) The bicyclo[2.2.1]heptane ring system is one of the most frequently encountered bicyclic structural types. It contains seven carbon atoms, as indicated by the suffix “-heptane.” The bridging groups contain two, two, and one carbon, respectively.

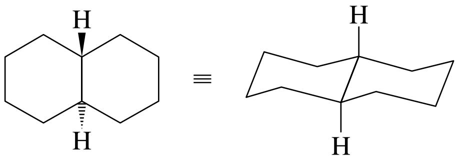


Bicyclo[2.2.1]heptane

Among the most important of the bicyclic hydrocarbons are the two stereoisomeric bicyclo[4.4.0]decanes, called *cis*- and *trans*-decalin. The hydrogen substituents at the ring junction positions are on the same side in *cis*-decalin and on opposite sides in *trans*-decalin. Both rings adopt the chair conformation in each stereoisomer.



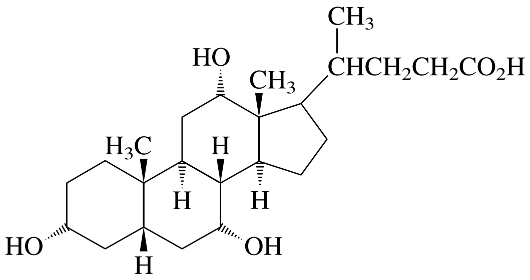
cis-Bicyclo[4.4.0]decane
(*cis*-decalin)



trans-Bicyclo[4.4.0]decane
(*trans*-decalin)

Make models of *cis*- and *trans*-decalin. Which is more stable?

Decalin ring systems appear as structural units in a large number of naturally occurring substances, particularly the steroids. Cholic acid, for example, a steroid present in bile that promotes digestion, incorporates *cis*-decalin and *trans*-decalin units into a rather complex *tetracyclic* structure.

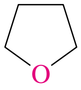


Cholic acid

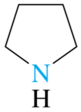
3.15 HETEROCYCLIC COMPOUNDS

Not all cyclic compounds are hydrocarbons. Many substances include an atom other than carbon, called a *heteroatom* (Section 1.7), as part of a ring. A ring that contains at least one heteroatom is called a **heterocycle,** and a substance based on a heterocyclic ring is a **heterocyclic compound.** Each of the following heterocyclic ring systems will be encountered in this text:

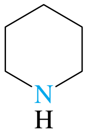
Ethylene oxide



Tetrahydrofuran



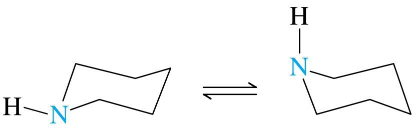
Pyrrolidine



Piperidine

The names cited are common names, which have been in widespread use for a long time and are acceptable in IUPAC nomenclature. We will introduce the systematic nomenclature of these ring systems as needed in later chapters.

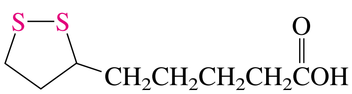
The shapes of heterocyclic rings are very much like those of their all-carbon analogs. Thus, six-membered heterocycles such as piperidine exist in a chair conformation analogous to cyclohexane.



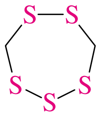
The hydrogen attached to nitrogen can be either axial or equatorial, and both chair conformations are approximately equal in stability.

PROBLEM 3.14 Draw or build a molecular model of what you would expect to be the most stable conformation of the piperidine derivative in which the hydrogen bonded to nitrogen has been replaced by methyl.

Sulfur-containing heterocycles are also common. Compounds in which sulfur is the heteroatom in three-, four-, five-, and six-membered rings, as well as larger rings, are all well known. Two interesting heterocyclic compounds that contain sulfur–sulfur bonds are *lipoic acid* and *lenthionine.*



Lipoic acid: a growth factor required by a variety of different organisms



Lenthionine: contributes to the odor of Shiitake mushrooms

Many heterocyclic systems contain double bonds and are related to arenes. The most important representatives of this class are described in Sections 11.21 and 11.22.

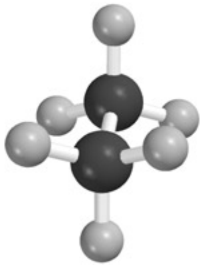
3.16 SUMMARY

In this chapter we explored the three-dimensional shapes of alkanes and cycloalkanes. The most important point to be taken from the chapter is that a molecule adopts the shape that minimizes its total **strain.** The sources of strain in alkanes and cycloalkanes are:

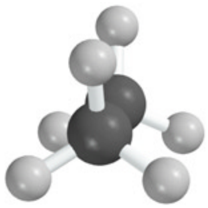
1. *Bond length distortion:* destabilization of a molecule that results when one or more of its bond distances are different from the normal values
2. *Angle strain:* destabilization that results from distortion of bond angles from their normal values
3. *Torsional strain:* destabilization that results from the eclipsing of bonds on adjacent atoms
4. *Van der Waals strain:* destabilization that results when atoms or groups on nonadjacent atoms are too close to one another

The various spatial arrangements available to a molecule by rotation about single bonds are called **conformations,** and **conformational analysis** is the study of the differences in stability and properties of the individual conformations. Rotation around carbon–carbon single bonds is normally very fast, occurring hundreds of thousands of times per second at room temperature. Molecules are rarely frozen into a single conformation but engage in rapid equilibration among the conformations that are energetically accessible.

Section 3.1 The most stable conformation of ethane is the **staggered** conformation. It is approximately 12 kJ/mol (3 kcal/mol) more stable than the **eclipsed,** which is the least stable conformation.



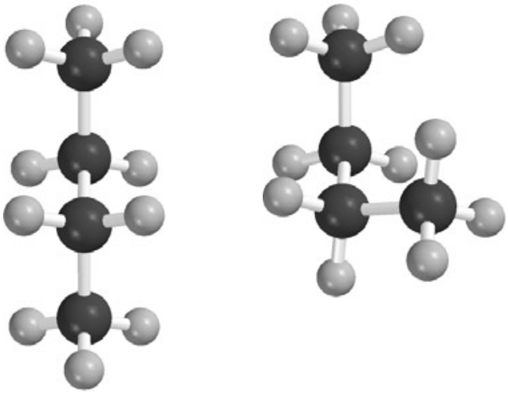
Staggered conformation of ethane
(most stable conformation)



Eclipsed conformation of ethane
(least stable conformation)

The difference in energy between the staggered and eclipsed forms is due almost entirely to the torsional strain in the eclipsed conformation. At any instant, almost all the molecules of ethane reside in the staggered conformation.

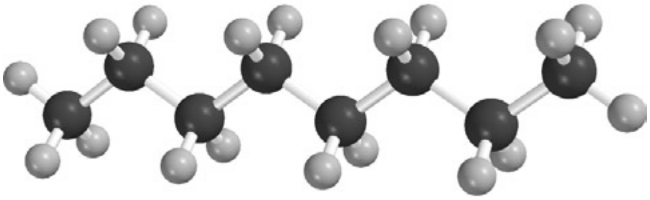
Section 3.2 The two staggered conformations of butane are not equivalent. The **anti** conformation is more stable than the **gauche.**



Anti conformation of butane Gauche conformation of butane

Neither conformation suffers torsional strain, because each has a staggered arrangement of bonds. The gauche conformation is less stable because of van der Waals strain involving the methyl groups.

Section 3.3 Higher alkanes adopt a zigzag conformation of the carbon chain in which all the bonds are staggered.



Octane

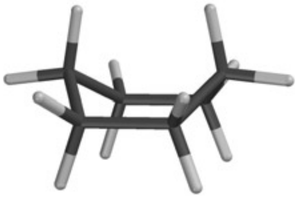
Section 3.4 Cyclopropane is the only cycloalkane in which all the ring carbons lie in the same plane. In all other cycloalkanes, the ring is nonplanar. A planar cycloalkane is destabilized by torsional strain and, in most cases, angle strain.

Cyclopropane

Section 3.5 Three conformations of cyclohexane have approximately tetrahedral angles at carbon: the chair, the boat, and the skew boat. The chair is by far the most stable; it is free of torsional strain, but the boat and skew boat are not. When a cyclohexane ring is present in a compound, it almost always adopts a chair conformation.

Chair

Skew boat



Boat

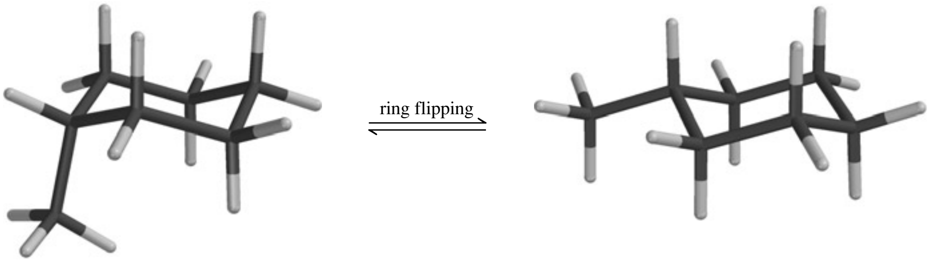
Section 3.6 The C—H bonds in the chair conformation of cyclohexane are not all equivalent but are divided into two sets of six each, called **axial** and **equatorial.**

Axial bonds to H in cyclohexane

Equatorial bonds to H in cyclohexane

Section 3.7 Conformational inversion (ring flipping) is rapid in cyclohexane and causes all axial bonds to become equatorial and vice versa. As a result, a monosubstituted derivative of cyclohexane adopts the chair conformation in which the substituent is equatorial (see next section). *No bonds are made or broken in this process.*

Section 3.8 A substituent is less crowded and more stable when it is equatorial than when it is axial on a cyclohexane ring. Ring flipping of a monosubstituted cyclohexane allows the substituent to become equatorial.



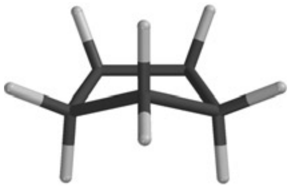
Methyl group axial (less stable)

Methyl group equatorial (more stable)

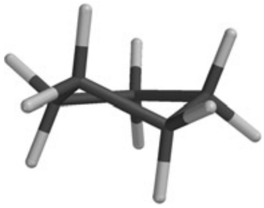
Branched substituents, especially *tert*-butyl, have an increased preference for the equatorial position.

Section 3.9 Cyclopropane is planar and strained (angle strain and torsional strain). Cyclobutane is nonplanar and less strained than cyclopropane.

Section 3.10 Cyclopentane has two nonplanar conformations that are of similar stability: the **envelope** and the **half-chair.**



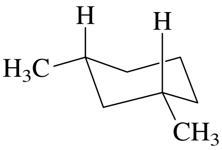
Envelope conformation of cyclopentane



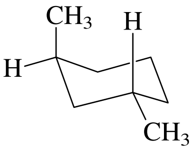
Half-chair conformation of cyclopentane

Section 3.11 Higher cycloalkanes have angles at carbon that are close to tetrahedral and are sufficiently flexible to adopt conformations that are free of torsional strain. They tend to be populated by several different conformations of similar stability.

Sections 3.12–3.13 **Stereoisomers** are isomers that have the same constitution but differ in the arrangement of atoms in space. *Cis*- and *trans*-1,3-dimethylcyclohexane are stereoisomers. The cis isomer is more stable than the trans.



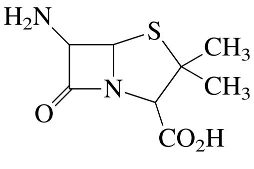
Most stable conformation of
cis-1,3-dimethylcyclohexane
(no axial methyl groups)



Most stable conformation of
trans-1,3-dimethylcyclohexane
(one axial methyl group)

Section 3.14 Cyclic hydrocarbons can contain more than one ring. **Spirocyclic** hydrocarbons are characterized by the presence of a single carbon that is common to two rings. **Bicyclic** alkanes contain two rings that share two or more atoms.

Section 3.15 Substances that contain one or more atoms other than carbon as part of a ring are called **heterocyclic** compounds. Rings in which the heteroatom is oxygen, nitrogen, or sulfur rank as both the most common and the most important.

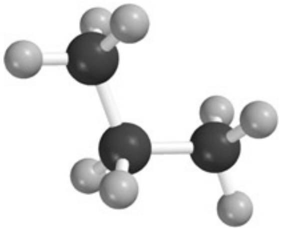


6-Aminopenicillanic acid
(bicyclic and heterocyclic)

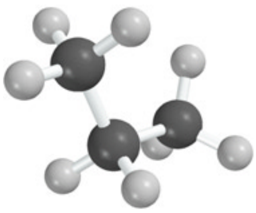
PROBLEMS

3.15 Like hydrogen peroxide, the inorganic substances hydrazine (H_2NNH_2) and hydroxylamine (H_2NOH) possess conformational mobility. Write structural representations or build molecular models of two different staggered conformations of (a) hydrazine and (b) hydroxylamine.

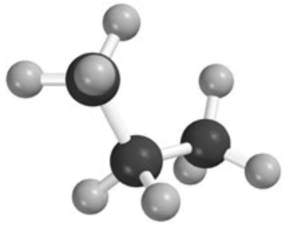
3.16 Of the three conformations of propane shown, which one is the most stable? Which one is the least stable? Why?



(*a*)



(*b*)



(*c*)

3.17 Sight down the C-2—C-3 bond, and draw Newman projection formulas for the

(a) Most stable conformation of 2,2-dimethylbutane

(b) Two most stable conformations of 2-methylbutane

(c) Two most stable conformations of 2,3-dimethylbutane

3.18 One of the staggered conformations of 2-methylbutane in Problem 3.17b is more stable than the other. Which one is more stable? Why?

3.19 Sketch an approximate potential energy diagram similar to that shown in Figures 3.4 and 3.7 for rotation about the carbon–carbon bond in 2,2-dimethylpropane. Does the form of the potential energy curve of 2,2-dimethylpropane more closely resemble that of ethane or that of butane?

3.20 Repeat Problem 3.19 for the case of 2-methylbutane.

3.21 One of the C—C—C angles of 2,2,4,4-tetramethylpentane is very much larger than the others. Which angle? Why?

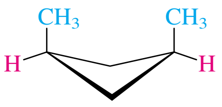
3.22 Even though the methyl group occupies an equatorial site, the conformation shown is not the most stable one for methylcyclohexane. Explain.

3.23 Which of the structures shown for the axial conformation of methylcyclohexane do you think is more stable, A or B? Why?

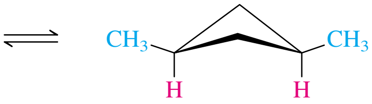
A

B

3.24 Which do you expect to be the more stable conformation of *cis*-1,3-dimethylcyclobutane, A or B? Why?



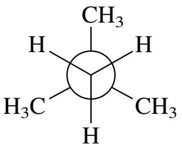
A



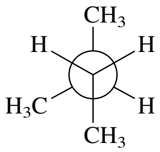
B

3.25 Determine whether the two structures in each of the following pairs represent *constitutional isomers,* different *conformations* of the same compound, or *stereoisomers* that cannot be interconverted by rotation about single bonds.

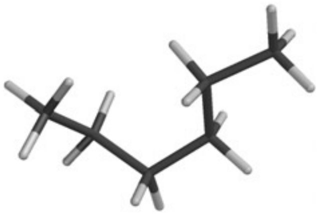
(a)



and



(b)



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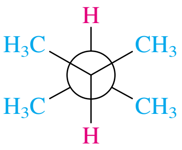
(c)



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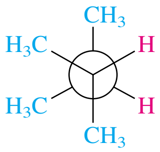
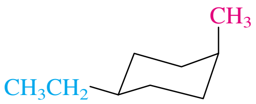


(d) *cis*-1,2-Dimethylcyclopentane and *trans*-1,3-dimethylcyclopentane

(e)



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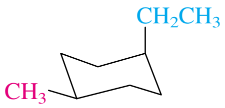
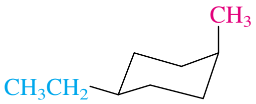


(f)



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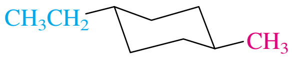
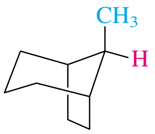


(g)



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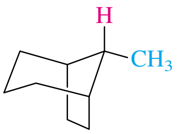


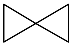
3.26 Excluding compounds that contain methyl or ethyl groups, write structural formulas for all the bicyclic isomers of (a) C_5H_8 and (b) C_6H_{10}.

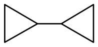
3.27 In each of the following groups of compounds, identify the one with the largest heat of combustion and the one with the smallest. In which cases can a comparison of heats of combustion be used to assess relative stability?

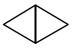
(a) Cyclopropane, cyclobutane, cyclopentane

(b) *cis*-1,2-Dimethylcyclopentane, methylcyclohexane, 1,1,2,2-tetramethylcyclopropane

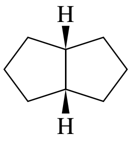
(c)

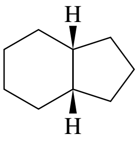


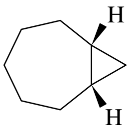




(d)







3.28 Write a structural formula for the most stable conformation of each of the following compounds:

(a) 2,2,5,5-Tetramethylhexane (Newman projection of conformation about C-3—C-4 bond)

(b) 2,2,5,5-Tetramethylhexane (zigzag conformation of entire molecule)

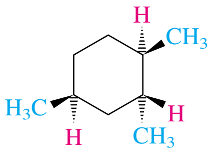
(c) *cis*-1-Isopropyl-3-methylcyclohexane

(d) *trans*-1-Isopropyl-3-methylcyclohexane

(e) *cis*-1-*tert*-Butyl-4-ethylcyclohexane

(f) *cis*-1,1,3,4-Tetramethylcyclohexane

(g)



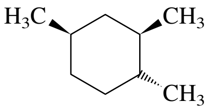
3.29 Identify the more stable stereoisomer in each of the following pairs, and give the reason for your choice:

(a) *cis*- or *trans*-1-Isopropyl-2-methylcyclohexane

(b) *cis*- or *trans*-1-Isopropyl-3-methylcyclohexane

(c) *cis*- or *trans*-1-Isopropyl-4-methylcyclohexane

(d)



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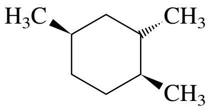

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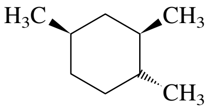

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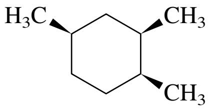

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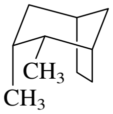

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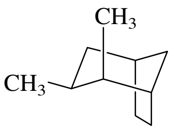
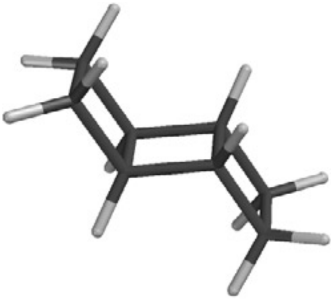
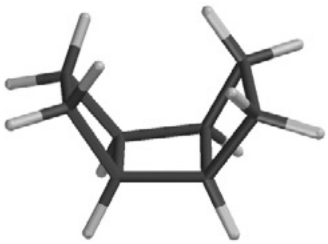


3.30 One stereoisomer of 1,1,3,5-tetramethylcyclohexane is 15 kJ/mol (3.7 kcal/mol) less stable than the other. Indicate which isomer is the less stable, and identify the reason for its decreased stability.

3.31 One of the following two stereoisomers is 20 kJ/mol (4.9 kcal/mol) less stable than the other. Indicate which isomer is the less stable, and identify the reason for its decreased stability.



A

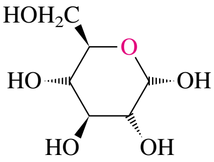


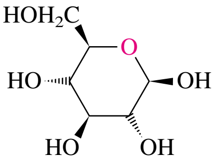
B

3.32 Cubane (C_8H_8) is the common name of a polycyclic hydrocarbon that was first synthesized in the early 1960s. As its name implies, its structure is that of a cube. How many rings are present in cubane?

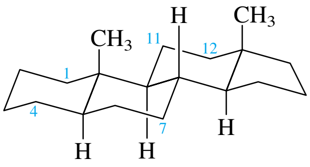
Cubane

3.33 The following are representations of two forms of glucose. The six-membered ring is known to exist in a chair conformation in each form. Draw clear representations of the most stable conformation of each. Are they two different conformations of the same molecule, or are they stereoisomers? Which substituents (if any) occupy axial sites?





3.34 A typical steroid skeleton is shown along with the numbering scheme used for this class of compounds. Specify in each case whether the designated substituent is axial or equatorial.



(a) Substituent at C-1 cis to the methyl groups

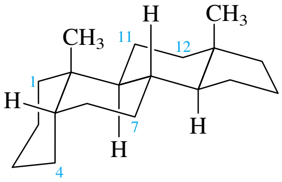
(b) Substituent at C-4 cis to the methyl groups

(c) Substituent at C-7 trans to the methyl groups

(d) Substituent at C-11 trans to the methyl groups

(e) Substituent at C-12 cis to the methyl groups

3.35 Repeat Problem 3.34 for the stereoisomeric steroid skeleton having a cis ring fusion between the first two rings.



3.36 (a) Write Newman projections for the gauche and anti conformations of 1,2-dichloroethane ($ClCH_2CH_2Cl$).

(b) The measured dipole moment of $ClCH_2CH_2Cl$ is 1.12 D. Which one of the following statements about 1,2-dichloroethane is false?

(1) It may exist entirely in the anti conformation.

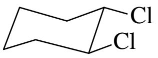
(2) It may exist entirely in the gauche conformation.

(3) It may exist as a mixture of anti and gauche conformations.

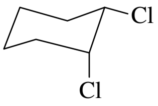
3.37 Compare the two staggered conformations of 1,1,2,2-tetrafluoroethane on *Learning By Modeling*. Do they differ in respect to their dipole moments? How?

3.38 The compound 2,2,4,4-tetramethylpentane [$(CH_3)_3CCH_2C(CH_3)_3$] is distinctive because it has an unusually large C—C—C bond angle. What carbons are involved? How large is the angle? What steric factor is responsible for increasing the size of this angle? One of the other bond angles is unusually small. Which one?

3.39 Structural drawings (molecular models, too) can be deceiving. For example, the chlorine atoms in 1,2-dichlorocyclohexane seem much closer to each other in a drawing of the trans stereoisomer than in the cis. Make a molecular model of each, and measure the distance between the chlorines. What do you find?

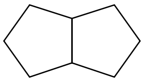


trans-1,2-Dichlorocyclohexane

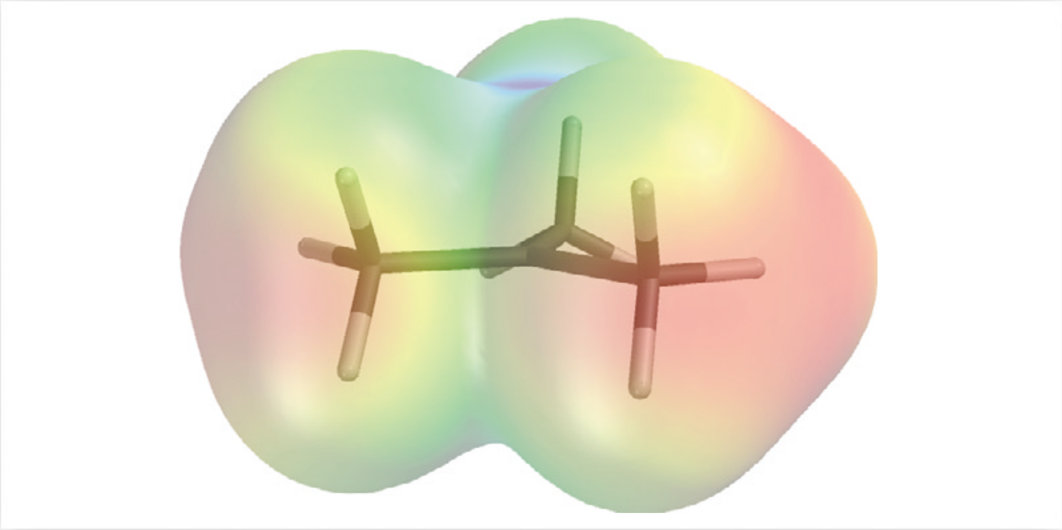


cis-1,2-Dichlorocyclohexane

3.40 Two stereoisomers of bicyclo[3.3.0]octane are possible. Make molecular models of both, and determine which is more stable.



Bicyclo[3.3.0]octane



CHAPTER 4

ALCOHOLS AND ALKYL HALIDES

Our first three chapters established some fundamental principles concerning the *structure* of organic molecules. In this chapter we begin our discussion of organic chemical *reactions* by directing attention to *alcohols* and *alkyl halides.* These two rank among the most useful classes of organic compounds because they often serve as starting materials for the preparation of numerous other families.

Two reactions that lead to alkyl halides will be described in this chapter. Both illustrate functional group transformations. In the first, the hydroxyl group of an alcohol is replaced by halogen on treatment with a hydrogen halide.

$$\underset{\text{Alcohol}}{\mathrm{R{-}OH}} + \underset{\text{Hydrogen halide}}{\mathrm{H{-}X}} \longrightarrow \underset{\text{Alkyl halide}}{\mathrm{R{-}X}} + \underset{\text{Water}}{\mathrm{H{-}OH}}$$

In the second, reaction with chlorine or bromine causes one of the hydrogen substituents of an alkane to be replaced by halogen.

$$\underset{\text{Alkane}}{\mathrm{R{-}H}} + \underset{\text{Halogen}}{\mathrm{X_2}} \longrightarrow \underset{\text{Alkyl halide}}{\mathrm{R{-}X}} + \underset{\text{Hydrogen halide}}{\mathrm{H{-}X}}$$

Both reactions are classified as *substitutions,* a term that describes the relationship between reactants and products—one functional group replaces another. In this chapter we go beyond the relationship of reactants and products and consider the *mechanism* of each reaction. A **mechanism** attempts to show *how* starting materials are converted into products during a chemical reaction.

While developing these themes of reaction and mechanism, we will also use alcohols and alkyl halides as vehicles to extend the principles of IUPAC nomenclature, continue to develop concepts of structure and bonding, and see how structure affects properties. A review of *acids and bases* constitutes an important part of this chapter in which a qualitative approach to proton-transfer equilibria will be developed that will be used throughout the remainder of the text.

4.1 IUPAC NOMENCLATURE OF ALKYL HALIDES

The IUPAC rules permit alkyl halides to be named in two different ways, called *functional class* nomenclature and *substitutive* nomenclature. In **functional class nomenclature** the alkyl group and the halide (*fluoride, chloride, bromide,* or *iodide*) are designated as separate words. The alkyl group is named on the basis of its longest continuous chain beginning at the carbon to which the halogen is attached.

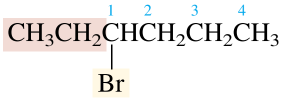
The IUPAC rules permit certain common alkyl group names to be used. These include *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, *tert*-butyl, and neopentyl (Section 2.10).

CH_3F

Methyl fluoride

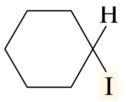
$CH_3CH_2CH_2CH_2CH_2Cl$

Pentyl chloride



$$\mathrm{CH_3CH_2\underset{\displaystyle Br}{\underset{|}{\overset{1}{C}}}H\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3}$$

1-Ethylbutyl bromide

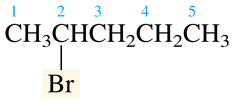


Cyclohexyl iodide

Substitutive nomenclature of alkyl halides treats the halogen as a *halo-* (*fluoro-, chloro-, bromo-,* or *iodo-*) *substituent* on an alkane chain. The carbon chain is numbered in the direction that gives the substituted carbon the lower locant.

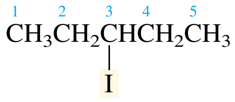
$\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2F$

1-Fluoropentane



$$\mathrm{\overset{1}{C}H_3\underset{\displaystyle Br}{\underset{|}{\overset{2}{C}}}H\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3}$$

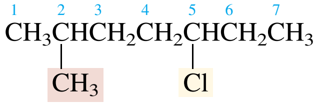
2-Bromopentane



$$\mathrm{\overset{1}{C}H_3\overset{2}{C}H_2\underset{\displaystyle I}{\underset{|}{\overset{3}{C}}}H\overset{4}{C}H_2\overset{5}{C}H_3}$$

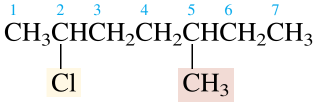
3-Iodopentane

When the carbon chain bears both a halogen and an alkyl substituent, the two substituents are considered of equal rank, and the chain is numbered so as to give the lower number to the substituent nearer the end of the chain.



$$\mathrm{\overset{1}{C}H_3\underset{\displaystyle CH_3}{\underset{|}{\overset{2}{C}}}H\overset{3}{C}H_2\overset{4}{C}H_2\underset{\displaystyle Cl}{\underset{|}{\overset{5}{C}}}H\overset{6}{C}H_2\overset{7}{C}H_3}$$

5-Chloro-2-methylheptane



$$\mathrm{\overset{1}{C}H_3\underset{\displaystyle Cl}{\underset{|}{\overset{2}{C}}}H\overset{3}{C}H_2\overset{4}{C}H_2\underset{\displaystyle CH_3}{\underset{|}{\overset{5}{C}}}H\overset{6}{C}H_2\overset{7}{C}H_3}$$

2-Chloro-5-methylheptane

PROBLEM 4.1 Write structural formulas, and give the functional class and substitutive names of all the isomeric alkyl chlorides that have the molecular formula C_4H_9Cl.

Substitutive names are preferred, but functional class names are sometimes more convenient or more familiar and are frequently encountered in organic chemistry.

Prior to the 1993 version of the IUPAC rules, the term "radicofunctional" was used instead of "functional class."

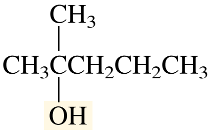
4.2 IUPAC NOMENCLATURE OF ALCOHOLS

Functional class names of alcohols are derived by naming the alkyl group that bears the hydroxyl substituent (—OH) and then adding *alcohol* as a separate word. The chain is always numbered beginning at the carbon to which the hydroxyl group is attached.

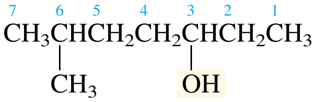
Substitutive names of alcohols are developed by identifying the longest continuous chain that bears the hydroxyl group and replacing the *-e* ending of the

Several alcohols are commonplace substances, well known by common names that reflect their origin (wood alcohol, grain alcohol) or use (rubbing alcohol). Wood alcohol is *methanol* (methyl alcohol, CH_3OH), grain alcohol is *ethanol* (ethyl alcohol, CH_3CH_2OH), and rubbing alcohol is *2-propanol* [isopropyl alcohol, $(CH_3)_2CHOH$].

corresponding alkane by the suffix *-ol*. The position of the hydroxyl group is indicated by number, choosing the sequence that assigns the lower locant to the carbon that bears the hydroxyl group.

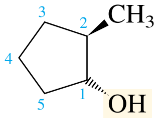
	CH_3CH_2OH	 $CH_3\underset{OH}{CH}CH_2CH_2CH_2CH_3$	 $CH_3\overset{CH_3}{\underset{OH}{C}}CH_2CH_2CH_3$
Functional class name:	Ethyl alcohol	1-Methylpentyl alcohol	1,1-Dimethylbutyl alcohol
Substitutive name:	Ethanol	2-Hexanol	2-Methyl-2-pentanol

Hydroxyl groups take precedence over (“outrank”) alkyl groups and halogen substituents in determining the direction in which a carbon chain is numbered.



$\overset{7}{C}H_3\underset{CH_3}{\overset{6}{C}H}\overset{5}{C}H_2\overset{4}{C}H_2\underset{OH}{\overset{3}{C}H}\overset{2}{C}H_2\overset{1}{C}H_3$

6-Methyl-3-heptanol
(not 2-methyl-5-heptanol)



trans-2-Methylcyclopentanol

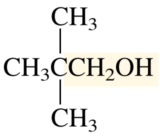
$F\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2OH$

3-Fluoro-1-propanol

PROBLEM 4.2 Write structural formulas, and give the functional class and substitutive names of all the isomeric alcohols that have the molecular formula $C_4H_{10}O$.

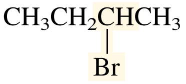
4.3 CLASSES OF ALCOHOLS AND ALKYL HALIDES

Alcohols and alkyl halides are classified as primary, secondary, or tertiary according to the classification of the carbon that bears the functional group (Section 2.10). Thus, *primary alcohols* and *primary alkyl halides* are compounds of the type RCH_2G (where G is the functional group), *secondary alcohols* and *secondary alkyl halides* are compounds of the type R_2CHG, and *tertiary alcohols* and *tertiary alkyl halides* are compounds of the type R_3CG.



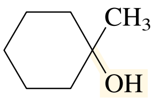
$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2OH$

2,2-Dimethyl-1-propanol
(a primary alcohol)

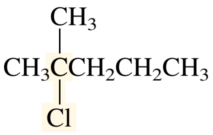


$CH_3CH_2\underset{Br}{CH}CH_3$

2-Bromobutane
(a secondary alkyl halide)



1-Methylcyclohexanol
(a tertiary alcohol)



$CH_3\overset{CH_3}{\underset{Cl}{C}}CH_2CH_2CH_3$

2-Chloro-2-methylpentane
(a tertiary alkyl halide)

PROBLEM 4.3 Classify the isomeric $C_4H_{10}O$ alcohols as being primary, secondary, or tertiary.

Many of the properties of alcohols and alkyl halides are affected by whether their functional groups are attached to primary, secondary, or tertiary carbons. We will see a number of cases in which a functional group attached to a primary carbon is more reactive than one attached to a secondary or tertiary carbon, as well as other cases in which the reverse is true.

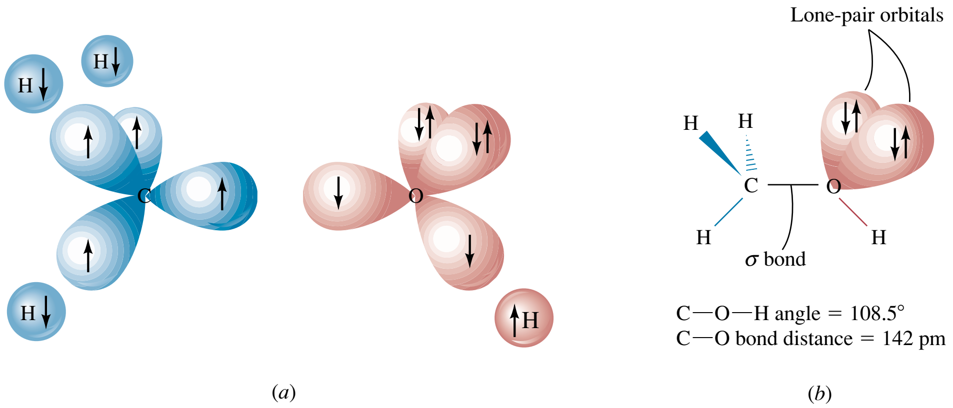
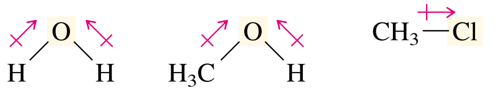


FIGURE 4.1 Orbital hybridization model of bonding in methanol. (*a*) The orbitals used in bonding are the 1*s* orbitals of hydrogen and sp^3-hybridized orbitals of carbon and oxygen. (*b*) The bond angles at carbon and oxygen are close to tetrahedral, and the carbon–oxygen σ bond is about 10 pm shorter than a carbon–carbon single bond.

4.4 BONDING IN ALCOHOLS AND ALKYL HALIDES

The carbon that bears the functional group is sp^3-hybridized in alcohols and alkyl halides. Figure 4.1 illustrates bonding in methanol. The bond angles at carbon are approximately tetrahedral, as is the C—O—H angle. A similar orbital hybridization model applies to alkyl halides, with the halogen substituent connected to sp^3-hybridized carbon by a σ bond. Carbon–halogen bond distances in alkyl halides increase in the order C—F (140 pm) < C—Cl (179 pm) < C—Br (197 pm) < C—I (216 pm).

Carbon–oxygen and carbon–halogen bonds are polar covalent bonds, and carbon bears a partial positive charge in alcohols ($^{\delta+}$C—O$^{\delta-}$) and in alkyl halides ($^{\delta+}$C—X$^{\delta-}$). The presence of these polar bonds makes alcohols and alkyl halides polar molecules. The dipole moments of methanol and chloromethane are very similar to each other and to water.



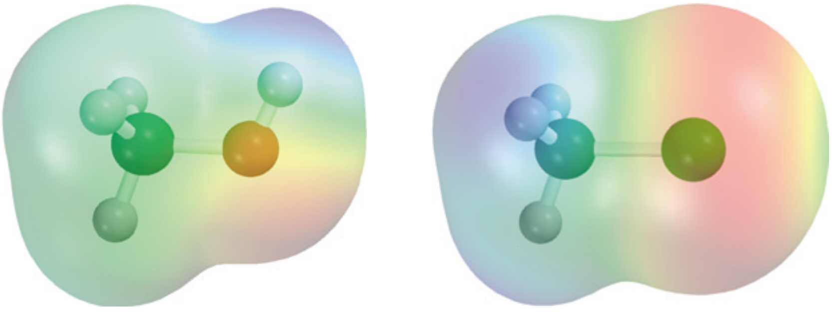
Water (μ = 1.8 D)

Methanol (μ = 1.7 D)

Chloromethane (μ = 1.9 D)

PROBLEM 4.4 Bromine is less electronegative than chlorine, yet methyl bromide and methyl chloride have very similar dipole moments. Why?

Figure 4.2 shows the distribution of electron density in methanol and chloromethane. Both are similar in that the sites of highest electrostatic potential (red) are near the electronegative atoms—oxygen and chlorine. The polarization of the bonds



Methanol (CH_3OH)

Chloromethane (CH_3Cl)

FIGURE 4.2 Electrostatic potential maps of methanol and chloromethane. The most positively charged regions are blue, the most negatively charged ones red. The electrostatic potential is most negative near oxygen in methanol and near chlorine in chloromethane.

to oxygen and chlorine, as well as their unshared electron pairs, contribute to the concentration of negative charge on these atoms.

Relatively simple notions of attractive forces between opposite charges are sufficient to account for many of the properties of chemical substances. You will find it helpful to keep the polarity of carbon–oxygen and carbon–halogen bonds in mind as we develop the properties of alcohols and alkyl halides in later sections.

4.5 PHYSICAL PROPERTIES OF ALCOHOLS AND ALKYL HALIDES: INTERMOLECULAR FORCES

Boiling Point. When describing the effect of alkane structure on boiling point in Section 2.14, we pointed out that the forces of attraction between neutral molecules are of three types listed here. The first two of these involve induced dipoles and are often referred to as *dispersion forces,* or *London forces.*

1. Induced-dipole/induced-dipole forces
2. Dipole/induced-dipole forces
3. Dipole–dipole forces

Induced-dipole/induced-dipole forces are the only intermolecular attractive forces available to nonpolar molecules such as alkanes. In addition to these forces, polar molecules engage in dipole–dipole and dipole/induced-dipole attractions. The **dipole–dipole attractive force** is easiest to visualize and is illustrated in Figure 4.3. Two molecules of a polar substance experience a mutual attraction between the positively polarized region of one molecule and the negatively polarized region of the other. As its name implies, the **dipole/induced-dipole force** combines features of both the induced-dipole/induced-dipole and dipole–dipole attractive forces. A polar region of one molecule alters the electron distribution in a nonpolar region of another in a direction that produces an attractive force between them.

Because so many factors contribute to the net intermolecular attractive force, it is not always possible to predict which of two compounds will have the higher boiling point. We can, however, use the boiling point behavior of selected molecules to inform us of the relative importance of various intermolecular forces and the structural features that influence them.

Consider three compounds similar in size and shape: the alkane propane, the alcohol ethanol, and the alkyl halide fluoroethane.

$CH_3CH_2CH_3$	CH_3CH_2OH	CH_3CH_2F
Propane (μ = 0 D)	Ethanol (μ = 1.7 D)	Fluoroethane (μ = 1.9 D)
bp: −42°C	bp: 78°C	bp: −32°C

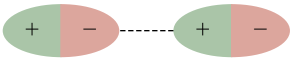


FIGURE 4.3 A dipole–dipole attractive force. Two molecules of a polar substance are oriented so that the positively polarized region of one and the negatively polarized region of the other attract each other.

Both polar compounds, ethanol and fluoroethane, have higher boiling points than the nonpolar propane. We attribute this to a combination of dipole/induced-dipole and dipole–dipole attractive forces that stabilize the liquid states of ethanol and fluoroethane, but that are absent in propane.

The most striking aspect of the data, however, is the much higher boiling point of ethanol compared with both propane and fluoroethane. This suggests that the attractive forces in ethanol must be unusually strong. Figure 4.4 shows that this force results from a dipole–dipole attraction between the positively polarized proton of the —OH group of one ethanol molecule and the negatively polarized oxygen of another. The term **hydrogen bonding** is used to describe dipole–dipole attractive forces of this type. The

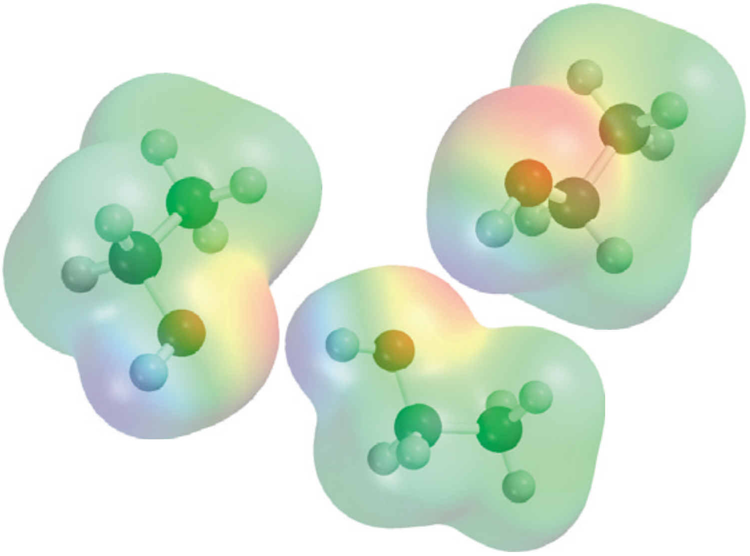


FIGURE 4.4 Hydrogen bonding in ethanol involves the oxygen of one molecule and the proton of an —OH group of another. Hydrogen bonding is much stronger than most other types of dipole–dipole attractive forces.

proton involved must be bonded to an electronegative element, usually oxygen or nitrogen. Protons in C—H bonds do not participate in hydrogen bonding. Thus fluoroethane, even though it is a polar molecule and engages in dipole–dipole attractions, does not form hydrogen bonds and, therefore, has a lower boiling point than ethanol.

Hydrogen bonding can be expected in molecules that have —OH or —NH groups. Individual hydrogen bonds are about 10–50 times weaker than typical covalent bonds, but their effects can be significant. More than other dipole–dipole attractive forces, intermolecular hydrogen bonds are strong enough to impose a relatively high degree of structural order on systems in which they are possible. As will be seen in Chapter 27, the three-dimensional structures adopted by proteins and nucleic acids, the organic molecules of life, are dictated by patterns of hydrogen bonds.

Hydrogen bonds between —OH groups are stronger than those between —NH groups, as a comparison of the boiling points of water (H_2O, 100°C) and ammonia (NH_3, −33°C) demonstrates.

PROBLEM 4.5 The constitutional isomer of ethanol, dimethyl ether (CH_3OCH_3), is a gas at room temperature. Suggest an explanation for this observation.

Table 4.1 lists the boiling points of some representative alkyl halides and alcohols. When comparing the boiling points of related compounds as a function of the *alkyl group,* we find that the boiling point increases with the number of carbon atoms, as it does with alkanes.

For a discussion concerning the boiling point behavior of alkyl halides, see the January 1988 issue of the *Journal of Chemical Education,* pp. 62–64.

TABLE 4.1 Boiling Points of Some Alkyl Halides and Alcohols

Name of alkyl group	Formula	Functional group X and boiling point, °C (1 atm)				
		X = F	X = Cl	X = Br	X = I	X = OH
Methyl	CH_3X	−78	−24	3	42	65
Ethyl	CH_3CH_2X	−32	12	38	72	78
Propyl	$CH_3CH_2CH_2X$	−3	47	71	103	97
Pentyl	$CH_3(CH_2)_3CH_2X$	65	108	129	157	138
Hexyl	$CH_3(CH_2)_4CH_2X$	92	134	155	180	157

With respect to the *halogen* in a group of alkyl halides, the boiling point increases as one descends the periodic table; alkyl fluorides have the lowest boiling points, alkyl iodides the highest. This trend matches the order of increasing *polarizability* of the halogens. **Polarizability** is the ease with which the electron distribution around an atom is distorted by a nearby electric field and is a significant factor in determining the strength of induced-dipole/induced-dipole and dipole/induced-dipole attractions. Forces that depend on induced dipoles are strongest when the halogen is a highly polarizable iodine, and weakest when the halogen is a nonpolarizable fluorine.

The boiling points of the chlorinated derivatives of methane increase with the number of chlorine atoms because of an increase in the induced-dipole/induced-dipole attractive forces.

	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
	Chloromethane (methyl chloride)	Dichloromethane (methylene dichloride)	Trichloromethane (chloroform)	Tetrachloromethane (carbon tetrachloride)
Boiling point:	−24°C	40°C	61°C	77°C

Fluorine is unique among the halogens in that increasing the number of fluorines does not produce higher and higher boiling points.

These boiling points illustrate why we should do away with the notion that boiling points always increase with increasing molecular weight.

	CH_3CH_2F	CH_3CHF_2	CH_3CF_3	CF_3CF_3
	Fluoroethane	1,1-Difluoroethane	1,1,1-Trifluoroethane	Hexafluoroethane
Boiling point:	−32°C	−25°C	−47°C	−78°C

Thus, although the difluoride CH_3CHF_2 boils at a higher temperature than CH_3CH_2F, the trifluoride CH_3CF_3 boils at a lower temperature than either of them. Even more striking is the observation that the hexafluoride CF_3CF_3 is the lowest boiling of any of the fluorinated derivatives of ethane. The boiling point of CF_3CF_3 is, in fact, only 11° higher than that of ethane itself. The reason for this behavior has to do with the very low polarizability of fluorine and a decrease in induced-dipole/induced-dipole forces that accompanies the incorporation of fluorine substituents into a molecule. Their weak intermolecular attractive forces give fluorinated hydrocarbons **(fluorocarbons)** certain desirable physical properties such as that found in the "no stick" *Teflon* coating of frying pans. Teflon is a *polymer* (Section 6.21) made up of long chains of $—CF_2CF_2—$units.

Solubility in Water. Alkyl halides and alcohols differ markedly from one another in their solubility in water. All alkyl halides are insoluble in water, but low-molecular-weight alcohols (methyl, ethyl, *n*-propyl, and isopropyl) are soluble in water in all proportions. Their ability to participate in intermolecular hydrogen bonding not only affects the boiling points of alcohols, but also enhances their water solubility. Hydrogen-bonded networks of the type shown in Figure 4.5, in which alcohol and water molecules associate with one another, replace the alcohol–alcohol and water–water hydrogen-bonded networks present in the pure substances.

Higher alcohols become more "hydrocarbon-like" and less water-soluble. 1-Octanol, for example, dissolves to the extent of only 1 mL in 2000 mL of water. As the alkyl chain gets longer, the hydrophobic effect (Section 2.14) becomes more important, to the point that it, more than hydrogen bonding, governs the solubility of alcohols.

Density. Alkyl fluorides and chlorides are less dense, and alkyl bromides and iodides more dense, than water.

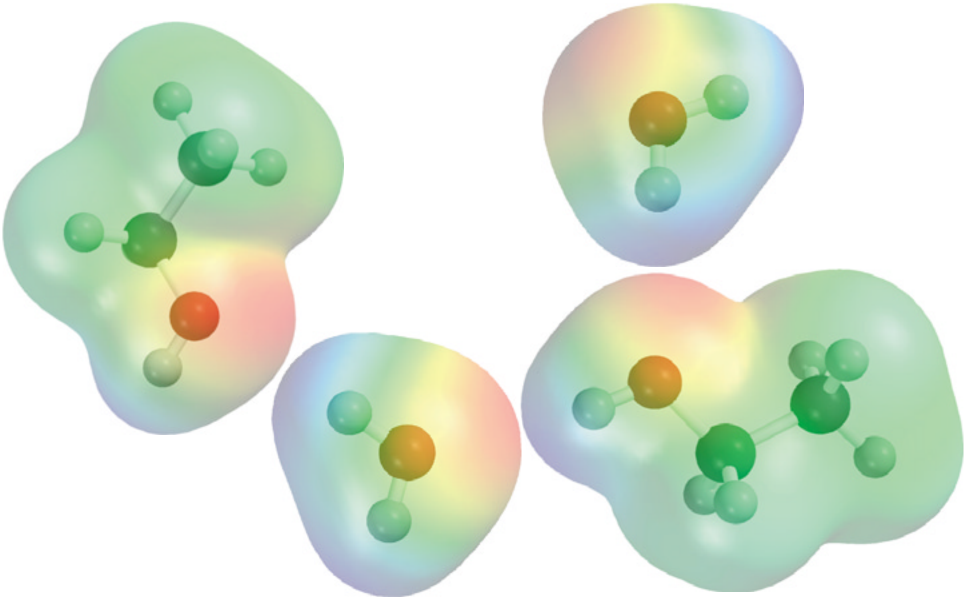


FIGURE 4.5 Hydrogen bonding between molecules of ethanol and water.

	$CH_3(CH_2)_6CH_2F$	$CH_3(CH_2)_6CH_2Cl$	$CH_3(CH_2)_6CH_2Br$	$CH_3(CH_2)_6CH_2I$
Density (20°C):	0.80 g/mL	0.89 g/mL	1.12 g/mL	1.34 g/mL

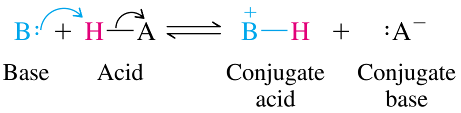
Because alkyl halides are insoluble in water, a mixture of an alkyl halide and water separates into two layers. When the alkyl halide is a fluoride or chloride, it is the upper layer and water is the lower. The situation is reversed when the alkyl halide is a bromide or an iodide. In these cases the alkyl halide is the lower layer. Polyhalogenation increases the density. The compounds CH_2Cl_2, $CHCl_3$, and CCl_4, for example, are all more dense than water.

All liquid alcohols have densities of approximately 0.8 g/mL and are, therefore, less dense than water.

4.6 ACIDS AND BASES: GENERAL PRINCIPLES

A solid understanding of acid–base chemistry is a big help in understanding chemical reactivity. This and the next section review some principles and properties of acids and bases and examine how these principles apply to alcohols.

According to the theory proposed by Svante Arrhenius, a Swedish chemist and winner of the 1903 Nobel Prize in chemistry, an acid ionizes in aqueous solution to liberate protons (H^+, hydrogen ions), whereas bases ionize to liberate hydroxide ions (HO^-). A more general theory of acids and bases was devised independently by Johannes Brønsted (Denmark) and Thomas M. Lowry (England) in 1923. In the Brønsted–Lowry approach, an acid is a **proton donor,** and a base is a **proton acceptor.**

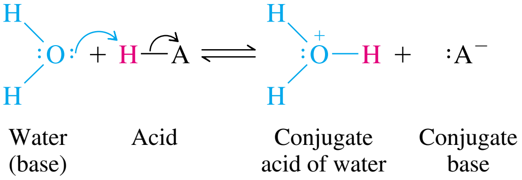


Curved arrow notation is used to show the electron pair of the base abstracting a proton from the acid. The pair of electrons in the H—A bond becomes an unshared pair in the anion $^-$:A. Curved arrows track **electron movement,** not atomic movement.

The Brønsted–Lowry definitions of acids and bases are widely used in organic chemistry. As noted in the preceding equation, the **conjugate acid** of a substance is formed when it accepts a proton from a suitable donor. Conversely, the proton donor is converted to its **conjugate base.** A conjugate acid–base pair always differ by a single proton.

PROBLEM 4.6 Write an equation for the reaction of ammonia (:NH_3) with hydrogen chloride (HCl). Use curved arrows to track electron movement, and identify the acid, base, conjugate acid, and conjugate base.

In aqueous solution, an acid transfers a proton to water. Water acts as a Brønsted base.



The systematic name for the conjugate acid of water (H_3O^+) is **oxonium ion.** Its common name is **hydronium ion.**

The strength of an acid is measured by its **acid dissociation constant** or **ionization constant K_a**.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Table 4.2 lists a number of Brønsted acids and their acid dissociation constants. Strong acids are characterized by K_a values that are greater than that for hydronium ion (H_3O^+, $K_a = 55$). Essentially every molecule of a strong acid transfers a proton to water in dilute aqueous solution. Weak acids have K_a values less than that of H_3O^+; they are incompletely ionized in dilute aqueous solution.

A convenient way to express acid strength is through the use of pK_a, defined as follows:

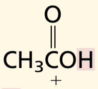
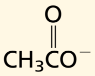
$$pK_a = -\log_{10} K_a$$

Thus, water, with $K_a = 1.8 \times 10^{-16}$, has a p$K_a$ of 15.7; ammonia, with $K_a \approx 10^{-36}$, has a pK_a of 36. The stronger the acid, the larger the value of its K_a and the smaller the value of pK_a. Water is a very weak acid, but is a far stronger acid than ammonia. Table 4.2 includes pK_a as well as K_a values for acids. Because both systems are widely used, you should practice converting K_a to pK_a and vice versa.

PROBLEM 4.7 Hydrogen cyanide (HCN) has a pK_a of 9.1. What is its K_a? Is HCN a strong or a weak acid?

An important part of the Brønsted–Lowry picture of acids and bases concerns the relative strengths of an acid and its conjugate base. The stronger the acid, the weaker the conjugate base, and vice versa. Ammonia (NH_3) is the second weakest acid in Table 4.2. Its conjugate base, amide ion (H_2N^-), is therefore the second strongest base. Hydroxide (HO^-) is a moderately strong base, much stronger than the halide ions F^-, Cl^-, Br^-, and I^-, which are very weak bases. Fluoride is the strongest base of the halides but is 10^{12} times less basic than hydroxide ion.

TABLE 4.2 Acid Dissociation Constants K_a and pK_a Values for Some Brønsted Acids*

Acid	Formula†	Dissociation constant, K_a	pK_a	Conjugate base
Hydrogen iodide	HI	$\approx 10^{10}$	≈ -10	I^-
Hydrogen bromide	HBr	$\approx 10^{9}$	≈ -9	Br^-
Hydrogen chloride	HCl	$\approx 10^{7}$	≈ -7	Cl^-
Sulfuric acid	$HOSO_2OH$	1.6×10^{5}	-4.8	$HOSO_2O^-$
Hydronium ion	$H-\overset{+}{O}H_2$	55	-1.7	H_2O
Hydrogen fluoride	HF	3.5×10^{-4}	3.5	F^-
Acetic acid	 $CH_3\overset{\overset{O}{\Vert}}{C}OH$	1.8×10^{-5}	4.7	 $CH_3\overset{\overset{O}{\Vert}}{C}O^-$
Ammonium ion	$H-\overset{+}{N}H_3$	5.6×10^{-10}	9.2	NH_3
Water	HOH	$1.8 \times 10^{-16‡}$	15.7	HO^-
Methanol	CH_3OH	$\approx 10^{-16}$	≈ 16	CH_3O^-
Ethanol	CH_3CH_2OH	$\approx 10^{-16}$	≈ 16	$CH_3CH_2O^-$
Isopropyl alcohol	$(CH_3)_2CHOH$	$\approx 10^{-17}$	≈ 17	$(CH_3)_2CHO^-$
tert-Butyl alcohol	$(CH_3)_3COH$	$\approx 10^{-18}$	≈ 18	$(CH_3)_3CO^-$
Ammonia	H_2NH	$\approx 10^{-36}$	≈ 36	H_2N^-
Dimethylamine	$(CH_3)_2NH$	$\approx 10^{-36}$	≈ 36	$(CH_3)_2N^-$

*Acid strength decreases from top to bottom of the table. Strength of conjugate base increases from top to bottom of the table.

†The most acidic proton—the one that is lost on ionization—is highlighted.

‡The "true" K_a for water is 1×10^{-14}. Dividing this value by 55.5 (the number of moles of water in 1 L of water) gives a K_a of 1.8×10^{-16} and puts water on the same concentration basis as the other substances in the table. A paper in the May 1990 issue of the *Journal of Chemical Education* (p. 386) outlines the justification for this approach. For a dissenting view, see the March 1992 issue of the *Journal of Chemical Education* (p. 255).

PROBLEM 4.8 As noted in Problem 4.7, hydrogen cyanide (HCN) has a pK_a of 9.1. Is cyanide ion (CN^-) a stronger base or a weaker base than hydroxide ion (HO^-)?

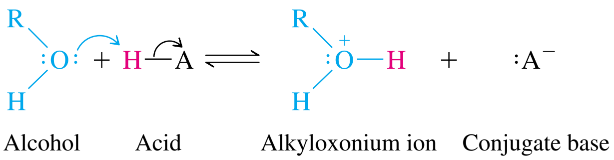
In any proton-transfer process the position of equilibrium favors formation of the weaker acid and the weaker base.

$$\text{Stronger acid} + \text{stronger base} \overset{K>1}{\rightleftharpoons} \text{weaker acid} + \text{weaker base}$$

This is one of the most important equations in chemistry.

Table 4.2 is set up so that the strongest acid is at the top of the acid column, with the strongest base at the bottom of the conjugate base column. An acid will transfer a proton to the conjugate base of any acid that lies below it in the table, and the equilibrium constant for the reaction will be greater than one.

Table 4.2 contains both inorganic and organic compounds. Organic compounds are similar to inorganic ones when the functional groups responsible for their acid–base properties are the same. Thus, alcohols (ROH) are similar to water (HOH) in both their Brønsted acidity (ability to donate a proton *from oxygen*) and Brønsted basicity (ability to accept a proton *on oxygen*). Just as proton transfer to a water molecule gives oxonium ion (hydronium ion, H_3O^+), proton transfer to an alcohol gives an **alkyloxonium ion** (ROH_2^+).



We shall see that several important reactions of alcohols involve strong acids either as reagents or as catalysts to increase the rate of reaction. In all these reactions the first step is formation of an alkyloxonium ion by proton transfer from the acid to the oxygen of the alcohol.

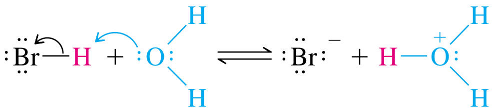
PROBLEM 4.9 Write an equation for proton transfer from hydrogen chloride to *tert*-butyl alcohol. Use curved arrows to track electron movement, and identify the acid, base, conjugate acid, and conjugate base.

PROBLEM 4.10 Is the equilibrium constant for proton transfer from hydrogen chloride to *tert*-butyl alcohol greater than 1 or less than 1?

Alkyl halides are neither very acidic nor very basic and are absent from Table 4.2. In general, compounds, including alkyl halides, in which all the protons are bonded to carbon are exceedingly weak acids—too weak to be included in the table.

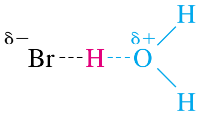
4.7 ACID–BASE REACTIONS: A MECHANISM FOR PROTON TRANSFER

Potential energy diagrams of the type used in Chapter 3 to describe conformational processes can also help us understand more about chemical reactions. Consider the transfer of a proton from hydrogen bromide to water:



A potential energy diagram for this reaction is shown in Figure 4.6. Because the transfer of a proton from hydrogen bromide to water is exothermic, the products are placed lower in energy than the reactants. The diagram depicts the reaction as occurring in a single **elementary step.** An elementary step is one that involves only one transition state. A reaction can proceed by way of a single elementary step, in which case it is described as a **concerted** reaction, or by a series of elementary steps. In the case of proton transfer from hydrogen bromide to water, breaking of the H—Br bond and making of the $H_2\overset{+}{O}$—H bond occur "in concert" with each other. The species present at the transition state is not a stable structure and cannot be isolated or examined directly. Its structure is assumed to be one in which the proton being transferred is partially bonded to both bromine and oxygen simultaneously, although not necessarily to the same extent.

Dashed lines in transition-state structures represent *partial* bonds, that is, bonds in the process of being made or broken.



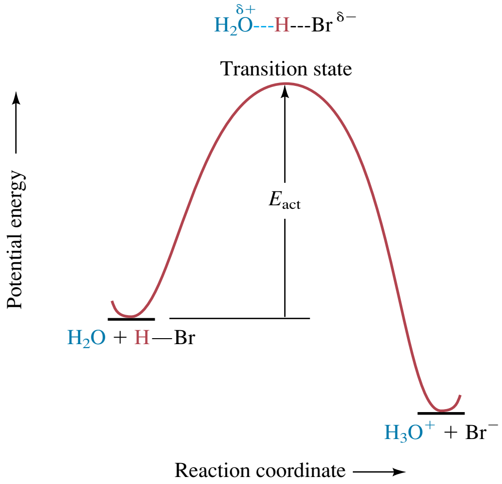


FIGURE 4.6 Energy diagram for concerted bimolecular proton transfer from hydrogen bromide to water.

The **molecularity** of an elementary step is given by the number of species that undergo a chemical change in that step. The elementary step

$$HBr + H_2O \rightleftharpoons Br^- + H_3O^+$$

is **bimolecular** because it involves one molecule of hydrogen bromide and one molecule of water.

PROBLEM 4.11 Represent the structure of the transition state for proton transfer from hydrogen chloride to *tert*-butyl alcohol.

Proton transfer from hydrogen bromide to water and alcohols ranks among the most rapid chemical processes and occurs almost as fast as the molecules collide with one another. Thus the height of the energy barrier separating reactants and products, the *activation energy* for proton transfer, must be quite low.

The concerted nature of proton transfer contributes to its rapid rate. The energy cost of breaking the H—Br bond is partially offset by the energy released in making the $H_2\overset{+}{O}$—H bond. Thus, the activation energy is far less than it would be for a hypothetical stepwise process involving an initial, unassisted ionization of the H—Br bond, followed by a combination of the resulting H^+ with water.

The 1967 Nobel Prize in chemistry was shared by Manfred Eigen, a German chemist who developed novel methods for measuring the rates of very fast reactions such as proton transfers.

4.8 PREPARATION OF ALKYL HALIDES FROM ALCOHOLS AND HYDROGEN HALIDES

Much of what organic chemists do is directed toward practical goals. Chemists in the pharmaceutical industry synthesize new compounds as potential drugs for the treatment of disease. Agricultural chemicals designed to increase crop yields include organic compounds used for weed control, insecticides, and fungicides. Among the "building block" molecules used as starting materials to prepare new substances, alcohols and alkyl halides are especially valuable.

The procedures to be described in the remainder of this chapter use either an alkane or an alcohol as the starting material for preparing an alkyl halide. By knowing how to prepare alkyl halides, we can better appreciate the material in later chapters, where alkyl halides figure prominently in key chemical transformations. The preparation of alkyl halides also serves as a focal point to develop the principles of reaction mechanisms. We'll begin with the preparation of alkyl halides from alcohols by reaction with hydrogen halides.

$$\mathrm{R{-}OH} + \mathrm{H{-}X} \longrightarrow \mathrm{R{-}X} + \mathrm{H{-}OH}$$

Alcohol Hydrogen halide Alkyl halide Water

The order of reactivity of the hydrogen halides parallels their acidity: HI > HBr > HCl >> HF. Hydrogen iodide is used infrequently, however, and the reaction of alcohols with hydrogen fluoride is not a useful method for the preparation of alkyl fluorides.

Among the various classes of alcohols, tertiary alcohols are observed to be the most reactive and primary alcohols the least reactive.

Increasing reactivity of alcohols
toward hydrogen halides

$$\mathrm{CH_3OH} < \mathrm{RCH_2OH} < \mathrm{R_2CHOH} < \mathrm{R_3COH}$$

Methyl Least reactive	Primary	Secondary	Tertiary Most reactive

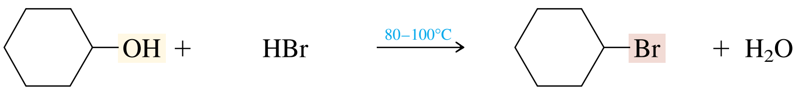
Tertiary alcohols are converted to alkyl chlorides in high yield within minutes on reaction with hydrogen chloride at room temperature and below.

$$\mathrm{(CH_3)_3COH} + \mathrm{HCl} \xrightarrow{25^\circ\mathrm{C}} \mathrm{(CH_3)_3CCl} + \mathrm{H_2O}$$

2-Methyl-2-propanol (*tert*-butyl alcohol)	Hydrogen chloride	2-Chloro-2-methylpropane (*tert*-butyl chloride) (78–88%)	Water

The efficiency of a synthetic transformation is normally expressed as a **percent yield,** or percentage of the *theoretical yield.* **Theoretical yield** is the amount of product that could be formed if the reaction proceeded to completion and did not lead to any products other than those given in the equation.

Secondary and primary alcohols do not react with hydrogen chloride at rates fast enough to make the preparation of the corresponding alkyl chlorides a method of practical value. Therefore, the more reactive hydrogen halide HBr is used; even then, elevated temperatures are required in order to increase the rate of reaction.



Cyclohexanol Hydrogen bromide Bromocyclohexane (73%) Water

$$\mathrm{CH_3(CH_2)_5CH_2OH} + \mathrm{HBr} \xrightarrow{120^\circ\mathrm{C}} \mathrm{CH_3(CH_2)_5CH_2Br} + \mathrm{H_2O}$$

1-Heptanol	Hydrogen bromide	1-Bromoheptane (87–90%)	Water

The same kind of transformation may be carried out by heating an alcohol with sodium bromide and sulfuric acid.

$$\mathrm{CH_3CH_2CH_2CH_2OH} \xrightarrow[\text{heat}]{\mathrm{NaBr,\ H_2SO_4}} \mathrm{CH_3CH_2CH_2CH_2Br}$$

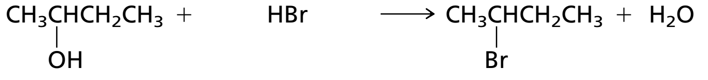
1-Butanol (*n*-butyl alcohol)	1-Bromobutane (70–83%) (*n*-butyl bromide)

We'll often find it convenient to write chemical equations in the abbreviated form shown here, in which reagents, especially inorganic ones, are not included in the body of the equation but instead are indicated over the arrow. Inorganic products—in this case, water—are usually omitted. These simplifications focus our attention on the organic reactant and its functional group transformation.

PROBLEM 4.12 Write chemical equations for the reaction that takes place between each of the following pairs of reactants:

(a) 2-Butanol and hydrogen bromide
(b) 3-Ethyl-3-pentanol and hydrogen chloride
(c) 1-Tetradecanol and hydrogen bromide

SAMPLE SOLUTION (a) An alcohol and a hydrogen halide react to form an alkyl halide and water. In this case 2-bromobutane was isolated in 73% yield.



$$\underset{\text{OH}}{CH_3\underset{|}{C}HCH_2CH_3} + HBr \longrightarrow \underset{\text{Br}}{CH_3\underset{|}{C}HCH_2CH_3} + H_2O$$

2-Butanol Hydrogen bromide 2-Bromobutane Water

4.9 MECHANISM OF THE REACTION OF ALCOHOLS WITH HYDROGEN HALIDES

The reaction of an alcohol with a hydrogen halide is a **substitution.** A halogen, usually chlorine or bromine, replaces a hydroxyl group as a substituent on carbon. Calling the reaction a substitution tells us the relationship between the organic reactant and its product but does not reveal the mechanism. In developing a mechanistic picture for a particular reaction, we combine some basic principles of chemical reactivity with experimental observations to deduce the most likely sequence of elementary steps.

Consider the reaction of *tert*-butyl alcohol with hydrogen chloride:

$$(CH_3)_3COH + HCl \longrightarrow (CH_3)_3CCl + H_2O$$

tert-Butyl alcohol	Hydrogen chloride	*tert*-Butyl chloride	Water

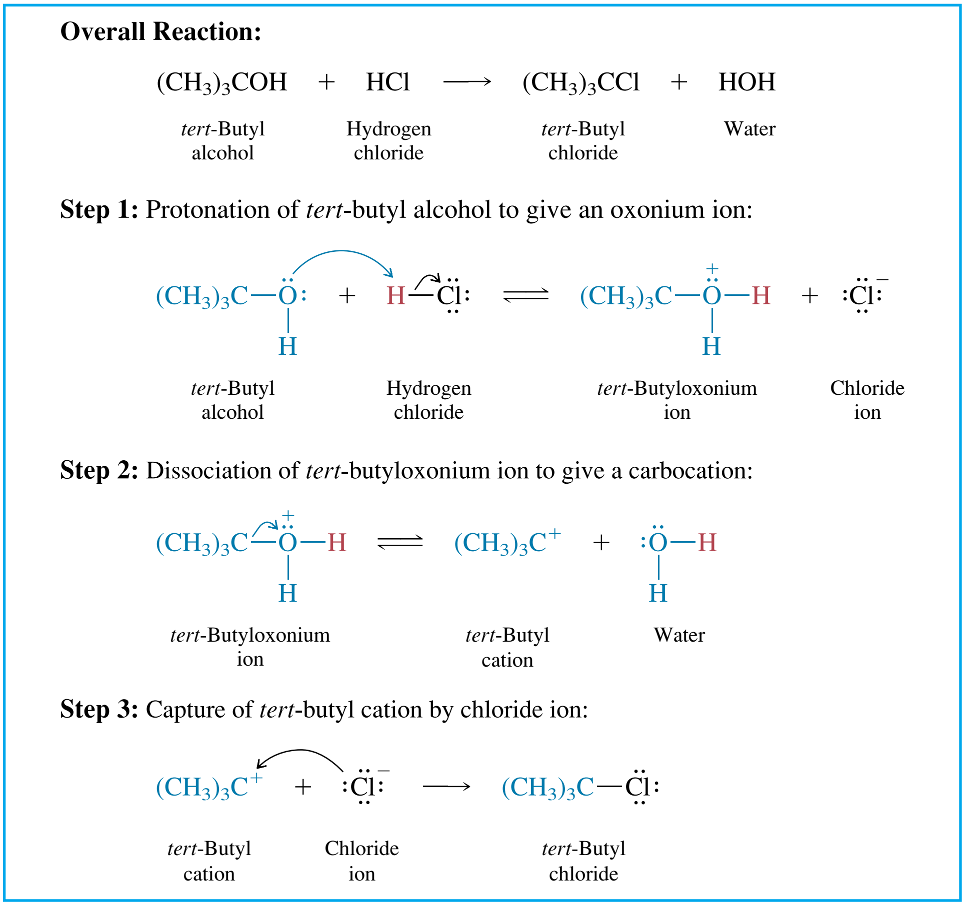
The generally accepted mechanism for this reaction is presented as a series of three elementary steps in Figure 4.7. We say "generally accepted" because a reaction mechanism can never be proved to be correct. A mechanism is our best present assessment of how a reaction proceeds and must account for all experimental observations. If new experimental data appear that conflict with the mechanism, the mechanism must be modified to accommodate them. If the new data are consistent with the proposed mechanism, our confidence grows that it is likely to be correct.

We already know about step 1 of the mechanism outlined in Figure 4.7; it is an example of a Brønsted acid–base reaction of the type discussed in Section 4.6 and formed the basis of Problems 4.9 through 4.11.

If you have not already written out the solutions to Problems 4.9 to 4.11, you should do so now.

Steps 2 and 3, however, are new to us. Step 2 involves dissociation of an alkyloxonium ion to a molecule of water and a **carbocation,** a species that contains a positively charged carbon. In step 3, this carbocation reacts with chloride ion to yield *tert*-butyl chloride. Both the alkyloxonium ion and the carbocation are **intermediates** in the reaction. They are not isolated, but are formed in one step and consumed in another during the passage of reactants to products. If we add the equations for steps 1 through 3 together, the equation for the overall process results. A valid reaction mechanism must

FIGURE 4.7 The mechanism of formation of *tert*-butyl chloride from *tert*-butyl alcohol and hydrogen chloride.

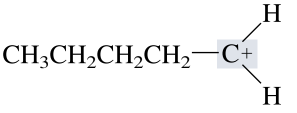


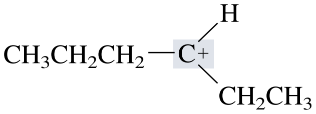
account for the consumption of all reactants and the formation of all products, be they organic or inorganic. So that we may better understand the chemistry expressed in steps 2 and 3, we need to examine carbocations in more detail.

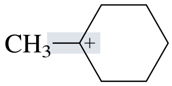
4.10 STRUCTURE, BONDING, AND STABILITY OF CARBOCATIONS

Carbocations are sometimes called *carbonium ions* or *carbenium ions.* An article in the November 1986 issue of the *Journal of Chemical Education,* pp. 930–933, traces the historical development of these and related terms.

Carbocations are classified as primary, secondary, or tertiary according to the number of carbons that are directly attached to the positively charged carbon. They are named by appending “cation” as a separate word after the IUPAC name of the appropriate alkyl group. The chain is numbered beginning with the positively charged carbon (the positive charge is always at C-1).


Pentyl cation
(primary carbocation)


1-Ethylbutyl cation
(secondary carbocation)


1-Methylcyclohexyl cation
(tertiary carbocation)


An electrostatic potential map of *tert*-butyl cation appears on the first page of this chapter.

Common names that have been incorporated into IUPAC nomenclature such as isopropyl, *sec*-butyl, and so on, are permitted. Thus 1,1-dimethylethyl cation $(CH_3)_3C^+$ may be called *tert*-butyl cation.

The properties of carbocations are intimately related to their structure, and so let's think about the bonding in methyl cation, CH_3^+. The positively charged carbon contributes three valence electrons, and each hydrogen contributes one for a total of six electrons, which are used to form three C—H σ bonds. As we saw in Section 1.17, carbon is sp^2-hybridized when it is bonded to three atoms or groups. We therefore choose the sp^2 hybridization model for bonding shown in Figure 4.8. Carbon forms σ bonds to three hydrogens by overlap of its sp^2 orbitals with hydrogen 1*s* orbitals. The three σ bonds are coplanar. Remaining on carbon is an unhybridized 2*p* orbital that contains no electrons. The axis of this empty *p* orbital is perpendicular to the plane defined by the three σ bonds.

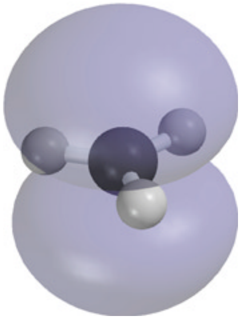
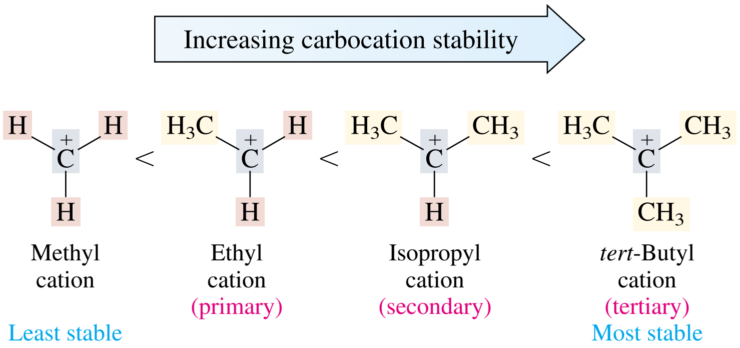


FIGURE 4.8 Structure of methyl cation CH_3^+. Carbon is sp^2-hybridized. Each hydrogen is attached to carbon by a σ bond formed by overlap of a hydrogen 1*s* orbital with an sp^2 hybrid orbital of carbon. All four atoms lie in the same plane. The unhybridized 2*p* orbital of carbon is unoccupied, and its axis is perpendicular to the plane of the atoms.

Evidence from a variety of sources convinces us that carbocations can exist, but are relatively unstable. When carbocations are involved in chemical reactions, it is as reactive intermediates, formed in one step and consumed rapidly thereafter.

Numerous studies have shown that the more stable a carbocation is, the faster it is formed. These studies also demonstrate that *alkyl groups directly attached to the positively charged carbon stabilize a carbocation.* Thus, the observed order of carbocation stability is



As carbocations go, CH_3^+ is particularly unstable, and its existence as an intermediate in chemical reactions has never been demonstrated. Primary carbocations, although more stable than CH_3^+, are still too unstable to be involved as intermediates in chemical reactions. The threshold of stability is reached with secondary carbocations. Many reactions, including the reaction of secondary alcohols with hydrogen halides, are believed to involve secondary carbocations. The evidence in support of tertiary carbocation intermediates is stronger yet.

PROBLEM 4.13 Of the isomeric $C_5H_{11}^+$ carbocations, which one is the most stable?

Because alkyl groups stabilize carbocations, we conclude that they release electrons to the positively charged carbon, dispersing the positive charge. They do this through a combination of effects. One involves polarization of the σ bonds to the positively charged carbon. As illustrated for ethyl cation in Figure 4.9, the positively charged carbon draws the electrons in its σ bonds toward itself and away from the atoms attached to it. Electrons in a C—C σ bond are more polarizable than those in a C—H bond, so replacing hydrogens by alkyl groups reduces the net charge on the sp^2-hybridized carbon. The electron-donating or electron-withdrawing effect of a group that is transmitted through σ bonds is called an **inductive effect.**

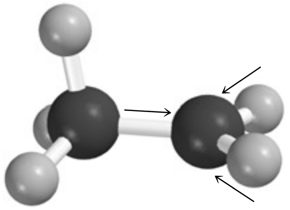
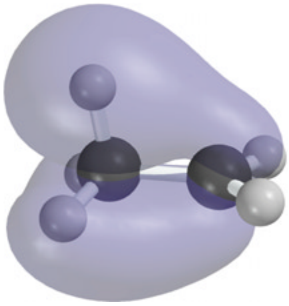


FIGURE 4.9 The charge in ethyl cation is stabilized by polarization of the electron distribution in the σ bonds to the positively charged carbon atom. Alkyl groups release electrons better than hydrogen.

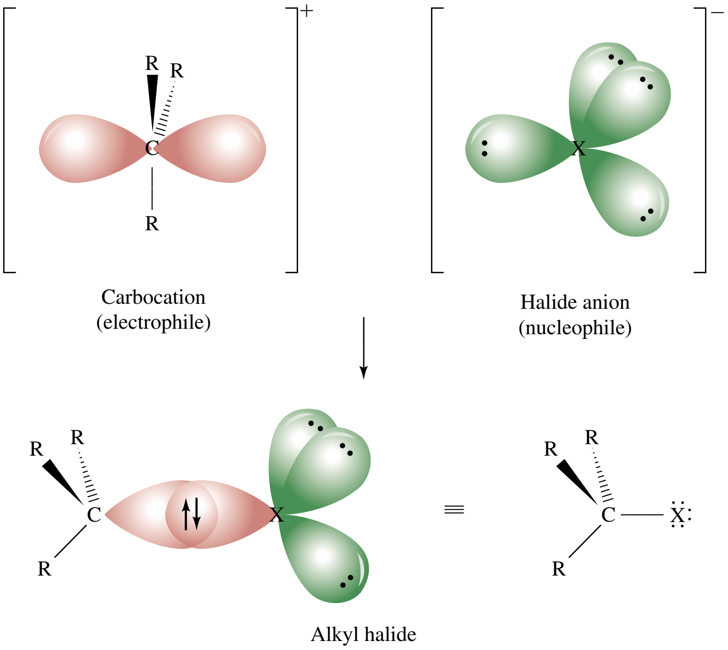
FIGURE 4.10 Hyperconjugation in ethyl cation. Ethyl cation is stabilized by delocalization of the electrons in the C—H bonds of the methyl group into the vacant 2*p* orbital of the positively charged carbon.



A second effect, called **hyperconjugation,** is also important. We'll again consider ethyl cation, but this time direct our attention to the electrons in the C—H bonds of the methyl group. Figure 4.10 illustrates how an orbital associated with the methyl group can overlap with the vacant *p* orbital of the positively charged carbon to give an extended orbital that encompasses both CH_3 and C^+. This allows the electrons of the methyl group to be shared by both carbons (thereby increasing their delocalization) and to stabilize the carbocation. Notice that according to hyperconjugation, electrons in the C—H bond of a $^+$C—C—H unit are more stabilizing than $^+$C—H electrons. Thus, successive replacement of the hydrogens attached to CH_3^+ by alkyl groups increases the opportunities for hyperconjugation, which is consistent with the observed order of increasing carbocation stability: methyl < primary < secondary < tertiary. Finally, although we have developed this picture for hyperconjugation of a $^+$C—C—H unit, it also applies to $^+$C—C—C as well as many others.

The positive charge on carbon and the vacant *p* orbital combine to make carbocations strongly **electrophilic** ("electron-loving," or "electron-seeking"). **Nucleophiles** are just the opposite. A nucleophile is "nucleus-seeking"; it has an unshared pair of electrons that it can use to form a covalent bond. Step 3 of the mechanism of the reaction of *tert*-butyl alcohol with hydrogen chloride is an example of a reaction between an electrophile and a nucleophile and is depicted from a structural perspective in Figure 4.11.

FIGURE 4.11 Combination of a carbocation and a halide anion to give an alkyl halide.



The crucial electronic interaction is between an unshared electron pair of the nucleophilic chloride anion and the vacant 2*p* orbital of the electrophilic carbocation.

Figure 4.12 maps the electrostatic potential in methyl cation and shows that the region of positive charge coincides with where we expect the vacant 2*p* orbital to be—centered on carbon and above and below the plane of the atoms.

A number of years ago G. N. Lewis extended our understanding of acid–base behavior to include reactions other than proton transfers. According to Lewis, *an acid is an electron-pair acceptor* and *a base is an electron-pair donor.* Thus, carbocations are electron-pair acceptors and are **Lewis acids.** Halide anions are electron-pair donors and are **Lewis bases.** It is generally true that electrophiles are Lewis acids, and nucleophiles are Lewis bases.

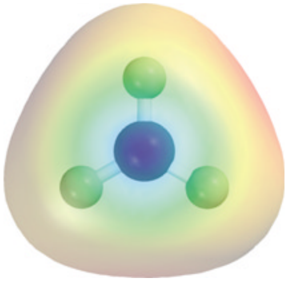
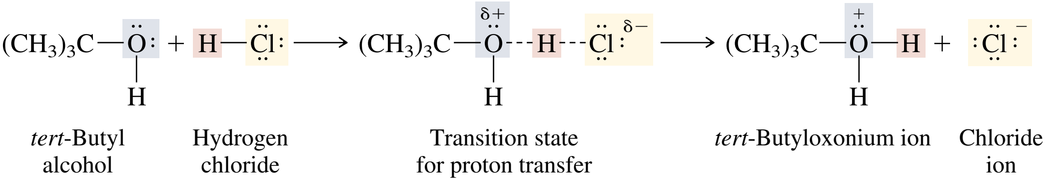


FIGURE 4.12 Electrostatic potential map of methyl cation (CH_3^+). The regions of lowest electron density are blue, are centered on carbon, and are located above and below the plane defined by the four atoms.

4.11 POTENTIAL ENERGY DIAGRAMS FOR MULTISTEP REACTIONS: THE S_N1 MECHANISM

The mechanism for the reaction of *tert*-butyl alcohol with hydrogen chloride presented in Figure 4.7 involves a sequence of three elementary steps. Each step has its own transition state, and the potential energy diagram in Figure 4.13 for the overall process is a composite of the energy diagrams for the three steps.

Reading from left to right in Figure 4.13, the first maximum corresponds to the transition state for proton transfer from hydrogen chloride to *tert*-butyl alcohol. This step is **bimolecular.** The proton that is transferred is partially bonded both to chlorine and to the oxygen of the alcohol at the transition state.



$$(CH_3)_3C-\underset{|\atop H}{\ddot{O}}: + H-\ddot{Cl}: \longrightarrow (CH_3)_3C-\underset{|\atop H}{\overset{\delta+}{\ddot{O}}}\text{---}H\text{---}\overset{\delta-}{\ddot{Cl}}: \longrightarrow (CH_3)_3C-\underset{|\atop H}{\overset{+}{\ddot{O}}}-H + :\ddot{Cl}:^-$$

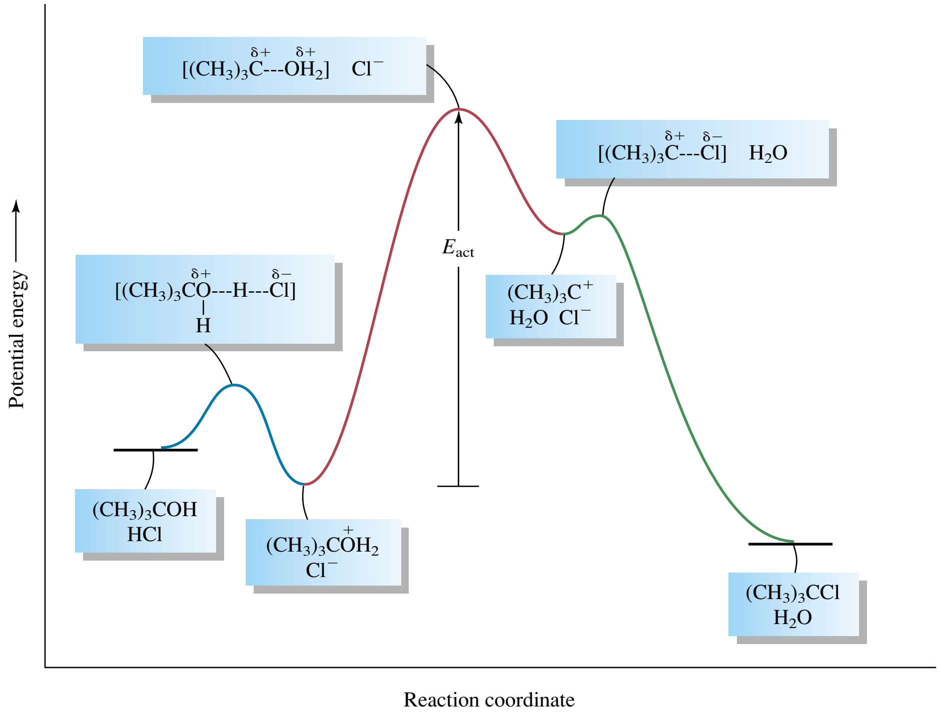
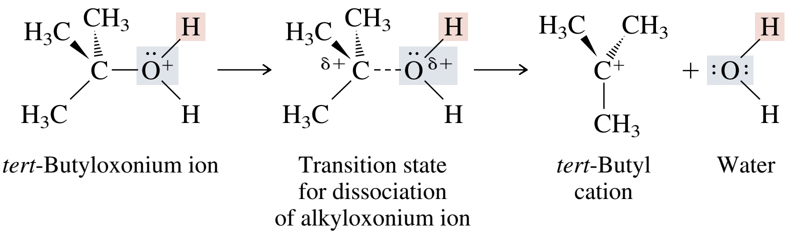


FIGURE 4.13 Energy diagram depicting the intermediates and transition states involved in the reaction of *tert*-butyl alcohol with hydrogen chloride.

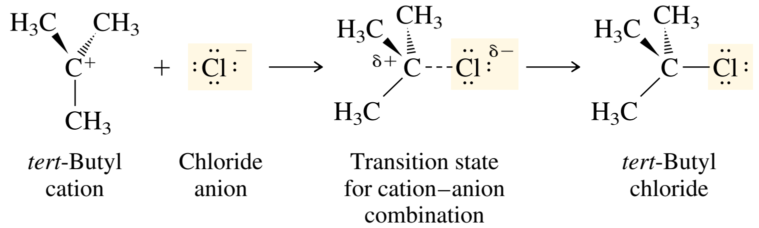
This is a rapid process, and therefore the activation energy for the first step is relatively low.

Once formed, the alkyloxonium ion dissociates by cleavage of its carbon–oxygen bond, giving a carbocation.



Only one species, the alkyloxonium ion, undergoes a chemical change in this step, making it **unimolecular.** Unlike the bimolecular proton transfer step that precedes it, in which formation of a new bond accompanies the cleavage of an old one, unimolecular dissociation of the alkyloxonium ion gives a carbocation without simultaneous formation of a new bond. Thus, the activation energy for carbocation formation is relatively high.

In the third step, the carbocation intermediate is captured by a chloride ion, and the energy barrier for this cation–anion combination is relatively low. The transition state is characterized by partial bond formation between the nucleophile (chloride anion) and the electrophile (*tert*-butyl cation).



Two species, the carbocation and the anion, react in this step, making it **bimolecular.** Note that molecularity refers only to individual elementary steps in a multistep mechanism, not to the overall reaction itself. Step 1 of the mechanism (proton transfer) is bimolecular, step 2 (dissociation of the alkyloxonium ion) is unimolecular, and step 3 (cation–anion combination) is bimolecular.

Of the three steps in the mechanism, step 2 has the highest activation energy and is the slowest step. A reaction can proceed no faster than its slowest step, which is referred to as the **rate-determining step.** In the reaction of *tert*-butyl alcohol with hydrogen chloride, formation of the carbocation by dissociation of the alkyloxonium ion is the rate-determining step.

Substitution reactions, of which the reaction of alcohols with hydrogen halides is but one example, will be discussed in more detail in Chapter 8. There, we will make extensive use of a shorthand notation for a mechanism originally introduced by Sir Christopher Ingold in the 1930s. Ingold proposed the symbol, S_N, to stand for *substitution nucleophilic,* to be followed by the number *1* or *2* according to whether the rate-determining step is unimolecular or bimolecular. The reaction of *tert*-butyl alcohol with hydrogen chloride, for example, is said to follow an **S_N1 mechanism** because its slow step (dissociation of *tert*-butyloxonium ion) is unimolecular.

4.12 EFFECT OF ALCOHOL STRUCTURE ON REACTION RATE

We saw in Section 4.8 that the reactivity of alcohols with hydrogen halides increases in the order primary < secondary < tertiary. To be valid, the mechanism proposed in Figure 4.7 and represented by the energy diagram in Figure 4.13 must account for this order of relative reactivity. When considering rate effects, we focus on the slow step of a reaction mechanism and analyze how that step is influenced by changes in reactants or reaction conditions.

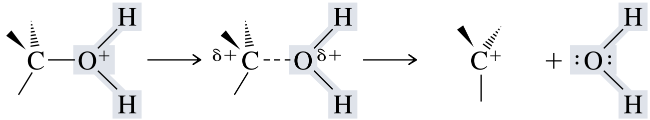
As mentioned, the slow step in the S_N1 mechanism is the dissociation of the alkyloxonium ion to the carbocation. The rate of this step is proportional to the concentration of the alkyloxonium ion:

$$\text{Rate} = k[\text{alkyloxonium ion}]$$

where k is a constant of proportionality called the *rate constant.* The value of k is related to the activation energy for alkyloxonium ion dissociation and is different for different alkyloxonium ions. A low activation energy implies a large value of k and a rapid rate of alkyloxonium ion dissociation. Conversely, a large activation energy is characterized by a small k for dissociation and a slow rate.

The rate of any chemical reaction increases with increasing temperature. Thus the value of k for a reaction is not constant, but increases as the temperature increases.

Consider what happens when the alkyloxonium ion dissociates to a carbocation and water. The positive charge resides mainly on oxygen in the alkyloxonium ion but is shared between oxygen and carbon at the transition state.



Alkyloxonium ion Transition state Carbocation Water

The transition state for carbocation formation begins to resemble the carbocation. If we assume that structural features that stabilize carbocations also stabilize transition states that have carbocation character, it follows that alkyloxonium ions derived from tertiary alcohols have a lower energy of activation for dissociation and are converted to their corresponding carbocations faster than those derived from secondary and primary alcohols. Figure 4.14 depicts the effect of alkyloxonium ion structure on the activation energy for, and thus the rate of, carbocation formation. Once the carbocation is formed, it is rapidly captured by halide ion, so that the rate of alkyl halide formation is governed by the rate of carbocation formation.

Inferring the structure of the transition state on the basis of what is known about the species that lead to it or may be formed by way of it is a practice with a long history in organic chemistry. A justification of this practice was advanced in 1955 by George S. Hammond, who reasoned that *if two states, such as a transition state and an intermediate derived from it, are similar in energy, then they are similar in structure.* This rationale is known as **Hammond's postulate.** In the formation of a carbocation from an alkyloxonium ion, the transition state is closer in energy to the carbocation than it is to the alkyloxonium ion, and so its structure more closely resembles the carbocation and it responds in a similar way to the stabilizing effects of alkyl substituents.

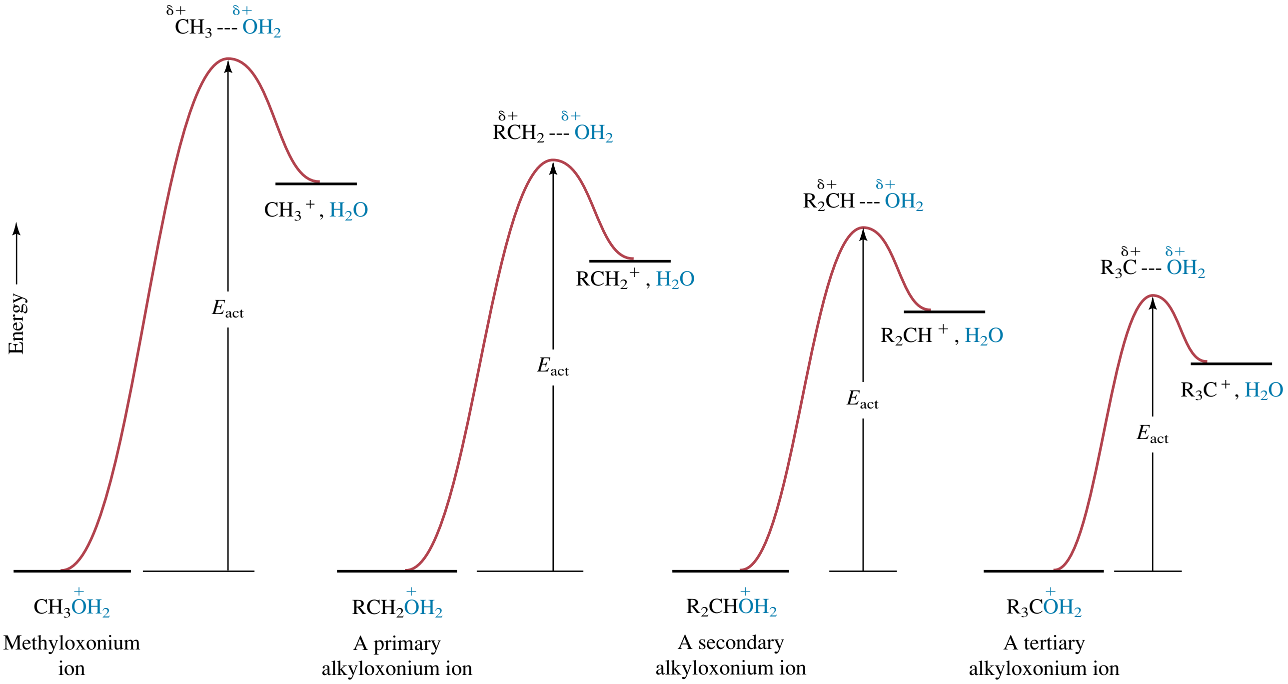
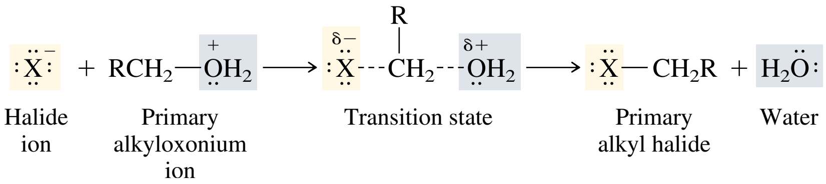


FIGURE 4.14 Diagrams comparing energies of activation for formation of carbocations from alkyloxonium ions of methyl, primary, secondary, and tertiary alcohols.

4.13 REACTION OF PRIMARY ALCOHOLS WITH HYDROGEN HALIDES. THE S_N2 MECHANISM

Unlike tertiary and secondary carbocations, primary carbocations are too high in energy to be intermediates in chemical reactions. Since primary alcohols are converted, albeit rather slowly, to alkyl halides on treatment with hydrogen halides, they must follow some other mechanism that avoids carbocation intermediates. This alternative mechanism is believed to be one in which the carbon–halogen bond begins to form before the carbon–oxygen bond of the alkyloxonium ion is completely broken.



The halide nucleophile helps to “push off” a water molecule from the alkyloxonium ion. According to this mechanism, both the halide ion and the alkyloxonium ion are involved in the same bimolecular elementary step. In Ingold’s terminology, introduced in Section 4.11 and to be described in detail in Chapter 8, nucleophilic substitutions characterized by a bimolecular rate-determining step are given the mechanistic symbol **S_N2.**

PROBLEM 4.14 1-Butanol and 2-butanol are converted to their corresponding bromides on being heated with hydrogen bromide. Write a suitable mechanism for each reaction, and assign each the appropriate symbol (S_N1 or S_N2).

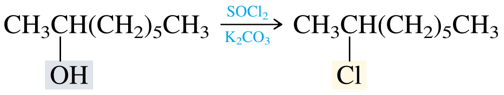
4.14 OTHER METHODS FOR CONVERTING ALCOHOLS TO ALKYL HALIDES

Alkyl halides are such useful starting materials for preparing other functional group types that chemists have developed several different methods for converting alcohols to alkyl halides. Two methods, based on the inorganic reagents *thionyl chloride* and *phosphorus tribromide,* bear special mention.

Thionyl chloride reacts with alcohols to give alkyl chlorides. The inorganic byproducts in the reaction, sulfur dioxide and hydrogen chloride, are both gases at room temperature and are easily removed, making it an easy matter to isolate the alkyl chloride.

$$\underset{\text{Alcohol}}{ROH} + \underset{\substack{\text{Thionyl}\\\text{chloride}}}{SOCl_2} \longrightarrow \underset{\substack{\text{Alkyl}\\\text{chloride}}}{RCl} + \underset{\substack{\text{Sulfur}\\\text{dioxide}}}{SO_2} + \underset{\substack{\text{Hydrogen}\\\text{chloride}}}{HCl}$$

Because tertiary alcohols are so readily converted to chlorides with hydrogen chloride, thionyl chloride is used mainly to prepare primary and secondary alkyl chlorides. Reactions with thionyl chloride are normally carried out in the presence of potassium carbonate or the weak organic base pyridine.



$$\underset{\textstyle OH}{CH_3CH(CH_2)_5CH_3} \xrightarrow[K_2CO_3]{SOCl_2} \underset{\textstyle Cl}{CH_3CH(CH_2)_5CH_3}$$

2-Octanol 2-Chlorooctane (81%)

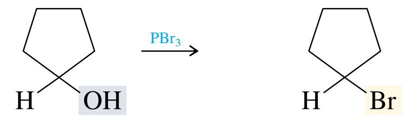
$$\underset{\text{2-Ethyl-1-butanol}}{(CH_3CH_2)_2CHCH_2OH} \xrightarrow[\text{pyridine}]{SOCl_2} \underset{\text{1-Chloro-2-ethylbutane (82\%)}}{(CH_3CH_2)_2CHCH_2Cl}$$

Phosphorus tribromide reacts with alcohols to give alkyl bromides and phosphorous acid.

$$\underset{\text{Alcohol}}{3ROH} + \underset{\substack{\text{Phosphorus}\\\text{tribromide}}}{PBr_3} \longrightarrow \underset{\substack{\text{Alkyl}\\\text{bromide}}}{3RBr} + \underset{\substack{\text{Phosphorous}\\\text{acid}}}{H_3PO_3}$$

Phosphorous acid is water-soluble and may be removed by washing the alkyl halide with water or with dilute aqueous base.

$$\underset{\text{Isobutyl alcohol}}{(CH_3)_2CHCH_2OH} \xrightarrow{PBr_3} \underset{\text{Isobutyl bromide (55–60\%)}}{(CH_3)_2CHCH_2Br}$$



Cyclopentanol Cyclopentyl bromide (78–84%)

Thionyl chloride and phosphorus tribromide are specialized reagents used to bring about particular functional group transformations. For this reason, we won't present the mechanisms by which they convert alcohols to alkyl halides, but instead will limit ourselves to those mechanisms that have broad applicability and enhance our knowledge of fundamental principles. In those instances you will find that a mechanistic understanding is of great help in organizing the reaction types of organic chemistry.

4.15 HALOGENATION OF ALKANES

The rest of this chapter describes a second method for preparing alkyl halides, one that uses alkanes as reactants. It involves substitution of a halogen atom for one of the alkane's hydrogens.

$$\underset{\text{Alkane}}{R{-}H} + \underset{\text{Halogen}}{X_2} \longrightarrow \underset{\text{Alkyl halide}}{R{-}X} + \underset{\text{Hydrogen halide}}{H{-}X}$$

The alkane is said to undergo *fluorination, chlorination, bromination,* or *iodination* according to whether X_2 is F_2, Cl_2, Br_2, or I_2, respectively. The general term is **halogenation. Chlorination** and **bromination** are the most widely used.

Volume II of *Organic Reactions,* an annual series that reviews reactions of interest to organic chemists, contains the statement "Most organic compounds burn or explode when brought in contact with fluorine."

The reactivity of the halogens decreases in the order $F_2 > Cl_2 > Br_2 > I_2$. Fluorine is an extremely aggressive oxidizing agent, and its reaction with alkanes is strongly exothermic and difficult to control. Direct fluorination of alkanes requires special equipment and techniques, is not a reaction of general applicability, and will not be discussed further.

Chlorination of alkanes is less exothermic than fluorination, and bromination less exothermic than chlorination. Iodine is unique among the halogens in that its reaction with alkanes is endothermic and alkyl iodides are never prepared by iodination of alkanes.

4.16 CHLORINATION OF METHANE

The gas-phase chlorination of methane is a reaction of industrial importance and leads to a mixture of chloromethane (CH_3Cl), dichloromethane (CH_2Cl_2), trichloromethane ($CHCl_3$), and tetrachloromethane (CCl_4) by sequential substitution of hydrogens.

Chlorination of methane provides approximately one-third of the annual U.S. production of chloromethane. The reaction of methanol with hydrogen chloride is the major synthetic method for the preparation of chloromethane.

$$\underset{\text{Methane}}{CH_4} + \underset{\text{Chlorine}}{Cl_2} \xrightarrow{400\text{–}440°C} \underset{\substack{\text{Chloromethane}\\ \text{(bp }-24°C)}}{CH_3Cl} + \underset{\substack{\text{Hydrogen}\\ \text{chloride}}}{HCl}$$

$$\underset{\text{Chloromethane}}{CH_3Cl} + \underset{\text{Chlorine}}{Cl_2} \xrightarrow{400\text{–}440°C} \underset{\substack{\text{Dichloromethane}\\ \text{(bp 40°C)}}}{CH_2Cl_2} + \underset{\substack{\text{Hydrogen}\\ \text{chloride}}}{HCl}$$

$$\underset{\text{Dichloromethane}}{CH_2Cl_2} + \underset{\text{Chlorine}}{Cl_2} \xrightarrow{400\text{–}440°C} \underset{\substack{\text{Trichloromethane}\\ \text{(bp 61°C)}}}{CHCl_3} + \underset{\substack{\text{Hydrogen}\\ \text{chloride}}}{HCl}$$

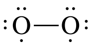
$$\underset{\text{Trichloromethane}}{CHCl_3} + \underset{\text{Chlorine}}{Cl_2} \xrightarrow{400\text{–}440°C} \underset{\substack{\text{Tetrachloromethane}\\ \text{(bp 77°C)}}}{CCl_4} + \underset{\substack{\text{Hydrogen}\\ \text{chloride}}}{HCl}$$

One of the chief uses of chloromethane is as a starting material from which silicone polymers are made. Dichloromethane is widely used as a paint stripper. Trichloromethane was once used as an inhalation anesthetic, but its toxicity caused it to be replaced by safer materials many years ago. Tetrachloromethane is the starting material for the preparation of several chlorofluorocarbons (CFCs), at one time widely used as refrigerant gases. In 1987, most of the world's industrialized nations agreed to phase out all uses of CFCs by the year 2000 because these compounds have been implicated in atmospheric processes that degrade the earth's ozone layer.

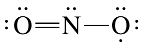
The chlorination of methane is carried out at rather high temperatures (400–440°C), even though each substitution in the series is exothermic. The high temperature provides the energy to initiate the reaction. The term "initiation step" has a specific meaning in organic chemistry, one that is related to the mechanism of the reaction. This mechanism, to be presented in Section 4.18, is fundamentally different from the mechanism by which alcohols react with hydrogen halides. Alcohols are converted to alkyl halides in reactions involving ionic (or "polar") intermediates—alkyloxonium ions and carbocations. The intermediates in the chlorination of methane and other alkanes are quite different; they are neutral ("nonpolar") species called **free radicals.**

4.17 STRUCTURE AND STABILITY OF FREE RADICALS

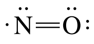
Free radicals are species that contain unpaired electrons. The octet rule notwithstanding, not all compounds have all of their electrons paired. Oxygen (O_2) is the most familiar example of a compound with unpaired electrons; it has two of them. Compounds that have an odd number of electrons, such as nitrogen dioxide (NO_2), must have at least one unpaired electron.



Oxygen



Nitrogen dioxide

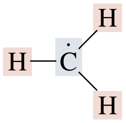


Nitrogen monoxide

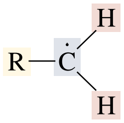
Nitrogen monoxide ("nitric oxide") is another stable free radical. Although known for hundreds of years, NO has only recently been discovered to be an extremely important biochemical messenger and moderator of so many biological processes that it might be better to ask "Which ones is it not involved in?"

The journal *Science* selected nitric oxide as its "Molecule of the Year" for 1992.

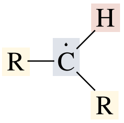
The free radicals that we usually see in carbon chemistry are much less stable than these. Simple alkyl radicals, for example, require special procedures for their isolation and study. We will encounter them here only as reactive intermediates, formed in one step of a reaction mechanism and consumed in the next. Alkyl radicals are classified as primary, secondary, or tertiary according to the number of carbon atoms directly attached to the carbon that bears the unpaired electron.



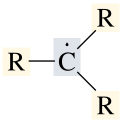
Methyl radical



Primary radical



Secondary radical

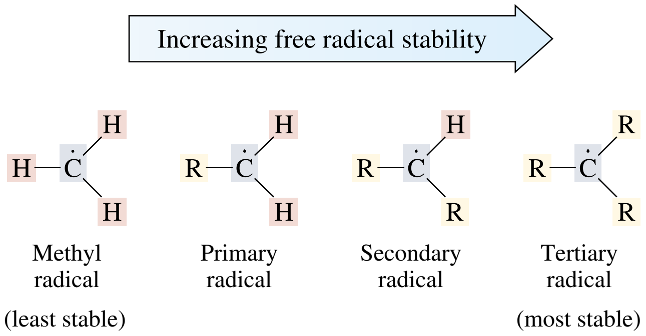


Tertiary radical

An alkyl radical is neutral and has one more electron than the corresponding carbocation. Thus, bonding in methyl radical may be approximated by simply adding an electron to the vacant 2*p* orbital of sp^2-hybridized carbon in methyl cation (Figure 4.15*a*). Alternatively, we could assume that carbon is sp^3-hybridized and place the unpaired electron in an sp^3 orbital (Figure 4.15*b*).

Of the two extremes, experimental studies indicate that the planar sp^2 model describes the bonding in alkyl radicals better than the pyramidal sp^3 model. Methyl radical is planar, and more highly substituted radicals such as *tert*-butyl radical are flattened pyramids closer in shape to that expected for sp^2-hybridized carbon than for sp^3.

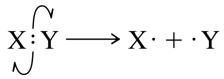
Free radicals, like carbocations, have an unfilled 2*p* orbital and are stabilized by substituents, such as alkyl groups, that release electrons. Consequently, the order of free-radical stability parallels that of carbocations.



PROBLEM 4.15 Write a structural formula for the most stable of the free radicals that have the formula C_5H_{11}.

Some of the evidence indicating that alkyl substituents stabilize free radicals comes from bond energies. The strength of a bond is measured by the energy required to break it. A covalent bond can be broken in two ways. In a **homolytic cleavage** a bond between two atoms is broken so that each of them retains one of the electrons in the bond.

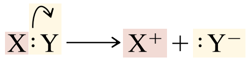
A curved arrow shown as a single-barbed fishhook ⌒ signifies the movement of *one* electron. "Normal" curved arrows ↷ track the movement of a *pair* of electrons.



$$X\!:\!Y \longrightarrow X\cdot + \cdot Y$$

Homolytic bond cleavage

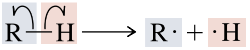
In contrast, in a **heterolytic cleavage** one fragment retains both electrons.



$$X\!:\!Y \longrightarrow X^+ + :\!Y^-$$

Heterolytic bond cleavage

We assess the relative stability of alkyl radicals by measuring the enthalpy change ($\Delta H°$) for the homolytic cleavage of a C—H bond in an alkane:



$$R\text{—}H \longrightarrow R\cdot + \cdot H$$

The more stable the radical, the lower the energy required to generate it by C—H bond homolysis.

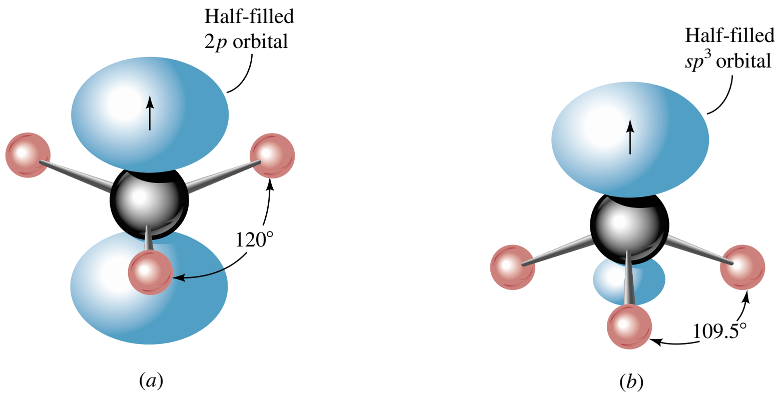


FIGURE 4.15 Orbital hybridization models of bonding in methyl radical. (*a*) If the structure of the CH_3 radical is planar, then carbon is sp^2-hybridized with an unpaired electron in a 2*p* orbital. (*b*) If CH_3 is pyramidal, carbon is sp^3-hybridized with an electron in an sp^3 orbital. Model (*a*) is more consistent with experimental observations.

TABLE 4.3 Bond Dissociation Energies of Some Representative Compounds*

	Bond dissociation energy			Bond dissociation energy	
Bond	**kJ/mol**	**(kcal/mol)**	**Bond**	**kJ/mol**	**(kcal/mol)**
Diatomic molecules					
H—H	435	(104)			
F—F	159	(38)	H—F	568	(136)
Cl—Cl	242	(58)	H—Cl	431	(103)
Br—Br	192	(46)	H—Br	366	(87.5)
I—I	150	(36)	H—I	297	(71)
Alkanes					
CH_3—H	435	(104)	CH_3—CH_3	368	(88)
CH_3CH_2—H	410	(98)	CH_3CH_2—CH_3	355	(85)
$CH_3CH_2CH_2$—H	410	(98)			
$(CH_3)_2CH$—H	397	(95)			
$(CH_3)_2CHCH_2$—H	410	(98)	$(CH_3)_2CH$—CH_3	351	(84)
$(CH_3)_3C$—H	380	(91)	$(CH_3)_3C$—CH_3	334	(80)
Alkyl halides					
CH_3—F	451	(108)	$(CH_3)_2CH$—F	439	(105)
CH_3—Cl	349	(83.5)	$(CH_3)_2CH$—Cl	339	(81)
CH_3—Br	293	(70)	$(CH_3)_2CH$—Br	284	(68)
CH_3—I	234	(56)	$(CH_3)_3C$—Cl	330	(79)
CH_3CH_2—Cl	338	(81)	$(CH_3)_3C$—Br	263	(63)
$CH_3CH_2CH_2$—Cl	343	(82)			
Water and alcohols					
HO—H	497	(119)	CH_3CH_2—OH	380	(91)
CH_3O—H	426	(102)	$(CH_3)_2CH$—OH	385	(92)
CH_3—OH	380	(91)	$(CH_3)_3C$—OH	380	(91)

*Bond dissociation energies refer to bond indicated in structural formula for each substance.

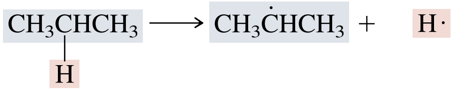
The energy required for homolytic bond cleavage is called the **bond dissociation energy (BDE).** A list of some bond dissociation energies is given in Table 4.3.

As the table indicates, C—H bond dissociation energies in alkanes are approximately 375 to 435 kJ/mol (90–105 kcal/mol). Homolysis of the H—CH_3 bond in methane gives methyl radical and requires 435 kJ/mol (104 kcal/mol). The dissociation energy of the H—CH_2CH_3 bond in ethane, which gives a primary radical, is somewhat less (410 kJ/mol, or 98 kcal/mol) and is consistent with the notion that ethyl radical (primary) is more stable than methyl.

The dissociation energy of the terminal C—H bond in propane is exactly the same as that of ethane. The resulting free radical is primary ($R\dot{C}H_2$) in both cases.

$$\underset{\text{Propane}}{CH_3CH_2CH_2{-}H} \longrightarrow \underset{\substack{n\text{-Propyl}\\ \text{radical}\\ \text{(primary)}}}{CH_3CH_2\dot{C}H_2} + \underset{\substack{\text{Hydrogen}\\ \text{atom}}}{H\cdot} \qquad \begin{array}{r}\Delta H^\circ = +410\text{ kJ}\\ (98\text{ kcal})\end{array}$$

Note, however, that Table 4.3 includes two entries for propane. The second entry corresponds to the cleavage of a bond to one of the hydrogens of the methylene (CH_2) group. It requires slightly less energy to break a C—H bond in the methylene group than in the methyl group.

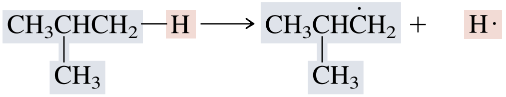


$$CH_3\underset{\displaystyle H}{\underset{|}{C}}HCH_3 \longrightarrow CH_3\dot{C}HCH_3 + H\cdot \qquad \Delta H^\circ = +397\text{ kJ } (95\text{ kcal})$$

Propane Isopropyl radical (secondary) Hydrogen atom

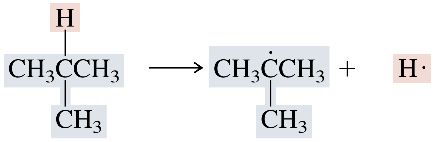
Since the starting material (propane) and one of the products (H·) are the same in both processes, the difference in bond dissociation energies is equal to the energy difference between an *n*-propyl radical (primary) and an isopropyl radical (secondary). As depicted in Figure 4.16, the secondary radical is 13 kJ/mol (3 kcal/mol) more stable than the primary radical.

Similarly, by comparing the bond dissociation energies of the two different types of C—H bonds in 2-methylpropane, we see that a tertiary radical is 30 kJ/mol (7 kcal/mol) more stable than a primary radical.



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2{-}H \longrightarrow CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\dot{C}H_2 + H\cdot \qquad \Delta H^\circ = +410\text{ kJ } (98\text{ kcal})$$

2-Methylpropane Isobutyl radical (primary) Hydrogen atom



$$CH_3\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}CH_3 \longrightarrow CH_3\underset{\displaystyle CH_3}{\underset{|}{\dot{C}}}CH_3 + H\cdot \qquad \Delta H^\circ = +380\text{ kJ } (91\text{ kcal})$$

2-Methylpropane *tert*-Butyl radical (tertiary) Hydrogen atom

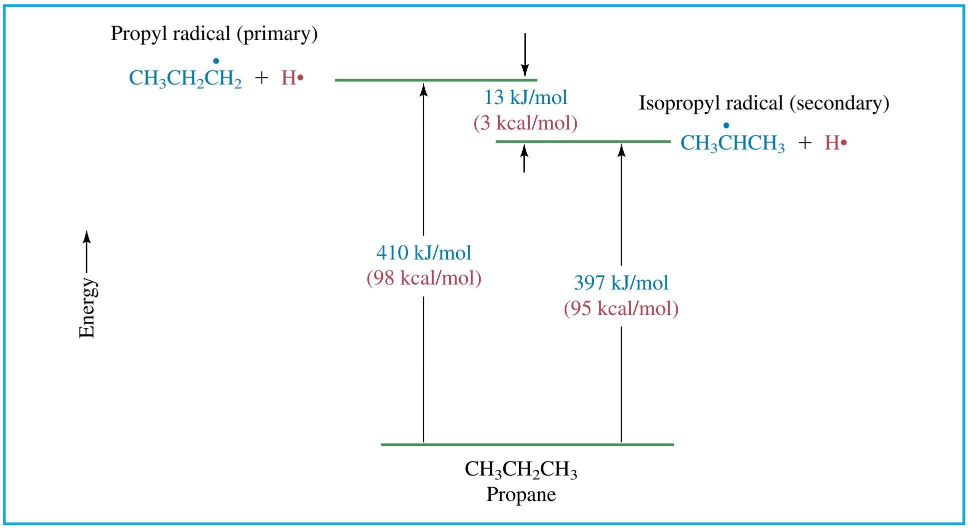


FIGURE 4.16 Diagram showing how bond dissociation energies of methylene and methyl C—H bonds in propane reveal a difference in stabilities between two isomeric free radicals. The secondary radical is more stable than the primary.

PROBLEM 4.16 Carbon–carbon bond dissociation energies have been measured for alkanes. Without referring to Table 4.3, identify the alkane in each of the following pairs that has the lower carbon–carbon bond dissociation energy, and explain the reason for your choice.

(a) Ethane or propane

(b) Propane or 2-methylpropane

(c) 2-Methylpropane or 2,2-dimethylpropane

SAMPLE SOLUTION (a) First write the equations that describe homolytic carbon–carbon bond cleavage in each alkane.

$$\underset{\text{Ethane}}{CH_3—CH_3} \longrightarrow \underset{\text{Two methyl radicals}}{\cdot CH_3 + \cdot CH_3}$$

$$\underset{\text{Propane}}{CH_3CH_2—CH_3} \longrightarrow \underset{\text{Ethyl radical}}{CH_3\dot{C}H_2} + \underset{\text{Methyl radical}}{\cdot CH_3}$$

Cleavage of the carbon–carbon bond in ethane yields two methyl radicals, whereas propane yields an ethyl radical and one methyl radical. Ethyl radical is more stable than methyl, and so less energy is required to break the carbon–carbon bond in propane than in ethane. The measured carbon–carbon bond dissociation energy in ethane is 368 kJ/mol (88 kcal/mol), and that in propane is 355 kJ/mol (85 kcal/mol).

Like carbocations, most free radicals are exceedingly reactive species—too reactive to be isolated but capable of being formed as transient intermediates in chemical reactions. Methyl radical, as we shall see in the following section, is an intermediate in the chlorination of methane.

4.18 MECHANISM OF METHANE CHLORINATION

The generally accepted mechanism for the chlorination of methane is presented in Figure 4.17. As we noted earlier (section 4.16), the reaction is normally carried out in the gas phase at high temperature. The reaction itself is strongly exothermic, but energy must be put into the system in order to get it going. This energy goes into breaking the weakest bond in the system, which, as we see from the bond dissociation energy data in Table 4.3, is the Cl—Cl bond with a bond dissociation energy of 242 kJ/mol (58 kcal/mol). The step in which Cl—Cl bond homolysis occurs is called the **initiation step.**

The bond dissociation energy of the other reactant, methane, is much higher. It is 435 kJ/mol (104 kcal/mol).

Each chlorine atom formed in the initiation step has seven valence electrons and is very reactive. Once formed, a chlorine atom abstracts a hydrogen atom from methane as shown in step 2 in Figure 4.17. Hydrogen chloride, one of the isolated products from the overall reaction, is formed in this step. A methyl radical is also formed, which then attacks a molecule of Cl_2 in step 3. Attack of methyl radical on Cl_2 gives chloromethane, the other product of the overall reaction, along with a chlorine atom which then cycles back to step 2, repeating the process. Steps 2 and 3 are called the **propagation steps** of the reaction and, when added together, give the overall equation for the reaction. Since one initiation step can result in a great many propagation cycles, the overall process is called a **free-radical chain reaction.**

PROBLEM 4.17 Write equations for the initiation and propagation steps for the formation of dichloromethane by free-radical chlorination of chloromethane.

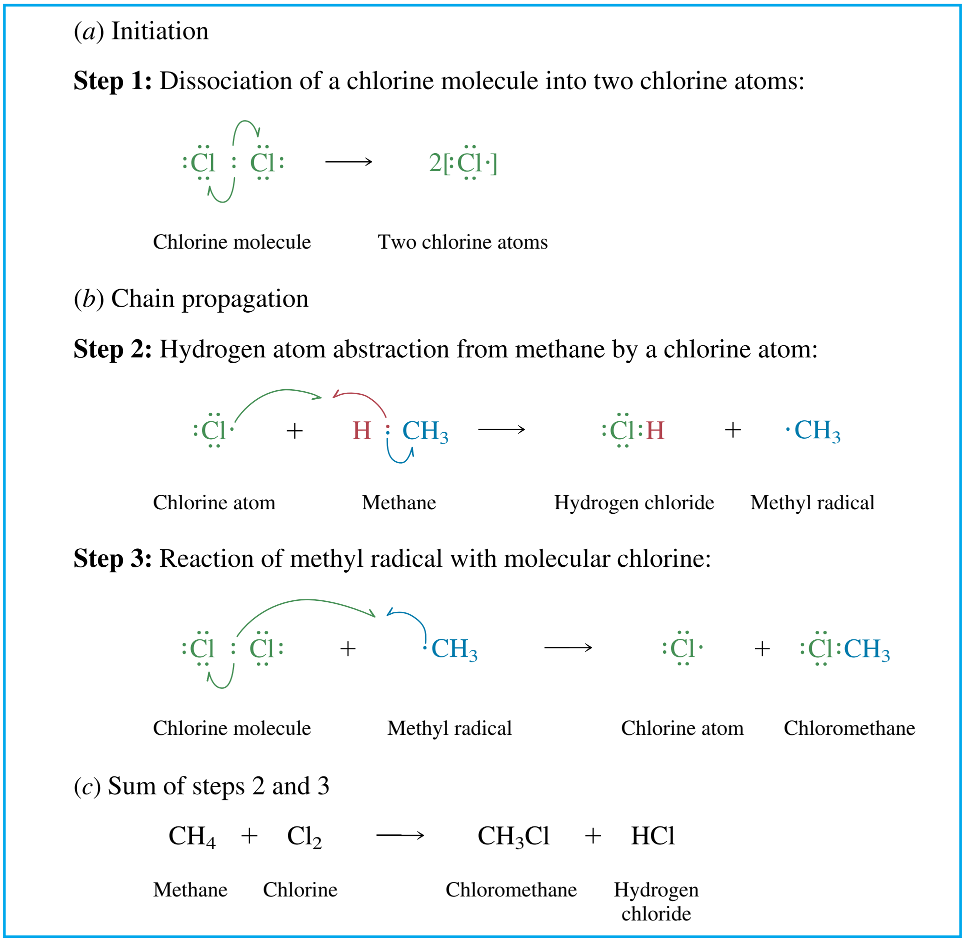
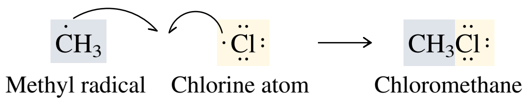


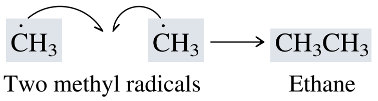
FIGURE 4.17 Equations describing the initiation and propagation steps in the free-radical mechanism for the chlorination of methane. Together the two propagation steps give the overall equation for the reaction.

In practice, side reactions intervene to reduce the efficiency of the propagation steps. The chain sequence is interrupted whenever two odd-electron species combine to give an even-electron product. Reactions of this type are called **chain-terminating steps.** Some commonly observed chain-terminating steps in the chlorination of methane are shown in the following equations.

Combination of a methyl radical with a chlorine atom:



Combination of two methyl radicals:



FROM BOND ENERGIES TO HEATS OF REACTION

You have seen that measurements of heats of reaction, such as heats of combustion, can provide quantitative information concerning the relative stability of constitutional isomers (Section 2.15) and stereoisomers (Section 3.12). The box in Section 2.15 described how heats of reaction can be manipulated arithmetically to generate heats of formation (ΔH_f°) for many molecules. The following material shows how two different sources of thermochemical information, heats of formation and bond dissociation energies (Table 4.3), can reveal whether a particular reaction is exothermic or endothermic and by how much.

Consider the chlorination of methane to chloromethane. The heats of formation of the reactants and products appear beneath the equation. These heats of formation for the chemical compounds are taken from published tabulations; the heat of formation of chlorine, as it is for all elements, is zero.

$$\begin{array}{lcccccc} & CH_4 & + & Cl_2 & \longrightarrow & CH_3Cl & + & HCl \\ \Delta H_f^\circ\text{: (kJ/mol)} & -74.8 & & 0 & & -81.9 & & -92.3 \end{array}$$

The overall heat of reaction is given by

$$\Delta H^\circ = \sum \text{(heats of formation of products)} - \sum \text{(heats of formation of reactants)}$$

$$\Delta H^\circ = (-81.9\text{ kJ} - 92.3\text{ kJ}) - (-74.8\text{ kJ}) = -99.4\text{ kJ}$$

Thus, the chlorination of methane is calculated to be an exothermic reaction on the basis of heat of formation data.

The same conclusion is reached using bond dissociation energies. The following equation shows the bond dissociation energies of the reactants and products taken from Table 4.3:

$$\begin{array}{lcccccc} & CH_4 & + & Cl_2 & \longrightarrow & CH_3Cl & + & HCl \\ \text{BDE: (kJ/mol)} & 435 & & 242 & & 349 & & 431 \end{array}$$

Because stronger bonds are formed at the expense of weaker ones, the reaction is exothermic and

$$\Delta H^\circ = \sum \text{(BDE of bonds broken)} - \sum \text{(BDE of bonds formed)}$$

$$\Delta H^\circ = (435\text{ kJ} + 242\text{ kJ}) - (349\text{ kJ} + 431\text{ kJ}) = -103\text{ kJ}$$

This value is in good agreement with that obtained from heat of formation data.

Compare chlorination of methane with iodination. The relevant bond dissociation energies are given in the equation.

$$\begin{array}{lcccccc} & CH_4 & + & I_2 & \longrightarrow & CH_3I & + & HI \\ \text{BDE: (kJ/mol)} & 435 & & 150 & & 234 & & 297 \end{array}$$

$$\Delta H^\circ = \sum \text{(BDE of bonds broken)} - \sum \text{(BDE of bonds formed)}$$

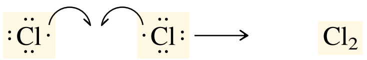
$$\Delta H^\circ = (435\text{ kJ} + 150\text{ kJ}) - (234\text{ kJ} + 297\text{ kJ}) = +54\text{ kJ}$$

A positive value for ΔH° signifies an **endothermic** reaction. The reactants are more stable than the products, and so iodination of alkanes is not a feasible reaction. You would not want to attempt the preparation of iodomethane by iodination of methane.

A similar analysis for fluorination of methane gives $\Delta H^\circ = -426$ kJ for its heat of reaction. Fluorination of methane is four times as exothermic as chlorination. A reaction this exothermic, if it also occurs at a rapid rate, can proceed with explosive violence.

Bromination of methane is exothermic, but less exothermic than chlorination. The value calculated from bond dissociation energies is $\Delta H^\circ = -30$ kJ. Although bromination of methane is energetically favorable, economic considerations cause most of the methyl bromide prepared commercially to be made from methanol by reaction with hydrogen bromide.

Combination of two chlorine atoms:



Two chlorine atoms Chlorine molecule

Termination steps are, in general, less likely to occur than the propagation steps. Each of the termination steps requires two free radicals to encounter each other in a medium that contains far greater quantities of other materials (methane and chlorine molecules) with which they can react. Although some chloromethane undoubtedly arises via direct combination of methyl radicals with chlorine atoms, most of it is formed by the propagation sequence shown in Figure 4.17.

4.19 HALOGENATION OF HIGHER ALKANES

Like the chlorination of methane, chlorination of ethane is carried out on an industrial scale as a high-temperature gas-phase reaction.

$$CH_3CH_3 + Cl_2 \xrightarrow{420°C} CH_3CH_2Cl + HCl$$

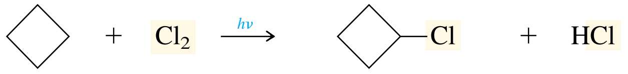
Ethane Chlorine Chloromethane (78%) (ethyl chloride) Hydrogen chloride

As in the chlorination of methane, it is often difficult to limit the reaction to monochlorination, and derivatives having more than one chlorine atom are also formed.

PROBLEM 4.18 Chlorination of ethane yields, in addition to ethyl chloride, a mixture of two isomeric dichlorides. What are the structures of these two dichlorides?

In the laboratory it is more convenient to use light, either visible or ultraviolet, as the source of energy to initiate the reaction. Reactions that occur when light energy is absorbed by a molecule are called **photochemical reactions.** Photochemical techniques permit the reaction of alkanes with chlorine to be performed at room temperature.

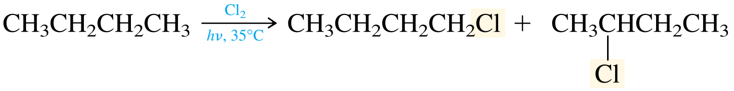
Photochemical energy is indicated by writing "light" or "*hν*" above the arrow. The symbol *hν* is equal to the energy of a light photon and will be discussed in more detail in Section 13.1.



Cyclobutane Chlorine Chlorocyclobutane (73%) (cyclobutyl chloride) Hydrogen chloride

Methane, ethane, and cyclobutane share the common feature that each one can give only a *single* monochloro derivative. All the hydrogens of cyclobutane, for example, are equivalent, and substitution of any one gives the same product as substitution of any other. Chlorination of alkanes in which all the hydrogens are not equivalent is more complicated in that a mixture of every possible monochloro derivative is formed, as the chlorination of butane illustrates:

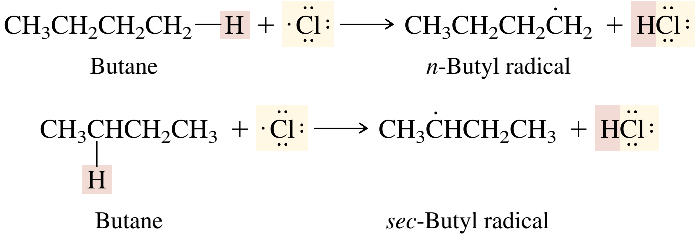
The percentages cited in this equation reflect the composition of the monochloride fraction of the product mixture rather than the isolated yield of each component.



$$CH_3CH_2CH_2CH_3 \xrightarrow[h\nu,\ 35°C]{Cl_2} CH_3CH_2CH_2CH_2Cl + CH_3\underset{\substack{|\\ Cl}}{C}HCH_2CH_3$$

Butane 1-Chlorobutane (28%) (*n*-butyl chloride) 2-Chlorobutane (72%) (*sec*-butyl chloride)

These two products arise because in one of the propagation steps a chlorine atom may abstract a hydrogen atom from either a methyl or a methylene group of butane.



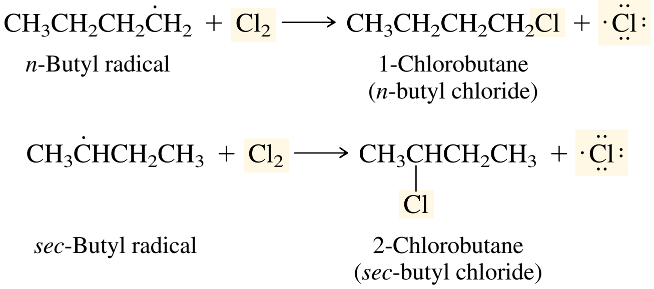
$$CH_3CH_2CH_2CH_2{-}H + \cdot\ddot{\underset{\cdot\cdot}{Cl}}\colon \longrightarrow CH_3CH_2CH_2\dot{C}H_2 + H\ddot{\underset{\cdot\cdot}{Cl}}\colon$$

Butane n-Butyl radical

$$CH_3\underset{\displaystyle H}{\underset{|}{C}}HCH_2CH_3 + \cdot\ddot{\underset{\cdot\cdot}{Cl}}\colon \longrightarrow CH_3\dot{C}HCH_2CH_3 + H\ddot{\underset{\cdot\cdot}{Cl}}\colon$$

Butane *sec*-Butyl radical

The resulting free radicals react with chlorine to give the corresponding alkyl chlorides. Butyl radical gives only 1-chlorobutane; *sec*-butyl radical gives only 2-chlorobutane.



$$CH_3CH_2CH_2\dot{C}H_2 + Cl_2 \longrightarrow CH_3CH_2CH_2CH_2Cl + \cdot\ddot{\underset{\cdot\cdot}{Cl}}\colon$$

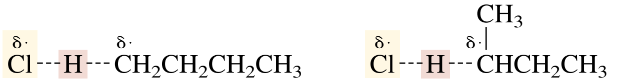
n-Butyl radical 1-Chlorobutane (*n*-butyl chloride)

$$CH_3\dot{C}HCH_2CH_3 + Cl_2 \longrightarrow CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3 + \cdot\ddot{\underset{\cdot\cdot}{Cl}}\colon$$

sec-Butyl radical 2-Chlorobutane (*sec*-butyl chloride)

If every collision of a chlorine atom with a butane molecule resulted in hydrogen abstraction, the *n*-butyl/*sec*-butyl radical ratio and, therefore, the 1-chloro/2-chlorobutane ratio, would be given by the relative numbers of hydrogens in the two equivalent methyl groups of $CH_3CH_2CH_2CH_3$ (six) compared with those in the two equivalent methylene groups (four). The product distribution expected on a *statistical* basis would be 60% 1-chlorobutane and 40% 2-chlorobutane. The *experimentally observed* product distribution, however, is 28% 1-chlorobutane and 72% 2-chlorobutane. *sec*-Butyl radical is therefore formed in greater amounts, and *n*-butyl radical in lesser amounts, than expected statistically.

The reason for this behavior stems from the greater stability of secondary compared with primary free radicals. The transition state for the step in which a chlorine atom abstracts a hydrogen from carbon has free-radical character at carbon.



$$\overset{\delta\cdot}{Cl}\text{---}H\text{---}\overset{\delta\cdot}{C}H_2CH_2CH_2CH_3 \qquad \overset{\delta\cdot}{Cl}\text{---}H\text{---}\overset{\overset{\displaystyle CH_3}{\delta\cdot|}}{C}HCH_2CH_3$$

Transition state for abstraction of a primary hydrogen

Transition state for abstraction of a secondary hydrogen

A secondary hydrogen is abstracted faster than a primary hydrogen because the transition state with secondary radical character is more stable than the one with primary radical character. The same factors that stabilize a secondary radical stabilize a transition state with secondary radical character more than one with primary radical character. Hydrogen atom abstraction from a CH_2 group occurs faster than from a CH_3 group. We can calculate how much faster a *single* secondary hydrogen is abstracted compared with a *single* primary hydrogen from the experimentally observed product distribution.

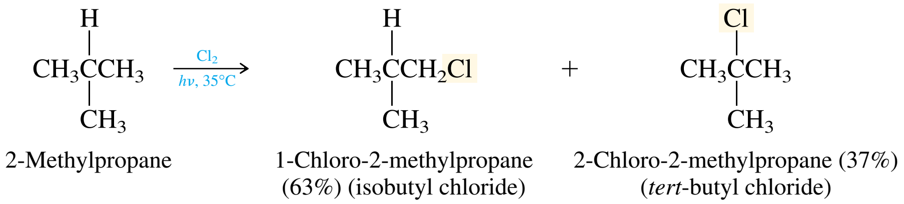
$$\frac{72\%\ \text{2-chlorobutane}}{28\%\ \text{1-chlorobutane}} = \frac{\text{rate of secondary H abstraction} \times 4\ \text{secondary hydrogens}}{\text{rate of primary H abstraction} \times 6\ \text{primary hydrogens}}$$

$$\frac{\text{Rate of secondary H abstraction}}{\text{Rate of primary H abstraction}} = \frac{72}{28} \times \frac{6}{4} = \frac{3.9}{1}$$

A single secondary hydrogen in butane is abstracted by a chlorine atom 3.9 times as fast as a single primary hydrogen.

PROBLEM 4.19 Assuming the relative rate of secondary to primary hydrogen atom abstraction to be the same in the chlorination of propane as it is in that of butane, calculate the relative amounts of propyl chloride and isopropyl chloride obtained in the free-radical chlorination of propane.

A similar study of the chlorination of 2-methylpropane established that a tertiary hydrogen is removed 5.2 times faster than each primary hydrogen.



$$\mathrm{(CH_3)_3CH} \xrightarrow[h\nu,\ 35^\circ\mathrm{C}]{\mathrm{Cl_2}} \mathrm{(CH_3)_2CHCH_2Cl} + \mathrm{(CH_3)_3CCl}$$

2-Methylpropane

1-Chloro-2-methylpropane (63%) (isobutyl chloride)

2-Chloro-2-methylpropane (37%) (*tert*-butyl chloride)

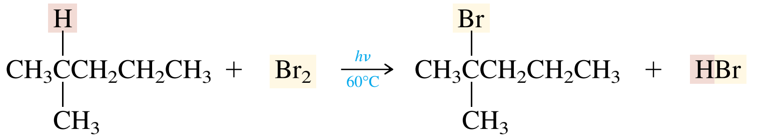
In summary then, the chlorination of alkanes is not very selective. The various kinds of hydrogens present in a molecule (tertiary, secondary, and primary) differ by only a factor of 5 in the relative rate at which each reacts with a chlorine atom.

	R_3CH >	R_2CH_2 >	RCH_3
	(tertiary)	(secondary)	(primary)
Relative rate (chlorination)	5.2	3.9	1

Bromine reacts with alkanes by a free-radical chain mechanism analogous to that of chlorine. There is an important difference between chlorination and bromination, however. Bromination is highly selective for substitution of *tertiary hydrogens*. The spread in reactivity among primary, secondary, and tertiary hydrogens is greater than 10^3.

	R_3CH >	R_2CH_2 >	RCH_3
	(tertiary)	(secondary)	(primary)
Relative rate (bromination)	1640	82	1

In practice, this means that when an alkane contains primary, secondary, and tertiary hydrogens, it is usually only the tertiary hydrogen that is replaced by bromine.



$$\mathrm{(CH_3)_2CHCH_2CH_2CH_3} + \mathrm{Br_2} \xrightarrow[60^\circ\mathrm{C}]{h\nu} \mathrm{(CH_3)_2CBrCH_2CH_2CH_3} + \mathrm{HBr}$$

2-Methylpentane | Bromine | 2-Bromo-2-methylpentane (76% isolated yield) | Hydrogen bromide

The yield cited in this reaction is the isolated yield of purified product. Isomeric bromides constitute only a tiny fraction of the crude product.

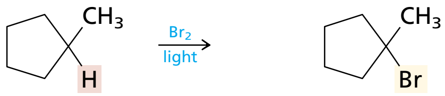
PROBLEM 4.20 Give the structure of the principal organic product formed by free-radical bromination of each of the following:

(a) Methylcyclopentane

(b) 1-Isopropyl-1-methylcyclopentane

(c) 2,2,4-Trimethylpentane

SAMPLE SOLUTION (a) Write the structure of the starting hydrocarbon, and identify any tertiary hydrogens that are present. The only tertiary hydrogen in methylcyclopentane is the one attached to C-1. This is the one replaced by bromine.



Methylcyclopentane 1-Bromo-1-methylcyclopentane

This difference in selectivity between chlorination and bromination of alkanes needs to be kept in mind when one wishes to prepare an alkyl halide from an alkane:

1. Since chlorination of an alkane yields every possible monochloride, it is used only when all the hydrogens in an alkane are equivalent.
2. Bromination is normally used only to prepare tertiary alkyl bromides from alkanes.

Selectivity is not an issue in the conversion of alcohols to alkyl halides. Except for certain limitations to be discussed in Section 8.15, the location of the halogen substituent in the product corresponds to that of the hydroxyl group in the starting alcohol.

4.20 SUMMARY

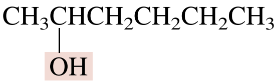
Chemical reactivity and functional group transformations involving the preparation of alkyl halides from alcohols and from alkanes are the main themes of this chapter. Although the conversions of an alcohol or an alkane to an alkyl halide are both classified as substitutions, they proceed by very different mechanisms.

Section 4.1 Alcohols and alkyl halides may be named using either **substitutive** or **functional class** nomenclature. In substitutive nomenclature alkyl halides are named as halogen derivatives of alkanes. The parent is the longest continuous chain that bears the halogen substituent, and in the absence of other substituents the chain is numbered from the direction that gives the lowest number to the carbon that bears the halogen. The functional class names of alkyl halides begin with the name of the alkyl group and end with the halide as a separate word.

$$CH_3\underset{\displaystyle Br}{\underset{|}{C}}HCH_2CH_2CH_2CH_3$$

Substitutive name: 2-Bromohexane
Functional class name: 1-Methylpentyl bromide

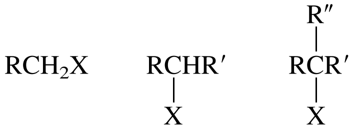
Section 4.2 The substitutive names of alcohols are derived by replacing the *-e* ending of an alkane with *-ol.* Functional class names of alcohols begin with the name of the alkyl group and end in the word "alcohol."



$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2CH_2CH_2CH_3$$

Substitutive name: 2-Hexanol
Functional class name: 1-Methylpentyl alcohol

Section 4.3 Alcohols (X = OH) and alkyl halides (X = F, Cl, Br, or I) are classified as primary, secondary, or tertiary according to the degree of substitution at the carbon that bears the functional group.

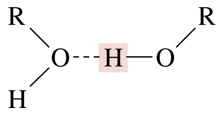


$$\mathrm{RCH_2X} \qquad \underset{\mathrm{X}}{\underset{|}{\mathrm{RCHR'}}} \qquad \underset{\mathrm{X}}{\underset{|}{\overset{\overset{\mathrm{R''}}{|}}{\mathrm{RCR'}}}}$$

Primary Secondary Tertiary

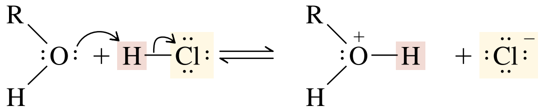
Section 4.4 The halogens (especially fluorine and chlorine) and oxygen are more electronegative than carbon, and the carbon–halogen bond in alkyl halides and the carbon–oxygen bond in alcohols are polar. Carbon is the positive end of the dipole and halogen or oxygen the negative end.

Section 4.5 Dipole/induced-dipole and dipole–dipole attractive forces make alcohols higher boiling than alkanes of similar molecular weight. The attractive force between —OH groups is called **hydrogen bonding.**



Hydrogen bonding between the hydroxyl group of an alcohol and water makes the water-solubility of alcohols greater than that of hydrocarbons. Low-molecular-weight alcohols [CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$, and $(CH_3)_2CHOH$] are soluble in water in all proportions. Alkyl halides are insoluble in water.

Section 4.6 **Brønsted acids** are proton donors; **Brønsted bases** are proton acceptors. Strong acids transfer protons to alcohols to form **alkyloxonium ions.** An alkyloxonium ion is the **conjugate acid** of an alcohol.



Alcohol (base) Alkyloxonium ion (conjugate acid)

Section 4.7 Proton transfer from a Brønsted acid to the oxygen of water is a single-step process and is very fast. It is a **bimolecular, concerted** process.

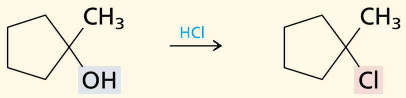
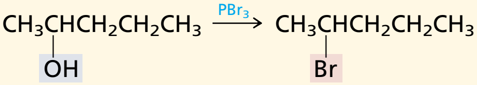
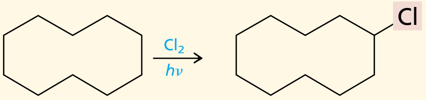
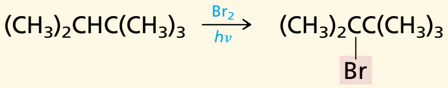
Section 4.8 See Table 4.4

Section 4.9 Secondary and tertiary alcohols react with hydrogen halides by a mechanism that involves formation of a carbocation intermediate in the rate-determining step.

$$(1)\quad \mathrm{ROH} + \mathrm{HX} \overset{\text{fast}}{\rightleftharpoons} \mathrm{R\overset{+}{O}H_2} + \mathrm{X^-}$$

Alcohol Hydrogen halide Alkyloxonium ion Halide anion

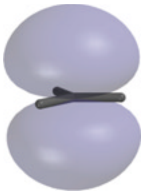
TABLE 4.4 Conversions of Alcohols and Alkanes to Alkyl Halides

Reaction (section) and comments	General equation and specific example(s)
Reactions of alcohols with hydrogen halides (Section 4.8) Alcohols react with hydrogen halides to yield alkyl halides. The reaction is useful as a synthesis of alkyl halides. The reactivity of hydrogen halides decreases in the order HI > HBr > HCl > HF. Alcohol reactivity decreases in the order tertiary > secondary > primary > methyl.	$\underset{\text{Alcohol}}{ROH} + \underset{\text{Hydrogen halide}}{HX} \longrightarrow \underset{\text{Alkyl halide}}{RX} + \underset{\text{Water}}{H_2O}$  1-Methylcyclopentanol 1-Chloro-1-methylcyclopentane (96%)
Reaction of alcohols with thionyl chloride (Section 4.14) Thionyl chloride is a synthetic reagent used to convert alcohols to alkyl chlorides.	$\underset{\text{Alcohol}}{ROH} + \underset{\text{Thionyl chloride}}{SOCl_2} \longrightarrow \underset{\text{Alkyl chloride}}{RCl} + \underset{\text{Sulfur dioxide}}{SO_2} + \underset{\text{Hydrogen chloride}}{HCl}$ $\underset{\text{1-Pentanol}}{CH_3CH_2CH_2CH_2CH_2OH} \xrightarrow[\text{pyridine}]{SOCl_2} \underset{\text{1-Chloropentane (80\%)}}{CH_3CH_2CH_2CH_2CH_2Cl}$
Reaction of alcohols with phosphorus tribromide (Section 4.14) As an alternative to converting alcohols to alkyl bromides with hydrogen bromide, the inorganic reagent phosphorus tribromide is sometimes used.	$\underset{\text{Alcohol}}{3ROH} + \underset{\text{Phosphorus tribromide}}{PBr_3} \longrightarrow \underset{\text{Alkyl bromide}}{3RBr} + \underset{\text{Phosphorous acid}}{H_3PO_3}$  $CH_3\underset{\underset{OH}{\mid}}{C}HCH_2CH_2CH_3 \xrightarrow{PBr_3} CH_3\underset{\underset{Br}{\mid}}{C}HCH_2CH_2CH_3$ 2-Pentanol 2-Bromopentane (67%)
Free-radical halogenation of alkanes (Sections 4.15 through 4.19) Alkanes react with halogens by substitution of a halogen for a hydrogen on the alkane. The reactivity of the halogens decreases in the order $F_2 > Cl_2 > Br_2 > I_2$. The ease of replacing a hydrogen decreases in the order tertiary > secondary > primary > methyl. Chlorination is not very selective and so is used only when all the hydrogens of the alkane are equivalent. Bromination is highly selective, replacing tertiary hydrogens much more readily than secondary or primary ones.	$\underset{\text{Alkane}}{RH} + \underset{\text{Halogen}}{X_2} \longrightarrow \underset{\text{Alkyl halide}}{RX} + \underset{\text{Hydrogen halide}}{HX}$  Cyclodecane Cyclodecyl chloride (64%)  $(CH_3)_2CHC(CH_3)_3 \xrightarrow[h\nu]{Br_2} (CH_3)_2\underset{\underset{Br}{\mid}}{C}C(CH_3)_3$ 2,2,3-Trimethylbutane 2-Bromo-2,3,3-trimethylbutane (80%)

$$\underset{\text{Alkyloxonium ion}}{R\overset{+}{O}H_2} \xrightarrow{\text{slow}} \underset{\text{Carbocation}}{R^+} + \underset{\text{Water}}{H_2O} \tag{2}$$

$$\underset{\text{Carbocation}}{R^+} + \underset{\text{Halide ion}}{X^-} \xrightarrow{\text{fast}} \underset{\text{Alkyl halide}}{RX} \tag{3}$$

Section 4.10 Carbocations contain a positively charged carbon with only three atoms or groups attached to it. This carbon is sp^2-hybridized and has a vacant $2p$ orbital.



Carbocations are stabilized by alkyl substituents attached directly to the positively charged carbon. Alkyl groups are *electron-releasing* substituents. Stability increases in the order:

(least stable) $CH_3^+ < R_2CH^+ < R_3C^+$ (most stable)

Carbocations are strongly **electrophilic** (Lewis acids) and react with **nucleophiles** (Lewis bases).

Section 4.11 The conversion of an alcohol to an alkyl halide on reaction with a hydrogen halide is a **nucleophilic substitution.** Nucleophilic substitutions (S_N) are classified as S_N1 or S_N2 according to whether the rate-determining step is unimolecular or bimolecular.

Section 4.12 The rates at which alcohols are converted to alkyl halides depends on the rate of carbocation formation: tertiary alcohols are most reactive; primary alcohols and methanol are least reactive.

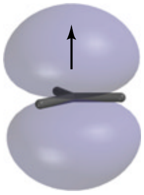
Section 4.13 Primary alcohols do not react with hydrogen halides by way of carbocation intermediates. The nucleophilic species (Br^-) attacks the alkyloxonium ion and "pushes off" a water molecule from carbon in a bimolecular step. This step is rate-determining, and the mechanism is S_N2.

Section 4.14 See Table 4.4

Section 4.15 See Table 4.4

Section 4.16 Methane reacts with Cl_2 to give chloromethane, dichloromethane, trichloromethane, and tetrachloromethane.

Section 4.17 Chlorination of methane, and halogenation of alkanes generally, proceed by way of **free-radical** intermediates. Alkyl radicals are neutral and have an unpaired electron on carbon.



Like carbocations, free radicals are stabilized by alkyl substituents. The order of free-radical stability parallels that of carbocation stability.

Section 4.18 The elementary steps (1) through (3) describe a free-radical chain mechanism for the reaction of an alkane with a halogen.

(1) (initiation step) $X_2 \longrightarrow 2X\cdot$

X_2	$2X\cdot$
Halogen molecule	Two halogen atoms

(2) (propagation step) $RH + X\cdot \longrightarrow R\cdot + HX$

RH	$X\cdot$	$R\cdot$	HX
Alkane	Halogen atom	Alkyl radical	Hydrogen halide

(3) (propagation step) $R\cdot + X_2 \longrightarrow RX + \cdot X$

$R\cdot$	X_2	RX	$\cdot X$
Alkyl radical	Halogen molecule	Alkyl halide	Halogen atom

Section 4.19 See Table 4.4

PROBLEMS

4.21 Write structural formulas for each of the following alcohols and alkyl halides:

(a) Cyclobutanol

(b) *sec*-Butyl alcohol

(c) 3-Heptanol

(d) *trans*-2-Chlorocyclopentanol

(e) 2,6-Dichloro-4-methyl-4-octanol

(f) *trans*-4-*tert*-Butylcyclohexanol

(g) 1-Cyclopropylethanol

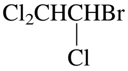
(h) 2-Cyclopropylethanol

4.22 Name each of the following compounds according to substitutive IUPAC nomenclature:

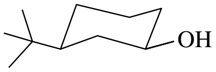
(a) $(CH_3)_2CHCH_2CH_2CH_2Br$

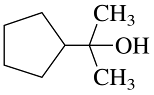
(b) $(CH_3)_2CHCH_2CH_2CH_2OH$

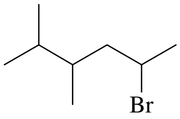
(c) Cl_3CCH_2Br

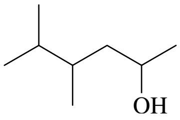
(d) 
$Cl_2CH\underset{\displaystyle Cl}{\underset{|}{C}}HBr$

(e) CF_3CH_2OH

(f) 

(g) 

(h) 

(i) 

4.23 Write structural formulas, or build molecular models for all the constitutionally isomeric alcohols of molecular formula $C_5H_{12}O$. Assign a substitutive and a functional class name to each one, and specify whether it is a primary, secondary, or tertiary alcohol.

4.24 A hydroxyl group is a somewhat "smaller" substituent on a six-membered ring than is a methyl group. That is, the preference of a hydroxyl group for the equatorial orientation is less pronounced than that of a methyl group. Given this information, write structural formulas or build molecular models for all the isomeric methylcyclohexanols, showing each one in its most stable conformation. Give the substitutive IUPAC name for each isomer.

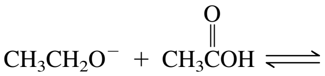
4.25 By assuming that the heat of combustion of the cis isomer was larger than the trans, structural assignments were made many years ago for the stereoisomeric 2-, 3-, and 4-methylcyclohexanols. This assumption is valid for two of the stereoisomeric pairs but is incorrect for the other. For which pair of stereoisomers is the assumption incorrect? Why?

4.26 (a) *Menthol,* used to flavor various foods and tobacco, is the most stable stereoisomer of 2-isopropyl-5-methylcyclohexanol. Draw or make a molecular model of its most stable conformation. Is the hydroxyl group cis or trans to the isopropyl group? To the methyl group?

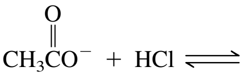
(b) *Neomenthol* is a stereoisomer of menthol. That is, it has the same constitution but differs in the arrangement of its atoms in space. Neomenthol is the second most stable stereoisomer of 2-isopropyl-5-methylcyclohexanol; it is less stable than menthol but more stable than any other stereoisomer. Write the structure, or make a molecular model of neomenthol in its most stable conformation.

4.27 Each of the following pairs of compounds undergoes a Brønsted acid–base reaction for which the equilibrium lies to the right. Give the products of each reaction, and identify the acid, the base, the conjugate acid, and the conjugate base.

(a) $HI + HO^- \rightleftharpoons$

(b)

$CH_3CH_2O^- + CH_3\overset{\overset{O}{\|}}{C}OH \rightleftharpoons$

(c) $HF + H_2N^- \rightleftharpoons$

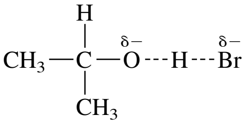
(d)

$CH_3\overset{\overset{O}{\|}}{C}O^- + HCl \rightleftharpoons$

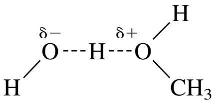
(e) $(CH_3)_3CO^- + H_2O \rightleftharpoons$

(f) $(CH_3)_2CHOH + H_2N^- \rightleftharpoons$

(g) $F^- + H_2SO_4 \rightleftharpoons$

4.28 Transition-state representations are shown for two acid–base reactions. For each one, write the equation for the reaction it represents in the direction for which the equilibrium lies to the right. Label the acid, the base, the conjugate acid, and the conjugate base, and use curved arrows to show the flow of electrons.

(a)


(b)


4.29 Calculate K_a for each of the following acids, given its pK_a. Rank the compounds in order of decreasing acidity.

(a) Aspirin: $pK_a = 3.48$

(b) Vitamin C (ascorbic acid): $pK_a = 4.17$

(c) Formic acid (present in sting of ants): $pK_a = 3.75$

(d) Oxalic acid (poisonous substance found in certain berries): $pK_a = 1.19$

4.30 The pK_a's of methanol (CH_3OH) and methanethiol (CH_3SH) are 16 and 11, respectively. Which is more basic, $KOCH_3$ or $KSCH_3$?

4.31 Write a chemical equation for the reaction of 1-butanol with each of the following:

(a) Sodium amide ($NaNH_2$)

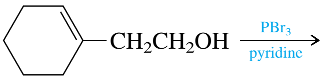
(b) Hydrogen bromide, heat

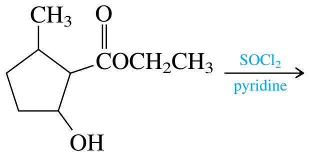
(c) Sodium bromide, sulfuric acid, heat

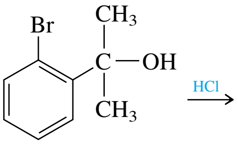
(d) Phosphorus tribromide

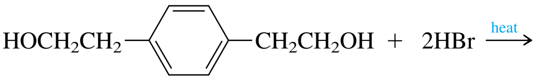
(e) Thionyl chloride

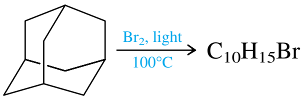
4.32 Each of the following reactions has been described in the chemical literature and involves an organic starting material somewhat more complex than those we have encountered so far. Nevertheless, on the basis of the topics covered in this chapter, you should be able to write the structure of the principal organic product of each reaction.

(a) 

(b) 

(c) 

(d) 

(e) 

4.33 Select the compound in each of the following pairs that will be converted to the corresponding alkyl bromide more rapidly on being treated with hydrogen bromide. Explain the reason for your choice.

(a) 1-Butanol or 2-butanol

(b) 2-Methyl-1-butanol or 2-butanol

(c) 2-Methyl-2-butanol or 2-butanol

(d) 2-Methylbutane or 2-butanol

(e) 1-Methylcyclopentanol or cyclohexanol

(f) 1-Methylcyclopentanol or *trans*-2-methylcyclopentanol

(g) 1-Cyclopentylethanol or 1-ethylcyclopentanol

4.34 Assuming that the rate-determining step in the reaction of cyclohexanol with hydrogen bromide to give cyclohexyl bromide is unimolecular, write an equation for this step. Use curved arrows to show the flow of electrons.

4.35 Assuming that the rate-determining step in the reaction of 1-hexanol with hydrogen bromide to give 1-bromohexane is an attack by a nucleophile on an alkyloxonium ion, write an equation for this step. Use curved arrows to show the flow of electrons.

4.36 Two stereoisomers of 1-bromo-4-methylcyclohexane are formed when *trans*-4-methylcyclohexanol reacts with hydrogen bromide. Write structural formulas or make molecular models of:

(a) *trans*-4-Methylcylohexanol

(b) The carbocation intermediate in this reaction

(c) The two stereoisomers of 1-bromo-4-methylcyclohexane

4.37 Basing your answers on the bond dissociation energies in Table 4.3, calculate which of the following reactions are endothermic and which are exothermic:

(a) $(CH_3)_2CHOH + HF \longrightarrow (CH_3)_2CHF + H_2O$

(b) $(CH_3)_2CHOH + HCl \longrightarrow (CH_3)_2CHCl + H_2O$

(c) $CH_3CH_2CH_3 + HCl \longrightarrow (CH_3)_2CHCl + H_2$

4.38 By carrying out the reaction at −78°C it is possible to fluorinate 2,2-dimethylpropane to yield $(CF_3)_4C$. Write a balanced chemical equation for this reaction.

4.39 In a search for fluorocarbons having anesthetic properties, 1,2-dichloro-1,1-difluoropropane was subjected to photochemical chlorination. Two isomeric products were obtained, one of which was identified as 1,2,3-trichloro-1,1-difluoropropane. What is the structure of the second compound?

4.40 Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

(a) A single monochloride

(b) Three isomeric monochlorides

(c) Four isomeric monochlorides

(d) Two isomeric dichlorides

4.41 In both the following exercises, assume that all the methylene groups in the alkane are equally reactive as sites of free-radical chlorination.

(a) Photochemical chlorination of heptane gave a mixture of monochlorides containing 15% 1-chloroheptane. What other monochlorides are present? Estimate the percentage of each of these additional $C_7H_{15}Cl$ isomers in the monochloride fraction.

(b) Photochemical chlorination of dodecane gave a monochloride fraction containing 19% 2-chlorododecane. Estimate the percentage of 1-chlorododecane present in that fraction.

4.42 Photochemical chlorination of 2,2,4-trimethylpentane gives four isomeric monochlorides.

(a) Write structural formulas for these four isomers.

(b) The two primary chlorides make up 65% of the monochloride fraction. Assuming that all the primary hydrogens in 2,2,4-trimethylpentane are equally reactive, estimate the percentage of each of the two primary chlorides in the product mixture.

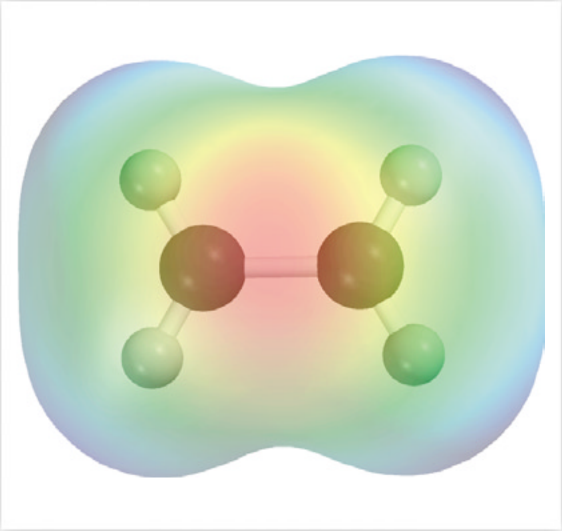
4.43 Photochemical chlorination of pentane gave a mixture of three isomeric monochlorides. The principal monochloride constituted 46% of the total, and the remaining 54% was approximately a 1 : 1 mixture of the other two isomers. Write structural formulas for the three monochloride isomers and specify which one was formed in greatest amount. (Recall that a secondary hydrogen is abstracted three times faster by a chlorine atom than a primary hydrogen.)

4.44 Cyclopropyl chloride has been prepared by the free-radical chlorination of cyclopropane. Write a stepwise mechanism for this reaction.

4.45 Deuterium oxide (D_2O) is water in which the protons (^1H) have been replaced by their heavier isotope deuterium (^2H). It is readily available and is used in a variety of mechanistic studies in organic chemistry and biochemistry. When D_2O is added to an alcohol (ROH), deuterium replaces the proton of the hydroxyl group.

$$ROH + D_2O \rightleftharpoons ROD + DOH$$

The reaction takes place extremely rapidly, and if D_2O is present in excess, all the alcohol is converted to ROD. This hydrogen–deuterium exchange can be catalyzed by either acids or bases. If D_3O^+ is the catalyst in acid solution and DO^- the catalyst in base, write reasonable reaction mechanisms for the conversion of ROH to ROD under conditions of (a) acid catalysis and (b) base catalysis.



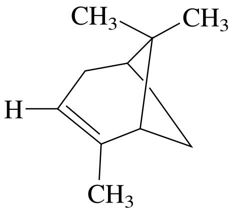
CHAPTER 5

STRUCTURE AND PREPARATION OF ALKENES: ELIMINATION REACTIONS

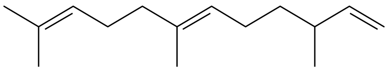
Alkenes are hydrocarbons that contain a carbon–carbon double bond. A carbon–carbon double bond is both an important structural unit and an important functional group in organic chemistry. The shape of an organic molecule is influenced by the presence of this bond, and the double bond is the site of most of the chemical reactions that alkenes undergo. Some representative alkenes include *isobutylene* (an industrial chemical), α-*pinene* (a fragrant liquid obtained from pine trees), and *farnesene* (a naturally occurring alkene with three double bonds).

$(CH_3)_2C{=}CH_2$

Isobutylene
(used in the production
of synthetic rubber)



α-Pinene
(a major constituent
of turpentine)



Farnesene
(present in the waxy coating
found on apple skins)

This chapter is the first of two dealing with alkenes; it describes their structure, bonding, and preparation. Chapter 6 discusses their chemical reactions.

5.1 ALKENE NOMENCLATURE

We give alkenes IUPAC names by replacing the *-ane* ending of the corresponding alkane with *-ene*. The two simplest alkenes are **ethene** and **propene.** Both are also well known by their common names *ethylene* and *propylene.*

$CH_2{=}CH_2$	$CH_3CH{=}CH_2$
IUPAC name: **ethene**	IUPAC name: **propene**
Common name: ethylene	Common name: propylene

Ethylene is an acceptable synonym for *ethene* in the IUPAC system. *Propylene, isobutylene,* and other common names ending in *-ylene* are not acceptable IUPAC names.

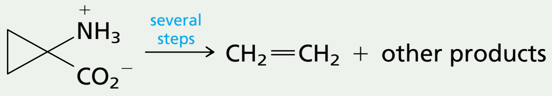
ETHYLENE

Ethylene was known to chemists in the eighteenth century and isolated in pure form in 1795. An early name for ethylene was *gaz oléfiant* (French for "oil-forming gas"), a term suggested to describe the fact that an oily liquid product is formed when two gases—ethylene and chlorine—react with each other.

$$\underset{\substack{\text{Ethylene}\\(\text{bp: }-104^\circ\text{C})}}{CH_2{=}CH_2} + \underset{\substack{\text{Chlorine}\\(\text{bp: }-34^\circ\text{C})}}{Cl_2} \longrightarrow \underset{\substack{\text{1,2-Dichloroethane}\\(\text{bp: }83^\circ\text{C})}}{ClCH_2CH_2Cl}$$

The term *gaz oléfiant* was the forerunner of the general term *olefin,* formerly used as the name of the class of compounds we now call *alkenes.*

Ethylene occurs naturally in small amounts as a plant hormone. Hormones are substances that act as messengers and play regulatory roles in biological processes. Ethylene is involved in the ripening of many fruits, in which it is formed in a complex series of steps from a compound containing a cyclopropane ring:



1-Amino-cyclopropane-carboxylic acid

Ethylene

Even minute amounts of ethylene can stimulate ripening, and the rate of ripening increases with the concentration of ethylene. This property is used to advantage, for example, in the marketing of bananas. Bananas are picked green in the tropics, kept green by being stored with adequate ventilation to limit the amount of ethylene present, and then induced to ripen at their destination by passing ethylene over the fruit.*

Ethylene is the cornerstone of the world's mammoth petrochemical industry and is produced in vast quantities. In a typical year the amount of ethylene produced in the United States (5×10^{10}lb) exceeds the combined weight of all of its people. In one process, ethane from natural gas is heated to bring about its dissociation into ethylene and hydrogen:

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow{750^\circ C} \underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{Hydrogen}}{H_2}$$

This reaction is known as **dehydrogenation** and is simultaneously both a source of ethylene and one of the methods by which hydrogen is prepared on an industrial scale. Most of the hydrogen so generated is subsequently used to reduce nitrogen to ammonia for the preparation of fertilizer.

Similarly, dehydrogenation of propane gives propene:

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow{750^\circ C} \underset{\text{Propene}}{CH_3CH{=}CH_2} + \underset{\text{Hydrogen}}{H_2}$$

Propene is the second most important petrochemical and is produced on a scale about half that of ethylene.

Almost any hydrocarbon can serve as a starting material for production of ethylene and propene. Cracking of petroleum (Section 2.13) gives ethylene and propene by processes involving cleavage of carbon–carbon bonds of higher molecular weight hydrocarbons.

The major uses of ethylene and propene are as starting materials for the preparation of polyethylene and polypropylene plastics, fibers, and films. These and other applications will be described in Chapter 6.

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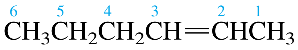
*For a review, see "Ethylene—An Unusual Plant Hormone" in the April 1992 issue of the *Journal of Chemical Education* (pp. 315–318).

The longest continuous chain that includes the double bond forms the base name of the alkene, and the chain is numbered in the direction that gives the doubly bonded carbons their lower numbers. The locant (or numerical position) of only one of the doubly bonded carbons is specified in the name; it is understood that the other doubly bonded carbon must follow in sequence.

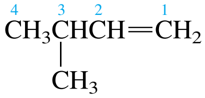

$\overset{1}{C}H_2{=}\overset{2}{C}H\overset{3}{C}H_2\overset{4}{C}H_3$

1-Butene
(not 1,2-butene)

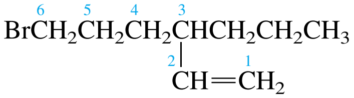

$\overset{6}{C}H_3\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H{=}\overset{2}{C}H\overset{1}{C}H_3$

2-Hexene
(not 4-hexene)

Carbon–carbon double bonds take precedence over alkyl groups and halogens in determining the main carbon chain and the direction in which it is numbered.

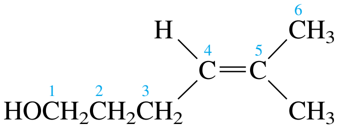

$CH_3CH(CH_3)CH{=}CH_2$

3-Methyl-1-butene
(not 2-methyl-3-butene)


$BrCH_2CH_2CH_2CH(CH{=}CH_2)CH_2CH_2CH_3$

6-Bromo-3-propyl-1-hexene
(longest chain that contains double bond is six carbons)

Hydroxyl groups, however, outrank the double bond. Compounds that contain both a double bond and a hydroxyl group use the combined suffix *-en* + *-ol* to signify that both functional groups are present.



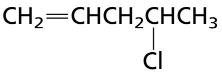
5-Methyl-4-hexen-1-ol
(not 2-methyl-2-hexen-6-ol)

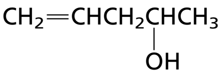
PROBLEM 5.1 Name each of the following using IUPAC nomenclature:

(a) $(CH_3)_2C{=}C(CH_3)_2$

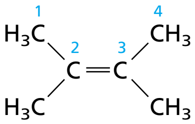
(b) $(CH_3)_3CCH{=}CH_2$

(c) $(CH_3)_2C{=}CHCH_2CH_2CH_3$

(d) 
$CH_2{=}CHCH_2CH(Cl)CH_3$

(e) 
$CH_2{=}CHCH_2CH(OH)CH_3$

SAMPLE SOLUTION (a) The longest continuous chain in this alkene contains four carbon atoms. The double bond is between C-2 and C-3, and so it is named as a derivative of 2-butene.



2,3-Dimethyl-2-butene

Identifying the alkene as a derivative of 2-butene leaves two methyl groups to be accounted for as substituents attached to the main chain. This alkene is 2,3-dimethyl-2-butene. (It is sometimes called *tetramethylethylene,* but that is a common name, not an IUPAC name.)

We noted in Section 2.10 that the common names of certain frequently encountered *alkyl* groups, such as isopropyl and *tert*-butyl, are acceptable in the IUPAC system. Three *alkenyl* groups—**vinyl, allyl,** and **isopropenyl**—are treated the same way.

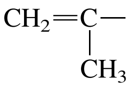
Vinyl chloride is an industrial chemical produced in large amounts (10^{10} lb/year in the United States) and is used in the preparation of poly(vinyl chloride). Poly(vinyl chloride), often called simply *vinyl,* has many applications, including siding for houses, wall coverings, and PVC piping.

$CH_2{=}CH{-}$ as in $CH_2{=}CHCl$

Vinyl — Vinyl chloride

$CH_2{=}CHCH_2{-}$ as in $CH_2{=}CHCH_2OH$

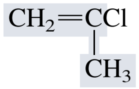
Allyl — Allyl alcohol



$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}$

Isopropenyl

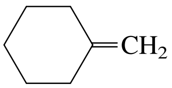
as in



$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}Cl$

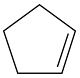
Isopropenyl chloride

When a CH_2 group is doubly bonded to a ring, the prefix *methylene* is added to the name of the ring.

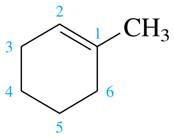


Methylenecyclohexane

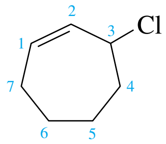
Cycloalkenes and their derivatives are named by adapting cycloalkane terminology to the principles of alkene nomenclature.



Cyclopentene



1-Methylcyclohexene



3-Chlorocycloheptene
(not 1-chloro-2-cycloheptene)

No locants are needed in the absence of substituents; it is understood that the double bond connects C-1 and C-2. Substituted cycloalkenes are numbered beginning with the double bond, proceeding through it, and continuing in sequence around the ring. The direction of numbering is chosen so as to give the lower of two possible locants to the substituent.

PROBLEM 5.2 Write structural formulas or build molecular models and give the IUPAC names of all the monochloro-substituted derivatives of cyclopentene.

5.2 STRUCTURE AND BONDING IN ALKENES

The structure of ethylene and the orbital hybridization model for the double bond were presented in Section 1.17. To review, Figure 5.1 depicts the planar structure of ethylene, its bond distances, and its bond angles. Each of the carbon atoms is sp^2-hybridized, and the double bond possesses a σ component and a π component. The σ component results when an sp^2 orbital of one carbon, oriented so that its axis lies along the internuclear axis, overlaps with a similarly disposed sp^2 orbital of the other carbon. Each sp^2 orbital contains one electron, and the resulting σ bond contains two of the four electrons of the double bond. The π bond contributes the other two electrons and is formed by a "side-by-side" overlap of singly occupied *p* orbitals of the two carbons.

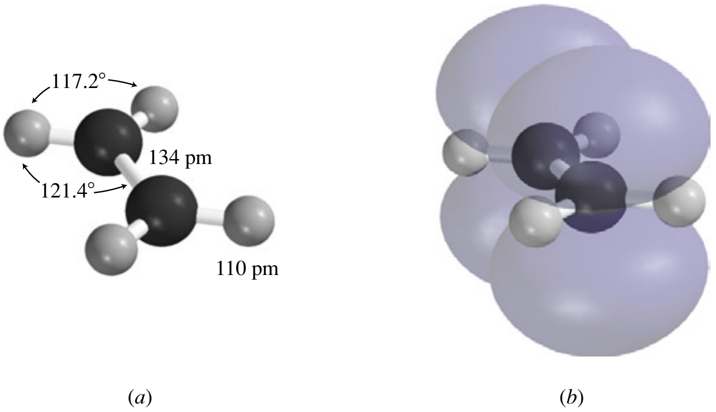
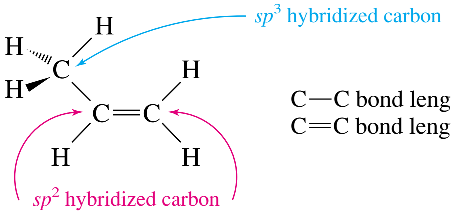


FIGURE 5.1 (*a*) The framework of σ bonds in ethylene showing bond distances in picometers and bond angles in degrees. All six atoms are coplanar. The carbon–carbon bond is a double bond made up of the σ component shown and the π component illustrated in *b*. (*b*) The *p* orbitals of two sp^2 hybridized carbons overlap to produce a π bond. An electron pair in the π bond is shared by the two carbons.

The simplest arithmetic approach subtracts the C—C σ bond energy of ethane (368 kJ/mol; 88 kcal/mol) from the C═C bond energy of ethylene (605 kJ/mol; 144.5 kcal/mol). This gives a value of 237 kJ/mol (56.5 kcal/mol) for the π bond energy.

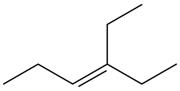
The double bond in ethylene is stronger than the C—C single bond in ethane, but it is not twice as strong. The C═C bond energy is 605 kJ/mol (144.5 kcal/mol) in ethylene versus 368 kJ/mol (88 kcal/mol) for the C—C bond in ethane. Chemists do not agree on exactly how to apportion the total C═C bond energy between its σ and π components, but all agree that the π bond is weaker than the σ bond.

There are two different types of carbon–carbon bonds in propene, $CH_3CH{=}CH_2$. The double bond is of the $\sigma + \pi$ type, and the bond to the methyl group is a σ bond formed by sp^3–sp^2 overlap.



C—C bond length = 150 pm
C═C bond length = 134 pm

PROBLEM 5.3 We can use bond-line formulas to represent alkenes in much the same way that we use them to represent alkanes. Consider the following alkene:



(a) What is the molecular formula of this alkene?
(b) What is its IUPAC name?
(c) How many carbon atoms are sp^2-hybridized in this alkene? How many are sp^3-hybridized?
(d) How many σ bonds are of the sp^2–sp^3 type? How many are of the sp^3–sp^3 type?

SAMPLE SOLUTION (a) Recall when writing bond-line formulas for hydrocarbons that a carbon occurs at each end and at each bend in a carbon chain. The appropriate number of hydrogens are attached so that each carbon has four bonds. Thus the compound shown is

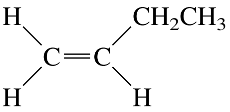
$$CH_3CH_2CH{=}C(CH_2CH_3)_2$$

The general molecular formula for an alkene is C_nH_{2n}. Ethylene is C_2H_4; propene is C_3H_6. Counting the carbons and hydrogens of the compound shown (C_8H_{16}) reveals that it, too, corresponds to C_nH_{2n}.

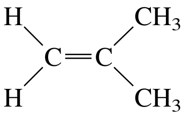
5.3 ISOMERISM IN ALKENES

Although ethylene is the only two-carbon alkene, and propene the only three-carbon alkene, there are *four* isomeric alkenes of molecular formula C_4H_8:

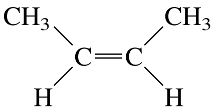
Make molecular models of *cis*-and *trans*-2-butene to verify that they are different.



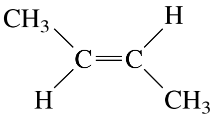
1-Butene



2-Methylpropene



cis-2-Butene



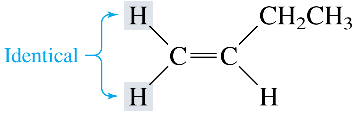
trans-2-Butene

1-Butene has an unbranched carbon chain with a double bond between C-1 and C-2. It is a constitutional isomer of the other three. Similarly, 2-methylpropene, with a branched carbon chain, is a constitutional isomer of the other three.

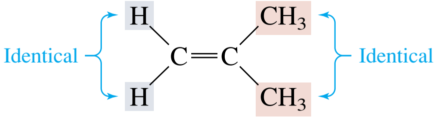
The pair of isomers designated *cis*- and *trans*-2-butene have the same constitution; both have an unbranched carbon chain with a double bond connecting C-2 and C-3. They differ from each other, however, in that the cis isomer has both of its methyl groups on the same side of the double bond, but the methyl groups in the trans isomer are on opposite sides of the double bond. Recall from Section 3.12 that isomers that have the same constitution but differ in the arrangement of their atoms in space are classified as *stereoisomers*. *cis*-2-Butene and *trans*-2-butene are stereoisomers, and the terms “cis” and “trans” specify the *configuration* of the double bond.

Stereoisomeric alkenes are sometimes referred to as *geometric isomers*.

Cis–trans stereoisomerism in alkenes is not possible when one of the doubly bonded carbons bears two identical substituents. Thus, neither 1-butene nor 2-methylpropene can have stereoisomers.



1-Butene
(no stereoisomers possible)



2-Methylpropene
(no stereoisomers possible)

PROBLEM 5.4 How many alkenes have the molecular formula C_5H_{10}? Write their structures and give their IUPAC names. Specify the configuration of stereoisomers as cis or trans as appropriate.

The activation energy for rotation about a typical carbon–carbon double bond is very high—on the order of 250 kJ/mol (about 60 kcal/mol). This quantity may be taken as a measure of the π bond contribution to the total C=C bond strength of 605 kJ/mol (144.5 kcal/mol) in ethylene and compares closely with the value estimated by manipulation of thermochemical data on page 171.

In principle, *cis*-2-butene and *trans*-2-butene may be interconverted by rotation about the C-2═C-3 *double* bond. However, unlike rotation about the C-2—C-3 *single* bond in butane, which is quite fast, interconversion of the stereoisomeric 2-butenes does not occur under normal circumstances. It is sometimes said that rotation about a carbon–carbon double bond is *restricted,* but this is an understatement. Conventional laboratory sources of heat do not provide enough thermal energy for rotation about the double bond in alkenes to take place. As shown in Figure 5.2, rotation about a double bond requires the *p* orbitals of C-2 and C-3 to be twisted from their stable parallel alignment—in effect, the π component of the double bond must be broken at the transition state.

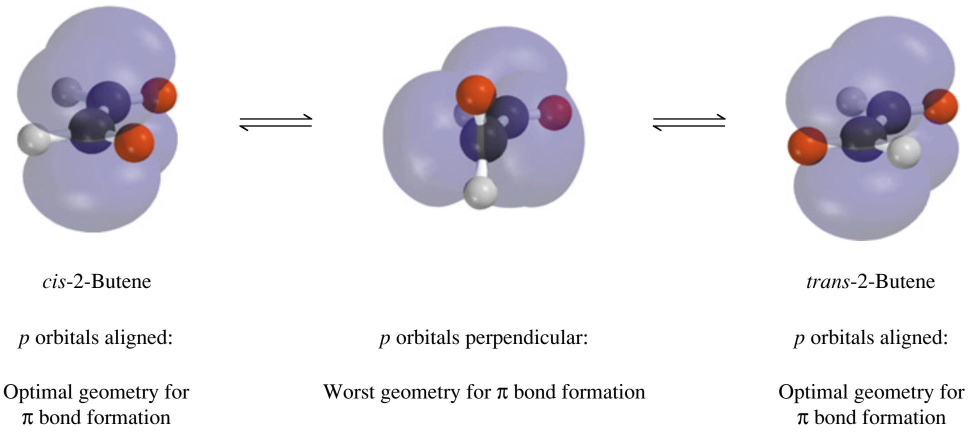
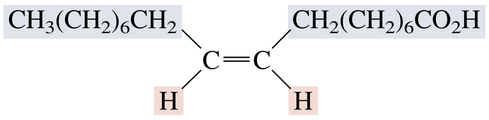


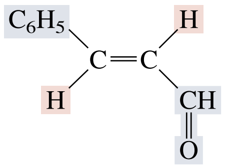
FIGURE 5.2 Interconversion of *cis*- and *trans*-2-butene proceeds by cleavage of the π component of the double bond. The red balls represent the two methyl groups.

5.4 NAMING STEREOISOMERIC ALKENES BY THE *E–Z* NOTATIONAL SYSTEM

When the groups on either end of a double bond are the same or are structurally similar to each other, it is a simple matter to describe the configuration of the double bond as cis or trans. Oleic acid, for example, a material that can be obtained from olive oil, has a cis double bond. Cinnamaldehyde, responsible for the characteristic odor of cinnamon, has a trans double bond.



Oleic acid



Cinnamaldehyde

PROBLEM 5.5 Female houseflies attract males by sending a chemical signal known as a *pheromone*. The substance emitted by the female housefly that attracts the male has been identified as *cis*-9-tricosene, $C_{23}H_{46}$. Write a structural formula, including stereochemistry, for this compound.

The terms "cis" and "trans" are ambiguous, however, when it is not obvious which substituent on one carbon is "similar" or "analogous" to a reference substituent on the other. Fortunately, a completely unambiguous system for specifying double bond stereochemistry has been developed based on an *atomic number* criterion for ranking substituents on the doubly bonded carbons. When atoms of higher atomic number are on the *same* side of the double bond, we say that the double bond has the ***Z*** configuration, where *Z* stands for the German word ***zusammen,*** meaning "together." When atoms of higher atomic number are on *opposite* sides of the double bond, we say that the configuration is ***E.*** The symbol *E* stands for the German word ***entgegen,*** meaning "opposite."

Z configuration
Higher ranked substituents (Cl and Br)
are on same side of double bond

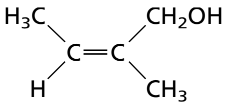
E configuration
Higher ranked substituents (Cl and Br)
are on opposite sides of double bond

The substituent groups on the double bonds of most alkenes are, of course, more complicated than in this example. The rules for ranking substituents, especially alkyl groups, are described in Table 5.1.

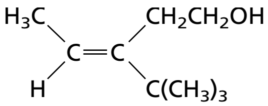
The priority rules were developed by R. S. Cahn and Sir Christopher Ingold (England) and Vladimir Prelog (Switzerland) in the context of a different aspect of organic stereochemistry; they will appear again in Chapter 7.

PROBLEM 5.6 Determine the configuration of each of the following alkenes as *Z* or *E* as appropriate:

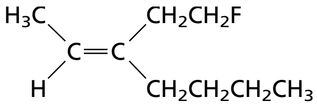
(a)



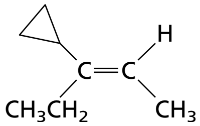
(c)



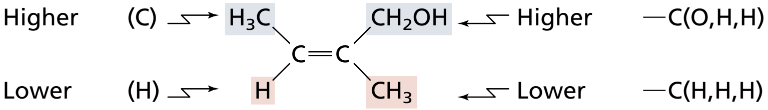
(b)



(d)



SAMPLE SOLUTION (a) One of the doubly bonded carbons bears a methyl group and a hydrogen. According to the rules of Table 5.1, methyl outranks hydrogen. The other carbon atom of the double bond bears a methyl and a —CH_2OH group. The —CH_2OH group is of higher priority than methyl.



Higher ranked substituents are on the same side of the double bond; the configuration is *Z.*

A table on the inside back cover (right page) lists some of the more frequently encountered atoms and groups in order of increasing precedence. You should not attempt to memorize this table, but should be able to derive the relative placement of one group versus another.

5.5 PHYSICAL PROPERTIES OF ALKENES

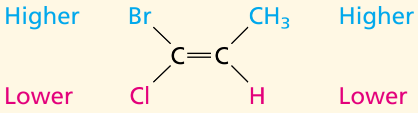
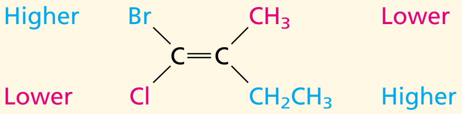
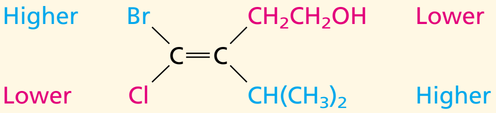
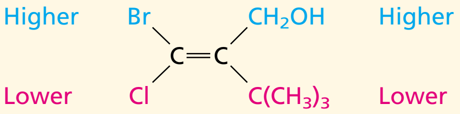
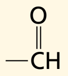
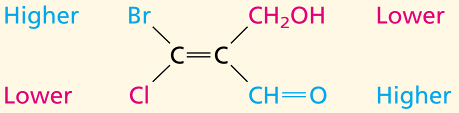
The physical properties of selected alkenes are collected in Appendix 1.

Alkenes resemble alkanes in most of their physical properties. The lower molecular weight alkenes through C_4H_8 are gases at room temperature and atmospheric pressure.

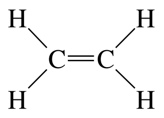
The dipole moments of most alkenes are quite small. Among the C_4H_8 isomers, 1-butene, *cis*-2-butene, and 2-methylpropene have dipole moments in the 0.3–0.5 D range; *trans*-2-butene has no dipole moment. Nevertheless, we can learn some things about alkenes by looking at the effect of substituents on dipole moments.

Experimental measurements of dipole moments give size, but not direction. We normally deduce the overall direction by examining the directions of individual bond

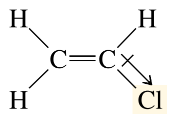
TABLE 5.1 Cahn–Ingold–Prelog Priority Rules

Rule	Example
1. Higher atomic number takes precedence over lower. Bromine (atomic number 35) outranks chlorine (atomic number 17). Methyl (C, atomic number 6) outranks hydrogen (atomic number 1).	The compound  has the *Z* configuration. Higher ranked atoms (Br and C of CH_3) are on the same side of the double bond.
2. When two atoms directly attached to the double bond are identical, compare the atoms attached with these two on the basis of their atomic numbers. Precedence is determined at the first point of difference: Ethyl [—C(**C**,H,H)] outranks methyl [—C(**H**,H,H)] Similarly, *tert*-butyl outranks isopropyl, and isopropyl outranks ethyl: $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3$ —C(C,C,C) > —C(C,C,H) > —C(C,H,H)	The compound  has the *E* configuration.
3. Work outward from the point of attachment, comparing all the atoms attached to a particular atom before proceeding further along the chain: $-CH(CH_3)_2$ [—C(C,**C**,H)] outranks $-CH_2CH_2OH$ [—C(C,**H**,H)]	The compound  has the *E* configuration.
4. When working outward from the point of attachment, always evaluate substituent atoms one by one, never as a group. Since oxygen has a higher atomic number than carbon, $-CH_2OH$ [—C(**O**,H,H)] outranks $-C(CH_3)_3$ [—C(**C**,C,C)]	The compound  has the *Z* configuration.
5. An atom that is multiply bonded to another atom is considered to be replicated as a substituent on that atom: $\overset{O}{\overset{\Vert}{-CH}}$ is treated as if it were —C(O,O,H) The group —CH═O [—C(O,**O**,H)] outranks $-CH_2OH$ [—C(O,**H**,H)]	The compound  has the *E* configuration.

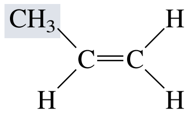
dipoles. With alkenes the basic question concerns the alkyl groups attached to C═C. *Does an alkyl group donate electrons to or withdraw electrons from a double bond?* This question can be approached by comparing the effect of an alkyl group, methyl for example, with other substituents.



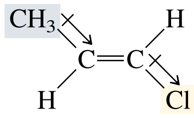
Ethylene
$\mu = 0$ D



Chloroethene
$\mu = 1.4$ D



Propene
$\mu = 0.3$ D



trans-1-Chloropropene
$\mu = 1.7$ D

Ethylene, of course, has no dipole moment. Replacing one of its hydrogens by chlorine gives chloroethene, which has a dipole moment of 1.4 D. The effect is much smaller when one of the hydrogens is replaced by methyl; $CH_3CH{=}CH_2$ has a dipole moment of only 0.3 D. Now place CH_3 and Cl trans to each other on the double bond. If methyl releases electrons better than H, then the dipole moment of *trans*-$CH_3CH{=}CHCl$ should be larger than that of $CH_2{=}CHCl$, because the effects of CH_3 and Cl reinforce each other. If methyl is electron attracting, the opposite should occur, and the dipole moment of *trans*-$CH_3CH{=}CHCl$ will be smaller than 1.4 D. In fact, the dipole moment of *trans*-$CH_3CH{=}CHCl$ is larger than that of $CH_2{=}CHCl$, indicating that a methyl group is an electron-donating substituent on the double bond.

A methyl group releases electrons to a double bond in much the same way that it releases electrons to the positively charged carbon of a carbocation—by an inductive effect and by hyperconjugation (Figure 5.3). Other alkyl groups behave similarly and, as we go along, we'll see several ways in which the electron-releasing effects of alkyl substituents influence the properties of alkenes. The first is described in the following section.

5.6 RELATIVE STABILITIES OF ALKENES

Earlier (Sections 2.15, 3.12) we saw how to use heats of combustion to compare the stabilities of isomeric alkanes. We can do the same thing with isomeric alkenes. Consider the heats of combustion of the four isomeric alkenes of molecular formula C_4H_8. All undergo combustion according to the equation

$$C_4H_8 + 6O_2 \longrightarrow 4CO_2 + 4H_2O$$

When the heats of combustion of the isomers are plotted on a common scale as in Figure 5.4, we see that the isomer of highest energy (the least stable one) is 1-butene, $CH_2{=}CHCH_2CH_3$. The isomer of lowest energy (most stable) is 2-methylpropene $(CH_3)_2C{=}CH_2$.

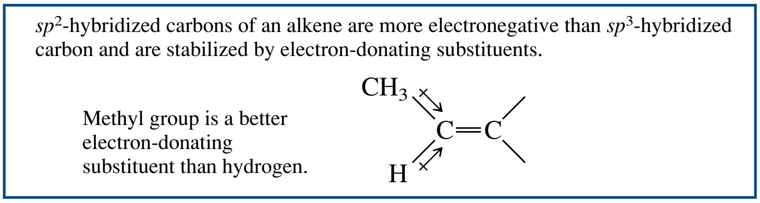


FIGURE 5.3 Alkyl groups donate electrons to sp^2-hybridized carbons of an alkene.

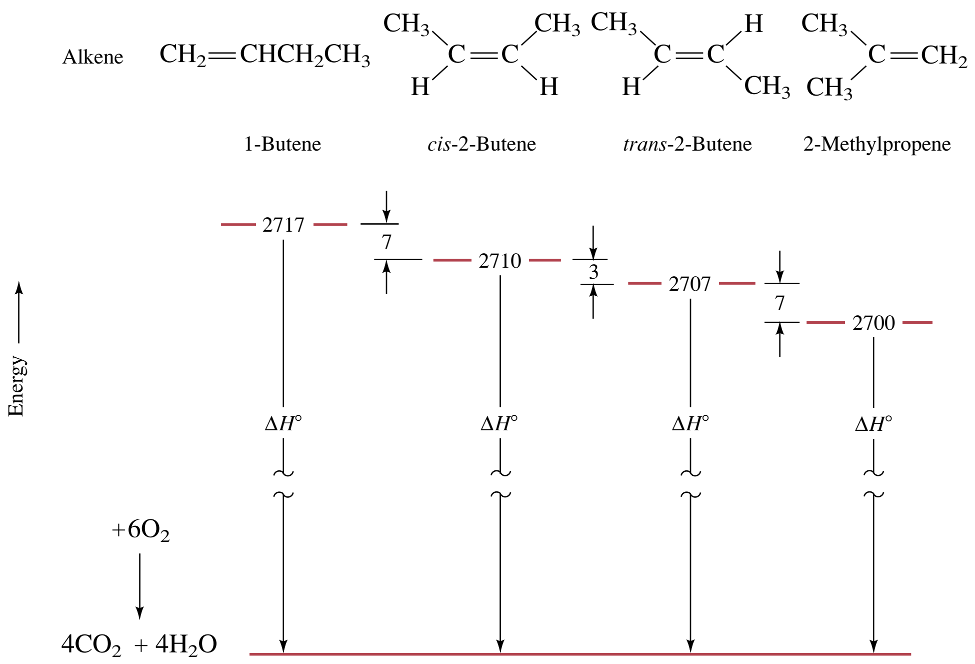


FIGURE 5.4 Heats of combustion of C_4H_8 alkene isomers plotted on a common scale. All energies are in kilojoules per mole. (An energy difference of 3 kJ/mol is equivalent to 0.7 kcal/mol; 7 kJ/mol is equivalent to 1.7 kcal/mol.)

Analogous data for a host of alkenes tell us that the most important factors governing alkene stability are:

1. *Degree of substitution* (alkyl substituents stabilize a double bond)
2. *Van der Waals strain* (destabilizing when alkyl groups are cis to each other)

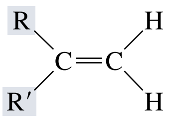
Degree of substitution. We classify double bonds as **monosubstituted, disubstituted, trisubstituted,** or **tetrasubstituted** according to the number of carbon atoms that are *directly* attached to the C=C structural unit.

Monosubstituted alkenes:

$RCH{=}CH_2$ as in $CH_3CH_2CH{=}CH_2$ (1-butene)

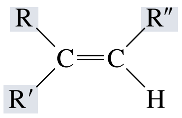
Disubstituted alkenes:
(R and R′ may be the same or different)

$RCH{=}CHR'$ as in $CH_3CH{=}CHCH_3$ (*cis-* or *trans*-2-butene)



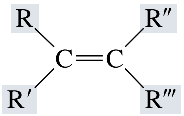
as in $(CH_3)_2C{=}CH_2$ (2-methylpropene)

Trisubstituted alkenes:
(R, R′, and R″ may be the same or different)

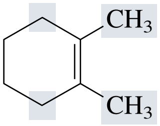


as in $(CH_3)_2C{=}CHCH_2CH_3$ (2-methyl-2-pentene)

Tetrasubstituted alkenes:
(R, R′, R″, and R‴ may be the same or different)



as in

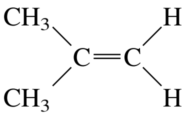


(1,2-dimethylcyclohexene)

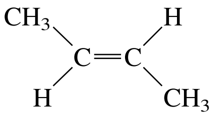
In the example shown, each of the highlighted ring carbons counts as a separate substituent on the double bond.

PROBLEM 5.7 Write structural formulas or build molecular models and give the IUPAC names for all the alkenes of molecular formula C_6H_{12} that contain a trisubstituted double bond. (Don't forget to include stereoisomers.)

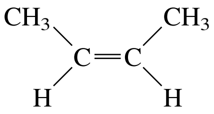
From the heats of combustion of the C_4H_8 alkenes in Figure 5.5 we see that each of the disubstituted alkenes



2-Methylpropene

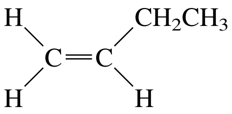


trans-2-Butene



cis-2-Butene

is more stable than the monosubstituted alkene



1-Butene

In general, alkenes with more highly substituted double bonds are more stable than isomers with less substituted double bonds.

PROBLEM 5.8 Give the structure or make a molecular model of the most stable C_6H_{12} alkene.

Like the sp^2-hybridized carbons of carbocations and free radicals, the sp^2-hybridized carbons of double bonds are electron attracting, and alkenes are stabilized by substituents that release electrons to these carbons. As we saw in the preceding section, alkyl groups are better electron-releasing substituents than hydrogen and are, therefore, better able to stabilize an alkene.

An effect that results when two or more atoms or groups interact so as to alter the electron distribution in a system is called an **electronic effect.** The greater stability of more highly substituted alkenes is an example of an electronic effect.

van der Waals strain. *Alkenes are more stable when large substituents are trans to each other than when they are cis.* As was seen in Figure 5.4, *trans*-2-butene has a lower heat of combustion and is more stable than *cis*-2-butene. The energy difference between the two is 3 kJ/mol (0.7 kcal/mol). The source of this energy difference is illustrated in

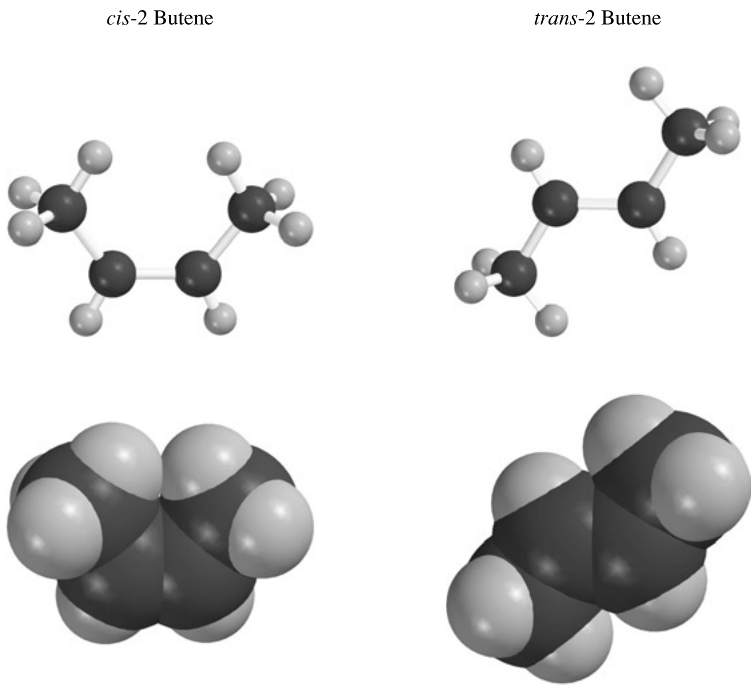


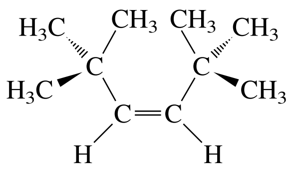
FIGURE 5.5 Ball-and-spoke and space-filling models of *cis*- and *trans*-2-butene. The space-filling model shows the serious van der Waals strain between two of the hydrogens in *cis*-2-butene. The molecule adjusts by expanding those bond angles that increase the separation between the crowded atoms. The combination of angle strain and van der Waals strain makes *cis*-2 butene less stable than *trans*-2-butene.

Figure 5.5, where it is seen that methyl groups approach each other very closely in *cis*-2-butene, but the trans isomer is free of strain. An effect that results when two or more atoms are close enough in space that a repulsion occurs between them is one type of **steric effect.** The greater stability of trans alkenes compared with their cis counterparts is an example of a steric effect.

A similar steric effect was seen in Section 3.12, where van der Waals strain between methyl groups on the same side of the ring made *cis*-1,2-dimethylcyclopropane less stable than its trans stereoisomer.

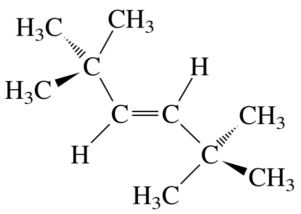
PROBLEM 5.9 Arrange the following alkenes in order of decreasing stability: 1-pentene; (*E*)-2-pentene; (*Z*)-2-pentene; 2-methyl-2-butene.

The difference in stability between stereoisomeric alkenes is even more pronounced with larger alkyl groups on the double bond. A particularly striking example compares *cis*- and *trans*-2,2,5,5-tetramethyl-3-hexene, in which the heat of combustion of the cis stereoisomer is 44 kJ/mol (10.5 kcal/mol) higher than that of the trans. The cis isomer is destabilized by the large van der Waals strain between the bulky *tert*-butyl groups on the same side of the double bond.



cis-2,2,5,5-Tetramethyl-3-hexene
Less stable

Energy difference =
44 kJ/mol
(10.5 kcal/mol)



trans-2,2,5,5-Tetramethyl-3-hexene
More stable

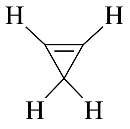
The common names of these alkenes are *cis*- and *trans*-di-*tert*-butylethylene. In cases such as this the common names are somewhat more convenient than the IUPAC names because they are more readily associated with molecular structure.

PROBLEM 5.10 Despite numerous attempts, the alkene 3,4-di-*tert*-butyl-2,2,5,5-tetramethyl-3-hexene has never been synthesized. Can you explain why? Try making a space-filling model of this compound.

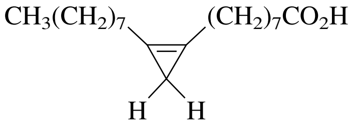
5.7 CYCLOALKENES

Double bonds are accommodated by rings of all sizes. The simplest cycloalkene, cyclopropene, was first synthesized in 1922. A cyclopropene ring is present in sterculic acid, a substance derived from one of the components of the oil present in the seeds of a tree (*Sterculia foelida*) that grows in the Philippines and Indonesia.

Sterculic acid and related substances are the subject of an article in the July 1982 issue of *Journal of Chemical Education* (pp. 539–543).



Cyclopropene

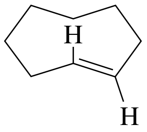


Sterculic acid

As we saw in Section 3.9, cyclopropane is destabilized by angle strain because its 60° bond angles are much smaller than the normal 109.5° angles associated with sp^3-hybridized carbon. Cyclopropene is even more strained because the deviation of the bond angles at its doubly bonded carbons from the normal sp^2 hybridization value of 120° is greater still. Cyclobutene has, of course, less angle strain than cyclopropene, and the angle strain of cyclopentene, cyclohexene, and higher cycloalkenes is negligible.

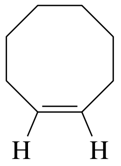
So far we have represented cycloalkenes by structural formulas in which the double bonds are of the cis configuration. If the ring is large enough, however, a trans stereoisomer is also possible. The smallest trans cycloalkene that is stable enough to be isolated and stored in a normal way is *trans*-cyclooctene.

Make molecular models of (*E*) and (*Z*)-cyclooctene and compare their H—C═C—H dihedral angles.



(*E*)-Cyclooctene
(*trans*-cyclooctene)
Less stable

Energy difference =
39 kJ/mol (9.2 kcal/mol)

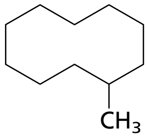


(*Z*)-Cyclooctene
(*cis*-cyclooctene)
More stable

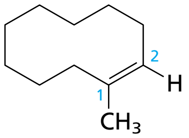
trans-Cycloheptene has been prepared and studied at low temperature (−90°C) but is too reactive to be isolated and stored at room temperature. Evidence has also been presented for the fleeting existence of the even more strained *trans*-cyclohexene as a reactive intermediate in certain reactions.

PROBLEM 5.11 Place a double bond in the carbon skeleton shown so as to represent

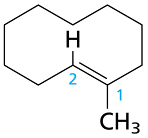
(a) (*Z*)-1-Methylcyclodecene
(b) (*E*)-1-Methylcyclodecene
(c) (*Z*)-3-Methylcyclodecene
(d) (*E*)-3-Methylcyclodecene
(e) (*Z*)-5-Methylcyclodecene
(f) (*E*)-5-Methylcyclodecene



SAMPLE SOLUTION (a) and (b) Since the methyl group must be at C-1, there are only two possible places to put the double bond:



(*Z*)-1-Methylcyclodecene



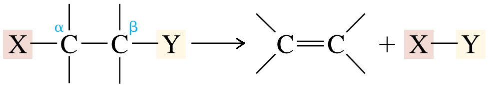
(*E*)-1-Methylcyclodecene

In the *Z* stereoisomer the two lower priority substituents—the methyl group and the hydrogen—are on the same side of the double bond. In the *E* stereoisomer these substituents are on opposite sides of the double bond. The ring carbons are the higher ranking substituents at each end of the double bond.

Because larger rings have more carbons with which to span the ends of a double bond, the strain associated with a trans cycloalkene decreases with increasing ring size. The strain eventually disappears when a 12-membered ring is reached and *cis* and *trans*-cyclododecene are of approximately equal stability. When the rings are larger than 12 membered, trans cycloalkenes are more stable than cis. In these cases, the ring is large enough and flexible enough that it is energetically similar to a noncyclic alkene. As in noncyclic cis alkenes, van der Waals strain between carbons on the same side of the double bond destabilizes a cis cycloalkene.

5.8 PREPARATION OF ALKENES: ELIMINATION REACTIONS

The rest of this chapter describes how alkenes are prepared by reactions of the type:



$$X-\overset{\alpha}{C}-\overset{\beta}{C}-Y \longrightarrow C=C + X-Y$$

Alkene formation requires that X and Y be substituents on adjacent carbon atoms. By making X the reference atom and identifying the carbon attached to it as the α carbon, we see that atom Y is a substituent on the β carbon. Carbons succeedingly more remote from the reference atom are designated γ, δ, and so on. Only β elimination reactions will be discussed in this chapter. [Beta (β) elimination reactions are also known as *1,2 eliminations.*]

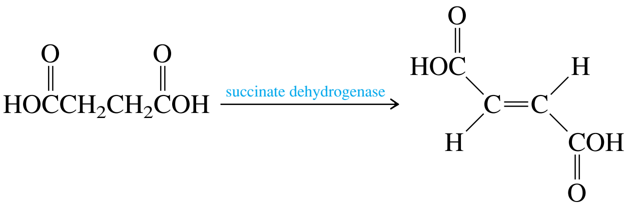
You are already familiar with one type of β elimination, having seen in Section 5.1 that ethylene and propene are prepared on an industrial scale by the high-temperature *dehydrogenation* of ethane and propane. Both reactions involve β elimination of H_2.

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow{750°C} \underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{Hydrogen}}{H_2}$$

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow{750°C} \underset{\text{Propene}}{CH_3CH{=}CH_2} + \underset{\text{Hydrogen}}{H_2}$$

Many reactions classified as dehydrogenations occur within the cells of living systems at 25°C. H_2 is not one of the products, however. Instead, the hydrogens are lost in separate steps of an enzyme-catalyzed process. The enzyme indicated in the reaction:

A quote from a biochemistry text is instructive here. “This is not an easy reaction in organic chemistry. It is, however, a very important type of reaction in metabolic chemistry and is an integral step in the oxidation of carbohydrates, fats, and several amino acids.” G. L. Zubay, *Biochemistry,* 4th ed., William C. Brown Publishers, 1996, p. 333.



Succinic acid

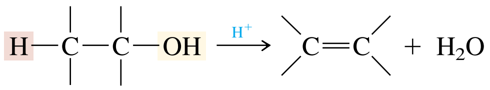
Fumaric acid

is a special kind, known as a *flavoprotein.*

Dehydrogenation of alkanes is not a practical *laboratory* synthesis for the vast majority of alkenes. The principal methods by which alkenes are prepared in the laboratory are two other β eliminations: the **dehydration of alcohols** and the **dehydrohalogenation of alkyl halides.** A discussion of these two methods makes up the remainder of this chapter.

5.9 DEHYDRATION OF ALCOHOLS

In the dehydration of alcohols, the H and OH are lost from adjacent carbons. An acid catalyst is necessary.



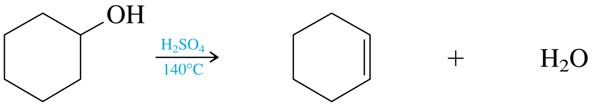
Alcohol Alkene Water

Before dehydrogenation of ethane became the dominant method, ethylene was prepared by heating ethyl alcohol with sulfuric acid.

$$CH_3CH_2OH \xrightarrow[160°C]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

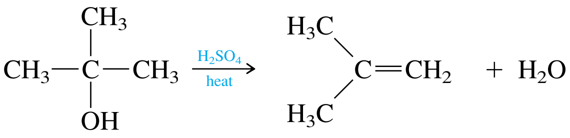
Ethyl alcohol Ethylene Water

Other alcohols behave similarly. Secondary alcohols undergo elimination at lower temperatures than primary alcohols,



Cyclohexanol Cyclohexene (79–87%) Water

and tertiary alcohols at lower temperatures than secondary alcohols.



2-Methyl-2-propanol 2-Methylpropene (82%) Water

HSO_4^- and H_3PO_4 are very similar in acid strength. Both are much weaker than H_2SO_4, which is a strong acid.

Sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) are the acids most frequently used in alcohol dehydrations. Potassium hydrogen sulfate ($KHSO_4$) is also often used.

PROBLEM 5.12 Identify the alkene obtained on dehydration of each of the following alcohols:

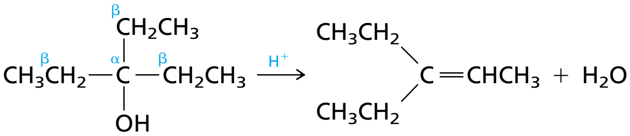
(a) 3-Ethyl-3-pentanol

(b) 1-Propanol

(c) 2-Propanol

(d) 2,3,3-Trimethyl-2-butanol

SAMPLE SOLUTION (a) The hydrogen and the hydroxyl are lost from adjacent carbons in the dehydration of 3-ethyl-3-pentanol.

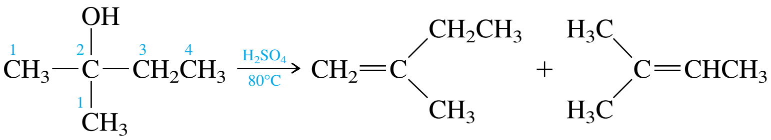


3-Ethyl-3-pentanol 3-Ethyl-2-pentene Water

The hydroxyl group is lost from a carbon that bears three equivalent ethyl substituents. Beta elimination can occur in any one of three equivalent directions to give the same alkene, 3-ethyl-2-pentene.

5.10 REGIOSELECTIVITY IN ALCOHOL DEHYDRATION: THE ZAITSEV RULE

In the preceding examples, including those of Problem 5.12, only a single alkene could be formed from each alcohol by β elimination. What about elimination in alcohols such as 2-methyl-2-butanol, in which dehydration can occur in two different directions to give alkenes that are constitutional isomers? Here, a double bond can be generated between C-1 and C-2 or between C-2 and C-3. Both processes occur but not nearly to the same extent. Under the usual reaction conditions 2-methyl-2-butene is the major product, and 2-methyl-1-butene the minor one.

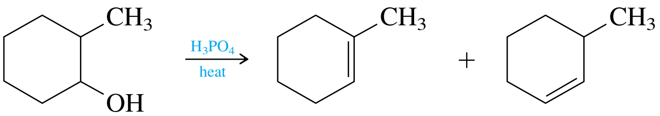


2-Methyl-2-butanol 2-Methyl-1-butene (10%) 2-Methyl-2-butene (90%)

Dehydration of this alcohol is selective in respect to its *direction.* Elimination occurs in the direction that leads to the double bond between C-2 and C-3 more than between C-2 and C-1. Reactions that can proceed in more than one direction, but in which one direction is preferred, are said to be *regioselective.*

The term "regioselective" was coined by Alfred Hassner, then at the University of Colorado, in a paper published in the *Journal of Organic Chemistry* in 1968.

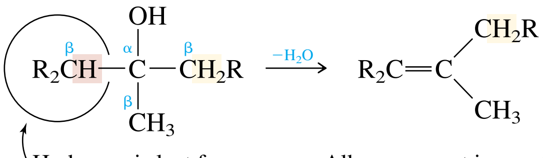
As a second example, consider the regioselective dehydration of 2-methylcyclohexanol to yield a mixture of 1-methylcyclohexene (major) and 3-methylcyclohexene (minor).



2-Methylcyclohexanol 1-Methylcyclohexene (84%) 3-Methylcyclohexene (16%)

Although Russian, Zaitsev published most of his work in German scientific journals, where his name was transliterated as *Saytzeff.* The spelling used here (*Zaitsev*) corresponds to the currently preferred style.

In 1875, Alexander M. Zaitsev of the University of Kazan (Russia) set forth a generalization describing the regioselectivity β-eliminations. **Zaitsev's rule** summarizes the results of numerous experiments in which alkene mixtures were produced by β elimination. In its original form, Zaitsev's rule stated that *the alkene formed in greatest amount is the one that corresponds to removal of the hydrogen from the β carbon having the fewest hydrogens.*

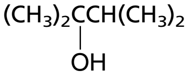


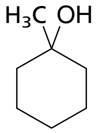
Hydrogen is lost from β-carbon having the fewest attached hydrogens

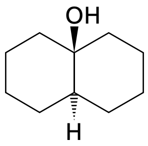
Alkene present in greatest amount in product

Zaitsev's rule as applied to the acid-catalyzed dehydration of alcohols is now more often expressed in a different way: *β elimination reactions of alcohols yield the most highly substituted alkene as the major product.* Since, as was discussed in Section 5.6, the most highly substituted alkene is also normally the most stable one, Zaitsev's rule is sometimes expressed as a preference for *predominant formation of the most stable alkene that could arise by β elimination.*

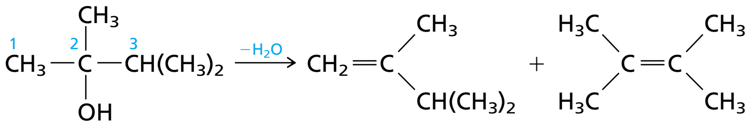
PROBLEM 5.13 Each of the following alcohols has been subjected to acid-catalyzed dehydration and yields a mixture of two isomeric alkenes. Identify the two alkenes in each case, and predict which one is the major product on the basis of the Zaitsev rule.

(a) 
$(CH_3)_2C(OH)CH(CH_3)_2$

(b) 

(c) 

SAMPLE SOLUTION (a) Dehydration of 2,3-dimethyl-2-butanol can lead to either 2,3-dimethyl-1-butene by removal of a C-1 hydrogen or to 2,3-dimethyl-2-butene by removal of a C-3 hydrogen.



2,3-Dimethyl-2-butanol

2,3-Dimethyl-1-butene (minor product)

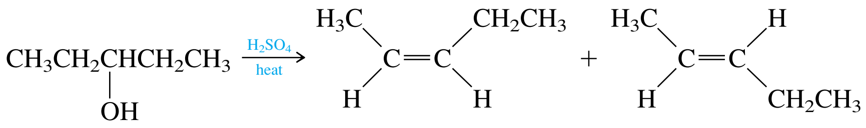
2,3-Dimethyl-2-butene (major product)

The major product is 2,3-dimethyl-2-butene. It has a tetrasubstituted double bond and is more stable than 2,3-dimethyl-1-butene, which has a disubstituted double bond. The major alkene arises by loss of a hydrogen from the β carbon that has fewer attached hydrogens (C-3) rather than from the β carbon that has the greater number of hydrogens (C-1).

5.11 STEREOSELECTIVITY IN ALCOHOL DEHYDRATION

In addition to being regioselective, alcohol dehydrations are **stereoselective.** A stereoselective reaction is one in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amounts than any other.

Alcohol dehydrations tend to produce the more stable stereoisomer of an alkene. Dehydration of 3-pentanol, for example, yields a mixture of *trans*-2-pentene and *cis*-2-pentene in which the more stable trans stereoisomer predominates.



3-Pentanol

cis-2-Pentene (25%)
(minor product)

trans-2-Pentene (75%)
(major product)

PROBLEM 5.14 What three alkenes are formed in the acid-catalyzed dehydration of 2-pentanol?

The biological dehydrogenation of succinic acid described in Section 5.8 is 100% stereoselective. Only fumaric acid, which has a trans double bond, is formed. High levels of stereoselectivity are characteristic of enzyme-catalyzed reactions.

5.12 THE MECHANISM OF ACID-CATALYZED DEHYDRATION OF ALCOHOLS

The dehydration of alcohols and the conversion of alcohols to alkyl halides by treatment with hydrogen halides (Section 4.8) are similar in two important ways:

1. Both reactions are promoted by acids.
2. The relative reactivity of alcohols decreases in the order tertiary > secondary > primary.

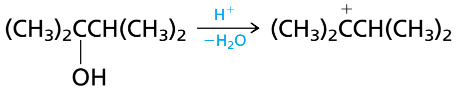
These common features suggest that carbocations are key intermediates in alcohol dehydration, just as they are in the conversion of alcohols to alkyl halides. Figure 5.6 portrays a three-step mechanism for the sulfuric acid-catalyzed dehydration of *tert*-butyl alcohol. Steps 1 and 2 describe the generation of *tert*-butyl cation by a process similar to that which led to its formation as an intermediate in the reaction of *tert*-butyl alcohol with hydrogen chloride. Step 3 in Figure 5.6, however, is new to us and is the step in which the double bond is formed.

Step 3 is an acid-base reaction in which the carbocation acts as a Brønsted acid, transferring a proton to a Brønsted base (water). This is the property of carbocations that is of the most significance to elimination reactions. Carbocations are strong acids; they are the conjugate acids of alkenes and readily lose a proton to form alkenes. Even weak bases such as water are sufficiently basic to abstract a proton from a carbocation.

Step 3 in Figure 5.6 shows water as the base which abstracts a proton from the carbocation. Other Brønsted bases present in the reaction mixture that can function in the same way include *tert*-butyl alcohol and hydrogen sulfate ion.

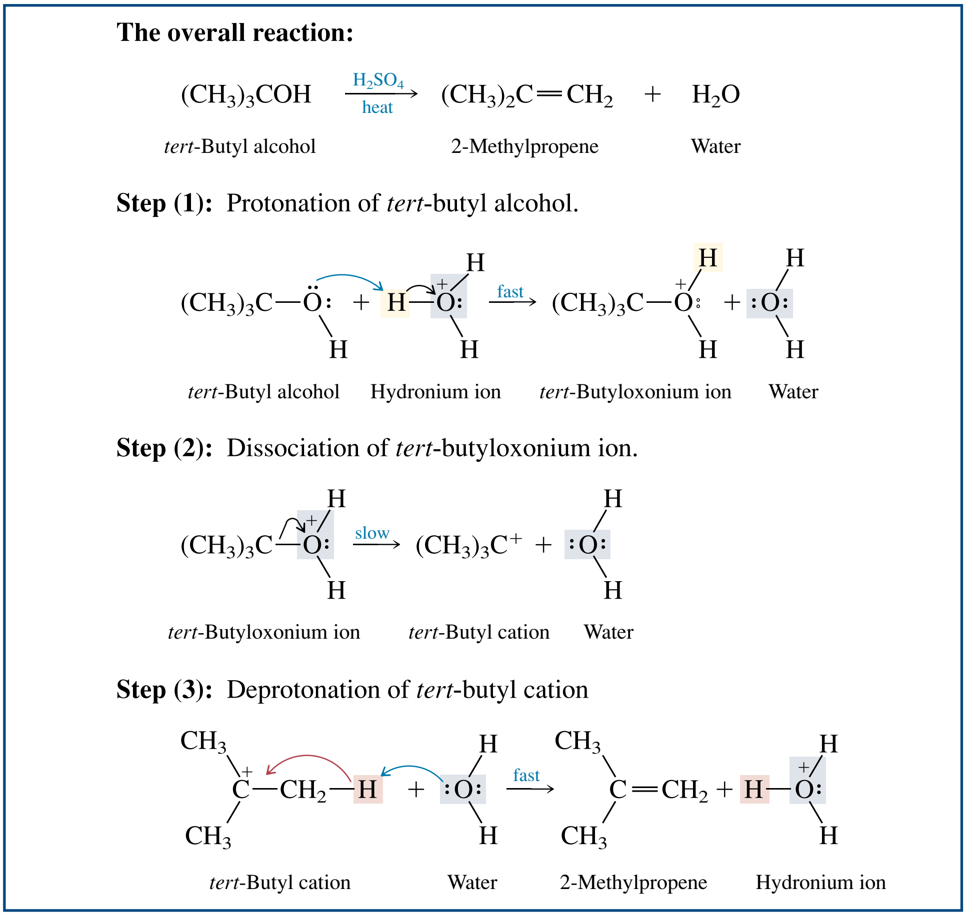
PROBLEM 5.15 Write a structural formula for the carbocation intermediate formed in the dehydration of each of the alcohols in Problem 5.13 (Section 5.10). Using curved arrows, show how each carbocation is deprotonated by water to give a mixture of alkenes.

SAMPLE SOLUTION (a) The carbon that bears the hydroxyl group in the starting alcohol is the one that becomes positively charged in the carbocation.

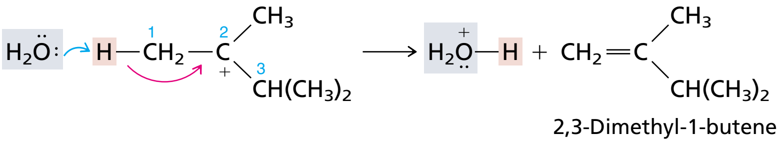


$$(CH_3)_2\underset{OH}{C}CH(CH_3)_2 \xrightarrow[-H_2O]{H^+} (CH_3)_2\overset{+}{C}CH(CH_3)_2$$

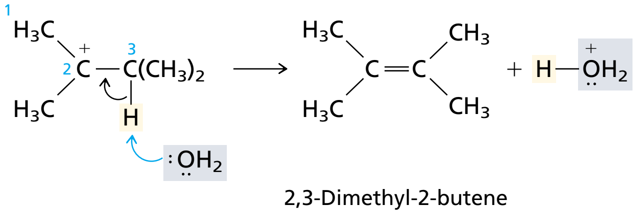
FIGURE 5.6 The mechanism for the acid-catalyzed dehydration of *tert*-butyl alcohol.



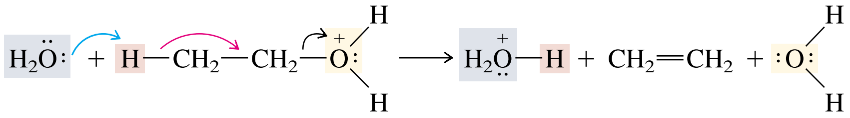
Water may remove a proton from either C-1 or C-3 of this carbocation. Loss of a proton from C-1 yields the minor product 2,3-dimethyl-1-butene. (This alkene has a disubstituted double bond.)



Loss of a proton from C-3 yields the major product 2,3-dimethyl-2-butene. (This alkene has a tetrasubstituted double bond.)



As noted earlier (Section 4.13) primary carbocations are too high in energy to be intermediates in most chemical reactions. If primary alcohols don't form primary carbocations, then how do they undergo elimination? A modification of our general mechanism for alcohol dehydration offers a reasonable explanation. For primary alcohols it is believed that a proton is lost from the alkyloxonium ion in the same step in which carbon–oxygen bond cleavage takes place. For example, the rate-determining step in the sulfuric acid-catalyzed dehydration of ethanol may be represented as:



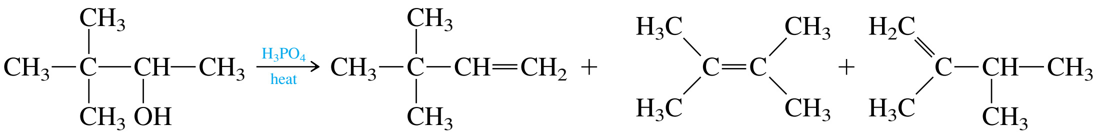
Water
Ethyloxonium ion
Hydronium ion
Ethylene
Water

Like tertiary alcohols, secondary alcohols normally undergo dehydration by way of carbocation intermediates.

In Chapter 4 you learned that carbocations could be captured by halide anions to give alkyl halides. In the present chapter, a second type of carbocation reaction has been introduced—a carbocation can lose a proton to form an alkene. In the next section a third aspect of carbocation behavior will be described, the *rearrangement* of one carbocation to another.

5.13 REARRANGEMENTS IN ALCOHOL DEHYDRATION

Some alcohols undergo dehydration to yield alkenes having carbon skeletons different from the starting alcohols. Not only has elimination taken place, but the arrangement of atoms in the alkene is different from that in the alcohol. A **rearrangement** is said to have occurred. An example of an alcohol dehydration that is accompanied by rearrangement is the case of 3,3-dimethyl-2-butanol. This is one of many such experiments carried out by F. C. Whitmore and his students at Pennsylvania State University in the 1930s as part of a general study of rearrangement reactions.



3,3-Dimethyl-2-butanol
3,3-Dimethyl-1-butene (3%)
2,3-Dimethyl-2-butene (64%)
2,3-Dimethyl-1-butene (33%)

A mixture of three alkenes was obtained in 80% yield, having the composition shown. The alkene having the same carbon skeleton as the starting alcohol, 3,3-dimethyl-1-butene, constituted only 3% of the alkene mixture. The two alkenes present in greatest amount, 2,3-dimethyl-2-butene and 2,3-dimethyl-1-butene, both have carbon skeletons different from that of the starting alcohol.

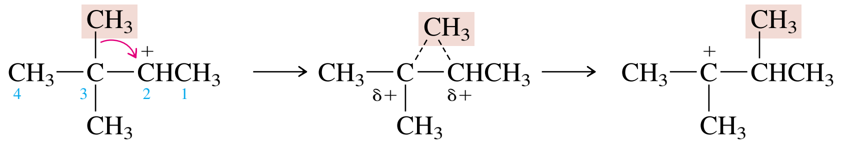
Whitmore proposed that the carbon skeleton rearrangement occurred in a separate step following carbocation formation. Once the alcohol was converted to the corresponding carbocation, that carbocation could either lose a proton to give an alkene having the same carbon skeleton or rearrange to a different carbocation, as shown in Figure 5.7. The rearranged alkenes arise by loss of a proton from the rearranged carbocation.

Why do carbocations rearrange? The answer is straightforward once we recall that tertiary carbocations are more stable than secondary carbocations (Section 4.10). Thus, rearrangement of a secondary to a tertiary carbocation is energetically favorable. As shown in Figure 5.7, the carbocation that is formed first in the dehydration of

3,3-dimethyl-2-butanol is secondary; the rearranged carbocation is tertiary. Rearrangement occurs, and almost all of the alkene products come from the tertiary carbocation.

To simplify the accompanying discussion, the carbons of the carbocation are numbered so as to correspond to their positions in the starting alcohol 3,3-dimethyl-2-butanol. These numbers are different from the locants in the IUPAC cation names, which are given under the structural formulas.

How do carbocations rearrange? To understand this we need to examine the structural change that takes place at the transition state. Again referring to the initial (secondary) carbocation intermediate in the dehydration of 3,3-dimethyl-2-butanol, rearrangement occurs when a methyl group shifts from C-3 to the positively charged carbon. The methyl group migrates with the pair of electrons that made up its original σ bond to C-3. In the curved arrow notation for this methyl migration, the arrow shows the movement of both the methyl group and the electrons in the σ bond.



1,2,2-Trimethylpropyl cation (secondary, less stable)

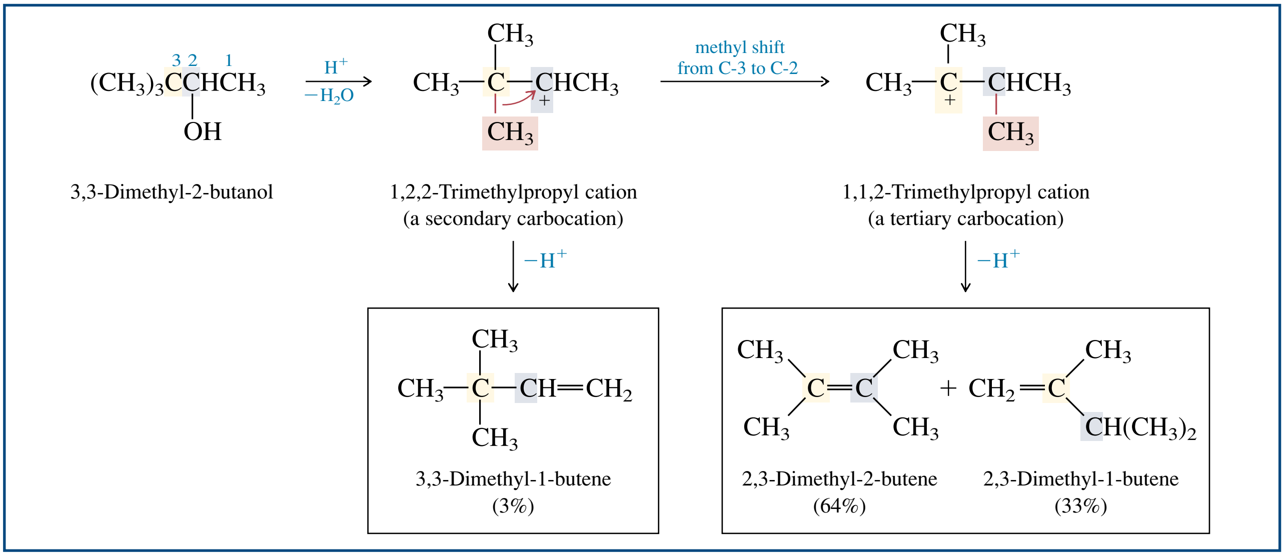
Transition state for methyl migration (dashed lines indicate partial bonds)

1,1,2-Trimethylpropyl cation (tertiary, more stable)

At the transition state for rearrangement, the methyl group is partially bonded both to its point of origin and to the carbon that will be its destination.

This rearrangement is shown in orbital terms in Figure 5.8. The relevant orbitals of the secondary carbocation are shown in structure (*a*), those of the transition state for rearrangement in (*b*), and those of the tertiary carbocation in (*c*). Delocalization of the *electrons* of the C—CH_3 σ bond into the vacant *p* orbital of the positively charged carbon by hyperconjugation is present in both (*a*) and (*c*), requires no activation energy, and stabilizes each carbocation. Migration of the *atoms* of the methyl group, however, occurs only when sufficient energy is absorbed by (*a*) to achieve the transition state (*b*). The activation energy is modest, and carbocation rearrangements are normally quite fast.

Once a carbocation is formed, anything that happens afterward happens rapidly.



3,3-Dimethyl-2-butanol

1,2,2-Trimethylpropyl cation (a secondary carbocation)

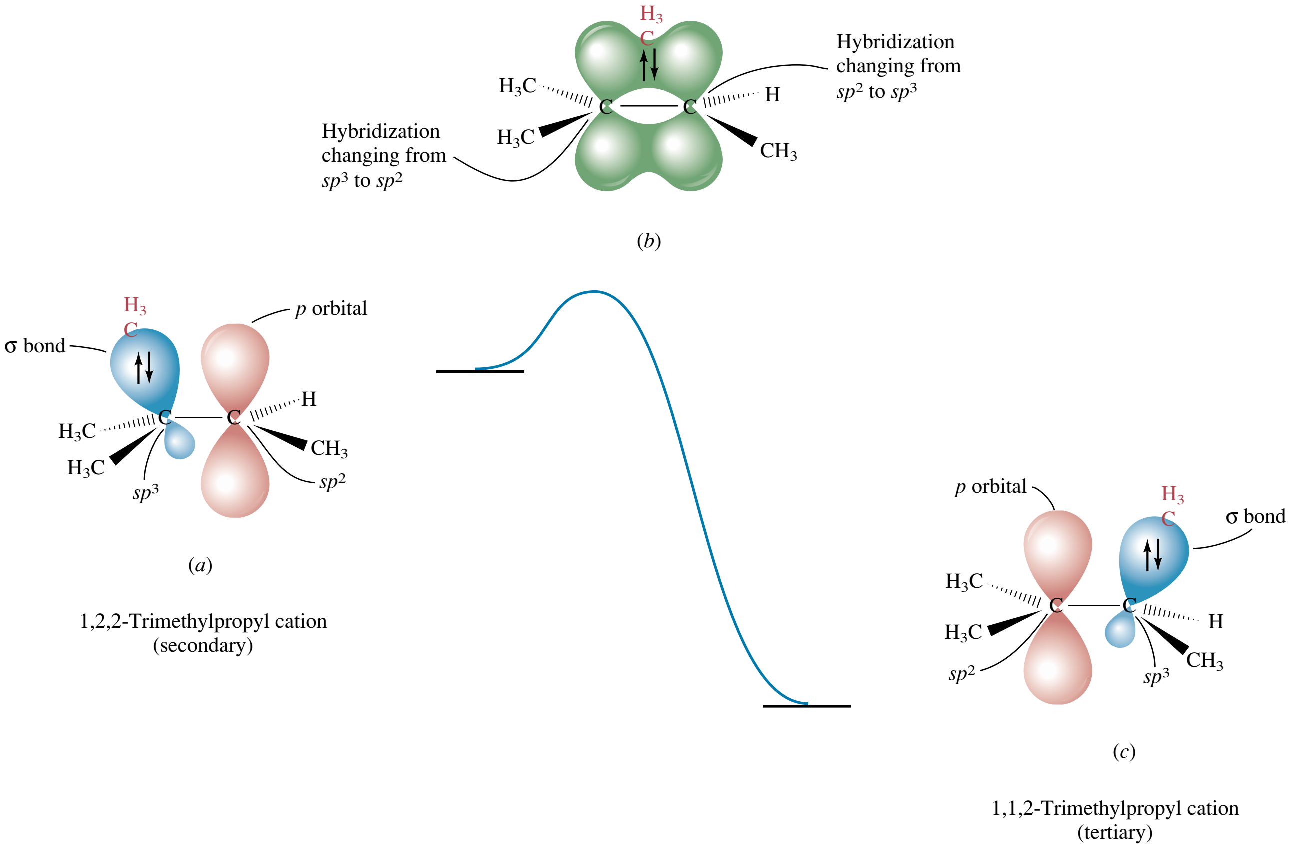
1,1,2-Trimethylpropyl cation (a tertiary carbocation)

3,3-Dimethyl-1-butene (3%)

2,3-Dimethyl-2-butene (64%)

2,3-Dimethyl-1-butene (33%)

FIGURE 5.7 The first formed carbocation from 3,3-dimethyl-2-butanol is secondary and rearranges to a more stable tertiary carbocation by a methyl migration. The major portion of the alkene products is formed by way of the tertiary carbocation.



1,2,2-Trimethylpropyl cation (secondary)

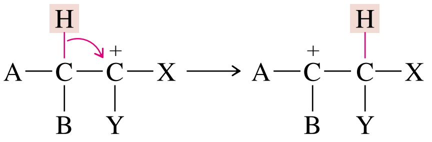
1,1,2-Trimethylpropyl cation (tertiary)

FIGURE 5.8 An orbital representation of methyl migration in 1,2,2-trimethylpropyl cation. Structure (*a*) is the initial secondary carbocation; structure (*b*) is the transition state for methyl migration, and structure (*c*) is the final tertiary carbocation.

PROBLEM 5.16 The alkene mixture obtained on dehydration of 2,2-dimethylcyclohexanol contains appreciable amounts of 1,2-dimethylcyclohexene. Give a mechanistic explanation for the formation of this product.

Alkyl groups other than methyl can also migrate to a positively charged carbon.

Many carbocation rearrangements involve migration of a hydrogen. These are called **hydride shifts.** The same requirements apply to hydride shifts as to alkyl group migrations; they proceed in the direction that leads to a more stable carbocation; the origin and destination of the migrating hydrogen are adjacent carbons, one of which must be positively charged; and the hydrogen migrates with a pair of electrons.



$$A-\underset{\displaystyle B}{\overset{\displaystyle H}{C}}-\underset{\displaystyle Y}{\overset{+}{C}}-X \longrightarrow A-\underset{\displaystyle B}{\overset{+}{C}}-\underset{\displaystyle Y}{\overset{\displaystyle H}{C}}-X$$

Hydride shift

Hydride shifts often occur during the dehydration of primary alcohols. Thus, although 1-butene would be expected to be the only alkene formed on dehydration of 1-butanol, it is in fact only a minor product. The major product is a mixture of *cis*- and *trans*-2-butene.

$$CH_3CH_2CH_2CH_2OH \xrightarrow[140\text{–}170°C]{H_2SO_4} CH_3CH_2CH{=}CH_2 + CH_3CH{=}CHCH_3$$

1-Butene (12%)

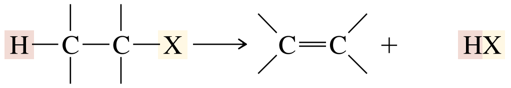
Mixture of *cis*-2-butene (32%) and *trans*-2-butene (56%)

A mechanism for the formation of these three alkenes is shown in Figure 5.9. Dissociation of the primary alkyloxonium ion is accompanied by a shift of hydride from C-2 to C-1. This avoids the formation of a primary carbocation, leading instead to a secondary carbocation in which the positive charge is at C-2. Deprotonation of this carbocation yields the observed products. (Some 1-butene may also arise directly from the primary alkyloxonium ion.)

This concludes discussion of our second functional group transformation involving *alcohols:* the first was the conversion of alcohols to alkyl halides (Chapter 4), and the second the conversion of alcohols to alkenes. In the remaining sections of the chapter the conversion of *alkyl halides* to alkenes by dehydrohalogenation is described.

5.14 DEHYDROHALOGENATION OF ALKYL HALIDES

Dehydrohalogenation is the loss of a hydrogen and a halogen from an alkyl halide. It is one of the most useful methods for preparing alkenes by β elimination.

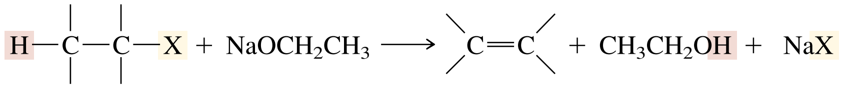


$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X} \longrightarrow \mathrm{C{=}C} + \mathrm{HX}$$

Alkyl halide Alkene Hydrogen halide

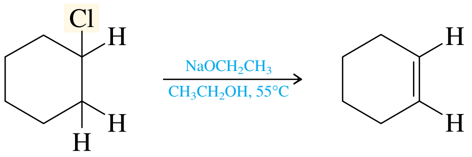
When applied to the preparation of alkenes, the reaction is carried out in the presence of a strong base, such as sodium ethoxide ($NaOCH_2CH_3$) in ethyl alcohol as solvent.

Sodium ethoxide is prepared by the reaction of sodium metal with ethanol.



$$\mathrm{H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}X} + NaOCH_2CH_3 \longrightarrow \mathrm{C{=}C} + CH_3CH_2OH + NaX$$

Alkyl halide Sodium ethoxide Alkene Ethyl alcohol Sodium halide



Cyclohexyl chloride Cyclohexene (100%)

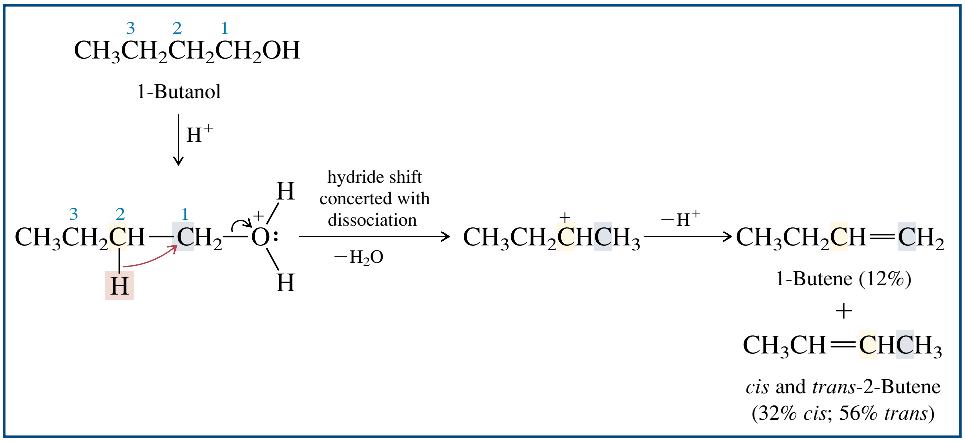


FIGURE 5.9 Dehydration of 1-butanol is accompanied by a hydride shift from C-2 to C-1.

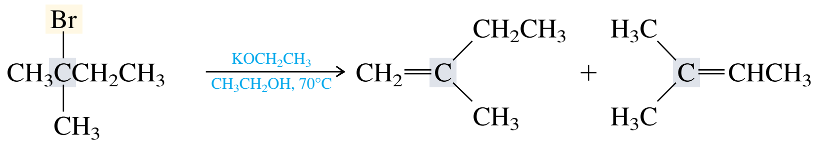
Similarly, sodium methoxide ($NaOCH_3$) is a suitable base and is used in methyl alcohol. Potassium hydroxide in ethyl alcohol is another base–solvent combination often employed in the dehydrohalogenation of alkyl halides. Potassium *tert*-butoxide [$KOC(CH_3)_3$] is the preferred base when the alkyl halide is primary; it is used in either *tert*-butyl alcohol or dimethyl sulfoxide as solvent.

Dimethyl sulfoxide has the structure $(CH_3)_2\overset{+}{\ddot{S}}{-}\ddot{\underset{\cdot\cdot}{O}}{:}^{-}$ and is commonly referred to as DMSO. It is a relatively inexpensive solvent, obtained as a byproduct in paper manufacture.

$$CH_3(CH_2)_{15}CH_2CH_2Cl \xrightarrow[\text{DMSO, 25°C}]{KOC(CH_3)_3} CH_3(CH_2)_{15}CH{=}CH_2$$

1-Chlorooctadecane 1-Octadecene (86%)

The regioselectivity of dehydrohalogenation of alkyl halides follows the Zaitsev rule; β elimination predominates in the direction that leads to the more highly substituted alkene.

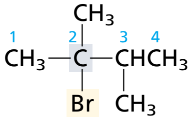


2-Bromo-2-methylbutane 2-Methyl-1-butene (29%) 2-Methyl-2-butene (71%)

PROBLEM 5.17 Write the structures of all the alkenes that can be formed by dehydrohalogenation of each of the following alkyl halides. Apply the Zaitsev rule to predict the alkene formed in greatest amount in each case.

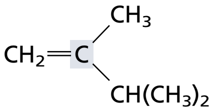
(a) 2-Bromo-2,3-dimethylbutane
(b) *tert*-Butyl chloride
(c) 3-Bromo-3-ethylpentane
(d) 2-Bromo-3-methylbutane
(e) 1-Bromo-3-methylbutane
(f) 1-Iodo-1-methylcyclohexane

SAMPLE SOLUTION (a) First analyze the structure of 2-bromo-2,3-dimethylbutane with respect to the number of possible β elimination pathways.



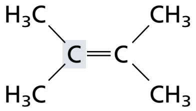
Bromine must be lost from C-2;
hydrogen may be lost from C-1 or from C-3

The two possible alkenes are



2,3-Dimethyl-1-butene
(minor product)

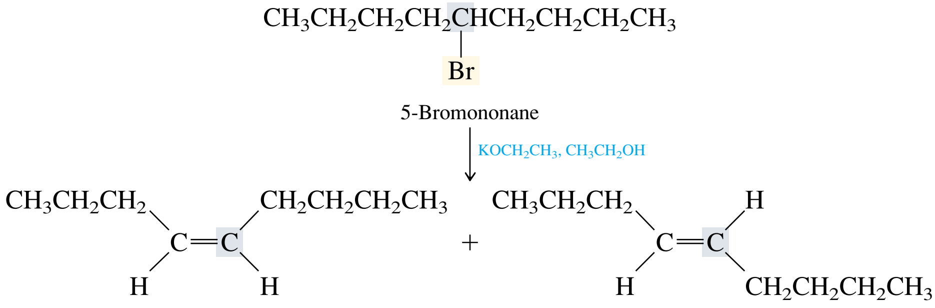
and



2,3-Dimethyl-2-butene
(major product)

The major product, predicted on the basis of Zaitsev's rule, is 2,3-dimethyl-2-butene. It has a tetrasubstituted double bond. The minor alkene has a disubstituted double bond.

In addition to being regioselective, dehydrohalogenation of alkyl halides is stereoselective and favors formation of the more stable stereoisomer. Usually, as in the case of 5-bromononane, the trans (or *E*) alkene is formed in greater amounts than its cis (or *Z*) stereoisomer.

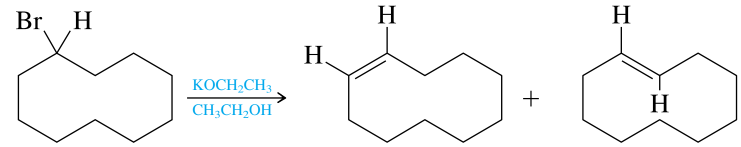


5-Bromononane

cis-4-Nonene (23%) + *trans*-4-Nonene (77%)

PROBLEM 5.18 Write structural formulas for all the alkenes that can be formed in the reaction of 2-bromobutane with potassium ethoxide.

Dehydrohalogenation of cycloalkyl halides lead exclusively to cis cycloalkenes when the ring has fewer than ten carbons. As the ring becomes larger, it can accommodate either a cis or a trans double bond, and large-ring cycloalkyl halides give mixtures of cis and trans cycloalkenes.



Bromocyclodecane

cis-Cyclodecene [(*Z*)-cyclodecene] (85%)

trans-Cyclodecene [(*E*)-cyclodecene] (15%)

5.15 MECHANISM OF THE DEHYDROHALOGENATION OF ALKYL HALIDES: THE E2 MECHANISM

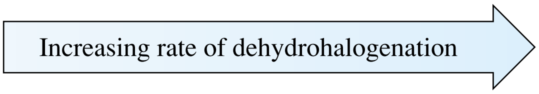
In the 1920s, Sir Christopher Ingold proposed a mechanism for dehydrohalogenation that is still accepted as a valid description of how these reactions occur. Some of the information on which Ingold based his mechanism included these facts:

1. *The reaction exhibits second-order kinetics; it is first-order in alkyl halide and first-order in base.*

$$\text{Rate} = k[\text{alkyl halide}][\text{base}]$$

Doubling the concentration of either the alkyl halide or the base doubles the reaction rate. Doubling the concentration of both reactants increases the rate by a factor of 4.

2. *The rate of elimination depends on the halogen, the reactivity of alkyl halides increasing with decreasing strength of the carbon–halogen bond.*



RF < RCl < RBr < RI

Alkyl fluoride
(slowest rate of elimination;
strongest carbon–halogen bond)

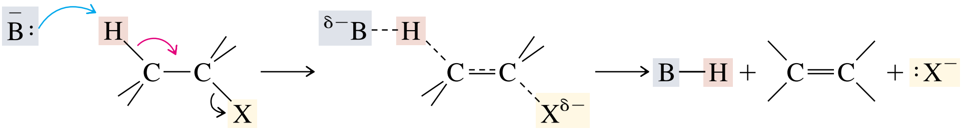
Alkyl iodide
(fastest rate of elimination;
weakest carbon–halogen bond)

Cyclohexyl bromide, for example, is converted to cyclohexene by sodium ethoxide in ethanol over 60 times faster than cyclohexyl chloride. Iodide is the best **leaving group** in a dehydrohalogenation reaction, fluoride the poorest leaving group. Fluoride is such a poor leaving group that alkyl fluorides are rarely used as starting materials in the preparation of alkenes.

What are the implications of second-order kinetics? Ingold reasoned that second-order kinetics suggest a bimolecular rate-determining step involving both a molecule of the alkyl halide and a molecule of base. He concluded that proton removal from the β carbon by the base occurs during the rate-determining step rather than in a separate step following the rate-determining step.

What are the implications of the effects of the various halide leaving groups? Since it is the halogen with the weakest bond to carbon that reacts fastest, Ingold concluded that the carbon–halogen bond breaks in the rate-determining step. The weaker the carbon–halogen bond, the easier it breaks.

On the basis of these observations, Ingold proposed a concerted (one-step) mechanism for dehydrohalogenation and gave it the mechanistic symbol **E2**, standing for **elimination bimolecular.**



Transition state for bimolecular elimination

In the E2 mechanism the three key elements

1. C—H bond breaking
2. C═C π bond formation
3. C—X bond breaking

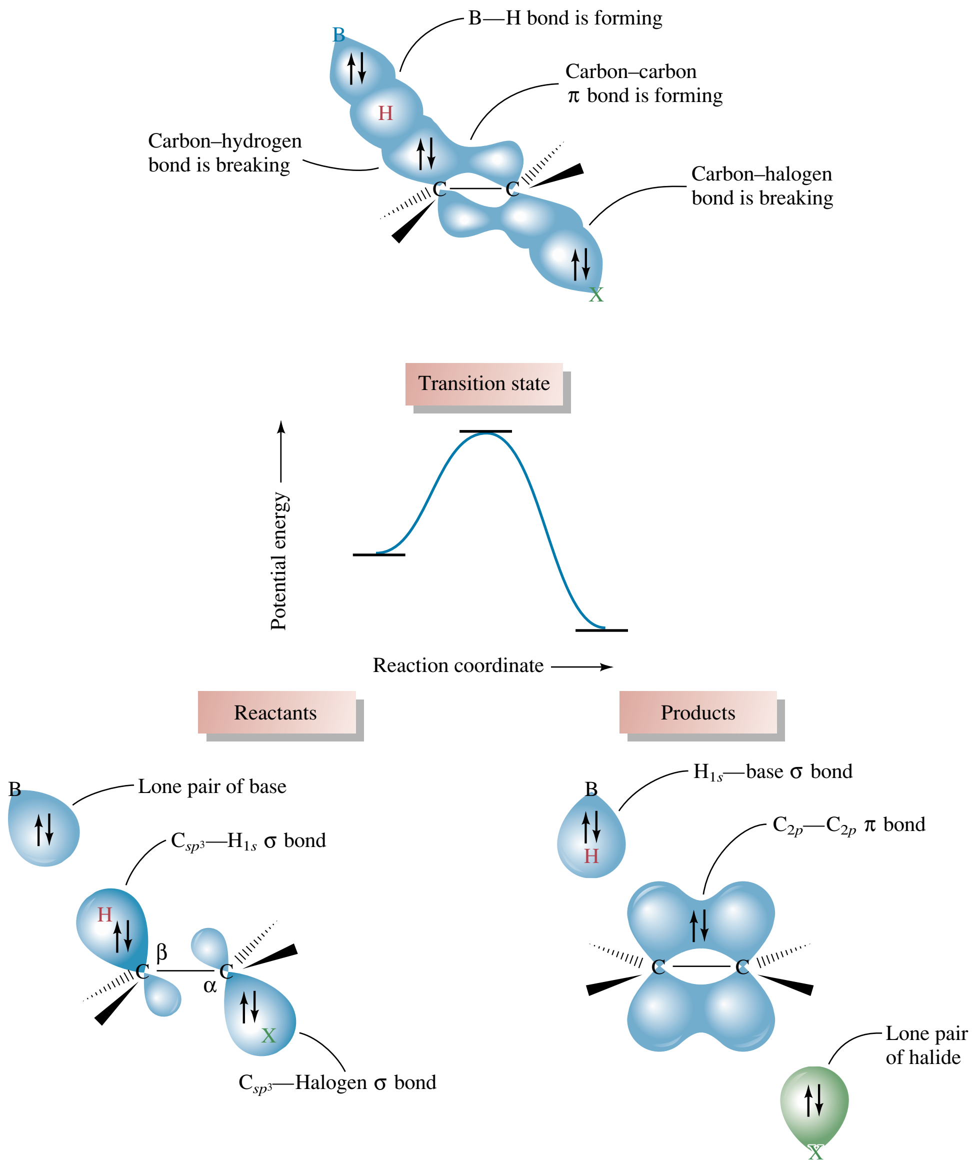
are all taking place at the same transition state. The carbon–hydrogen and carbon–halogen bonds are in the process of being broken, the base is becoming bonded to the hydrogen, a π bond is being formed, and the hybridization of carbon is changing from sp^3 to sp^2. An energy diagram for the E2 mechanism is shown in Figure 5.10.

PROBLEM 5.19 Use curved arrows to track electron movement in the dehydrohalogenation of *tert*-butyl chloride by sodium methoxide by the E2 mechanism.

The regioselectivity of elimination is accommodated in the E2 mechanism by noting that a partial double bond develops at the transition state. Since alkyl groups stabilize double bonds, they also stabilize a partially formed π bond in the transition state. The more stable alkene therefore requires a lower energy of activation for its formation and predominates in the product mixture because it is formed faster than a less stable one.

Ingold was a pioneer in applying quantitative measurements of reaction rates to the understanding of organic reaction mechanisms. Many of the reactions to be described in this text were studied by him and his students during the period of about 1920 to 1950. The facts disclosed by Ingold's experiments have been verified many times. His interpretations, although considerably refined during the decades that followed his

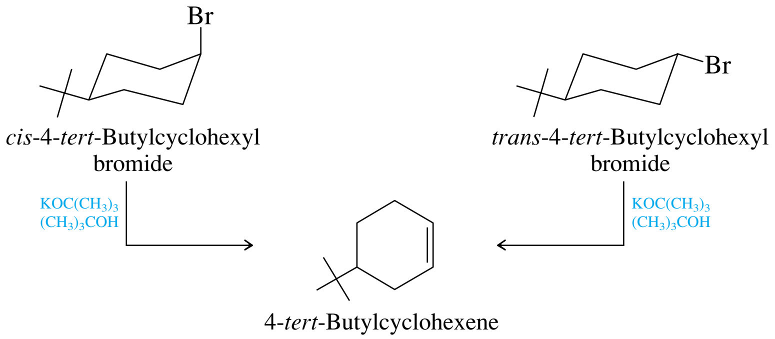
FIGURE 5.10 Potential energy diagram for concerted E2 elimination of an alkyl halide.



original reports, still serve us well as a starting point for understanding how the fundamental processes of organic chemistry take place. Beta-elimination of alkyl halides by the E2 mechanism is one of those fundamental processes.

5.16 ANTI ELIMINATION IN E2 REACTIONS: STEREOELECTRONIC EFFECTS

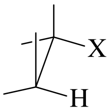
Further insight into the E2 mechanism comes from stereochemical studies. One such experiment compares the rates of elimination of the cis and trans isomers of 4-*tert*-butylcyclohexyl bromide.



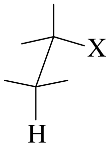
Although both stereoisomers yield 4-*tert*-butylcyclohexene as the only alkene, they do so at quite different rates. The cis isomer reacts over 500 times faster than the trans.

The difference in reaction rate results from different degrees of π bond development in the E2 transition state. Since π overlap of *p* orbitals requires their axes to be parallel, π bond formation is best achieved when the four atoms of the H—C—C—X unit lie in the same plane at the transition state. The two conformations that permit this relationship are termed *syn periplanar* and *anti periplanar.*

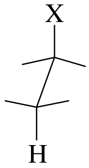
The *peri*- in *periplanar* means "almost" or "nearly." Although coplanarity of the *p* orbitals is the best geometry for the E2 process, modest deviations from this ideal can be tolerated.



Syn periplanar;
orbitals aligned but
bonds are eclipsed



Gauche;
orbitals not aligned for
double bond formation



Anti periplanar;
orbitals aligned and
bonds are staggered

Because adjacent bonds are eclipsed when the H—C—C—X unit is syn periplanar, a transition state having this geometry is less stable than one that has an anti periplanar relationship between the proton and the leaving group.

As Figure 5.11 shows, bromine is axial in the most stable conformation of *cis*-4-*tert*-butylcyclohexyl bromide, but it is equatorial in the trans stereoisomer. An axial bromine is anti periplanar with respect to the axial hydrogens at C-2 and C-6, and so

cis-4-*tert*-Butylcyclohexyl bromide

Axial halide is in proper orientation for anti elimination with respect to axial hydrogens on adjacent carbon atoms. Dehydrobromination is rapid.

trans-4-*tert*-Butylcyclohexyl bromide

Equatorial halide is gauche to axial and equatorial hydrogens on adjacent carbon; cannot undergo anti elimination in this conformation. Dehydrobromination is slow.

FIGURE 5.11 Conformations of *cis*- and *trans*-4-*tert*-butylcyclohexyl bromide and their relationship to the preference for an anti periplanar arrangement of proton and leaving group.

the proper geometry between the proton and the leaving group is already present in the cis bromide, which undergoes E2 elimination rapidly. The less reactive stereoisomer, the trans bromide, has an equatorial bromine in its most stable conformation. An equatorial bromine is not anti periplanar with respect to any of the hydrogens that are β to it. The relationship between an equatorial leaving group and all the C-2 and C-6 hydrogens is gauche. In order to undergo E2 elimination, the trans bromide must adopt a geometry in which the ring is strained. The transition state for its elimination is therefore higher in energy, and reaction is slower.

PROBLEM 5.20 Use curved arrow notation to show the bonding changes in the reaction of *cis*-4-*tert*-butylcyclohexyl bromide with potassium *tert*-butoxide. Be sure your drawing correctly represents the spatial relationship between the leaving group and the proton that is lost.

Effects that arise because one spatial arrangement of electrons (or orbitals or bonds) is more stable than another are called **stereoelectronic effects.** *There is a stereoelectronic preference for the anti periplanar arrangement of proton and leaving group in E2 reactions.*

5.17 A DIFFERENT MECHANISM FOR ALKYL HALIDE ELIMINATION: THE E1 MECHANISM

The E2 mechanism is a concerted process in which the carbon–hydrogen and carbon–halogen bonds both break in the same elementary step. What if these bonds break in separate steps?

One possibility is the two-step mechanism of Figure 5.12, in which the carbon–halogen bond breaks first to give a carbocation intermediate, followed by deprotonation of the carbocation in a second step.

The alkyl halide, in this case 2-bromo-2-methylbutane, ionizes to a carbocation and a halide anion by a heterolytic cleavage of the carbon–halogen bond. Like the dissociation of an alkyloxonium ion to a carbocation, this step is rate-determining. Because the rate-determining step is unimolecular—it involves only the alkyl halide and not the base—this mechanism is known by the symbol **E1,** standing for **elimination unimolecular.** It exhibits first-order kinetics.

$$\text{Rate} = k[\text{alkyl halide}]$$

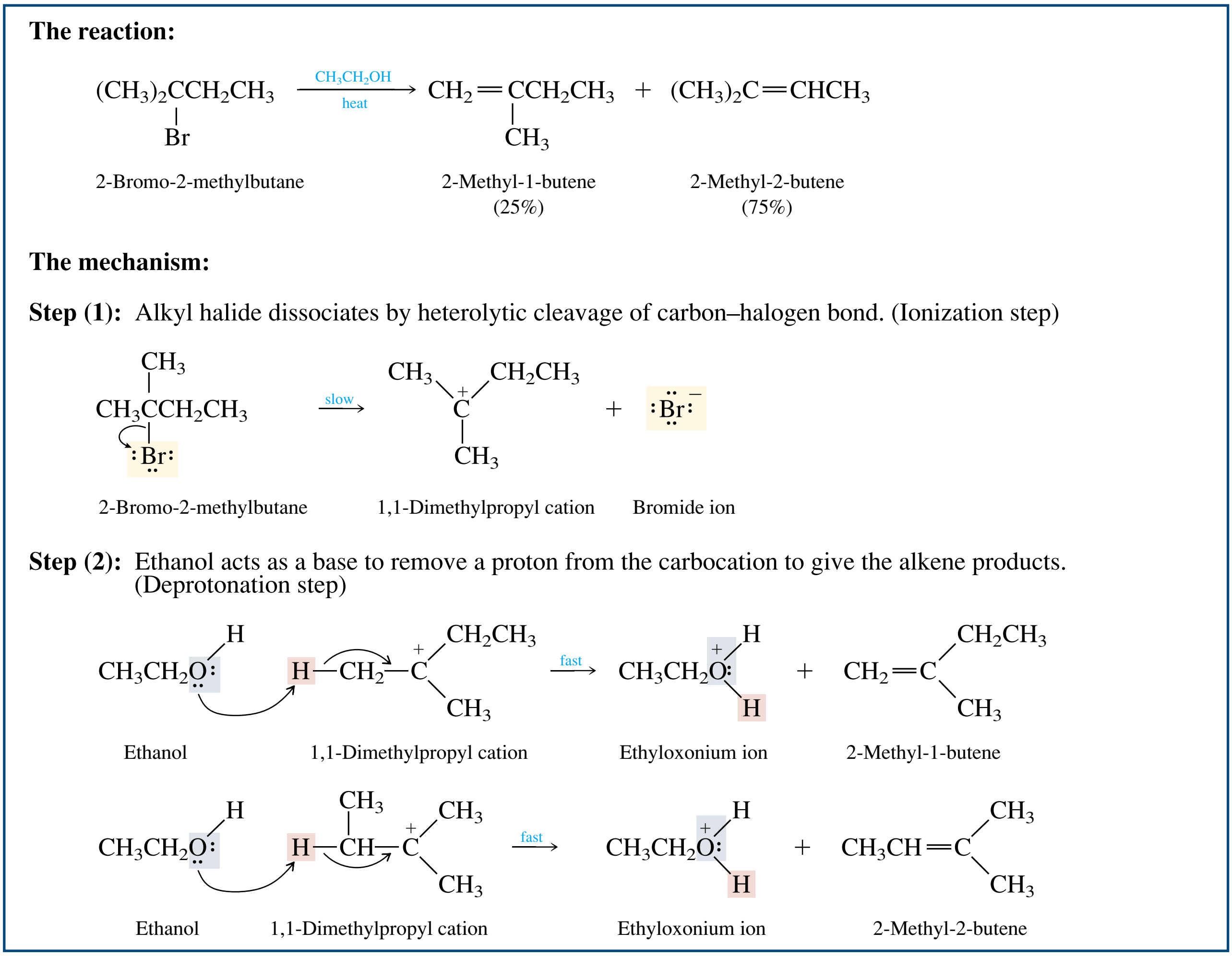
Typically, elimination by the E1 mechanism is observed only for tertiary and some secondary alkyl halides, and then only when the base is weak or in low concentration. The reactivity order parallels the ease of carbocation formation.

Increasing rate of elimination
by the E1 mechanism

$$\text{RCH}_2\text{X} < \text{R}_2\text{CHX} < \text{R}_3\text{CX}$$

Primary alkyl halide
slowest rate of
E1 elimination

Tertiary alkyl halide
fastest rate of
E1 elimination



The reaction:

The mechanism:

Step (1): Alkyl halide dissociates by heterolytic cleavage of carbon–halogen bond. (Ionization step)

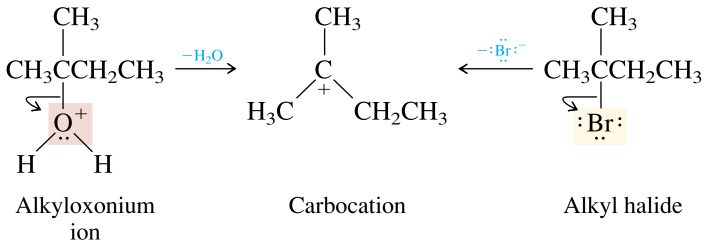
Step (2): Ethanol acts as a base to remove a proton from the carbocation to give the alkene products. (Deprotonation step)

FIGURE 5.12 The E1 mechanism for the dehydrohalogenation of 2-bromo-2-methylbutane in ethanol.

Because the carbon–halogen bond breaks in the slow step, the rate of the reaction depends on the leaving group. Alkyl iodides have the weakest carbon–halogen bond and are the most reactive; alkyl fluorides have the strongest carbon–halogen bond and are the least reactive.

The best examples of E1 eliminations are those carried out in the absence of added base. In the example cited in Figure 5.12, the base that abstracts the proton from the carbocation intermediate is a very weak one; it is a molecule of the solvent, ethyl alcohol. At even modest concentrations of strong base, elimination by the E2 mechanism is much faster than E1 elimination.

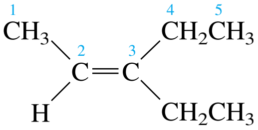
There is a strong similarity between the mechanism shown in Figure 5.12 and the one shown for alcohol dehydration in Figure 5.6. Indeed, we can describe the acid-catalyzed dehydration of alcohols as an E1 elimination of their conjugate acids. The main difference between the dehydration of 2-methyl-2-butanol and the dehydrohalogenation of 2-bromo-2-methylbutane is the source of the carbocation. When the alcohol is the substrate, it is the corresponding alkyloxonium ion that dissociates to form the carbocation. The alkyl halide ionizes directly to the carbocation.



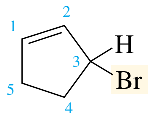
Like alcohol dehydrations, E1 reactions of alkyl halides can be accompanied by carbocation rearrangements. Eliminations by the E2 mechanism, on the other hand, normally proceed without rearrangement. Consequently, if one wishes to prepare an alkene from an alkyl halide, conditions favorable to E2 elimination should be chosen. In practice this simply means carrying out the reaction in the presence of a strong base.

5.18 SUMMARY

Section 5.1 Alkenes and cycloalkenes contain carbon–carbon double bonds. According to **IUPAC nomenclature,** alkenes are named by substituting *-ene* for the *-ane* suffix of the alkane that has the same number of carbon atoms as the longest continuous chain that includes the double bond. The chain is numbered in the direction that gives the lower number to the first-appearing carbon of the double bond. The double bond takes precedence over alkyl groups and halogens in dictating the direction of numbering, but is outranked by the hydroxyl group.



3-Ethyl-2-pentene

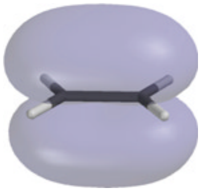


3-Bromocyclopentene

$\overset{4}{C}H_2{=}\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_2OH$

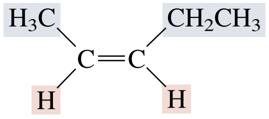
3-Buten-1-ol

Section 5.2 Bonding in alkenes is described according to an sp^2 orbital hybridization model. The double bond unites two sp^2-hybridized carbon atoms and is made of a σ component and a π component. The σ bond arises by overlap of an sp^2 hybrid orbital on each carbon. The π bond is weaker than the σ bond and results from a side-by-side overlap of p orbitals.

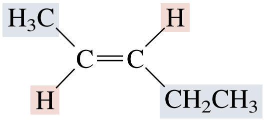


Sections 5.3–5.4 Isomeric alkenes may be either **constitutional isomers** or **stereoisomers.** There is a sizable barrier to rotation about a carbon–carbon double bond, which corresponds to the energy required to break the π component of the double bond. Stereoisomeric alkenes are configurationally stable under normal conditions. The **configurations** of stereoisomeric alkenes

are described according to two notational systems. One system adds the prefix *cis-* to the name of the alkene when similar substituents are on the same side of the double bond and the prefix *trans-* when they are on opposite sides. The other ranks substituents according to a system of rules based on atomic number. The prefix *Z* is used for alkenes that have higher ranked substituents on the same side of the double bond; the prefix *E* is used when higher ranked substituents are on opposite sides.



cis-2-Pentene
[(*Z*)-2-pentene]



trans-2-Pentene
[(*E*)-2-pentene]

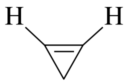
Section 5.5 Alkenes are relatively nonpolar. Alkyl substituents donate electrons to an sp^2-hybridized carbon to which they are attached slightly better than hydrogen does.

Section 5.6 Electron release from alkyl substituents stabilizes a double bond. In general, the order of alkene stability is:

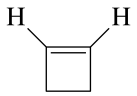
1. Tetrasubstituted alkenes ($R_2C{=}CR_2$) are the most stable.
2. Trisubstituted alkenes ($R_2C{=}CHR$) are next.
3. Among disubstituted alkenes, *trans*-RCH=CHR is normally more stable than *cis*-RCH=CHR. Exceptions are cycloalkenes, cis cycloalkenes being more stable than trans when the ring contains fewer than 11 carbons. Terminally disubstituted alkenes ($R_2C{=}CH_2$) may be slightly more or less stable than RCH=CHR, depending on their substituents.
4. Monosubstituted alkenes ($RCH{=}CH_2$) have a more stabilized double bond than ethylene (unsubstituted) but are less stable than disubstituted alkenes.

The greater stability of more highly substituted double bonds is an example of an **electronic effect.** The decreased stability that results from van der Waals strain between cis substituents is an example of a **steric effect.**

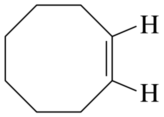
Section 5.7 Cycloalkenes that have trans double bonds in rings smaller than 12 members are less stable than their cis stereoisomers. *trans*-Cyclooctene can be isolated and stored at room temperature, but *trans*-cycloheptene is not stable above −30°C.



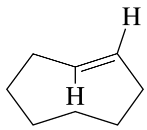
Cyclopropene



Cyclobutene



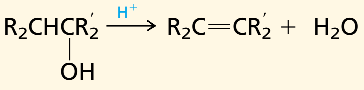
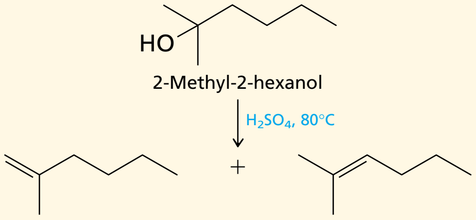
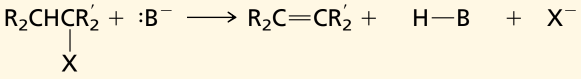
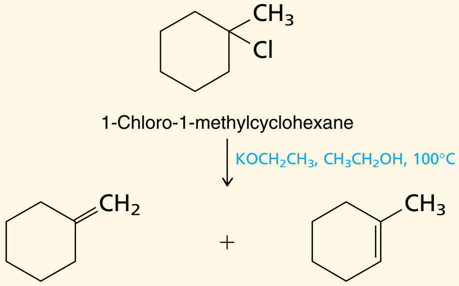
cis-Cyclooctene



trans-Cyclooctene

Section 5.8 Alkenes are prepared by **β elimination** of alcohols and alkyl halides. These reactions are summarized with examples in Table 5.2. In both cases, β elimination proceeds in the direction that yields the more highly substituted double bond **(Zaitsev's rule).**

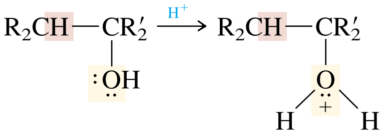
TABLE 5.2 Preparation of Alkenes by Elimination Reactions of Alcohols and Alkyl Halides

Reaction (section) and comments	General equation and specific example
Dehydration of alcohols (Sections 5.9–5.13) Dehydration requires an acid catalyst; the order of reactivity of alcohols is tertiary > secondary > primary. Elimination is regioselective and proceeds in the direction that produces the most highly substituted double bond. When stereoisomeric alkenes are possible, the more stable one is formed in greater amounts. A carbocation intermediate is involved, and sometimes rearrangements take place during elimination.	 $R_2CH\underset{OH}{C}R'_2 \xrightarrow{H^+} R_2C{=}CR'_2 + H_2O$ Alcohol Alkene Water  2-Methyl-2-hexanol H_2SO_4, 80°C 2-Methyl-1-hexene (19%) 2-Methyl-2-hexene (81%)
Dehydrohalogenation of alkyl halides (Sections 5.14–5.16) Strong bases cause a proton and a halide to be lost from adjacent carbons of an alkyl halide to yield an alkene. Regioselectivity is in accord with the Zaitsev rule. The order of halide reactivity is I > Br > Cl > F. A concerted E2 reaction pathway is followed, carbocations are not involved, and rearrangements do not normally occur. An anti periplanar arrangement of the proton being removed and the halide being lost characterizes the transition state.	 $R_2CH\underset{X}{C}R'_2 + :B^- \longrightarrow R_2C{=}CR'_2 + H{-}B + X^-$ Alkyl halide Base Alkene Conjugate acid of base Halide  1-Chloro-1-methylcyclohexane $KOCH_2CH_3$, CH_3CH_2OH, 100°C Methylenecyclohexane (6%) 1-Methylcyclohexene (94%)

Sections 5.9–5.11 See Table 5.2.

Section 5.12 Secondary and tertiary alcohols undergo **dehydration** by way of carbocation intermediates.

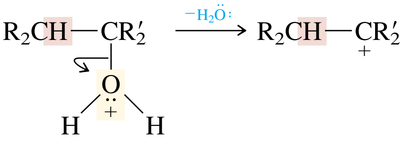
Step 1



$R_2CH{-}\underset{:\ddot{O}H}{C}R'_2 \xrightarrow{H^+} R_2CH{-}\underset{H-\overset{+}{\ddot{O}}-H}{C}R'_2$

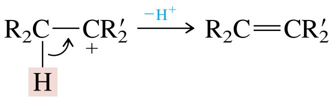
Alcohol Alkyloxonium ion

Step 2



$R_2CH{-}\underset{H-\overset{+}{\ddot{O}}-H}{C}R'_2 \xrightarrow{-H_2\ddot{O}:} R_2CH{-}\underset{+}{C}R'_2$

Alkyloxonium ion Carbocation

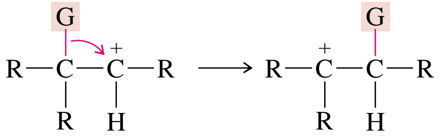
Step 3 

$$R_2\underset{\substack{|\\ H}}{C}-\overset{+}{C}R'_2 \xrightarrow{-H^+} R_2C{=}CR'_2$$

Carbocation Alkene

Primary alcohols do not dehydrate as readily as secondary or tertiary alcohols, and their dehydration does not involve a primary carbocation. A proton is lost from the β carbon in the same step in which carbon–oxygen bond cleavage occurs.

Section 5.13 Alkene synthesis via alcohol dehydration is complicated by **carbocation rearrangements.** A less stable carbocation can rearrange to a more stable one by an alkyl group migration or by a hydride shift, opening the possibility for alkene formation from two different carbocations.

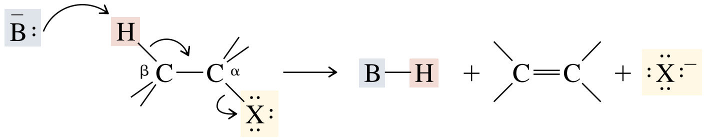


Secondary carbocation Tertiary carbocation

(G is a migrating group; it may be either a hydrogen or an alkyl group)

Section 5.14 See Table 5.2.

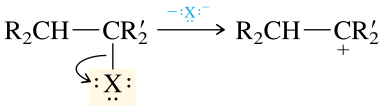
Section 5.15 **Dehydrohalogenation** of alkyl halides by alkoxide bases is not complicated by rearrangements, because carbocations are not intermediates. The **bimolecular (E2) mechanism** is a concerted process in which the base abstracts a proton from the β carbon while the bond between the halogen and the α carbon undergoes heterolytic cleavage.



Base Alkyl halide Conjugate acid of base Alkene Halide ion

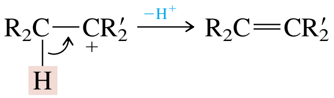
Section 5.16 The preceding equation shows the proton H and the halogen X in the **anti periplanar** relationship that is required for elimination by the E2 mechanism.

Section 5.17 In the absence of a strong base, alkyl halides eliminate by the **unimolecular (E1) mechanism.** The E1 mechanism involves rate-determining ionization of the alkyl halide to a carbocation, followed by deprotonation of the carbocation.

Step 1 

$$R_2CH-\underset{\substack{|\\ :\ddot{X}:}}{C}R'_2 \xrightarrow{-:\ddot{X}:^-} R_2CH-\overset{}{\underset{+}{C}}R'_2$$

Alkyl halide Carbocation

Step 2 

$$R_2\underset{\substack{|\\ H}}{C}-\overset{+}{C}R'_2 \xrightarrow{-H^+} R_2C{=}CR'_2$$

Carbocation Alkene

PROBLEMS

5.21 Write structural formulas for each of the following:

(a) 1-Heptene
(b) 3-Ethyl-2-pentene
(c) *cis*-3-Octene
(d) *trans*-1,4-Dichloro-2-butene
(e) (*Z*)-3-Methyl-2-hexene
(f) (*E*)-3-Chloro-2-hexene
(*g*) 1-Bromo-3-methylcyclohexene
(h) 1-Bromo-6-methylcyclohexene
(i) 4-Methyl-4-penten-2-ol
(j) Vinylcycloheptane
(k) 1,1-Diallylcyclopropane
(l) *trans*-1-Isopropenyl-3-methylcyclohexane

5.22 Write a structural formula or build a molecular model and give a correct IUPAC name for each alkene of molecular formula C_7H_{14} that has a *tetrasubstituted* double bond.

5.23 Give the IUPAC names for each of the following compounds:

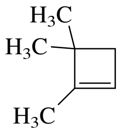
(a) $(CH_3CH_2)_2C{=}CHCH_3$

(b) $(CH_3CH_2)_2C{=}C(CH_2CH_3)_2$

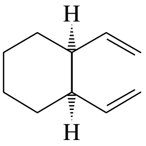
(c) $(CH_3)_3CCH{=}CCl_2$

(d)

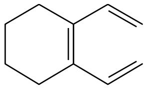
(e)



(f)



(g)

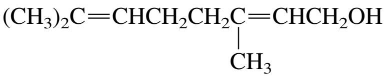


5.24 (a) A hydrocarbon isolated from fish oil and from plankton was identified as 2,6,10,14-tetramethyl-2-pentadecene. Write its structure.

(b) Alkyl isothiocyanates are compounds of the type $RN{=}C{=}S$. Write a structural formula for *allyl isothiocyanate,* a pungent-smelling compound isolated from mustard.

5.25 (a) The sex attractant of the Mediterranean fruit fly is (*E*)-6-nonen-1-ol. Write a structural formula or build a molecular model for this compound, showing the stereochemistry of the double bond.

(b) Geraniol is a naturally occurring substance present in the fragrant oil of many plants. It has a pleasing, roselike odor. Geraniol is the *E* isomer of



$$(CH_3)_2C{=}CHCH_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CHCH_2OH$$

Write a structural formula or build a molecular model for geraniol, showing its stereochemistry.

(c) Nerol is a naturally occurring substance that is a stereoisomer of geraniol. Write its structure or build a molecular model.

(d) The sex attractant of the codling moth is the 2*Z*, 6*E* stereoisomer of

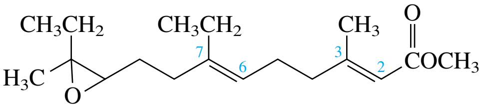
$$CH_3CH_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CHCH_2CH_2\underset{\underset{\displaystyle CH_2CH_3}{|}}{C}{=}CHCH_2OH$$

Write the structure of this substance or build a molecular model in a way that clearly shows its stereochemistry.

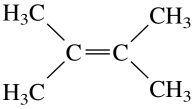
(e) The sex pheromone of the honeybee is the *E* stereoisomer of the compound shown. Write a structural formula or build a molecular model for this compound.

$$CH_3\overset{\overset{O}{\|}}{C}(CH_2)_4CH_2CH{=}CHCO_2H$$

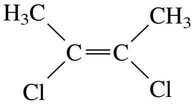
(f) A growth hormone from the cecropia moth has the structure shown. Express the stereochemistry of the double bonds according to the *E–Z* system.



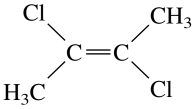
5.26 Which one of the following has the largest dipole moment (is the most polar)? Compare your answer with the calculated dipole moments on the *Learning By Modeling* CD.



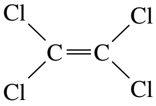
A



B



C



D

5.27 Match each alkene with the appropriate heat of combustion:

Heats of combustion (kJ/mol): 5293; 4658; 4650; 4638; 4632

Heats of combustion (kcal/mol): 1264.9; 1113.4; 1111.4; 1108.6; 1107.1

(a) 1-Heptene

(b) 2,4-Dimethyl-1-pentene

(c) 2,4-Dimethyl-2-pentene

(d) (*Z*)-4,4-Dimethyl-2-pentene

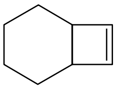
(e) 2,4,4-Trimethyl-2-pentene

5.28 Choose the more stable alkene in each of the following pairs. Explain your reasoning.

(a) 1-Methylcyclohexene or 3-methylcyclohexene

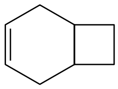
(b) Isopropenylcyclopentane or allylcyclopentane

(c)



Bicyclo[4.2.0]oct-7-ene

or

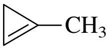


Bicyclo[4.2.0]oct-3-ene

(d) (*Z*)-Cyclononene or (*E*)-cyclononene

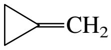
(e) (*Z*)-Cyclooctadecene or (*E*)-cyclooctadecene

5.29 (a) Suggest an explanation for the fact that 1-methylcyclopropene is some 42 kJ/mol (10 kcal/mol) less stable than methylenecyclopropane.



1-Methylcyclopropene

is less stable than



Methylenecyclopropane

(b) On the basis of your answer to part (a), compare the expected stability of 3-methylcyclopropene with that of 1-methylcyclopropene and that of methylenecyclopropane.

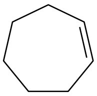
5.30 How many alkenes would you expect to be formed from each of the following alkyl bromides under conditions of E2 elimination? Identify the alkenes in each case.

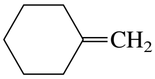
(a) 1-Bromohexane
(b) 2-Bromohexane
(c) 3-Bromohexane
(d) 2-Bromo-2-methylpentane
(e) 2-Bromo-3-methylpentane
(f) 3-Bromo-2-methylpentane
(g) 3-Bromo-3-methylpentane
(h) 3-Bromo-2,2-dimethylbutane

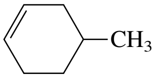
5.31 Write structural formulas for all the alkene products that could reasonably be formed from each of the following compounds under the indicated reaction conditions. Where more than one alkene is produced, specify the one that is the major product.

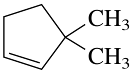
(a) 1-Bromo-3,3-dimethylbutane (potassium *tert*-butoxide, *tert*-butyl alcohol, 100°C)
(b) 1-Methylcyclopentyl chloride (sodium ethoxide, ethanol, 70°C)
(c) 3-Methyl-3-pentanol (sulfuric acid, 80°C)
(d) 2,3-Dimethyl-2-butanol (phosphoric acid, 120°C)
(e) 3-Iodo-2,4-dimethylpentane (sodium ethoxide, ethanol, 70°C)
(f) 2,4-Dimethyl-3-pentanol (sulfuric acid, 120°C)

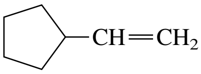
5.32 Choose the compound of molecular formula $C_7H_{13}Br$ that gives each alkene shown as the *exclusive* product of E2 elimination.

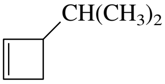
(a) 

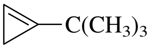
(b) 

(c) 

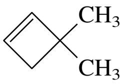
(d) 

(e) 

(f) 

(g) 

5.33 Give the structures of two different alkyl bromides both of which yield the indicated alkene as the *exclusive* product of E2 elimination.

(a) $CH_3CH{=}CH_2$
(b) $(CH_3)_2C{=}CH_2$
(c) $BrCH{=}CBr_2$
(d) 

5.34 (a) Write the structures or build molecular models of all the isomeric alkyl bromides having the molecular formula $C_5H_{11}Br$.

(b) Which one undergoes E1 elimination at the fastest rate?
(c) Which one is incapable of reacting by the E2 mechanism?
(d) Which ones can yield only a single alkene on E2 elimination?
(e) For which isomer does E2 elimination give two alkenes which are not constitutional isomers?
(f) Which one yields the most complex mixture of alkenes on E2 elimination?

5.35 (a) Write the structures or build molecular models of all the isomeric alcohols having the molecular formula $C_5H_{12}O$.

(b) Which one will undergo acid-catalyzed dehydration most readily?

(c) Write the structure of the most stable C_5H_{11} carbocation.

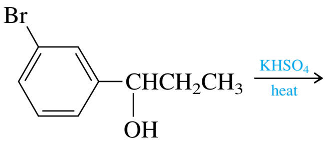
(d) Which alkenes may be derived from the carbocation in part (c)?

(e) Which alcohols can yield the carbocation in part (c) by a process involving a hydride shift?

(f) Which alcohols can yield the carbocation in part (c) by a process involving a methyl shift?

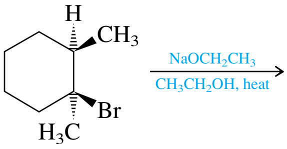
5.36 Predict the major organic product of each of the following reactions. In spite of the structural complexity of some of the starting materials, the functional group transformations are all of the type described in this chapter.

(a)

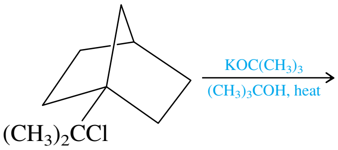


(b) $ICH_2CH(OCH_2CH_3)_2 \xrightarrow[(CH_3)_3COH,\ heat]{KOC(CH_3)_3}$

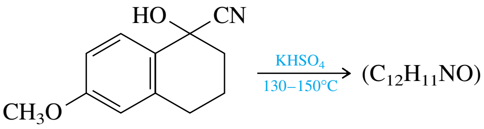
(c)



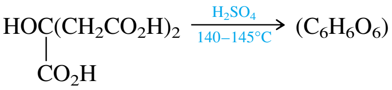
(d)



(e)



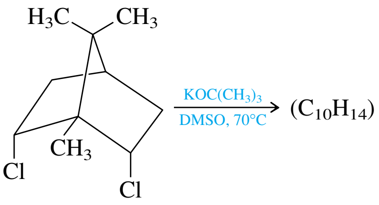
(f)



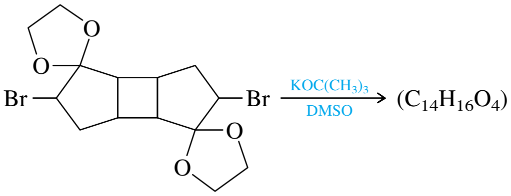
$$HO\underset{\textstyle CO_2H}{C}(CH_2CO_2H)_2 \xrightarrow[140\text{–}145°C]{H_2SO_4} (C_6H_6O_6)$$

Citric acid

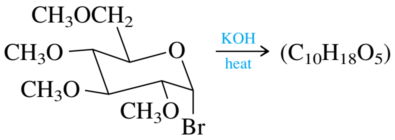
(g)



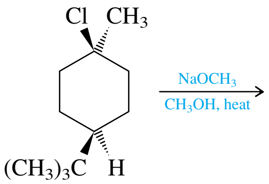
(h)



(i)



(j)



5.37 Evidence has been reported in the chemical literature that the reaction

$$(CH_3CH_2)_2CHCH_2Br + KNH_2 \longrightarrow (CH_3CH_2)_2C{=}CH_2 + NH_3 + KBr$$

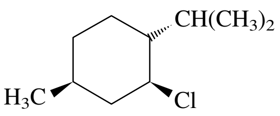
proceeds by the E2 mechanism. Use curved arrow notation to represent the flow of electrons for this process.

5.38 The rate of the reaction

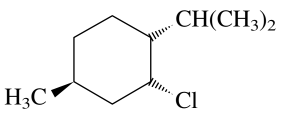
$$(CH_3)_3CCl + NaSCH_2CH_3 \longrightarrow (CH_3)_2C{=}CH_2 + CH_3CH_2SH + NaCl$$

is first-order in $(CH_3)_3CCl$ and first-order in $NaSCH_2CH_3$. Give the symbol (E1 or E2) for the most reasonable mechanism, and use curved arrow notation to represent the flow of electrons.

5.39 Menthyl chloride and neomenthyl chloride have the structures shown. One of these stereoisomers undergoes elimination on treatment with sodium ethoxide in ethanol much more readily than the other. Which reacts faster, menthyl chloride or neomenthyl chloride? Why? (Molecular models will help here.)



Menthyl chloride



Neomenthyl chloride

5.40 The stereoselectivity of elimination of 5-bromononane on treatment with potassium ethoxide was described in Section 5.14. Draw Newman projections or make molecular models of 5-bromononane showing the conformations that lead to *cis*-4-nonene and *trans*-4-nonene, respectively. Identify the proton that is lost in each case, and suggest a mechanistic explanation for the observed stereoselectivity.

5.41 In the acid-catalyzed dehydration of 2-methyl-1-propanol, what carbocation would be formed if a hydride shift accompanied cleavage of the carbon–oxygen bond in the alkyloxonium ion? What ion would be formed as a result of a methyl shift? Which pathway do you think will predominate, a hydride shift or a methyl shift?

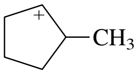
5.42 Each of the following carbocations has the potential to rearrange to a more stable one. Write the structure of the rearranged carbocation.

(a) $CH_3CH_2CH_2^{+}$

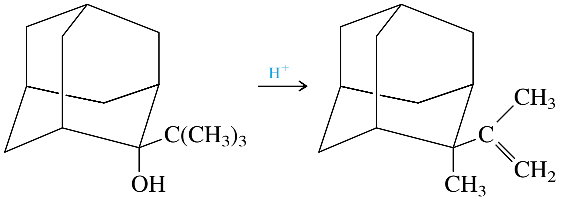
(b) $(CH_3)_2CH\overset{+}{C}HCH_3$

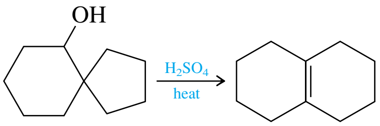
(c) $(CH_3)_3C\overset{+}{C}HCH_3$

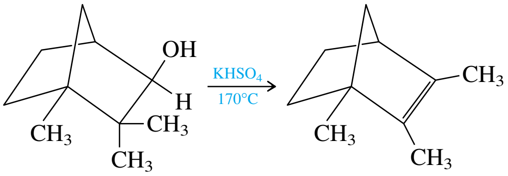
(d) $(CH_3CH_2)_3CCH_2^+$

(e) 

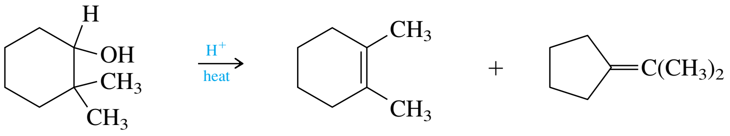
5.43 Write a sequence of steps depicting the mechanisms of each of the following reactions:

(a) 

(b) 

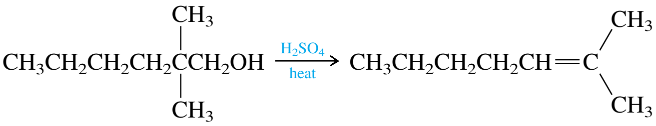
(c) 

5.44 In Problem 5.16 (Section 5.13) we saw that acid-catalyzed dehydration of 2,2-dimethylcyclohexanol afforded 1,2-dimethylcyclohexene. To explain this product we must write a mechanism for the reaction in which a methyl shift transforms a secondary carbocation to a tertiary one. Another product of the dehydration of 2,2-dimethylcyclohexanol is isopropylidenecyclopentane. Write a mechanism to rationalize its formation.



2,2-Dimethylcyclohexanol 1,2-Dimethylcyclohexene Isopropylidenecyclopentane

5.45 Acid-catalyzed dehydration of 2,2-dimethyl-1-hexanol gave a number of isomeric alkenes including 2-methyl-2-heptene as shown in the following formula.



$$CH_3CH_2CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2OH \xrightarrow[\text{heat}]{H_2SO_4} CH_3CH_2CH_2CH_2CH{=}C\begin{matrix}CH_3\\CH_3\end{matrix}$$

(a) Write a stepwise mechanism for the formation of 2-methyl-2-heptene.

(b) What other alkenes do you think are formed in this reaction?

5.46 Compound A (C_4H_{10}) gives two different monochlorides on photochemical chlorination. Treatment of either of these monochlorides with potassium *tert*-butoxide in dimethyl sulfoxide gives the same alkene B (C_4H_8) as the only product. What are the structures of compound A, the two monochlorides, and alkene B?

5.47 Compound A (C_6H_{14}) gives three different monochlorides on photochemical chlorination. One of these monochlorides is inert to E2 elimination. The other two monochlorides yield the same alkene B (C_6H_{12}) on being heated with potassium *tert*-butoxide in *tert*-butyl alcohol. Identify compound A, the three monochlorides, and alkene B.