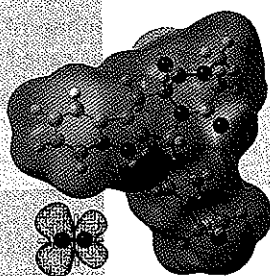


# RADICAL REACTIONS



*Nitric oxide and Cialis®*

## **Radicals in Biology, Medicine, and Industry**

Radicals are chemical species containing unpaired electrons. Radical reactions are of vital importance in biology and medicine. Radical reactions are ubiquitous in living things, because radicals are produced in the normal course of metabolism. Radicals are all *around* us, too, because molecular oxygen ( $\cdot\ddot{\text{O}}-\ddot{\text{O}}\cdot$ ) is itself a diradical (Section 10.11A). Another radical, one that was never suspected to be very important in normal cell function, is nitric oxide ( $\cdot\ddot{\text{N}}=\ddot{\text{O}}\cdot$ ). It has been shown, however, that nitric oxide plays a remarkable number of important roles in living systems. Although in its free form nitric oxide is a relatively unstable and potentially toxic gas, in biological systems it is involved in blood pressure regulation and blood clotting, neurotransmission, and the immune response against tumor cells. Nitric oxide has taken the spotlight as one of nature's most surprising yet ubiquitous chemical messengers. Pharmaceuticals such as Cialis®, Levitra®, and Viagra® prolong the effect of nitric oxide signaling in a vital biochemical pathway (Section 10.11B). Models of nitric oxide and Cialis® are shown above.

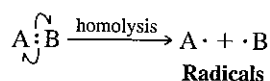
Because radicals are highly reactive, however, they are also capable of randomly damaging all components of the body. Accordingly, they are believed to be important in the "aging process" in the sense that radicals are involved in the development of the chronic diseases that are life limiting. For example, there is growing evidence that radical reactions are important in the development of cancers and in the development of atherosclerosis. A naturally occurring radical called superoxide ( $\text{O}_2^{\cdot-}$ ) paradoxically is associated with both the immune response against pathogens and at the same time the development of certain diseases. An enzyme called superoxide dismutase regulates the level of superoxide in the body (Section 10.11A). Radicals in cigarette smoke have been implicated in inactivation of an antiprotease in the lungs, an inactivation that leads to the development of emphysema. Calicheamicin, a natural product from bacteria, has clinical potential for fighting tumor cells by cleaving their DNA by a radical reaction (Section 10.11C).

Radical reactions are important in many industrial processes as well. We shall learn in Section 10.10 how radical reactions are used to produce a whole class of useful "plastics" or *polymers* such as polyethylene, Teflon, and polystyrene. (Additional information is provided in Special Topic A, which follows this chapter.) Radical reactions are also central to the "cracking" process by which gasoline and other fuels are made from petroleum. Moreover, the combustion process by which these fuels are converted to energy involves radical reactions (Section 10.11C).

## 10.1 Introduction

So far almost all of the reactions whose mechanisms we have studied have been **ionic reactions**. Ionic reactions are those in which covalent bonds break **heterolytically** and in which ions are involved as reactants, intermediates, or products.

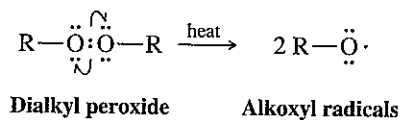
Another broad category of reactions has mechanisms that involve **homolysis** of covalent bonds with the production of intermediates possessing unpaired electrons called **radicals** (or **free radicals**):



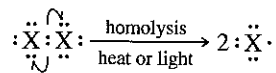
This simple example illustrates the way we use **single-barbed** curved arrows to show the movement of a **single electron** (not of an electron pair as we have done earlier). In this instance, each group, A and B, comes away with one of the electrons of the covalent bond that joined them.

### 10.1A Production of Radicals

Energy must be supplied to cause homolysis of covalent bonds (Section 10.2), and this is usually done in two ways: by heating or by irradiation with light. For example, compounds with an oxygen–oxygen single bond, called **peroxides**, undergo homolysis readily when heated, because the oxygen–oxygen bond is weak. The products are two radicals, called alkoxy radicals:



Halogen molecules ( $\text{X}_2$ ) also contain a relatively weak bond. As we shall soon see, halogens undergo homolysis readily when heated or when irradiated with light of a wavelength that can be absorbed by the halogen molecule:



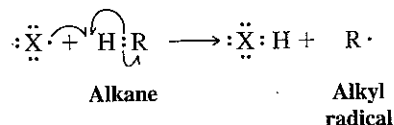
The products of this homolysis are halogen atoms, and because halogen atoms contain an unpaired electron, they are radicals.

### 10.1B Reactions of Radicals

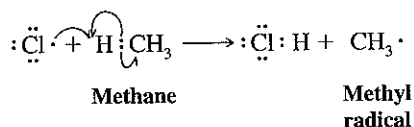
Almost all small radicals are short-lived, highly reactive species. When they collide with other molecules, they tend to react in a way that leads to pairing of their unpaired electron. One way they can do this is by abstracting an atom from another molecule. For example, a halogen atom may abstract a hydrogen atom from an alkane. This **hydrogen abstraction**

gives the halogen atom an electron (from the hydrogen atom) to pair with its unpaired electron. Notice, however, that the other product of this abstraction is *another radical*, in this case, an alkyl radical,  $R\cdot$ :

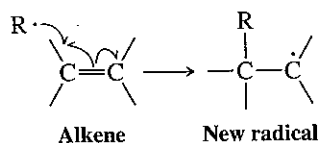
**General Reaction**



**Specific Example**

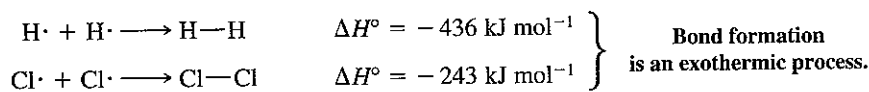


This behavior is characteristic of **radical reactions**. Consider another example, one that shows another way in which radicals can react: They can combine with a compound containing a multiple bond to produce a new, larger radical. (We shall study reactions of this type in Section 10.10.)



## 10.2 Homolytic Bond Dissociation Energies

When atoms combine to form molecules, energy is released as covalent bonds form. The molecules of the products have lower enthalpy than the separate atoms. When hydrogen atoms combine to form hydrogen molecules, for example, the reaction is *exothermic*; it evolves 436 kJ of heat for every mole of hydrogen that is produced. Similarly, when chlorine atoms combine to form chlorine molecules, the reaction evolves 243 kJ mol<sup>-1</sup> of chlorine produced:



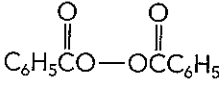
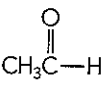
To break covalent bonds, energy must be supplied. Reactions in which only bond breaking occurs are always endothermic. The energy required to break the covalent bonds of hydrogen or chlorine homolytically is exactly equal to that evolved when the separate atoms combine to form molecules. In the bond cleavage reaction, however,  $\Delta H^\circ$  is positive:



The energies required to break covalent bonds homolytically have been determined experimentally for many types of covalent bonds. These energies are called **homolytic bond dissociation energies**, and they are usually abbreviated by the symbol  $DH^\circ$ . The homolytic bond dissociation energies of hydrogen and chlorine, for example, might be written in the following way:



**TABLE 10.1** Single-Bond Homolytic Dissociation Energies  $DH^\circ$  at 25°C<sup>a</sup>

$A:B \longrightarrow A\cdot + B\cdot$			
Bond Broken (shown in red)	kJ $\text{mol}^{-1}$	Bond Broken (shown in red)	kJ $\text{mol}^{-1}$
H—H	436	(CH <sub>3</sub> ) <sub>2</sub> CH—Br	298
D—D	443	(CH <sub>3</sub> ) <sub>2</sub> CH—I	222
F—F	159	(CH <sub>3</sub> ) <sub>2</sub> CH—OH	402
Cl—Cl	243	(CH <sub>3</sub> ) <sub>2</sub> CH—OCH <sub>3</sub>	359
Br—Br	193	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> —H	422
I—I	151	(CH <sub>3</sub> ) <sub>3</sub> C—H	400
H—F	570	(CH <sub>3</sub> ) <sub>3</sub> C—Cl	349
H—Cl	432	(CH <sub>3</sub> ) <sub>3</sub> C—Br	292
H—Br	366	(CH <sub>3</sub> ) <sub>3</sub> C—I	227
H—I	298	(CH <sub>3</sub> ) <sub>3</sub> C—OH	400
CH <sub>3</sub> —H	440	(CH <sub>3</sub> ) <sub>3</sub> C—OCH <sub>3</sub>	348
CH <sub>3</sub> —F	461	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> —H	375
CH <sub>3</sub> —Cl	352	CH <sub>2</sub> =CHCH <sub>2</sub> —H	369
CH <sub>3</sub> —Br	293	CH <sub>2</sub> =CH—H	465
CH <sub>3</sub> —I	240	C <sub>6</sub> H <sub>5</sub> —H	474
CH <sub>3</sub> —OH	387	HC≡C—H	547
CH <sub>3</sub> —OCH <sub>3</sub>	348	CH <sub>3</sub> —CH <sub>3</sub>	378
CH <sub>3</sub> CH <sub>2</sub> —H	421	CH <sub>3</sub> CH <sub>2</sub> —CH <sub>3</sub>	371
CH <sub>3</sub> CH <sub>2</sub> —F	444	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —CH <sub>3</sub>	374
CH <sub>3</sub> CH <sub>2</sub> —Cl	353	CH <sub>3</sub> CH <sub>2</sub> —CH <sub>2</sub> CH <sub>3</sub>	343
CH <sub>3</sub> CH <sub>2</sub> —Br	295	(CH <sub>3</sub> ) <sub>2</sub> CH—CH <sub>3</sub>	371
CH <sub>3</sub> CH <sub>2</sub> —I	233	(CH <sub>3</sub> ) <sub>3</sub> C—CH <sub>3</sub>	363
CH <sub>3</sub> CH <sub>2</sub> —OH	393	HO—H	499
CH <sub>3</sub> CH <sub>2</sub> —OCH <sub>3</sub>	352	HOO—H	356
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —H	423	HO—OH	214
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —F	444	(CH <sub>3</sub> ) <sub>3</sub> CO—OC(CH <sub>3</sub> ) <sub>3</sub>	157
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —Cl	354		139
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —Br	294	CH <sub>3</sub> CH <sub>2</sub> O—OCH <sub>3</sub>	184
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —I	239	CH <sub>3</sub> CH <sub>2</sub> O—H	431
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —OH	395		364
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> —OCH <sub>3</sub>	355		
(CH <sub>3</sub> ) <sub>2</sub> CH—H	413		
(CH <sub>3</sub> ) <sub>2</sub> CH—F	439		
(CH <sub>3</sub> ) <sub>2</sub> CH—Cl	355		

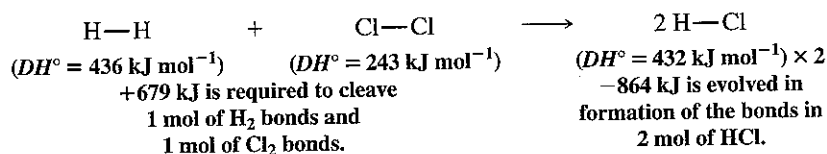
<sup>a</sup>Data compiled from the *National Institute of Standards (NIST) Standard Reference Database Number 69*, July 2001 Release, accessed via *NIST Chemistry WebBook* (<http://webbook.nist.gov/chemistry/>). Copyright 2000. From *CRC Handbook of Chemistry and Physics, Updated 3rd Electronic Edition*; Lide, David R., ed. Reproduced by permission of Routledge/Taylor & Francis Group, LLC.  $DH^\circ$  values were obtained directly or calculated from heat of formation ( $H_f^\circ$ ) data using the equation  $DH^\circ[A-B] = H_f[A\cdot] + H_f[B\cdot] - H_f[A-B]$ .

The homolytic bond dissociation energies of a variety of covalent bonds are listed in Table 10.1 above.

## 10.2A Homolytic Bond Dissociation Energies and Heats of Reaction

Bond dissociation energies have, as we shall see, a variety of uses. They can be used, for example, to calculate the enthalpy change ( $\Delta H^\circ$ ) for a reaction. To make such a calculation (see following reaction), we must remember that **for bond breaking  $\Delta H^\circ$  is positive and for bond formation  $\Delta H^\circ$  is negative**. Let us consider, for example, the reaction of

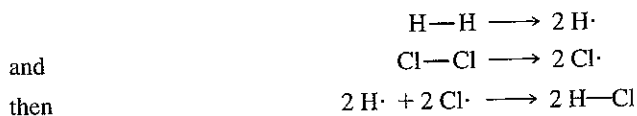
hydrogen and chlorine to produce 2 mol of hydrogen chloride. From Table 10.1 we get the following values of  $DH^\circ$ :



Overall, the reaction of 1 mol of  $\text{H}_2$  and 1 mol of  $\text{Cl}_2$  to form 2 mol of  $\text{HCl}$  is exothermic:

$$\Delta H^\circ = (-864 \text{ kJ} + 679 \text{ kJ}) = -185 \text{ kJ} \quad \text{for 2 mol HCl produced}$$

For the purpose of our calculation, we have assumed a particular pathway, which amounts to



This is not the way the reaction actually occurs. Nevertheless, the heat of reaction,  $\Delta H^\circ$ , is a thermodynamic quantity that is dependent *only* on the initial and final states of the reacting molecules. Here,  $\Delta H^\circ$  is independent of the path followed (Hess's law), and, for this reason, our calculation is valid.

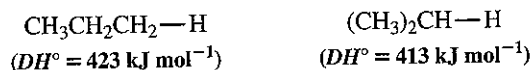
Calculate the heat of reaction,  $\Delta H^\circ$ , for the following reactions:

### Review Problem 10.1

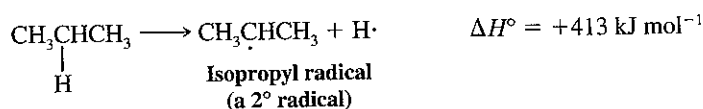
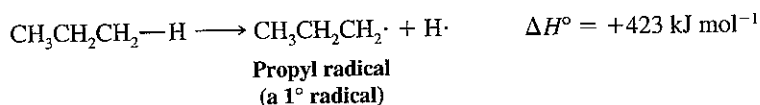
- (a)  $\text{H}_2 + \text{F}_2 \longrightarrow 2 \text{HF}$   
 (b)  $\text{CH}_4 + \text{F}_2 \longrightarrow \text{CH}_3\text{F} + \text{HF}$   
 (c)  $\text{CH}_4 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{HCl}$   
 (d)  $\text{CH}_4 + \text{Br}_2 \longrightarrow \text{CH}_3\text{Br} + \text{HBr}$   
 (e)  $\text{CH}_4 + \text{I}_2 \longrightarrow \text{CH}_3\text{I} + \text{HI}$   
 (f)  $\text{CH}_3\text{CH}_3 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{HCl}$   
 (g)  $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{CHClCH}_3 + \text{HCl}$   
 (h)  $(\text{CH}_3)_3\text{CH} + \text{Cl}_2 \longrightarrow (\text{CH}_3)_3\text{CCl} + \text{HCl}$

## 10.2B Homolytic Bond Dissociation Energies and the Relative Stabilities of Radicals

Homolytic bond dissociation energies also provide us with a convenient way to estimate the relative stabilities of radicals. If we examine the data given in Table 10.1, we find the following values of  $DH^\circ$  for the primary and secondary C—H bonds of propane:



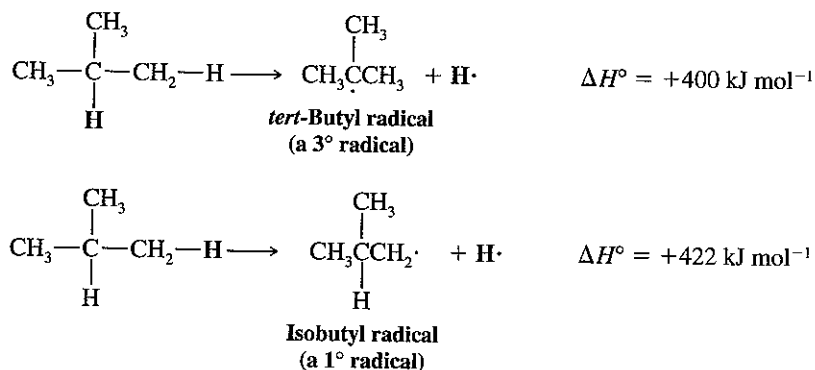
This means that for the reaction in which the designated C—H bonds are broken homolytically, the values of  $\Delta H^\circ$  are those given here.



These reactions resemble each other in two respects: They both begin with the same alkane (propane), and they both produce an alkyl radical and a hydrogen atom. They differ, however, in the amount of energy required and in the type of carbon radical produced. These two differences are related to each other.

Alkyl radicals are classified as being 1°, 2°, or 3° on the basis of the carbon atom that has the unpaired electron. More energy must be supplied to produce a primary alkyl radical (the propyl radical) from propane than is required to produce a secondary carbon radical (the isopropyl radical) from the same compound. This must mean that the primary radical has absorbed more energy and thus has greater *potential energy*. Because the relative stability of a chemical species is inversely related to its potential energy, the secondary radical must be the *more stable* radical (Fig. 10.1a). In fact, the secondary isopropyl radical is more stable than the primary propyl radical by 10 kJ mol<sup>-1</sup>.

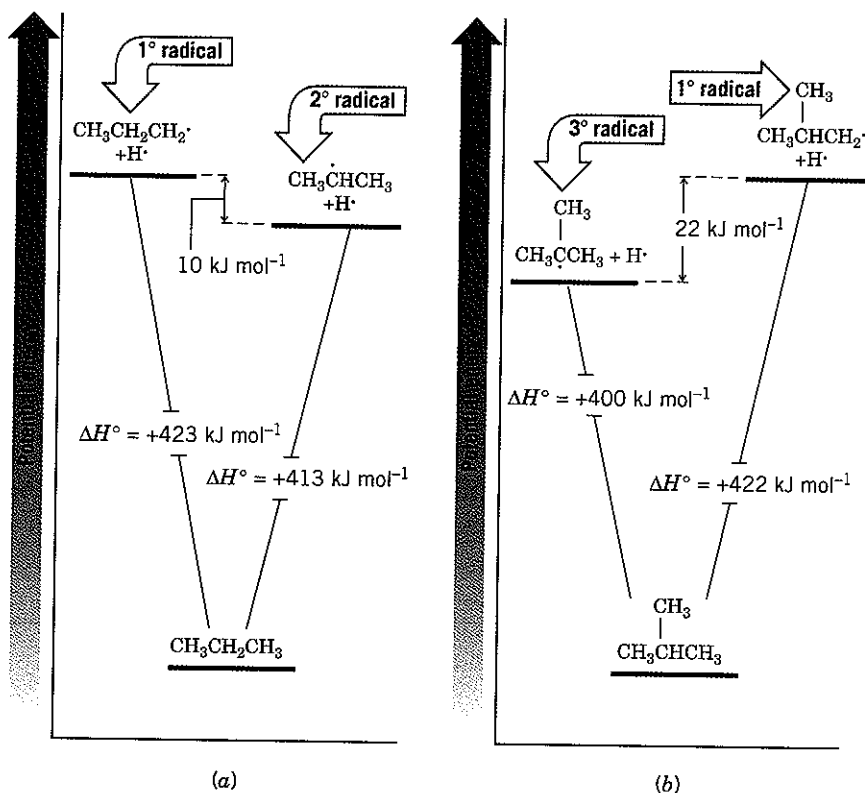
We can use the data in Table 10.1 to make a similar comparison of the *tert*-butyl radical (a 3° radical) and the isobutyl radical (a 1° radical) relative to isobutane:



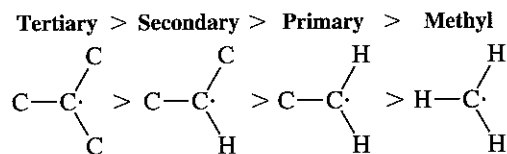
Knowing the relative stability of radicals is important for predicting reactions.

Here we find (Fig. 10.1b) that the difference in stability of the two radicals is even larger. The tertiary radical is more stable than the primary radical by 22 kJ mol<sup>-1</sup>.

**FIGURE 10.1** (a) Comparison of the potential energies of the propyl radical (+H·) and the isopropyl radical (+H·) relative to propane. The isopropyl radical (a 2° radical) is more stable than the 1° radical by 10 kJ mol<sup>-1</sup>. (b) Comparison of the potential energies of the *tert*-butyl radical (+H·) and the isobutyl radical (+H·) relative to isobutane. The 3° radical is more stable than the 1° radical by 22 kJ mol<sup>-1</sup>.



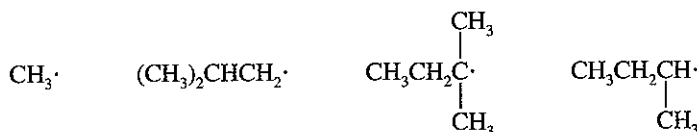
The kind of pattern that we find in these examples is found with alkyl radicals generally; overall, their relative stabilities are the following:



The order of stability of alkyl radicals is the same as for carbocations (Section 6.11B), and the reasons are similar. Although alkyl radicals are uncharged, the carbon that bears the odd electron is *electron deficient*. Therefore, alkyl groups attached to this carbon provide a stabilizing effect through hyperconjugation, and the more alkyl groups bonded to it, the more stable the radical is.

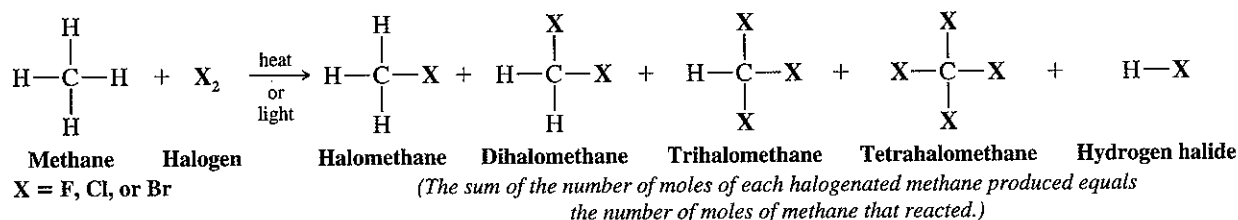
List the following radicals in order of decreasing stability:

Review Problem 10.2

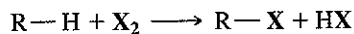


## 10.3 The Reactions of Alkanes with Halogens

Methane, ethane, and other alkanes react with the first three members of the halogen family: fluorine, chlorine, and bromine. Alkanes do not react appreciably with iodine. With methane the reaction produces a mixture of halomethanes and a hydrogen halide:



The reaction of an alkane with a halogen is a **substitution reaction**, called **halogenation**. The general reaction to produce a monohaloalkane can be written as follows:



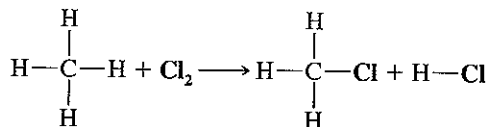
In these reactions a halogen atom replaces one or more of the hydrogen atoms of the alkane.

### 10.3A Multiple Substitution Reactions versus Selectivity

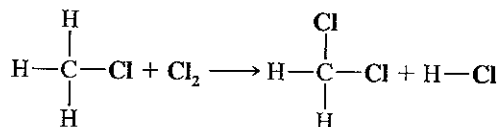
One complicating characteristic of alkane halogenations is that multiple substitution reactions almost always occur. As we saw above, the halogenation of methane produces a mixture of monohalomethane, dihalomethane, trihalomethane, and tetrahalomethane. This happens because all hydrogen atoms attached to carbon are capable of reacting with fluorine, chlorine, or bromine.

Let us consider the reaction that takes place between chlorine and methane as an example. If we mix methane and chlorine (both substances are gases at room temperature) and then either heat the mixture or irradiate it with light, a reaction begins to occur vigorously. At the

outset, the only compounds that are present in the mixture are chlorine and methane, and the only reaction that can take place is one that produces chloromethane and hydrogen chloride:



As the reaction progresses, however, the concentration of chloromethane in the mixture increases, and a second substitution reaction begins to occur. Chloromethane reacts with chlorine to produce dichloromethane:



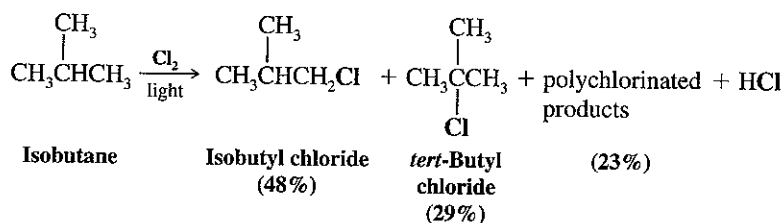
The dichloromethane produced can then react to form trichloromethane, and trichloromethane, as it accumulates in the mixture, can react with chlorine to produce tetrachloromethane. Each time a substitution of —Cl for —H takes place, a molecule of H—Cl is produced.

### Study Problem

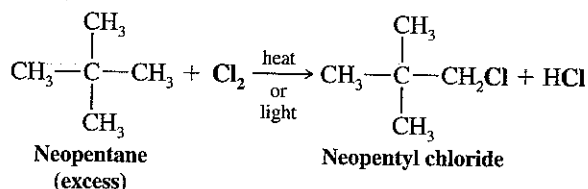
If the goal of a synthesis is to prepare chloromethane ( $\text{CH}_3\text{Cl}$ ), its formation can be maximized and the formation of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  minimized by using a large excess of methane in the reaction mixture. Explain why this is possible.

**ANSWER** The use of a large excess of methane maximizes the probability that chlorine will attack methane molecules because the concentration of methane in the mixture will always be relatively large. It also minimizes the probability that chlorine will attack molecules of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$ , because their concentrations will always be relatively small. After the reaction is over, the unreacted excess methane can be recovered and recycled.

**Chlorination** of most higher alkanes gives a mixture of isomeric monochloro products as well as more highly halogenated compounds. Chlorine is relatively *unselective*; it does not discriminate greatly among the different types of hydrogen atoms (primary, secondary, and tertiary) in an alkane. An example is the light-promoted chlorination of isobutane:



Because alkane chlorinations usually yield a complex mixture of products, they are not generally useful as synthetic methods when our goal is the preparation of a specific alkyl chloride. An exception is the halogenation of an alkane (or cycloalkane) whose hydrogen atoms are *all equivalent*. [Equivalent hydrogen atoms are defined as those which on replacement by some other group (e.g., chlorine) yield the same compound.] Neopentane, for example, can form only one monohalogenation product, and the use of a large excess of neopentane minimizes polychlorination:



Bromine is generally less reactive toward alkanes than chlorine, and bromine is *more selective* in the site of attack when it does react. We shall examine this topic further in Section 10.6A.



Chlorination is unselective.

## 10.4 Chlorination of Methane: Mechanism of Reaction

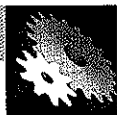
The *halogenation* reactions of alkanes take place by a radical mechanism. Let us begin our study of them by examining a simple example of an alkane halogenation—the reaction of methane with chlorine that takes place in the gas phase:



Several important experimental observations can be made about this reaction:

- The reaction is promoted by heat or light.** At room temperature methane and chlorine do not react at a perceptible rate as long as the mixture is kept away from light. Methane and chlorine do react, however, at room temperature if the gaseous reaction mixture is irradiated with UV light at a wavelength absorbed by  $\text{Cl}_2$ , and they react in the dark if the gaseous mixture is heated to temperatures greater than  $100^\circ\text{C}$ .
- The light-promoted reaction is highly efficient.** A relatively small number of light photons permits the formation of relatively large amounts of chlorinated product.

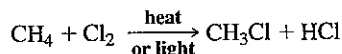
A mechanism that is consistent with these observations has several steps, shown below. The first step involves the fragmentation of a chlorine molecule, by heat or light, into two chlorine atoms. The second step involves hydrogen abstraction by a chlorine atom.



### A MECHANISM FOR THE REACTION

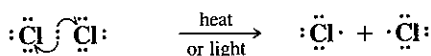
#### Radical Chlorination of Methane

#### REACTION



#### MECHANISM

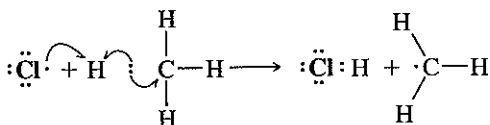
Step 1



Under the influence of heat or light a molecule of chlorine dissociates; each atom takes one of the bonding electrons.

This step produces two highly reactive chlorine atoms.

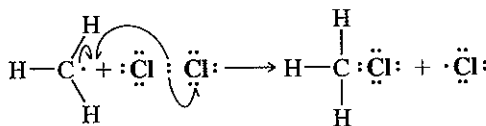
Step 2



A chlorine atom abstracts a hydrogen atom from a methane molecule.

This step produces a molecule of hydrogen chloride and a methyl radical.

Step 3



A methyl radical abstracts a chlorine atom from a chlorine molecule.

This step produces a molecule of methyl chloride and a chlorine atom. The chlorine atom can now cause a repetition of step 2.



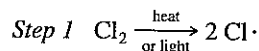
Remember: These conventions are used in illustrating reaction mechanisms in this text.

- Arrows  $\curvearrowright$  or  $\curvearrowleft$  always show the direction of movement of electrons.
- Single-barbed arrows  $\curvearrowright$  show the attack (or movement) of an unpaired electron.
- Double-barbed arrows  $\curvearrowright$  show the attack (or movement) of an electron pair.

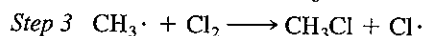
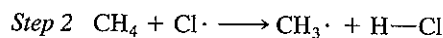
In step 3 the highly reactive methyl radical reacts with a chlorine molecule by abstracting a chlorine atom. This results in the formation of a molecule of chloromethane (one of the ultimate products of the reaction) and a *chlorine atom*. The latter product is particularly significant, for the chlorine atom formed in step 3 can attack another methane molecule and cause a repetition of step 2. Then, step 3 is repeated, and so forth, for hundreds or thousands of times. (With each repetition of step 3 a molecule of chloromethane is produced.) This type of sequential, stepwise mechanism, in which each step generates the reactive intermediate that causes the next cycle of the reaction to occur, is called a **chain reaction**.

Step 1 is called the **chain-initiating step**. In the chain-initiating step *radicals are created*. Steps 2 and 3 are called **chain-propagating steps**. In chain-propagating steps *one radical generates another*.

#### Chain Initiation



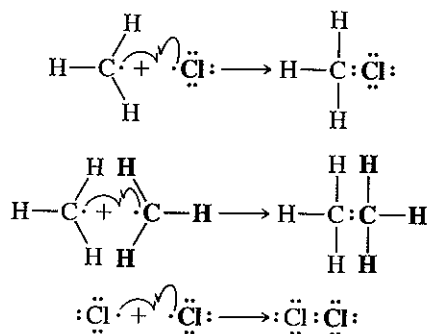
#### Chain Propagation



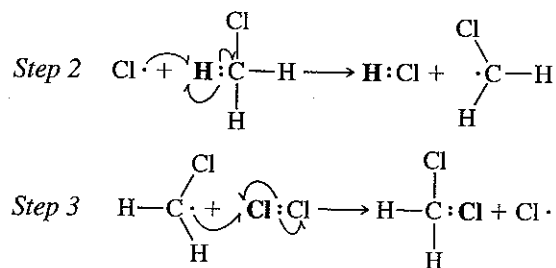
The chain nature of the reaction accounts for the observation that the light-promoted reaction is highly efficient. The presence of a relatively few atoms of chlorine at any given moment is all that is needed to cause the formation of many thousands of molecules of chloromethane.

What causes the chains to terminate? Why does one photon of light not promote the chlorination of all of the methane molecules present? We know that this does not happen because we find that, at low temperatures, continuous irradiation is required or the reaction slows and stops. The answer to these questions is the existence of **chain-terminating steps**: steps that happen infrequently but occur often enough to *use up one or both of the reactive intermediates*. The continuous replacement of intermediates used up by chain-terminating steps requires continuous irradiation. Plausible chain-terminating steps are as follows.

#### Chain Termination



Our radical mechanism also explains how the reaction of methane with chlorine produces the more highly halogenated products,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$  (as well as additional  $\text{HCl}$ ). As the reaction progresses, chloromethane ( $\text{CH}_3\text{Cl}$ ) accumulates in the mixture and its hydrogen atoms, too, are susceptible to abstraction by chlorine. Thus chloromethyl radicals are produced that lead to dichloromethane ( $\text{CH}_2\text{Cl}_2$ ).



Then step 2 is repeated, then step 3 is repeated, and so on. Each repetition of step 2 yields a molecule of HCl, and each repetition of step 3 yields a molecule of CH<sub>2</sub>Cl<sub>2</sub>.

Suggest a method for separating the mixture of CH<sub>4</sub>, CH<sub>3</sub>Cl, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and CCl<sub>4</sub> that is formed when methane is chlorinated. (You may want to consult a handbook.) What analytical method could be used to separate this mixture and give structural information about each component? How would the molecular ion peaks in their respective mass spectra differ on the basis of the number of chlorines (remember that chlorine has two predominant isotopes, <sup>35</sup>Cl and <sup>37</sup>Cl)?

**Review Problem 10.3**

When methane is chlorinated, among the products found are traces of chloroethane. How is it formed? Of what significance is its formation?

**Review Problem 10.4**

If our goal is to synthesize CCl<sub>4</sub> in maximum yield, this can be accomplished by using a large excess of chlorine. Explain.

**Review Problem 10.5**

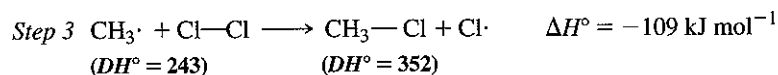
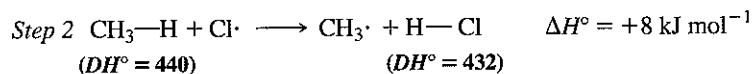
## 10.5 Chlorination of Methane: Energy Changes

We saw in Section 10.2A that we can calculate the overall heat of reaction from bond dissociation energies. We can also calculate the heat of reaction for each individual step of a mechanism:

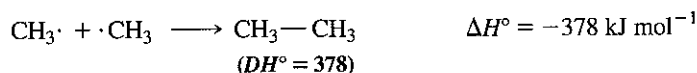
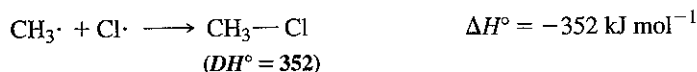
### Chain Initiation



### Chain Propagation



### Chain Termination



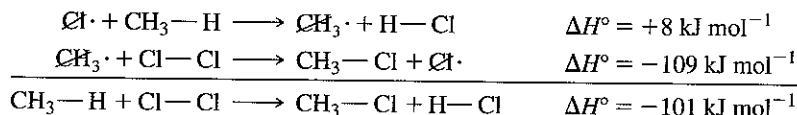
In the chain-initiating step only one bond is broken—the bond between two chlorine atoms—and no bonds are formed. The heat of reaction for this step is simply the bond dissociation energy for a chlorine molecule, and it is highly endothermic.

In the chain-terminating steps bonds are formed, but no bonds are broken. As a result, all of the chain-terminating steps are highly exothermic.

Each of the chain-propagating steps, on the other hand, requires the breaking of one bond and the formation of another. The value of  $\Delta H^\circ$  for each of these steps is the difference between the bond dissociation energy of the bond that is broken and the bond dissociation energy for the bond that is formed. The first chain-propagating step is slightly endothermic ( $\Delta H^\circ = +8 \text{ kJ mol}^{-1}$ ), but the second is exothermic by a large amount ( $\Delta H^\circ = -109 \text{ kJ mol}^{-1}$ ).

**Review Problem 10.6** Assuming the same mechanism applies, calculate  $\Delta H^\circ$  for the chain-initiating, chain-propagating, and chain-terminating steps involved in the fluorination of methane.

The addition of the chain-propagating steps yields the overall equation for the chlorination of methane:



and the addition of the values of  $\Delta H^\circ$  for the individual chain-propagating steps yields the overall value of  $\Delta H^\circ$  for the reaction.

**Review Problem 10.7** Show how you can use the chain-propagating steps (see Review Problem 10.6) to calculate the overall value of  $\Delta H^\circ$  for the fluorination of methane.

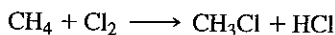
### 10.5A The Overall Free-Energy Change

For many reactions the entropy change is so small that the term  $T\Delta S^\circ$  in the expression

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

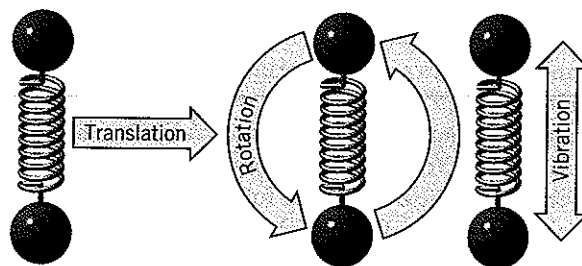
is almost zero, and  $\Delta G^\circ$  is approximately equal to  $\Delta H^\circ$ . This happens when the reaction is one in which the relative order of reactants and products is about the same. Recall (Section 3.9) that entropy measures the relative disorder or randomness of a system. For a chemical system the relative disorder of the molecules can be related to the number of *degrees of freedom* available to the molecules and their constituent atoms. Degrees of freedom are associated with ways in which *movement or changes in relative position can occur*. Molecules have three sorts of degrees of freedom: translational degrees of freedom associated with movements of the whole molecule through space, rotational degrees of freedom associated with the tumbling motions of the molecule, and vibrational degrees of freedom associated with the stretching and bending motion of atoms about the bonds that connect them (Fig. 10.2). If the atoms of the products of a reaction have more degrees of freedom available than they did as reactants, the entropy change ( $\Delta S^\circ$ ) for the reaction will be positive. If, on the other hand, the atoms of the products are more constrained (have fewer degrees of freedom) than the reactants, a negative  $\Delta S^\circ$  results.

Consider the reaction of methane with chlorine:

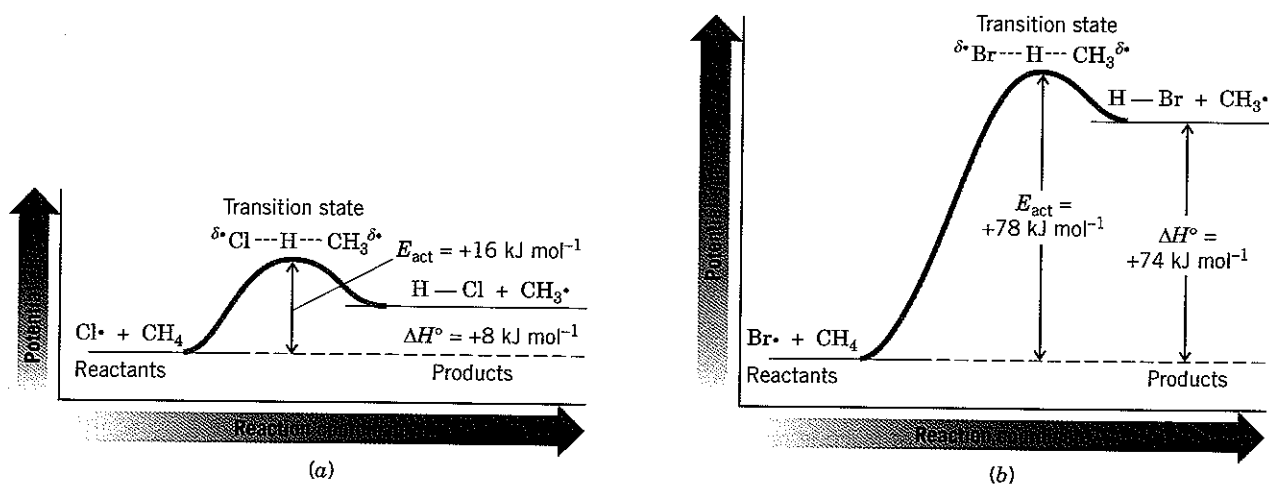


Here, 2 mol of the products are formed from the same number of moles of the reactants. Thus the number of translational degrees of freedom available to products and reactants is the same. Furthermore,  $\text{CH}_3\text{Cl}$  is a tetrahedral molecule like  $\text{CH}_4$ , and  $\text{HCl}$  is a

**FIGURE 10.2** Translational, rotational, and vibrational degrees of freedom for a simple diatomic molecule.







**FIGURE 10.3** Potential energy diagrams for (a) the reaction of a chlorine atom with methane and (b) the reaction of a bromine atom with methane.

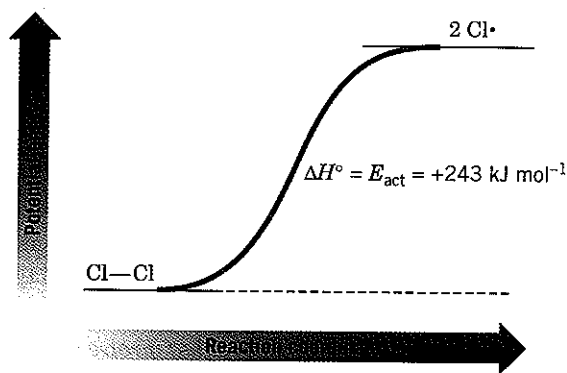
potential energy diagrams in Fig. 10.3. In each case the path from reactants to products is from a lower energy plateau to a higher one. In each case the intervening energy hill is higher still, and since the energy of activation is the vertical (energy) distance between the plateau of reactants and the top of this hill, the energy of activation exceeds the heat of reaction.

3. **The energy of activation of a gas-phase reaction where bonds are broken homolytically but no bonds are formed is equal to  $\Delta H^\circ$ .**\* An example of this type of reaction is the chain-initiating step in the chlorination of methane—the dissociation of chlorine molecules into chlorine atoms:



The potential energy diagram for this reaction is shown in Fig. 10.4.

**FIGURE 10.4** Potential energy diagram for the dissociation of a chlorine molecule into chlorine atoms.



4. **The energy of activation for a gas-phase reaction in which small radicals combine to form molecules is usually zero.** In reactions of this type the problem of nonsimultaneous bond formation and bond rupture does not exist; only one process occurs: that of bond formation. All of the chain-terminating steps in the chlorination of methane fall into this category. An example is the combination of two methyl radicals to form a molecule of ethane:

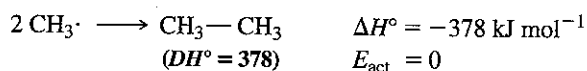
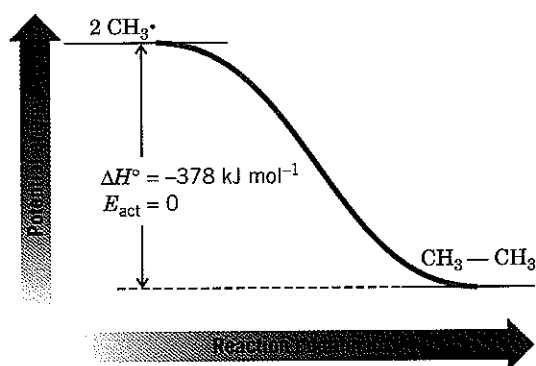


Figure 10.5 illustrates the potential energy changes that occur in this reaction.

\*This rule applies only to radical reactions taking place in the gas phase. It does not apply to reactions taking place in solution, especially where ions are involved, because solvation energies are also important.



**FIGURE 10.5** Potential energy diagram for the combination of two methyl radicals to form a molecule of ethane.

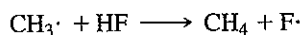
When pentane is heated to a very high temperature, radical reactions take place that produce (among other products) methane, ethane, propane, and butane. This type of change is called **thermal cracking**. Among the reactions that take place are the following:

- (1)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \longrightarrow \text{CH}_3\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\cdot$
- (2)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\cdot$
- (3)  $\text{CH}_3\cdot + \text{CH}_3\cdot \longrightarrow \text{CH}_3\text{CH}_3$
- (4)  $\text{CH}_3\cdot + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \longrightarrow \text{CH}_4 + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$
- (5)  $\text{CH}_3\cdot + \text{CH}_3\text{CH}_2\cdot \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_3$
- (6)  $\text{CH}_3\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\cdot \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

- (a) For which of these reactions would you expect  $E_{\text{act}}$  to equal zero?
- (b) To be greater than zero?
- (c) To equal  $\Delta H^\circ$ ?

### Review Problem 10.8

The energy of activation for the first chain-propagating step in the fluorination of methane (cf. Review Problem 10.6) is known to be  $+5.0 \text{ kJ mol}^{-1}$ . The energy of activation for the second chain-propagating step is known to be very small. Assuming that it is  $+1.0 \text{ kcal mol}^{-1}$ , then (a) and (b) sketch potential energy diagrams for these two chain-propagating steps. Sketch a potential energy diagram for (c) the chain-initiating step in the fluorination of methane and (d) the chain-terminating step that produces  $\text{CH}_3\text{F}$ . (e) Sketch a potential energy diagram for the following reaction:



### Review Problem 10.9

## 10.5C Reaction of Methane with Other Halogens

The *reactivity* of one substance toward another is measured by the *rate* at which the two substances react. A reagent that reacts very rapidly with a particular substance is said to be highly reactive toward that substance. One that reacts slowly or not at all under the same experimental conditions (e.g., concentration, pressure, and temperature) is said to have a low relative reactivity or to be unreactive. The reactions of the halogens (fluorine, chlorine, bromine, and iodine) with methane show a wide spread of relative reactivities. Fluorine is most reactive—so reactive, in fact, that without special precautions mixtures of fluorine and methane explode. Chlorine is the next most reactive. However, the chlorination of methane is easily controlled by the judicious control of heat and light. Bromine is much less reactive toward methane than chlorine, and iodine is so unreactive that for all practical purposes we can say that no reaction takes place.

If the mechanisms for fluorination, bromination, and iodination of methane are the same as for its chlorination, we can explain the wide variation in reactivity of the halogens by a careful examination of  $\Delta H^\circ$  and  $E_{\text{act}}$  for each step.

## FLUORINATION

	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$E_{\text{act}}$ (kJ mol <sup>-1</sup> )
<i>Chain Initiation</i>		
$\text{F}_2 \longrightarrow 2 \text{F}\cdot$	+159	+159
<i>Chain Propagation</i>		
$\text{F}\cdot + \text{CH}_4 \longrightarrow \text{HF} + \text{CH}_3\cdot$	-130	+5.0
$\text{CH}_3\cdot + \text{F}_2 \longrightarrow \text{CH}_3\text{F} + \text{F}\cdot$	<u>-302</u>	Small
Overall $\Delta H^\circ = -432$		

The chain-initiating step in **fluorination** is highly endothermic and thus has a high energy of activation.

If we did not know otherwise, we might carelessly conclude from the energy of activation of the chain-initiating step alone that fluorine would be quite unreactive toward methane. (If we then proceeded to try the reaction, as a result of this careless assessment, the results would be literally disastrous.) We know, however, that the chain-initiating step occurs only infrequently relative to the chain-propagating steps. One initiating step is able to produce thousands of fluorination reactions. As a result, the high activation energy for this step is not an impediment to the reaction.

Chain-propagating steps, by contrast, cannot afford to have high energies of activation. If they do, the highly reactive intermediates are consumed by chain-terminating steps before the chains progress very far. Both of the chain-propagating steps in fluorination have very small energies of activation. This allows a relatively large fraction of energetically favorable collisions even at room temperature. Moreover, the overall heat of reaction,  $\Delta H^\circ$ , is very large. This means that as the reaction occurs, a large quantity of heat is evolved. This heat may accumulate in the mixture faster than it dissipates to the surroundings, causing the temperature to rise and with it a rapid increase in the frequency of additional chain-initiating steps that would generate additional chains. These two factors, the low energy of activation for the chain-propagating steps and the large overall heat of reaction, account for the high reactivity of fluorine toward methane. (Fluorination reactions can be controlled. This is usually accomplished by diluting both the hydrocarbon and the fluorine with an inert gas such as helium before bringing them together. The reaction is also carried out in a reactor packed with copper shot. The copper, by absorbing the heat produced, moderates the reaction.)

## CHLORINATION

	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$E_{\text{act}}$ (kJ mol <sup>-1</sup> )
<i>Chain Initiation</i>		
$\text{Cl}_2 \longrightarrow 2 \text{Cl}\cdot$	+243	+243
<i>Chain Propagation</i>		
$\text{Cl}\cdot + \text{CH}_4 \longrightarrow \text{HCl} + \text{CH}_3\cdot$	+8	+16
$\text{CH}_3\cdot + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$	<u>-109</u>	Small
Overall $\Delta H^\circ = -101$		

The higher energy of activation of the first chain-propagating step (the hydrogen abstraction step) in the chlorination of methane (+16 kJ mol<sup>-1</sup>), compared to the lower energy of activation (+5.0 kJ mol<sup>-1</sup>) in the fluorination, partly explains the lower reactivity of chlorine. The greater energy required to break the chlorine-chlorine bond in the initiating step (243 kJ mol<sup>-1</sup> for Cl<sub>2</sub> versus 159 kJ mol<sup>-1</sup> for F<sub>2</sub>) has some effect, too. However, the much greater overall heat of reaction in fluorination probably plays the greatest role in accounting for the much greater reactivity of fluorine.

## BROMINATION

	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$E_{\text{act}}$ (kJ mol <sup>-1</sup> )
<i>Chain Initiation</i>		
$\text{Br}_2 \longrightarrow 2 \text{Br}\cdot$	+193	+193
<i>Chain Propagation</i>		
$\text{Br}\cdot + \text{CH}_4 \longrightarrow \text{HBr} + \text{CH}_3\cdot$	+74	+78
$\text{CH}_3\cdot + \text{Br}_2 \longrightarrow \text{CH}_3\text{Br} + \text{Br}\cdot$	<u>-100</u>	Small
Overall $\Delta H^\circ = -26$		

In contrast to chlorination, the hydrogen atom abstraction step in **bromination** has a very high energy of activation ( $E_{\text{act}} = 78 \text{ kJ mol}^{-1}$ ). This means that only a very tiny fraction of all of the collisions between bromine atoms and methane molecules will be energetically effective even at a temperature of  $300^\circ\text{C}$ . Bromine, as a result, is much less reactive toward methane than chlorine, even though the net reaction is slightly exothermic.

#### IODINATION

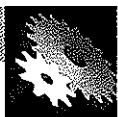
	$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$E_{\text{act}}$ (kJ mol <sup>-1</sup> )
<i>Chain Initiation</i>		
$\text{I}_2 \longrightarrow 2 \text{I}\cdot$	+151	+151
<i>Chain Propagation</i>		
$\text{I}\cdot + \text{CH}_4 \longrightarrow \text{HI} + \text{CH}_3\cdot$	+142	+140
$\text{CH}_3\cdot + \text{I}_2 \longrightarrow \text{CH}_3\text{I} + \text{I}\cdot$	-89	Small
Overall $\Delta H^\circ = +53$		

The thermodynamic quantities for **iodination** of methane make it clear that the chain-initiating step is not responsible for the observed order of reactivities:  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ . The iodine–iodine bond is even weaker than the fluorine–fluorine bond. On this basis alone, one would predict iodine to be the most reactive of the halogens. This clearly is not the case. Once again, it is the hydrogen atom–abstraction step that correlates with the experimentally determined order of reactivities. The energy of activation of this step in the iodine reaction ( $140 \text{ kJ mol}^{-1}$ ) is so large that only two collisions out of every  $10^{12}$  have sufficient energy to produce reactions at  $300^\circ\text{C}$ . As a result, iodination is not a feasible reaction experimentally.

Before we leave this topic, one further point needs to be made. We have given explanations of the relative reactivities of the halogens toward methane that have been based on energy considerations alone. This has been possible *only because the reactions are quite similar and thus have similar entropy changes*. Had the reactions been of different types, this kind of analysis would not have been proper and might have given incorrect explanations.

## 10.6 Halogenation of Higher Alkanes

Higher alkanes react with halogens by the same kind of chain mechanism as those that we have just seen. Ethane, for example, reacts with chlorine to produce chloroethane (ethyl chloride). The mechanism is as follows:

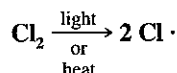


### A MECHANISM FOR THE REACTION

#### Radical Halogenation of Ethane

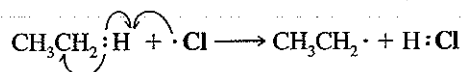
##### Chain Initiation

Step 1

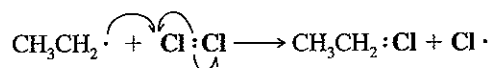


##### Chain Propagation

Step 2

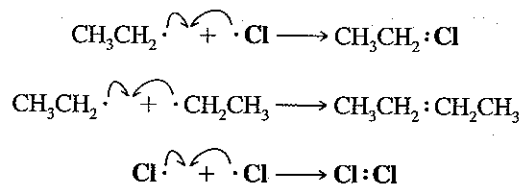


Step 3



Chain propagation continues with steps 2, 3, 2, 3, and so on.

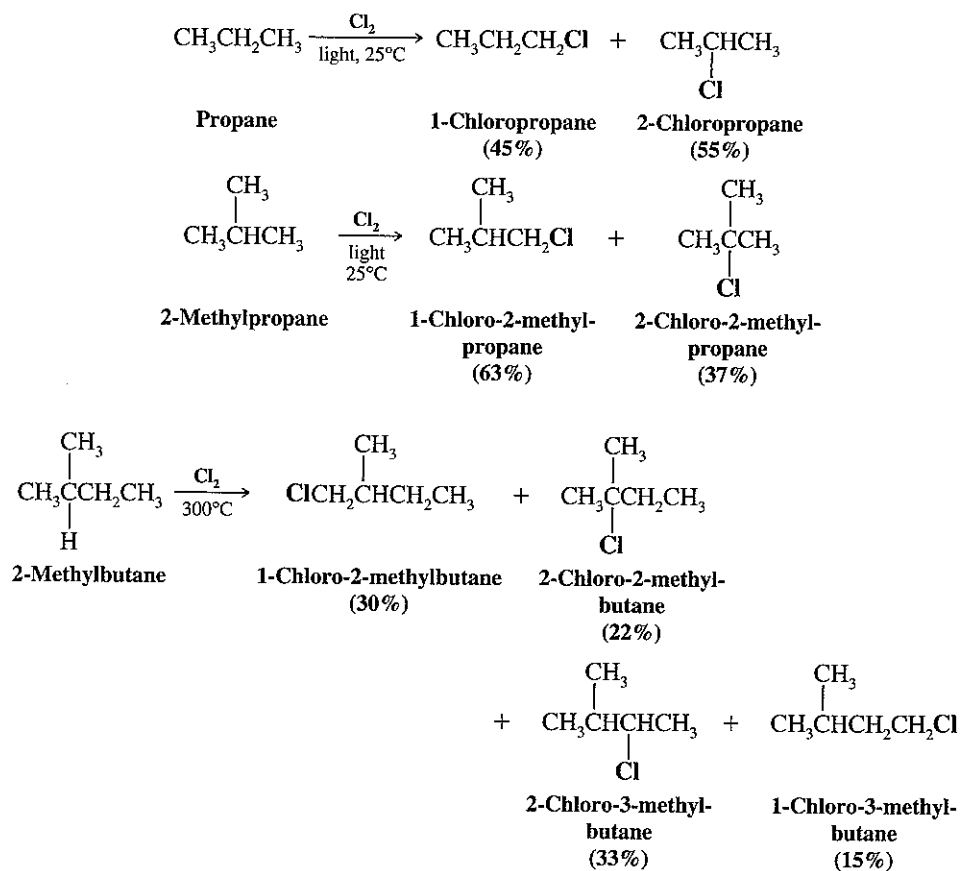
## Chain Termination



**Review Problem 10.10** The energy of activation for the hydrogen atom-abstraction step in the chlorination of ethane is  $4.2 \text{ kJ mol}^{-1}$ . (a) Use the homolytic bond dissociation energies in Table 10.1 to calculate  $\Delta H^\circ$  for this step. (b) Sketch a potential energy diagram for the hydrogen atom-abstraction step in the chlorination of ethane similar to that for the chlorination of methane shown in Fig. 10.3a. (c) When an equimolar mixture of methane and ethane is chlorinated, the reaction yields far more chloroethane than chloromethane ( $\sim 400$  molecules of chloroethane for every molecule of chloromethane). Explain this greater yield of chloroethane.

**Review Problem 10.11** When ethane is chlorinated, 1,1-dichloroethane and 1,2-dichloroethane, as well as more highly chlorinated ethanes, are formed in the mixture (see Section 10.3A). Write chain mechanisms accounting for the formation of 1,1-dichloroethane and 1,2-dichloroethane.

Chlorination of most alkanes whose molecules contain more than two carbon atoms gives a mixture of isomeric monochloro products (as well as more highly chlorinated compounds). Several examples follow. The percentages given are based on the total amount of monochloro products formed in each reaction.



The ratios of products that we obtain from chlorination reactions of higher alkanes are not identical with what we would expect if all the hydrogen atoms of the alkane were equally reactive. We find that there is a correlation between reactivity of different hydrogen atoms and the type of hydrogen atom ( $1^\circ$ ,  $2^\circ$ , or  $3^\circ$ ) being replaced. The tertiary hydrogen atoms of an alkane are most reactive, secondary hydrogen atoms are next most reactive, and primary hydrogen atoms are the least reactive (see Review Problem 10.12).

- (a) What percentages of 1-chloropropane and 2-chloropropane would you expect to obtain from the chlorination of propane if  $1^\circ$  and  $2^\circ$  hydrogen atoms were equally reactive? (b) What percentages of 1-chloro-2-methylpropane and 2-chloro-2-methylpropane would you expect from the chlorination of 2-methylpropane if the  $1^\circ$  and  $3^\circ$  hydrogen atoms were equally reactive? (c) Compare these calculated answers with the results actually obtained (above) and justify the assertion that the order of reactivity of the hydrogen atoms is  $3^\circ > 2^\circ > 1^\circ$ .

Review Problem 10.12

We can account for the relative reactivities of the primary, secondary, and tertiary hydrogen atoms in a chlorination reaction on the basis of the homolytic bond dissociation energies we saw earlier (Table 10.1). Of the three types, breaking a tertiary C—H bond requires the least energy, and breaking a primary C—H bond requires the most. Since the step in which the C—H bond is broken (i.e., the hydrogen atom-abstraction step) determines the location or orientation of the chlorination, we would expect the  $E_{\text{act}}$  for abstracting a tertiary hydrogen atom to be least and the  $E_{\text{act}}$  for abstracting a primary hydrogen atom to be greatest. Thus tertiary hydrogen atoms should be most reactive, secondary hydrogen atoms should be the next most reactive, and primary hydrogen atoms should be the least reactive.

The differences in the rates with which primary, secondary, and tertiary hydrogen atoms are replaced by chlorine are not large, however. Chlorine, as a result, does not discriminate among the different types of hydrogen atoms in a way that makes chlorination of higher alkanes a generally useful laboratory synthesis. (Alkane chlorinations do find use in some industrial processes, especially in those instances where mixtures of alkyl chlorides can be used.)

Chlorination reactions of certain alkanes can be used for laboratory preparations. Examples are the preparation of chlorocyclopropane from cyclopropane and chlorocyclobutane from cyclobutane. What structural feature of these molecules makes this possible?

Review Problem 10.13

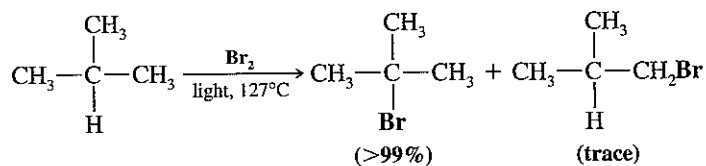
Each of the following alkanes reacts with chlorine to give a single monochloro substitution product. On the basis of this information, deduce the structure of each alkane.

Review Problem 10.14

- (a)  $\text{C}_5\text{H}_{10}$  (b)  $\text{C}_8\text{H}_{18}$  (c)  $\text{C}_5\text{H}_{12}$

### 10.6A Selectivity of Bromine

Bromine is less reactive toward alkanes in general than chlorine, but bromine is more *selective* in the site of attack when it does react. Bromine shows a much greater ability to discriminate among the different types of hydrogen atoms. The reaction of 2-methylpropane and bromine, for example, gives almost exclusive replacement of the tertiary hydrogen atom:



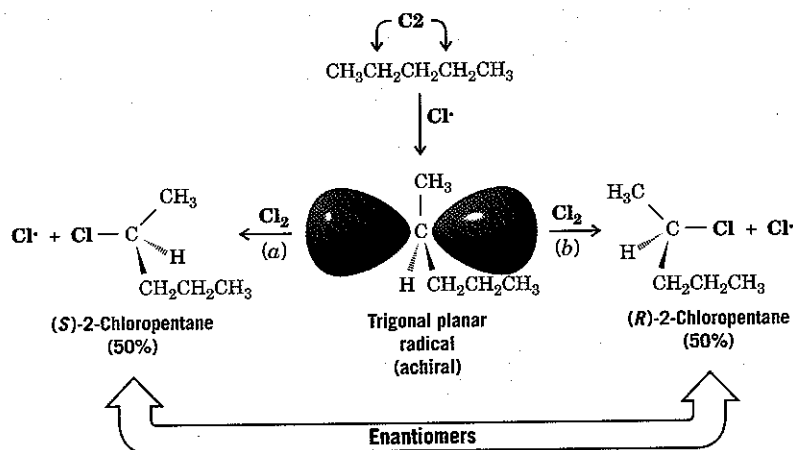
Bromination is selective.



The reaction will lead to the products shown here, as well as more highly chlorinated products. (We can use an excess of pentane to minimize multiple chlorinations.) Neither 1-chloropentane nor 3-chloropentane contains a chirality center, but 2-chloropentane does, and it is *obtained as a racemic form*. If we examine the mechanism we shall see why.

### A MECHANISM FOR THE REACTION

#### The Stereochemistry of Chlorination at C2 of Pentane



Abstraction of a hydrogen atom from C2 produces a trigonal planar radical that is achiral. This radical then reacts with chlorine at either face [by path (a) or path (b)]. Because the radical is achiral, the probability of reaction by either path is the same; therefore, the two enantiomers are produced in equal amounts, and a racemic form of 2-chloropentane results.

#### 10.8A Generation of a Second Chirality Center in a Radical Halogenation

Let us now examine what happens when a chiral molecule (containing one chirality center) reacts so as to yield a product with a second chirality center. As an example consider what happens when (*S*)-2-chloropentane undergoes chlorination at C3 (other products are formed, of course, by chlorination at other carbon atoms). The results of chlorination at C3 are shown in the box at the top of page 448.

The products of the reactions are (2*S*,3*S*)-2,3-dichloropentane and (2*S*,3*R*)-2,3-dichloropentane. These two compounds are **diastereomers**. (They are stereoisomers but they are not mirror images of each other.) The two diastereomers are *not* produced in equal amounts. Because the intermediate radical itself is chiral, reactions at the two faces are not equally likely. The radical reacts with chlorine to a greater extent at one face than the other (although we cannot easily predict which). That is, the presence of a chirality center in the radical (at C2) influences the reaction that introduces the new chirality center (at C3).

Both of the 2,3-dichloropentane diastereomers are chiral and, therefore, each exhibits optical activity. Moreover, because the two compounds are *diastereomers*, they have different physical properties (e.g., different melting points and boiling points) and are separable by conventional means (by gas chromatography or by careful fractional distillation).

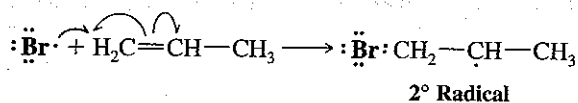
Consider the chlorination of (*S*)-2-chloropentane at C4. (a) Write stereochemical structures for the products that would be obtained and give each its proper (*R,S*) designation. (b) What is the stereoisomeric relationship between these products? (c) Are both products chiral? (d) Are both optically active? (e) Could the products be separated by conventional means? (f) What other dichloropentanes would be obtained by chlorination of (*S*)-2-chloropentane? (g) Which of these are optically active?

Review Problem 10.16



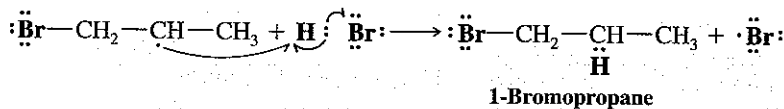


Step 3



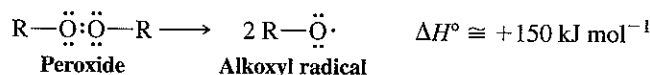
A bromine atom adds to the double bond to produce the more stable 2° radical.

Step 4

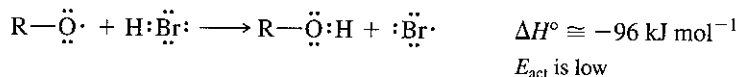


The 2° radical abstracts a hydrogen atom from HBr. This leads to the product and regenerates a bromine atom. Then repetitions of steps 3 and 4 lead to a chain reaction.

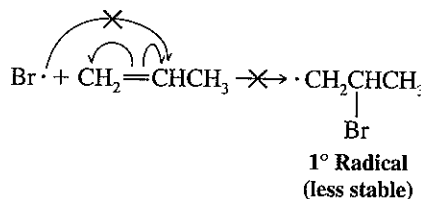
Step 1 is the simple homolytic cleavage of the peroxide molecule to produce two alkoxy radicals. The oxygen–oxygen bond of peroxides is weak, and such reactions are known to occur readily:



Step 2 of the mechanism, abstraction of a hydrogen atom by the radical, is exothermic and has a low energy of activation:



Step 3 of the mechanism determines the final orientation of bromine in the product. It occurs as it does because a *more stable secondary radical* is produced and because *attack at the primary carbon atom is less hindered*. Had the bromine attacked propene at the secondary carbon atom, a less stable, primary radical would have been the result,



and attack at the secondary carbon atom would have been more hindered.

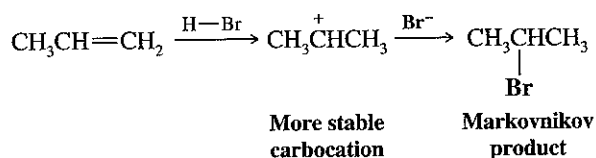
Step 4 of the mechanism is simply the abstraction of a hydrogen atom from hydrogen bromide by the radical produced in step 3. This hydrogen atom abstraction produces a bromine atom that can bring about step 3 again; then step 4 occurs again—a chain reaction.

### 10.9A Summary of Markovnikov versus Anti-Markovnikov Addition of HBr to Alkenes

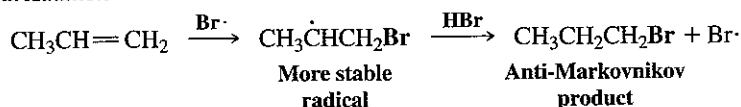
We can now see the contrast between the two ways that HBr can add to an alkene. In the *absence* of peroxides, the reagent that attacks the double bond first is a proton. Because a proton is small, steric effects are unimportant. It attaches itself to a carbon atom by an ionic mechanism so as to form the more stable carbocation. The result is Markovnikov addition. Polar, protic solvents favor this process.



A tip for alkyl halide synthesis.

**Ionic Addition**

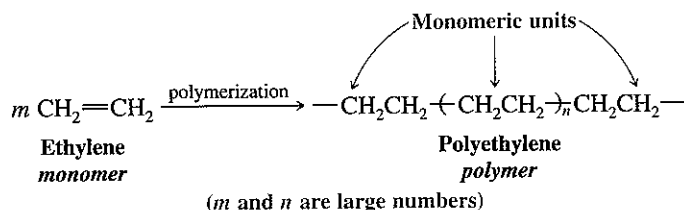
In the *presence* of peroxides, the reagent that attacks the double bond first is the larger bromine atom. It attaches itself to the less hindered carbon atom by a radical mechanism, so as to form the more stable radical intermediate. The result is anti-Markovnikov addition. Nonpolar solvents are preferable for reactions involving radicals.

**Radical Addition**

## 10.10 Radical Polymerization of Alkenes: Chain-Growth Polymers

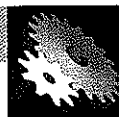
Polymers are substances that consist of very large molecules called **macromolecules** that are made up of many repeating subunits. The molecular subunits that are used to synthesize polymers are called **monomers**, and the reactions by which monomers are joined together are called **polymerizations**. Many polymerizations can be initiated by radicals.

Ethylene (ethene), for example, is the monomer that is used to synthesize the familiar polymer called *polyethylene*.



Because polymers such as polyethylene are made by addition reactions, they are often called **chain-growth polymers** or **addition polymers**. Let us now examine in some detail how polyethylene is made.

Ethylene polymerizes by a radical mechanism when it is heated at a pressure of 1000 atm with a small amount of an organic peroxide (called a diacyl peroxide).

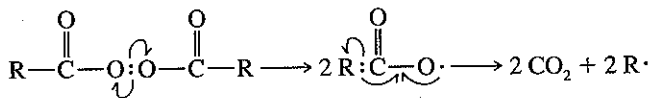


### A MECHANISM FOR THE REACTION

#### Radical Polymerization of Ethene

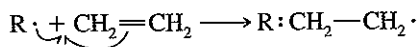
**Chain Initiation**

Step 1



Diacyl peroxide

Step 2



The diacyl peroxide dissociates and releases carbon dioxide gas. Alkyl radicals are produced, which in turn initiate chains.



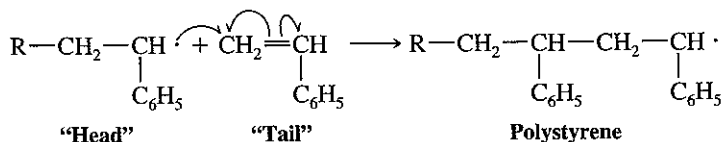
Table 10.2 lists several other common chain-growth polymers. Further information on each is provided in Special Topic A.

**TABLE 10.2** Other Common Chain-Growth Polymers

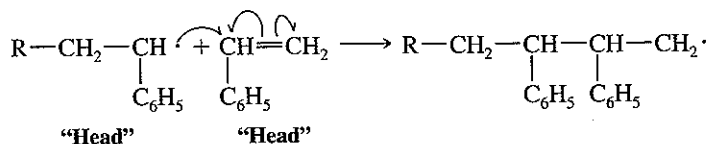
Monomer	Polymer	Names
$\text{CH}_2=\text{CHCH}_3$	$\left(\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}\right)_n$	Polypropylene
$\text{CH}_2=\text{CHCl}$	$\left(\text{CH}_2-\underset{\text{Cl}}{\text{CH}}\right)_n$	Poly(vinyl chloride), PVC
$\text{CH}_2=\text{CHCN}$	$\left(\text{CH}_2-\underset{\text{CN}}{\text{CH}}\right)_n$	Polyacrylonitrile, Orlon
$\text{CF}_2=\text{CF}_2$	$\left(\text{CF}_2-\text{CF}_2\right)_n$	Poly(tetrafluoroethene), Teflon
$\text{CH}_2=\underset{\text{CH}_3}{\text{C}}\text{CO}_2\text{CH}_3$	$\left(\text{CH}_2-\underset{\text{CO}_2\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}\right)_n$	Poly(methyl methacrylate), Lucite, Plexiglas, Perspex

Can you suggest an explanation that accounts for the fact that the radical polymerization of styrene ( $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$ ) to produce polystyrene occurs in a head-to-tail fashion,

**Review Problem 10.19**

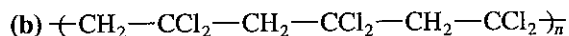
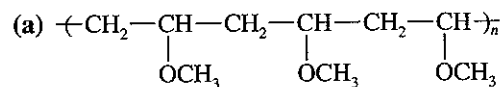


rather than the head-to-head manner shown here?

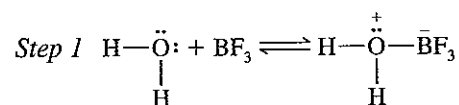


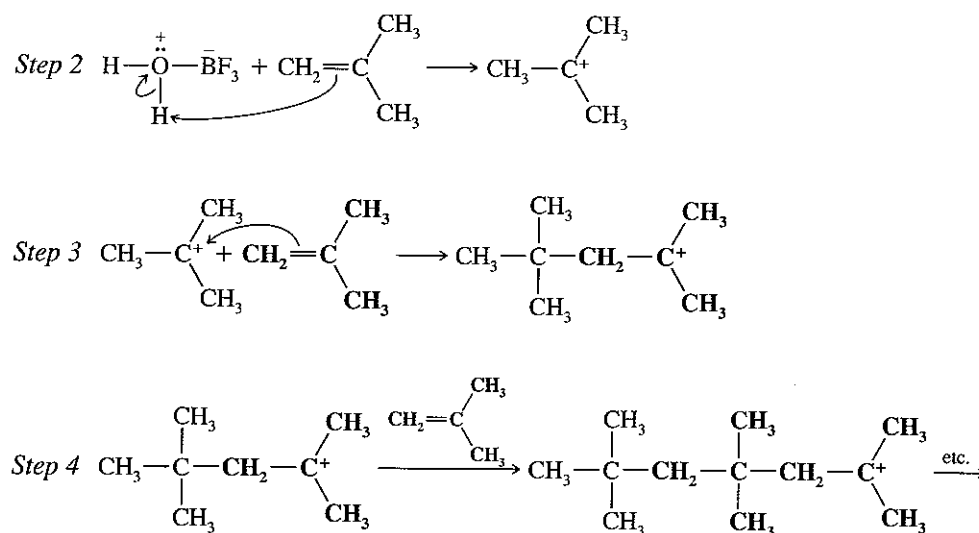
Outline a general method for the synthesis of each of the following polymers by radical polymerization. Show the monomers that you would use.

**Review Problem 10.20**



Alkenes also polymerize when they are treated with strong acids. The growing chains in acid-catalyzed polymerizations are *cations* rather than radicals. The following reactions illustrate the cationic polymerization of isobutylene:

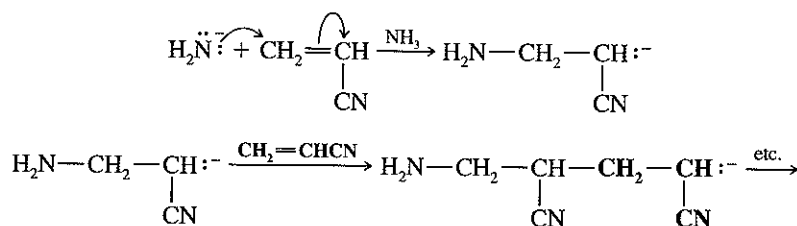




The catalysts used for cationic polymerizations are usually Lewis acids that contain a small amount of water. The polymerization of isobutylene illustrates how the catalyst ( $\text{BF}_3$  and  $\text{H}_2\text{O}$ ) functions to produce growing cationic chains.

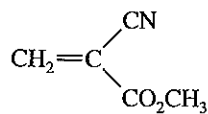
**Review Problem 10.21** Alkenes such as ethene, vinyl chloride, and acrylonitrile do not undergo cationic polymerization very readily. On the other hand, isobutylene undergoes cationic polymerization rapidly. Provide an explanation for this behavior.

Alkenes containing electron-withdrawing groups polymerize in the presence of strong bases. Acrylonitrile, for example, polymerizes when it is treated with sodium amide ( $\text{NaNH}_2$ ) in liquid ammonia. The growing chains in this polymerization are anions:



Anionic polymerization of acrylonitrile is less important in commercial production than the radical process illustrated in Special Topic A.

**Review Problem 10.22** The remarkable adhesive called “superglue” is a result of anionic polymerization. Superglue is a solution containing purified methyl  $\alpha$ -cyanoacrylate:



Methyl  $\alpha$ -cyanoacrylate

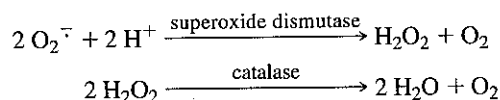
Methyl cyanoacrylate can be polymerized by anions such as hydroxide ion, but it is even polymerized by traces of water found on the surfaces of the two objects that are being glued together. (These two objects, unfortunately, have often been two fingers of the person doing the gluing.) Show how methyl  $\alpha$ -cyanoacrylate would undergo anionic polymerization.

## 10.11 Other Important Radical Reactions

Radical mechanisms are important in understanding many other organic reactions. We shall see other examples in later chapters, but let us examine a few important radicals and radical reactions here: oxygen and superoxide, the combustion of alkanes, DNA cleavage, autoxidation, antioxidants, and some reactions of chlorofluoromethanes that have threatened the protective layer of ozone in the stratosphere.

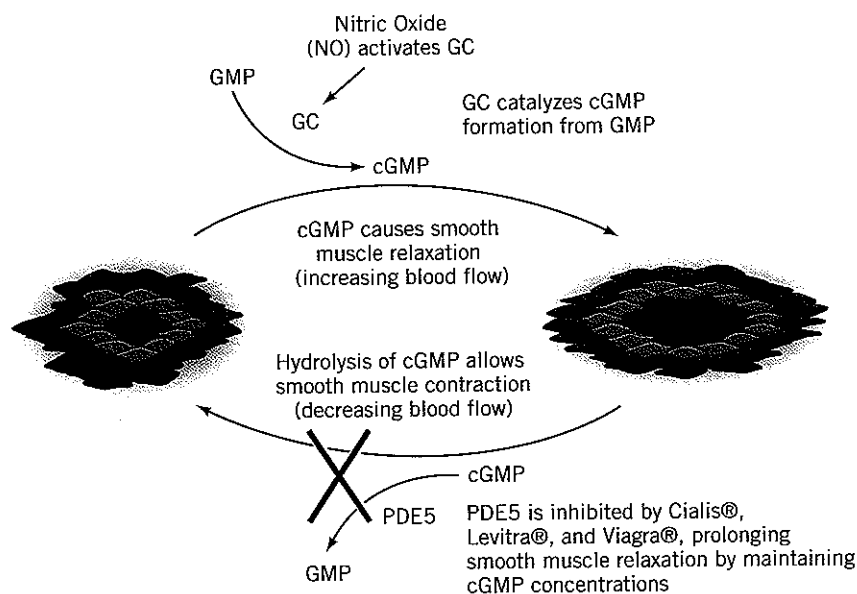
## 10.11A Molecular Oxygen and Superoxide

One of the most important radicals (and one that we encounter every moment of our lives) is molecular oxygen. Molecular oxygen in the ground state is a diradical with one unpaired electron on each oxygen. As a radical, oxygen can abstract hydrogen atoms just like other radicals we have seen. This is one way oxygen is involved in combustion reactions (Section 10.11C) and autoxidation (Section 10.11D). In biological systems, oxygen is an electron acceptor. When molecular oxygen accepts one electron, it becomes a radical anion called superoxide ( $\text{O}_2^-$ ). Superoxide is involved in both positive and negative physiological roles: The immune system uses superoxide in its defense against pathogens, yet superoxide is also suspected of being involved in degenerative disease processes associated with aging and oxidative damage to healthy cells. The enzyme superoxide dismutase regulates the level of superoxide by catalyzing conversion of superoxide to hydrogen peroxide and molecular oxygen. Hydrogen peroxide, however, is also harmful because it can produce hydroxyl ( $\text{HO}\cdot$ ) radicals. The enzyme catalase helps to prevent release of hydroxyl radicals by converting hydrogen peroxide to water and oxygen:



## 10.11B Nitric Oxide

Nitric oxide, synthesized in the body from the amino acid arginine, serves as a chemical messenger in a variety of biological processes, including blood pressure regulation and the immune response (see the chapter opening vignette). Its role in relaxation of smooth muscle in vascular tissues is shown in Fig. 10.7.

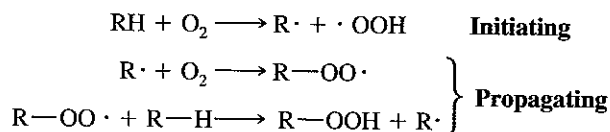


**FIGURE 10.7** Nitric oxide (NO) activates guanylate cyclase (GC), leading to production of cyclic guanosine monophosphate (cGMP). cGMP signals processes that cause smooth muscle relaxation, ultimately resulting in increased blood flow to certain tissues. Phosphodiesterase V (PDE5) degrades cGMP, leading to smooth muscle contraction and a reduction of blood flow. Cialis®, Levitra®, and Viagra® take their effect by inhibiting PDE5, thus maintaining concentrations of cGMP and sustaining smooth muscle relaxation and tissue engorgement. (Reprinted with permission from Christianson, *Accounts of Chemical Research*, 38, p. 197, Figure 6b, 2005. Copyright 2005 by American Chemical Society.)

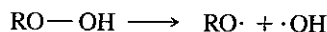
The 1998 Nobel Prize in Physiology or Medicine was awarded to R. F. Furchgott, L. J. Ignarro, and F. Murad for their discovery that NO is an important signaling molecule.

## 10.11C Combustion of Alkanes

When alkanes react with oxygen (e.g., in oil and gas furnaces and in internal combustion engines) a complex series of reactions takes place, ultimately converting the alkane to carbon dioxide and water (Section 4.10A). Although our understanding of the detailed mechanism of combustion is incomplete, we do know that the important reactions occur by radical chain mechanisms with chain-initiating and chain-propagating steps such as the following reactions:



One product of the second chain-propagating step is R—OOH, called an alkyl hydroperoxide. The oxygen–oxygen bond of an alkyl hydroperoxide is quite weak, and it can break and produce radicals that can initiate other chains:



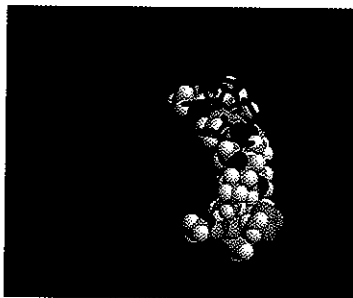
## THE CHEMISTRY OF...

Calicheamicin  $\gamma_1^I$ : A Radical Device for Slicing the Backbone of DNA

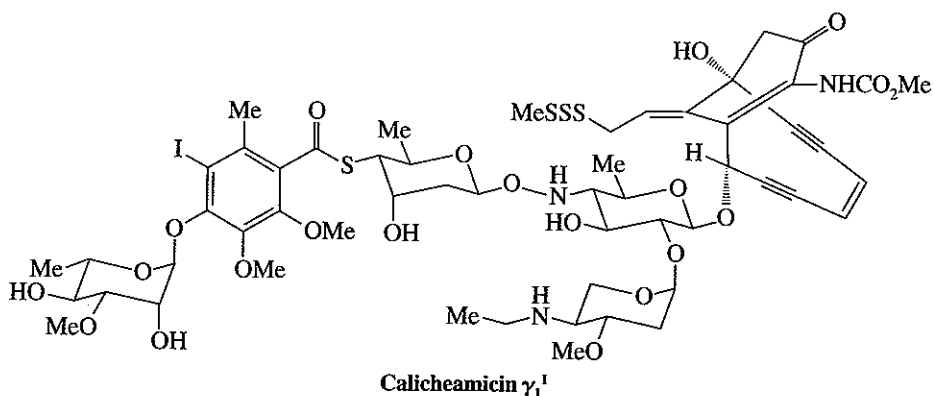
The beautiful architecture of calicheamicin  $\gamma_1^I$  conceals a lethal reactivity. Calicheamicin  $\gamma_1^I$  binds to the minor groove of DNA where its unusual enediyne (pronounced *ēn dī īn*) moiety reacts to form a highly effective device for slicing the backbone of DNA. A model of calicheamicin bound to DNA is shown below, along with its structural formula. Calicheamicin  $\gamma_1^I$  and its analogs are of great clinical interest because they are extraordinarily deadly for cancer cells, having been shown to initiate apoptosis (programmed cell death). Indeed, research on calicheamicin has since led to development of the drug Mylotarg, now used to treat some cases of acute myelogenous leukemia. Mylotarg carries two calicheamicin “warheads” on an antibody that delivers it specifically to the cancerous cells. In nature, bacteria called *Micromonospora echinospora* synthesize calicheamicin  $\gamma_1^I$  as part of their normal metabolism, presumably as a chemi-

cal defense against other organisms. The laboratory synthesis of this complex molecule by the research group of K. C. Nicolaou (Scripps Research Institute, University of California, San Diego), on the other hand, represents a *tour de force* achievement in synthetic organic chemistry. Synthesis of calicheamicin and analogs, as well as investigations by many other researchers, has led to fascinating insights about its mechanism of action and biological properties.

The DNA-slicing property of calicheamicin  $\gamma_1^I$  arises because it acts as a molecular machine for producing carbon radicals. A carbon radical is a highly reactive and unstable intermediate that has an unpaired electron. Once formed, a carbon radical can become a stable molecule again by removing a proton and one electron (i.e., a hydrogen atom) from another molecule. In this way, its unpaired electron becomes part of a bonding electron pair.

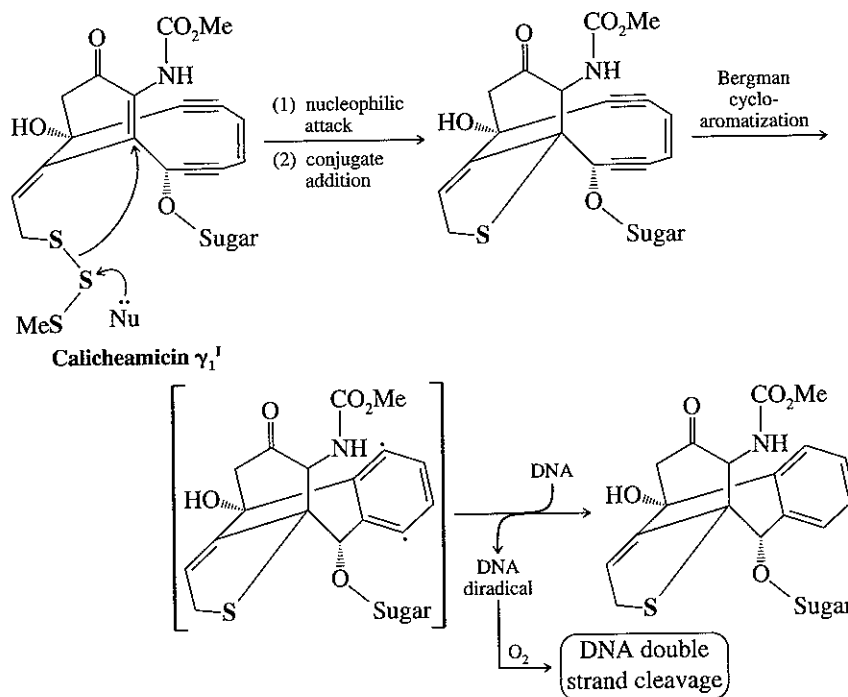


Calicheamicin bound to DNA. (PDB ID: 2PIK. Kumar, R. A.; Ikemoto, N., and Patel, D. J., Solution structure of the calicheamicin  $\gamma_1^I$ -DNA complex, *J. Mol. Biol.* **1997**, 265, 187.) [Calicheamicin  $\gamma_1^I$  structure from *Chemistry and Biology*, **1994**, 1(1), 26. Reprinted by permission of current Biology, Ltd., London.



(Other paths to achieve this are possible, too). The molecule that lost the hydrogen atom, however, becomes a new reactive radical intermediate. When the radical weaponry of each calicheamicin  $\gamma_1^I$  is activated, it removes a hydrogen

atom from the backbone of DNA. This leaves the DNA molecule as an unstable radical intermediate which, in turn, results in double-strand cleavage of the DNA and cell death.

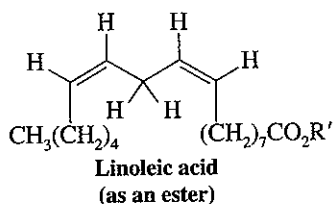


In Problem 10.30 and in "The Chemistry of . . . Calicheamicin  $\gamma_1^I$  Activation for Cleavage of DNA" box in Chapter 17 we shall revisit calicheamicin  $\gamma_1^I$  to consider the

reactions that remodel its structure into a machine for producing radicals.

### 10.11D Autoxidation

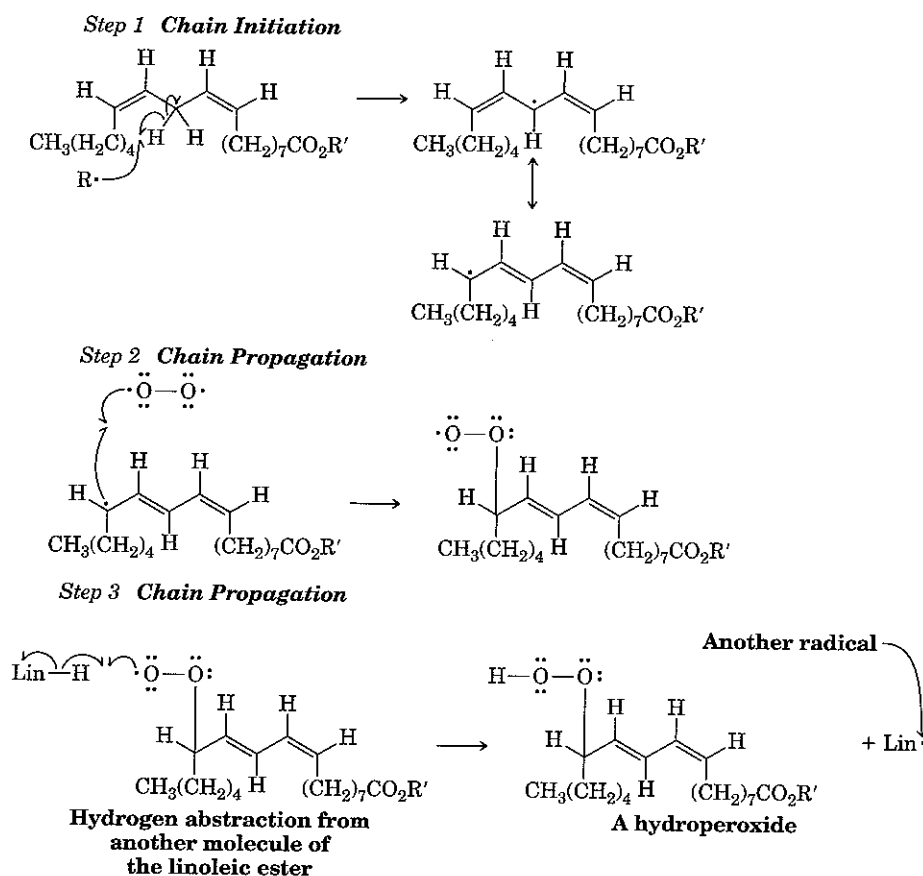
Linoleic acid is an example of a *polyunsaturated fatty acid*, the kind of polyunsaturated acid that occurs as an ester in **polyunsaturated fats** (Section 7.13, "The Chemistry of . . . Hydrogenation in the Food Industry," and Chapter 23). By polyunsaturated, we mean that the compound contains two or more double bonds:



Polyunsaturated fats occur widely in the fats and oils that are components of our diets. They are also widespread in the tissues of the body where they perform numerous vital functions.

The hydrogen atoms of the  $-\text{CH}_2-$  group located between the two double bonds of linoleic ester (Lin-H) are especially susceptible to abstraction by radicals (we shall see why in Chapter 13). Abstraction of one of these hydrogen atoms produces a new radical (Lin $\cdot$ ) that can react with oxygen in a chain reaction that belongs to a general type of

**FIGURE 10.8** Autoxidation of a linoleic acid ester. In step 1 the reaction is initiated by the attack of a radical on one of the hydrogen atoms of the  $-\text{CH}_2-$  group between the two double bonds; this hydrogen abstraction produces a radical that is a resonance hybrid. In step 2 this radical reacts with oxygen in the first of two chain-propagating steps to produce an oxygen-containing radical, which in step 3 can abstract a hydrogen from another molecule of the linoleic ester ( $\text{Lin}-\text{H}$ ). The result of this second chain-propagating step is the formation of a hydroperoxide and a radical ( $\text{Lin}\cdot$ ) that can bring about a repetition of step 2.



reaction called **autoxidation** (Fig. 10.8). The result of autoxidation is the formation of a hydroperoxide. Autoxidation is a process that occurs in many substances; for example, autoxidation is responsible for the development of the rancidity that occurs when fats and oils spoil and for the spontaneous combustion of oily rags left open to the air. Autoxidation also occurs in the body, and here it may cause irreversible damage.



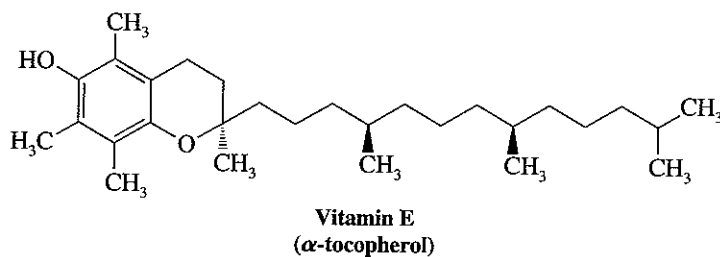
## THE CHEMISTRY OF...

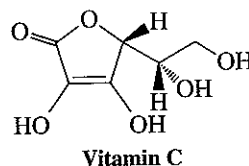
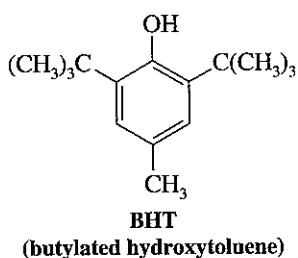
### Antioxidants

Autoxidation is inhibited when compounds called antioxidants are present that can rapidly "trap" peroxy radicals by reacting with them to give stabilized radicals that do not continue the chain.

Vitamin E ( $\alpha$ -tocopherol) is capable of acting as a radical trap, and one of the important roles that vitamin E plays in

the body may be in inhibiting radical reactions that could cause cell damage. Vitamin C is also an antioxidant, although recent work indicates that supplements over 500 mg per day may have prooxidant effects. Compounds such as BHT are added to foods to prevent autoxidation. BHT is also known to trap radicals.

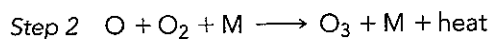
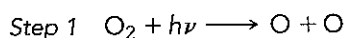




## THE CHEMISTRY OF...

### Ozone Depletion and Chlorofluorocarbons (CFCs)

In the stratosphere at altitudes of about 25 km, very high-energy (very short wavelength) UV light converts diatomic oxygen ( $O_2$ ) into ozone ( $O_3$ ). The reactions that take place may be represented as follows:



where M is some other particle that can absorb some of the energy released in the second step.

The ozone produced in step 2 can also interact with high-energy UV light in the following way:



The oxygen atom formed in step 3 can cause a repetition of step 2, and so forth. The net result of these steps is to convert highly energetic UV light into heat. This is important because the existence of this cycle shields Earth from radiation that is destructive to living organisms. This shield makes life possible on Earth's surface. Even a relatively small increase in high-energy UV radiation at Earth's surface would cause a large increase in the incidence of skin cancers.

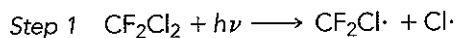
Production of chlorofluoromethanes (and of chlorofluoroethanes) called chlorofluorocarbons (CFCs) or *freons* began in 1930. These compounds have been used as refrigerants, solvents, and propellants in aerosol cans. Typical freons are trichlorofluoromethane,  $CFCl_3$  (called Freon-11), and dichlorodifluoromethane,  $CF_2Cl_2$  (called Freon-12).



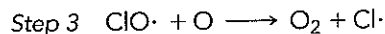
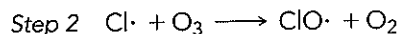
By 1974 world freon production was about 2 billion pounds annually. Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In June 1974 F. S. Rowland and M. J. Molina published an article indicating, for the first time, that in the stratosphere freon is able to initiate radical chain reactions that can upset the natural ozone balance. The 1995 Nobel Prize in Chemistry was awarded to P. J. Crutzen, M. J. Molina,

and F. S. Rowland for their combined work in this area. The reactions that take place are the following. (Freon-12 is used as an example.)

#### Chain Initiation



#### Chain Propagation



In the chain-initiating step, UV light causes homolytic cleavage of one C—Cl bond of the freon. The chlorine atom thus produced is the real villain; it can set off a chain reaction that destroys thousands of molecules of ozone before it diffuses out of the stratosphere or reacts with some other substance.

In 1975 a study by the National Academy of Sciences supported the predictions of Rowland and Molina, and since January 1978 the use of freons in aerosol cans in the United States has been banned.

In 1985 a hole was discovered in the ozone layer above Antarctica. Studies done since then strongly suggest that chlorine atom destruction of the ozone is a factor in the formation of the hole. This ozone hole has continued to grow in size, and such a hole has also been discovered in the Arctic ozone layer. Should the ozone layer be depleted, more of the sun's damaging rays would penetrate to the surface of Earth.

Recognizing the global nature of the problem, the "Montreal Protocol" was initiated in 1987. This treaty required the signing nations to reduce their production and consumption of chlorofluorocarbons. Accordingly, the industrialized nations of the world ceased production of chlorofluorocarbons as of January 1, 1996, and over 120 nations have now signed the Montreal Protocol. Increased worldwide understanding of stratospheric ozone depletion, in general, has accelerated the phasing out of chlorofluorocarbons.



## Key Terms and Concepts

- |  |  |
|--|--|
| Addition polymers Section 10.10                  | Homolytic bond dissociation energy ( $DH^\circ$ ) Section 10.2 |
| Anti-Markovnikov addition of HBr Section 10.9    | Hydrogen abstraction Section 10.1B                             |
| Autoxidation Section 10.11D                      | Iodination Section 10.5C                                       |
| Bromination Sections 10.5C, 10.6A                | Ionic reaction Sections 3.1A, 10.1                             |
| Chain-growth polymers Section 10.10              | Macromolecules Section 10.10                                   |
| Chain reactions Sections 10.4–10.6, 10.10, 10.11 | Monomers Section 10.10   |
| Chlorination Sections 10.3A, 10.5                | Peroxide Section 10.1A   |
| Energy of activation, $E_{act}$ Section 10.5B    | Polymerizations Section 10.10                                  |
| Fluorination Section 10.5C                       | Radical addition to alkenes Sections 10.9, 10.10               |
| Freon Section 10.11D                             | Radicals Sections 10.1, 10.6, 10.7                             |
| Halogenation Sections 10.3–10.6, 10.8            | Radical reactions Section 10.1B                                |
| Homolysis Section 10.1                           | Substitution reaction Section 10.3                             |

## Exercises

- 10.23** The radical reaction of propane with chlorine yields (in addition to more highly halogenated compounds) 1-chloropropane and 2-chloropropane. Write chain-initiating and chain-propagating steps showing how each compound is formed.
- 10.24** In addition to more highly chlorinated products, chlorination of butane yields a mixture of compounds with the formula  $C_4H_9Cl$ . (a) Taking stereochemistry into account, how many different isomers with the formula  $C_4H_9Cl$  would you expect to be produced? (b) If the mixture of  $C_4H_9Cl$  isomers were subjected to fractional distillation or gas chromatography, how many fractions would you expect to obtain? (c) Which fractions would be optically inactive? (d) Which would you be able to resolve into enantiomers? (e) Predict the features in their  $^1H$  and  $^{13}C$  DEPT NMR spectra that would differentiate among the isomers separated by GC or distillation. (f) How could fragmentation in their mass spectra be used to differentiate the isomers?
- 10.25** Chlorination of (*R*)-2-chlorobutane yields a mixture of isomers with the formula  $C_4H_8Cl_2$ . (a) How many different isomers would you expect to be produced? Write their structures. (b) If the mixture of  $C_4H_8Cl_2$  isomers were subjected to fractional distillation, how many fractions would you expect to obtain? (c) Which of these fractions would be optically active?
- 10.26** Peroxides are often used to initiate radical chain reactions such as alkane halogenations. (a) Examine the bond energies in Table 10.1 and give reasons that explain why peroxides are especially effective as radical initiators. (b) Illustrate your answer by outlining how di-*tert*-butyl peroxide,  $(CH_3)_3CO-OC(CH_3)_3$ , might initiate an alkane halogenation.
- 10.27** List in order of decreasing stability all of the radicals that can be obtained by abstraction of a hydrogen atom from 2-methylbutane.
- 10.28** Starting with the compound or compounds indicated in each part and using any other needed reagents, outline syntheses of each of the following compounds. (You need not repeat steps carried out in earlier parts of this problem.)
- Iodoethane from ethane
  - Diethyl ether from ethane
  - Cyclopentene from cyclopentane
  - 2-Bromo-3-methylbutane from 2-methylbutane
  - 2-Butyne from methane and acetylene
  - 2-Butanol from ethane and acetylene
  - Ethyl azide ( $CH_3CH_2N_3$ ) from ethane



## Problems

- 10.29** The relative stability of a series of primary, secondary, and tertiary alkyl radicals can be compared using R—CH<sub>3</sub> carbon–carbon bond dissociation energies instead of R—H bond dissociation energies (the method used in Section 10.2B). Bond dissociation energies ( $DH^\circ$ ) needed to make such a comparison for various R—CH<sub>3</sub> species can be calculated from values for the heat of formation ( $H_f$ ) of radicals R·, CH<sub>3</sub>·, and the molecule R—CH<sub>3</sub> using the following equation:  $DH^\circ[\text{R—R}'] = H_f[\text{R}\cdot] + H_f[\text{CH}_3\cdot] - H_f[\text{R—CH}_3]$ . Using the data below, calculate the R—CH<sub>3</sub> bond dissociation energies for the examples given, and from your results compare the relative stabilities of the respective primary, secondary, and tertiary radicals in this series.

Chemical Species	$H_f$ (Heat of Formation, kJ mol <sup>-1</sup> )
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> —CH <sub>3</sub>	-146.8
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )—CH <sub>3</sub>	-153.7
(CH <sub>3</sub> ) <sub>3</sub> C—CH <sub>3</sub>	-167.9
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ·	80.9
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )·	69
(CH <sub>3</sub> ) <sub>3</sub> C·	48
CH <sub>3</sub> ·	147

- 10.30** Draw mechanism arrows to show electron movements in the Bergman cycloaromatization reaction that leads to the diradical believed responsible for the DNA-cleaving action of the antitumor agent calicheamicin (see “The Chemistry of . . . Calicheamicin” in Section 10.11C).
- 10.31** In the radical chlorination of 2,2-dimethylhexane, chlorine substitution occurs much more rapidly at C5 than it does at a typical secondary carbon (e.g., C2 in butane). Review the discussion on radical polymerization and then suggest an explanation for the enhanced rate of substitution at C5 in 2,2-dimethylhexane.
- 10.32** Hydrogen peroxide and ferrous sulfate react to produce hydroxyl radical (HO·), as reported in 1894 by English chemist H. J. H. Fenton. When *tert*-butyl alcohol is treated with HO· generated this way, it affords a crystalline reaction product X, mp 92°, which has these spectral properties:  
**MS:** heaviest mass peak is at  $m/z$  131  
**IR:** 3620, 3350 (broad), 2980, 2940, 1385, 1370 cm<sup>-1</sup>  
**<sup>1</sup>H NMR:** sharp singlets at  $\delta$  1.22, 1.58, and 2.95 (6 : 2 : 1 area ratio)  
**<sup>13</sup>C NMR:**  $\delta$  28 (CH<sub>3</sub>), 35 (CH<sub>2</sub>), 68 (C)  
 Draw the structure of X and write a mechanism for its formation.

## Challenge Problems

-  **10.33** Molecular orbital calculations can be used to model the location of electron density from unpaired electrons in a radical. Open the molecular models on the book's website for the methyl, ethyl, and *tert*-butyl radicals. The gray wire mesh surfaces in these models represent volumes enclosing electron density from unpaired electrons. What do you notice about the distribution of unpaired electron density in the ethyl radical and *tert*-butyl radical, as compared to the methyl radical? What bearing does this have on the relative stabilities of the radicals in this series?
-  **10.34** If one were to try to draw the simplest Lewis structure for molecular oxygen, the result might be the following ( $\ddot{\text{O}}=\ddot{\text{O}}$ ). However, it is known from the properties of molecular oxygen and experiments that O<sub>2</sub> contains two unpaired electrons, and therefore, the Lewis structure above is incorrect. To understand the structure of O<sub>2</sub>, it is necessary to employ a molecular orbital representation. To do so, we will need to recall (1) the shapes of bonding and antibonding  $\sigma$  and  $\pi$  molecular orbitals, (2) that each orbital can contain a maximum of two electrons, (3) that molecular oxygen has 16 electrons in total, and (4) that the two unpaired electrons in oxygen occupy separate degenerate (equal-energy) orbitals. Now, open the molecular model on the book's website for oxygen and examine its molecular orbitals in sequence from the HOMO-7 orbital to the LUMO. [HOMO-7 means the seventh orbital in energy below the highest occupied molecular orbital (HOMO), HOMO-6 means the sixth below the HOMO, and so forth.] Orbitals HOMO-7 through HOMO-4 represent the  $\sigma 1s$ ,  $\sigma 1s^*$ ,  $\sigma 2s$ , and  $\sigma 2s^*$  orbitals, respectively, each containing a pair of electrons.

- (a) What type of orbital is represented by HOMO-3 and HOMO-2? [Hint: What types of orbitals are possible for second-row elements like oxygen, and which orbitals have already been used?]
- (b) What type of orbital is HOMO-1? [Hint: The  $\sigma 2s$  and  $\sigma 2s^*$  orbitals are already filled, as are the HOMO-3 and HOMO-2 orbitals identified in part (b). What bonding orbital remains?]
- (c) The orbitals designated HOMO and LUMO in  $O_2$  have the same energy (they are degenerate), and each contains one of the unpaired electrons of the oxygen molecule. What type of orbital are these?



### Learning Group Problems

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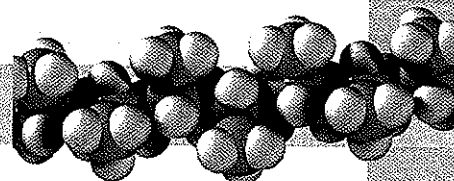
1. (a) Draw structures for all organic products that would result when an *excess* of *cis*-1,3-dimethylcyclohexane reacts with  $Br_2$  in the presence of heat and light. Use three-dimensional formulas to show stereochemistry.
- (b) Draw structures for all organic products that would result when an *excess* of *cis*-1,3-dimethylcyclohexane reacts with  $Cl_2$  in the presence of heat and light. Use three-dimensional formulas to show stereochemistry.
- (c) As an alternative, use *cis*-1,2-dimethylcyclohexane to answer parts (a) and (b) above.
2. (a) Propose a synthesis of 2-methoxypropene starting with propane and methane as the sole source for carbon atoms. You may use any other reagents necessary. Devise a retrosynthetic analysis first.
- (b) 2-Methoxypropene will form a polymer when treated with a radical initiator. Write the structure of this polymer and a mechanism for the polymerization reaction assuming a radical mechanism initiated by a diacyl peroxide.

# CHAIN-GROWTH POLYMERS

SPECIAL  
TOPIC

A

Polypropylene (syndiotactic)



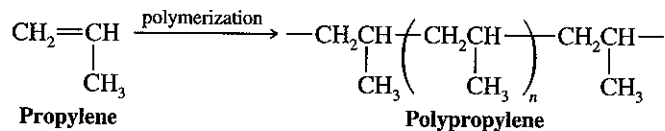
The names *Orlon*, *Plexiglas*, *Lucite*, *polyethylene*, and *Teflon* are now familiar to most of us. These “plastics” or polymers are used in the construction of many objects around us—from the clothing we wear to portions of the houses we live in. Yet all of these compounds were unknown 100 years ago. The development of the processes by which synthetic polymers are made, more than any other single factor, was responsible for the remarkable growth of the chemical industry in the twentieth century.

At the same time, some scientists are now expressing concern about the reliance we have placed on these synthetic materials. Because they are the products of laboratory and industrial processes rather than processes that occur in nature, nature often has no way of disposing of many of them. Although progress has been made in the development of “biodegradable plastics” in recent years, many materials are still used that are not biodegradable. Although most of these objects are combustible, incineration is not always a feasible method of disposal because of attendant air pollution.

Not all polymers are synthetic. Many naturally occurring compounds are polymers as well. Silk and wool are polymers that we call proteins. The starches of our diet are polymers and so is the cellulose of cotton and wood.

Polymers are compounds that consist of very large molecules made up of many repeating subunits. The molecular subunits that are used to synthesize polymers are called *monomers*, and the reactions by which monomers are joined together are called polymerization reactions.

Propylene (propene), for example, can be polymerized to form *polypropylene*. This polymerization occurs by a chain reaction, and, as a consequence, polymers such as polypropylene are called *chain-growth* or *addition polymers*:



As we saw in Section 10.10, alkenes are convenient starting materials for the preparation of chain-growth polymers. The addition reactions occur through radical, cationic, or anionic mechanisms depending on how they are initiated. The following examples illustrate these mechanisms. All of these reactions are chain reactions: