

# ALKANES

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**A**lthough this chapter is concerned with the chemistry of only one class of compounds, saturated hydrocarbons or alkanes, several fundamental principles are developed that we shall use extensively in later chapters. The study of some of these principles has been associated traditionally more with physical chemistry than with organic chemistry. We include them here, at the beginning of our discussion of organic reactions, because they provide a sound basis for understanding the key questions concerning the practical use of organic reactions. Is the equilibrium point of a given reaction far enough toward the desired products to be useful? Can conditions be found in which the reaction will take place at a practical rate? How can unwanted side reactions be suppressed?

Initially, we will be concerned with the physical properties of alkanes and how these properties can be correlated by the important concept of homology. This will be followed by a brief survey of the occurrence and uses of hydrocarbons, with special reference to the petroleum industry. Chemical reactions of alkanes then will be discussed, with special emphasis on combustion and substitution reactions. These reactions are employed to illustrate how we can predict and use energy changes—particularly  $\Delta H$ , the heat evolved or absorbed by a reacting system, which often can be estimated from bond energies. Then we consider some of the problems involved in predicting reaction rates in the context of a specific reaction, the chlorination of methane. The example is complex, but it has the virtue that we are able to break the overall reaction into quite simple steps.

Before proceeding further, it will be well to reiterate what an alkane is, lest you be confused as to the difference between alkanes and alkenes. **Alkanes** are compounds of carbon and hydrogen only, without double bonds, triple

bonds, or rings. They all conform to the general formula  $C_nH_{2n+2}$  and sometimes are called **paraffin** hydrocarbons, open-chain saturated hydrocarbons, or **acyclic** hydrocarbons. The nomenclature of alkanes has been discussed in Chapter 3, and you may find it well to review Section 3-1 before proceeding.

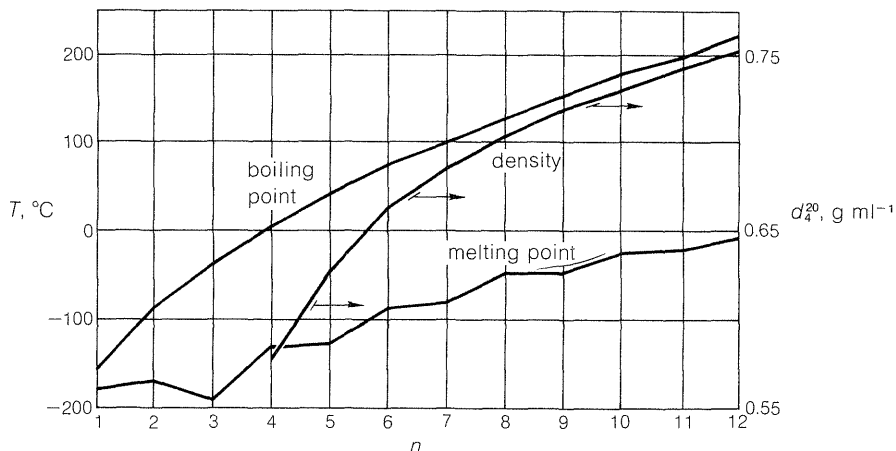
#### 4-1 PHYSICAL PROPERTIES OF ALKANES. THE CONCEPT OF HOMOLOGY

The series of straight-chain alkanes, in which  $n$  is the number of carbons in the chain, shows a remarkably smooth gradation of physical properties (see Table 4-1 and Figure 4-1). As  $n$  increases, each additional  $CH_2$  group contributes a fairly constant increment to the boiling point and density, and to a lesser extent to the melting point. This makes it possible to estimate the properties of an unknown member of the series from those of its neighbors. For example, the boiling points of hexane and heptane are  $69^\circ$  and  $98^\circ$ , respectively. Thus a difference in structure of one  $CH_2$  group for these compounds makes a difference in boiling point of  $29^\circ$ ; we would predict the boiling point of the next higher member, octane, to be  $98^\circ + 29^\circ = 127^\circ$ , which is close to the actual boiling point of  $126^\circ$ .

**Table 4-1**  
Physical Properties of Alkanes,  $CH_3(CH_2)_{n-1}H$

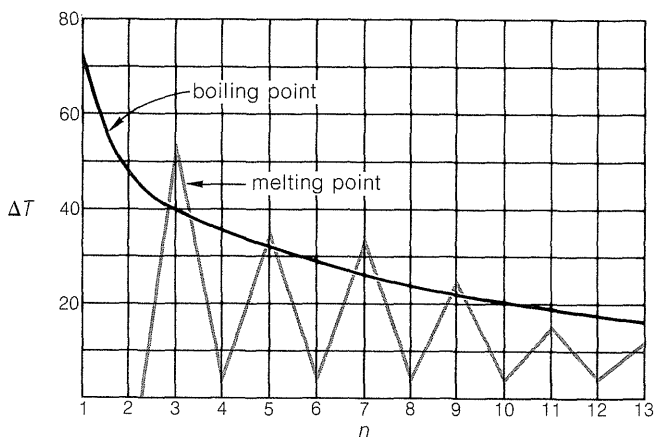
$n$	Name	Bp, $^\circ C$ (760 mm)	Mp, $^\circ C$	Density at $20^\circ$ , $d_4^{20}$ , g ml $^{-1}$
1	methane	-161.5	-183	0.424 <sup>a</sup>
2	ethane	-88.6	-172	0.546 <sup>a</sup>
3	propane	-42.1	-188	0.501 <sup>b</sup>
4	butane	-0.5	-135	0.579 <sup>b</sup>
5	pentane	36.1	-130	0.626
6	hexane	68.7	-95	0.659
7	heptane	98.4	-91	0.684
8	octane	125.7	-57	0.703
9	nonane	150.8	-54	0.718
10	decane	174.1	-30	0.730
11	undecane	195.9	-26	0.740
12	dodecane	216.3	-10	0.749
15	pentadecane	270.6	10	0.769
20	eicosane	342.7	37	0.786 <sup>c</sup>
30	triacontane	446.4	66	0.810 <sup>c</sup>

<sup>a</sup>At the boiling point. <sup>b</sup>Under pressure. <sup>c</sup>For the supercooled liquid.



**Figure 4-1** Dependence on  $n$  of melting points, boiling points, and densities ( $d_4^{20}$ ) of continuous-chain alkanes,  $\text{CH}_3(\text{CH}_2)_{n-1}\text{H}$

Members of a group of compounds, such as the alkanes, that have similar chemical structures and graded physical properties, and which differ from one another by the number of atoms in the structural backbone, are said to constitute a *homologous series*. When used to forecast the properties of unknown members of the series, the concept of *homology* works most satisfactorily for the higher-molecular-weight members because the introduction of additional  $\text{CH}_2$  groups makes a smaller relative change in the overall composition of such molecules. This is better seen from Figure 4-2, which shows



**Figure 4-2** Dependence of  $\Delta T$  (difference in boiling and melting points between consecutive members of the series of continuous-chain alkanes) on  $n$  (number of carbon atoms)

how  $\Delta T$ , the differences in boiling points and melting points between consecutive members of the homologous series of continuous-chain alkanes, changes with the number of carbons,  $n$ .

Branched-chain alkanes do not exhibit the same smooth gradation of physical properties as do the continuous-chain alkanes. Usually there is too great a variation in molecular structure for regularities to be apparent. Nevertheless, in any one set of isomeric hydrocarbons, volatility increases with increased branching. This can be seen from the data in Table 4-2, which lists the physical properties of the five hexane isomers. The most striking feature of the data is the  $19^\circ$  difference between the boiling points of hexane and 2,2-dimethylbutane.

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**Exercise 4-1** Use the data of Tables 4-1 and 4-2 to estimate the boiling points of tetradecane, heptadecane, 2-methylhexane, and 2,2-dimethylpentane.

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**Table 4-2**  
Physical Properties of Hexane Isomers

Isomer	Structure	Bp, °C	Mp, °C	Density at 20°, $d_4^{20}$ , g ml <sup>-1</sup>
hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	68.7	-94	0.659
3-methylpentane	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \end{array}$	63.3	-118	0.664
2-methylpentane	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3 \end{array}$	60.3	-154	0.653
2,3-dimethylbutane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3\text{CH}-\text{CHCH}_3 \end{array}$	58.0	-129	0.661
2,2-dimethylbutane	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{CCH}_2\text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	49.7	-98	0.649

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Homology hardly can be overestimated as a practical aid for the organic chemist to cope with the large numbers of compounds with which he works. In the simplest approximation, the members of a homologous series are assumed to have essentially the same properties, except for increases in boiling point and melting point as shown in Figure 4-1 for alkanes. This generally will be true, except when the number of carbons is small and when the hydrocarbon chain has polar substituents. To explain briefly, consider com-

$$\delta^- \quad \delta^+$$
 pounds such as alcohols, ROH, which have polar O---H groups. As we indicated in Section 1-3, polarity causes molecules to associate with one another, which decreases their volatility, raises melting points, increases solubility in polar liquids, and decreases solubility in nonpolar liquids. This explains why methanol, CH<sub>3</sub>OH, is much less volatile and much more water-soluble than methane, CH<sub>4</sub>. But we find that the water-solubility of alcohols falls off rapidly with the length of the carbon chain, certainly faster than expected for a simple homologous series effect. Whereas methanol, CH<sub>3</sub>OH, and ethanol, CH<sub>3</sub>CH<sub>2</sub>OH, are completely soluble in water, butanol, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, is only slightly soluble. This illustrates the conflicting properties conferred on molecules by polar groups compared to nonpolar hydrocarbon groups, and points up that large changes in physical properties can be expected in the early part of a homologous series until the hydrocarbon chain is sufficiently long, usually six or more carbons, so that the hydrocarbon parts dominate over the polar parts of the molecules.

**Exercise 4-2** Write detailed structures and predict which compound in each pair would have (1) the lower boiling point and (2) the higher water solubility.

- a.** H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, H<sub>3</sub>CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>      **d.** CH<sub>3</sub>CO<sub>2</sub>H, HCO<sub>2</sub>CH<sub>3</sub>  
**b.** CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>OH                      **e.** CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>CO<sub>2</sub>H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CO<sub>2</sub>H  
**c.** CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, (CH<sub>3</sub>)<sub>3</sub>COH

## 4-2 CHEMICAL REACTIONS OF ALKANES. COMBUSTION OF ALKANES

As a class, alkanes generally are unreactive. The names saturated hydrocarbon, or “paraffin,” which literally means “not enough affinity” [L. *par(um)*, not enough, + *affins*, affinity], arise because their chemical “affinity” for most common reagents may be regarded as “saturated” or satisfied. Thus none of the C–H or C–C bonds in a typical saturated hydrocarbon, for example ethane, are attacked at ordinary temperatures by a strong acid, such as sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), or by an oxidizing agent, such as bromine (in the dark), oxygen, or potassium permanganate (KMnO<sub>4</sub>). Under ordinary conditions, ethane is

similarly stable to reducing agents such as hydrogen, even in the presence of catalysts such as platinum, palladium, or nickel.

However, all saturated hydrocarbons are attacked by oxygen at elevated temperatures and, if oxygen is in excess, complete combustion to carbon dioxide and water occurs. Vast quantities of hydrocarbons from petroleum are utilized as fuels for the production of heat and power by combustion, although it is becoming quite clear that few of the nations of the world are going to continue to satisfy their needs (or desires) for energy through use of petroleum the way it has been possible in the past.

Petroleums differ considerably in composition depending on their source. However, a representative petroleum<sup>1</sup> on distillation yields the following fractions:

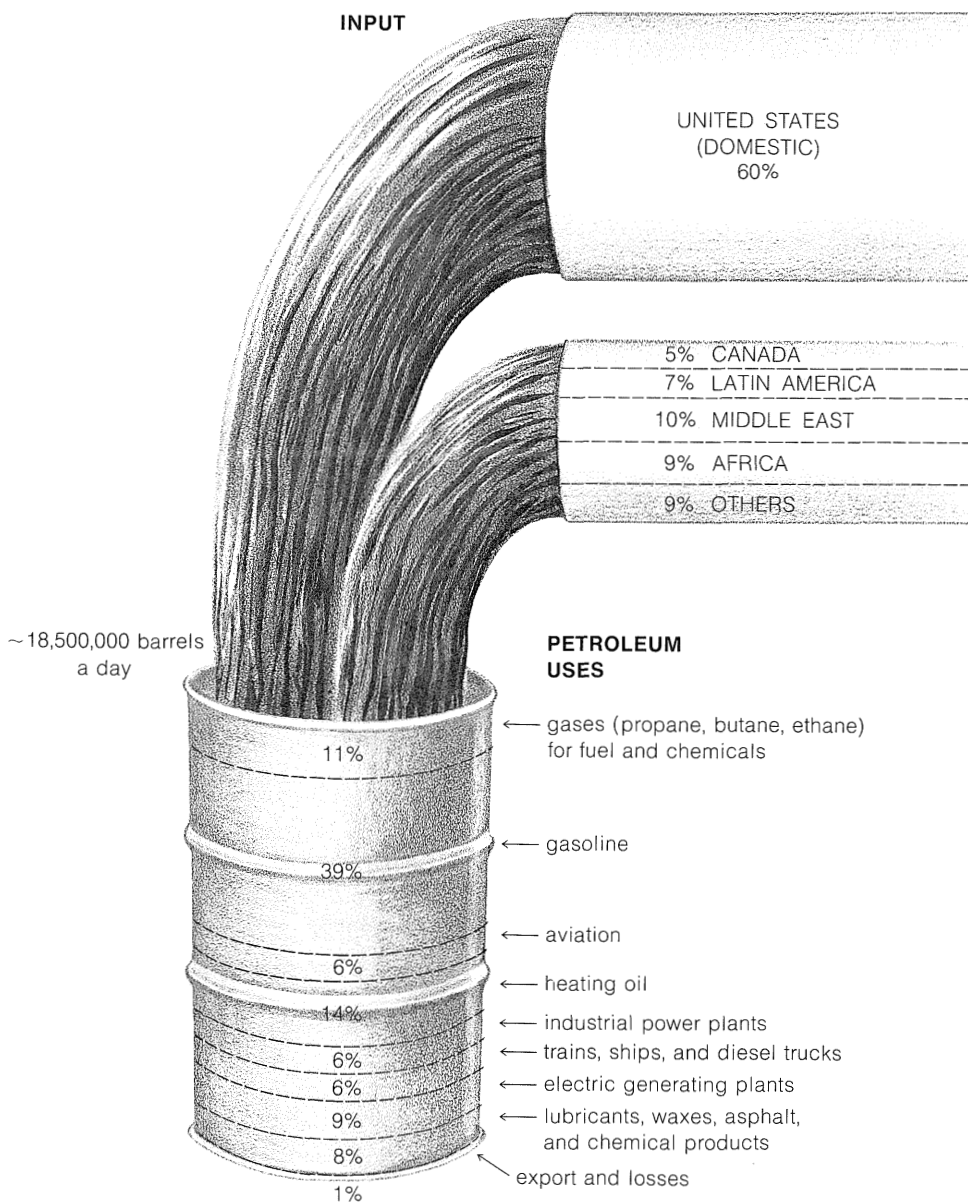
1. *Gas* fraction, boiling point up to 40°, contains normal and branched alkanes from C<sub>1</sub> to C<sub>5</sub>. Natural gas is mainly methane and ethane. "Bottled" gas (liquefied petroleum gas) is mainly propane and butane.
2. *Gasoline*, boiling point from 40° to 180°, contains mostly hydrocarbons from C<sub>6</sub> to C<sub>10</sub>. Over 100 compounds have been identified in gasoline, and these include continuous-chain and branched alkanes, cycloalkanes, and alkylbenzenes (arenes). The branched alkanes make better gasoline than their continuous-chain isomers because they give less "knock" in high-compression gasoline engines.
3. *Kerosine*, boiling point 180° to 230°, contains hydrocarbons from C<sub>11</sub> to C<sub>12</sub>. Much of this fraction is utilized as jet engine fuels or is "cracked" to simpler alkanes (and alkenes).
4. *Light gas oil*, boiling point 230° to 305°, C<sub>13</sub> to C<sub>17</sub>, is utilized as diesel and furnace fuels.
5. *Heavy gas oil and light lubricating distillate*, boiling point 305° to 405°, C<sub>18</sub> to C<sub>25</sub>.
6. *Lubricants*, boiling point 405° to 515°, C<sub>26</sub> to C<sub>38</sub>, familiarly encountered as paraffin wax and petroleum jelly (Vaseline).
7. The distillation residues are known as *asphalts*.

The way in which petroleum is refined and the uses for it depend very much on supply and demand, which always are changing. However, the situation for the United States in 1974 is summarized in Figure 4-3, which shows roughly how much of one barrel of oil (160 liters) is used for specific purposes.

In the past three decades, petroleum technology has outpaced coal technology, and we now are reliant on petroleum as the major source of fuels and chemicals. Faced with dwindling oil reserves, however, it is inevitable that coal again will become a major source of raw materials. When coal is heated at high temperatures in the absence of air, it carbonizes to *coke* and gives off a gaseous mixture of compounds. Some of these gases condense to a black viscous oil (*coal tar*), others produce an aqueous condensate called *ammoniacal liquors*, and some remain gaseous (*coal gas*). The residue is coke, which is used both as a fuel and as a source of carbon for the production of steel. The major component in coal gas is methane. Coal tar is an incredible mixture of compounds, mostly hydrocarbons, a substantial number of which are arenes. Coal and coal tar can be utilized to produce alkanes, but the technology involved

<sup>1</sup>See F. D. Rossini, "Hydrocarbons in Petroleum," *J. Chem. Educ.* **37**, 554 (1960).

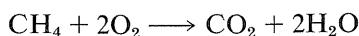
is more complex and costly than petroleum refining. It seems inevitable that the cost of hydrocarbon fuel will continue to rise as supply problems become more difficult. And there is yet no answer to what will happen when the world's limited quantities of petroleum and coal are exhausted.



**Figure 4-3** Sources and uses of petroleum in the United States in 1976

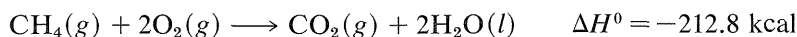
### 4-3 COMBUSTION. HEATS OF REACTION. BOND ENERGIES

All hydrocarbons are attacked by oxygen at elevated temperatures and, if oxygen is in excess, complete combustion occurs to carbon dioxide and water:

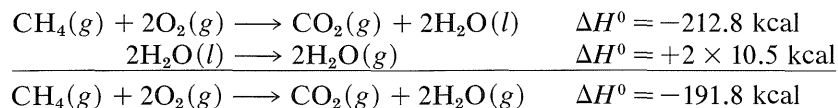


The heat evolved in this process—the heat of the combustion reaction,  $\Delta H$ —is a measure of the amount of energy stored in the C–C and C–H bonds of the hydrocarbon compared to the energy stored in the products, carbon dioxide and water. It can be measured experimentally with considerable accuracy and generally is reported as  $\Delta H^0$  the amount of heat (in kilocalories)<sup>2</sup> liberated on complete combustion of one mole of hydrocarbon when the reactants and the products are in standard states, and at the same temperature, usually 25°. <sup>3</sup> Not all chemical reactions that occur spontaneously liberate heat—some actually absorb heat. By convention,  $\Delta H^0$  is given a *negative* sign when heat is evolved (**exothermic reaction**) and a *positive* sign when heat is absorbed (**endothermic reaction**). The heat evolved or absorbed also is called the **enthalpy change**.

For the combustion of 1 mole of methane at 25°, we find by experiment (corrected from constant volume to constant pressure, if necessary) that the reaction is exothermic by 212.8 kcal. This statement can be expressed as follows:



The symbol (*g*) denotes that the reactants and products are in the gaseous state except for the water, which is liquid (*l*). If we wish to have  $\Delta H^0$  with gaseous water  $\text{H}_2\text{O}(g)$  as the product we have to make a correction for the heat of vaporization of water (10.5 kcal mole<sup>-1</sup> at 25°):



<sup>2</sup>In this book we use kilocalories in place of the presently recommended (SI) joules for units of energy. As of the date of writing, it is not clear just how general the use of the joule will become among chemists. To convert calories to joules (or kcal to kJ), multiply by 4.184.

<sup>3</sup>You may wonder how a reaction, such as combustion of methane, can occur at 25°. The fact is that the reaction can be carried out at any desired temperature. The important thing is that the  $\Delta H^0$  value we are talking about here is the heat liberated or absorbed when you start with the reactants at 25° and finish with the products at 25°. As long as  $\Delta H^0$  is defined this way, it does not matter at what temperature the reaction actually occurs. Standard states for gases are 1 atm partial pressure. Standard states for liquids or solids usually are the pure liquid or solid at 1 atm external pressure.



The task of measuring the heats of all chemical reactions is a formidable one and about as practical as counting grains of sand on the beach. However, it is of practical interest to be able to estimate heats of reaction, and this can be done quite simply with the aid of bond energies. The necessary bond energies are given in Table 4-3, and it is important to notice that they apply only to *complete dissociation of gaseous substances to gaseous atoms at 25°C*. Also, they do not apply, without suitable corrections, to many compounds, such as benzene, that have more than one double bond. This limitation will be discussed in Chapters 6 and 21.

To calculate  $\Delta H^0$  for the combustion of one mole of methane, first we break bonds as follows, using 98.7 kcal mole<sup>-1</sup> for the energy of each of the

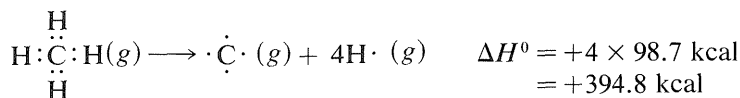
**Table 4-3**Bond Energies (kcal mole<sup>-1</sup> at 25°C)<sup>a</sup>

Diatomic Molecules					
H—H	104.2	F—F	37.5	H—F	135.9
O=O	118.9	Cl—Cl	58.1	H—Cl	103.1
N≡N	226.8	Br—Br	46.4	H—Br	87.4
C=O <sup>b</sup>	257.3	I—I	36.5	H—I	71.4
Polyatomic Molecules					
C—H	98.7	C—C	82.6	C—F	116
N—H	93.4	C=C	145.8	C—Cl	81
O—H	110.6	C≡C	199.6	C—Br	68
S—H	83	C—N	72.8	C—I	51
P—H	76	C=N	147	C—S	65
N—N	39	C≡N	212.6	C=S <sup>c</sup>	128
N=N	100	C—O	85.5	N—F	65
O—O	35	C=O <sup>d</sup>	192.0	N—Cl	46
S—S	54	C=O <sup>e</sup>	166	O—F	45
N—O	53	C=O <sup>f</sup>	176	O—Cl	52
N=O	145	C=O <sup>g</sup>	179	O—Br	48

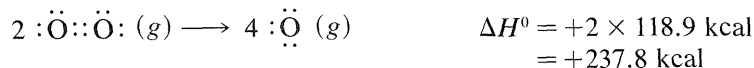
<sup>a</sup>The bond energies for diatomic molecules in this table are from the extensive and up-to-date compilation of J. A. Kerr, M. J. Parsonage, and A. F. Trotman-Dickenson in the *Handbook of Chemistry and Physics*, 55th ed., CRC Press, 1975, pp. F-204 to F-208; those for polyatomic molecules are from L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

<sup>b</sup>Carbon monoxide. <sup>c</sup>For carbon disulfide. <sup>d</sup>For carbon dioxide. <sup>e</sup>For formaldehyde. <sup>f</sup>Other aldehydes. <sup>g</sup>Ketones.

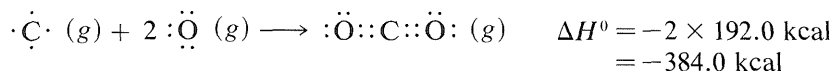
C–H bonds,



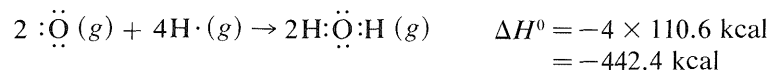
and then 118.9 kcal mole<sup>-1</sup> for the energy of the double bond in oxygen:



Then we make bonds, using 192 kcal mole<sup>-1</sup> for each O=C bond in carbon dioxide,



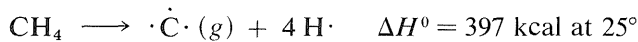
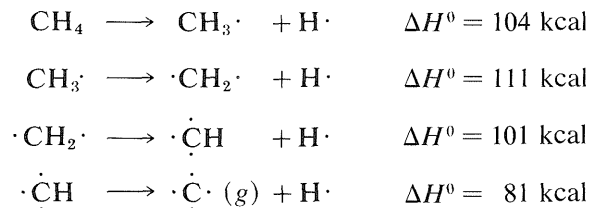
and 110.6 kcal mole<sup>-1</sup> for each of the H–O bonds in water:



The net sum of these  $\Delta H^0$  values is  $394.8 + 237.8 - 384.0 - 442.4 = -193.8$  kcal, which is reasonably close to the value of  $-191.8$  kcal for the heat of combustion of one mole of methane determined experimentally.

The same type of procedure can be used to estimate  $\Delta H^0$  values for many other kinds of reactions of organic compounds in the vapor phase at 25°. Moreover, if appropriate heats of vaporization are available, it is straightforward to compute  $\Delta H^0$  for vapor-phase reactions of substances which are normally liquids or solids at 25°. The special problems that arise when solutions and ionic substances are involved are considered in Chapters 8 and 11.

It is important to recognize that the bond energies listed in Table 4-3 for all molecules other than diatomic molecules are *average* values. That the C–H bond energy is stated to be 98.7 kcal does not mean that, if the hydrogens of methane were detached one by one, 98.7 kcal would have to be put in at each step. Actually, the experimental evidence is in accord with quite different energies for the separate dissociation steps:



The moral is that we should try to avoid using the bond energies in Table 4-3 as a measure of  $\Delta H^0$  for the dissociation of just one bond in a polyatomic molecule. For this we need what are called *bond-dissociation energies*, some of which are given in Table 4-6. The values given have been selected to emphasize

how structure influences bond energy. Thus, C–H bond energies in alkanes decrease in the order primary > secondary > tertiary; likewise, C–H bonds decrease in strength along the series  $\text{C}\equiv\text{C}-\text{H} > \text{C}=\text{C}-\text{H} > \text{C}-\text{C}-\text{H}$ .

How accurate are  $\Delta H^0$  values calculated from bond energies? Generally quite good, provided nonbonded interactions between the atoms are small and the bond angles and distances are close to the normal values (see Section 2-2B). A few examples of calculated and experimental heats of combustion of some hydrocarbons are given in Table 4-4. Negative discrepancies represent heats of combustion *smaller* than expected from the average bond energies and positive values correspond to *larger* than expected heats of combustion.

**Table 4-4**

Calculated and Experimental Heats of Combustion of Gaseous Hydrocarbons at 25°C

Hydrocarbon	$\Delta H^0$ of combustion, calculated from bond energies, kcal mole <sup>-1</sup>	$\Delta H^0$ of combustion, experimental values, <sup>a</sup> kcal mole <sup>-1</sup>	Discrepancy, kcal mole <sup>-1</sup>
CH <sub>4</sub>	-193.8	-191.8	-2.0
CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>	-634.4	-635.1	+0.7
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{CH}_3 \end{array}$	-634.4	-633.1	-1.3
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	-1221.8	-1223.0	+1.2
$\begin{array}{c} \text{CH}_3 \text{ CH}_3 \\   \quad   \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\   \quad   \\ \text{CH}_3 \text{ CH}_3 \end{array}$	-1221.8	-1218.9	-2.9
$\begin{array}{c} \text{CH}_2 \\ / \quad \backslash \\ \text{CH}_2-\text{CH}_2 \end{array}$	-440.6	-468.3	+27.7
$\begin{array}{c} \text{CH}_2 \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}_2 \\   \quad   \\ \text{CH}_2 \quad \text{CH}_2 \\ \backslash \quad / \\ \text{CH}_2 \end{array}$	-881.1	-881.8	+0.7

<sup>a</sup>Based on the individual heats of formation compiled by D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley and Sons, Inc., New York, 1969.

Comparing isomers in Table 4-4, we see that 2-methylpropane and 2,2,3,3-tetramethylbutane give off less heat when burned than do butane and octane, and this is a rather general characteristic result of chain branching.

Cyclopropane has a  $\Delta H^\circ$  of combustion  $27.7 \text{ kcal mole}^{-1}$  greater than expected from bond energies, and this clearly is associated with the abnormal C–C–C bond angles in the ring. These matters will be discussed in detail in Chapter 12. For cyclohexane, which has normal bond angles, the heat of combustion is close to the calculated value.

**Exercise 4-3** The heat of combustion of 1 mole of liquid decane to give carbon dioxide and liquid water is 1620.1 kcal. The heat of vaporization of decane at  $25^\circ$  is  $11.7 \text{ kcal mole}^{-1}$ . Calculate the heat of combustion that would be observed for all the participants in the vapor phase.

**Exercise 4-4** Kilogram for kilogram, would the combustion of gaseous methane or of liquid decane (to  $\text{CO}_2$  and liquid water) give more heat?

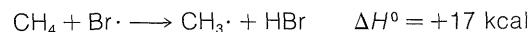
**Exercise 4-5** Use the bond-energy table (4-3) to calculate  $\Delta H^\circ$  for the following reactions in the vapor phase at  $25^\circ$ :

- $\text{CH}_3\text{CH}_2\text{CH}_3 + 5\text{O}_2 \longrightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$
- $\text{CH}_4 + \frac{3}{2}\text{O}_2 \longrightarrow \text{CO} + 2\text{H}_2\text{O}$
- $\text{CO} + 3\text{H}_2 \longrightarrow \text{CH}_4 + \text{H}_2\text{O}$

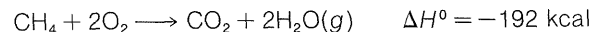
**Exercise 4-6** Calculate  $\Delta H^\circ$  for  $\text{C}(\text{s}) \longrightarrow \text{C}(\text{g})$  from the heat of combustion of 1 gram-atom of carbon to  $\text{CO}_2$  as 94.05 kcal, and the bond energies in Table 4-3.

**Exercise 4-7** The dissociation  $\text{HO—H} \longrightarrow \text{HO}\cdot + \text{H}\cdot$  for gaseous water at  $25^\circ$  has  $\Delta H^\circ$  equal to +119.9 kcal. What is  $\Delta H^\circ$  for dissociation of the O–H bond of  $\text{HO}\cdot$ ?

**Exercise 4-8** Methane reacts slowly with bromine atoms and it has been established that  $\Delta H^\circ$  for the following reaction is 17 kcal per mole of  $\text{CH}_4$ :



- Calculate the C–H bond strength of  $\text{CH}_4$  from this result and any other required bond energies you choose to employ.
- The heat of the following reaction in the vapor state is 192 kcal per mole of  $\text{CH}_4$ :



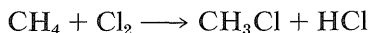
From  $\Delta H^\circ$  and any other required bond energies in Table 4-3, compute a second C–H bond-energy value for methane.

- Consider whether the two C–H bond-energy values obtained in Parts **a** and **b** should be the same in theory and experiment, provided that the experimental error is small.

## 4-4 HALOGENATION OF ALKANES. ENERGIES AND RATES OF REACTIONS

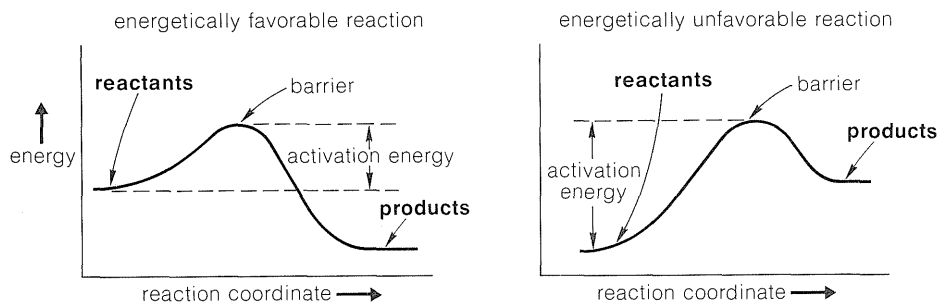
The economies of the highly industrialized nations of the world are based in large part on energy and chemicals produced from petroleum. Although the most important and versatile intermediates for conversion of petroleum to chemicals are compounds with double or triple bonds, it also is possible to prepare many valuable substances by *substitution reactions of alkanes*. In such substitutions, a hydrogen is removed from a carbon chain and another atom or group of atoms becomes attached in its place.

A simple example of a substitution reaction is the formation of chloromethane from methane and chlorine:



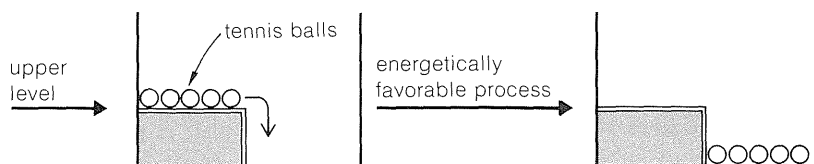
The equation for the reaction is simple, the ingredients are cheap, and the product is useful. However, if we want to decide in advance whether such a reaction is actually feasible, we have to know more. Particularly, we have to know whether the reaction proceeds in the direction it is written and, if so, whether conditions can be found under which it proceeds at a convenient rate. Obviously, if one were to mix methane and chlorine and find that, at most, only 1% conversion to the desired product occurred and that the 1% conversion could be achieved only after a day or so of strong heating, this reaction would be both too unfavorable and too slow for an industrial process.

One way of visualizing the problems involved is with energy diagrams, which show the energy in terms of some arbitrary **reaction coordinate** that is a measure of progress between the initial and final states (Figure 4-4). Diagrams such as Figure 4-4 may not be familiar to you, and a mechanical analogy may be helpful to provide better understanding of the very important ideas involved. Consider a two-level box containing a number of tennis balls. An analog to an energetically favorable reaction would be to have all of the balls

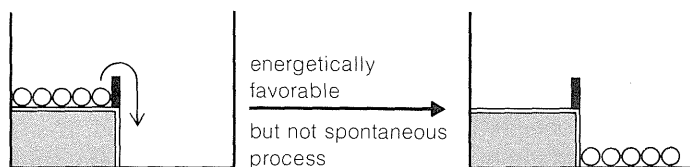


**Figure 4-4** Schematic energy diagrams for reactions that are energetically favorable and unfavorable when proceeding from left to right along the reaction coordinate

on the upper level where any disturbance would cause them to roll down to the lower level under the influence of gravity, thereby losing energy.



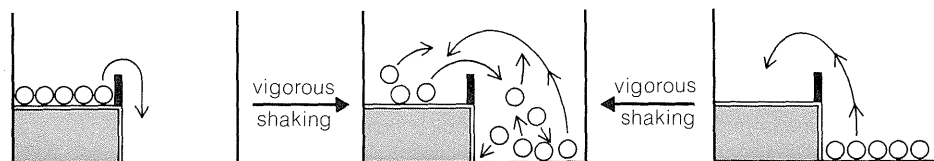
If the upper level is modified and a low fence added to hold the balls in place, it will be just as energetically favorable as when the fence is not there for the balls to be at the lower level. The difference is that the process will not occur *spontaneously* without some major disturbance. We can say there is an **energy barrier** to occurrence of the favorable process.



The situation here has a parallel in the left side of Figure 4-4 where we show an energy barrier to the spontaneous conversion of reactants to products for an energetically favorable chemical reaction.

Now, if we shake the box hard enough, the balls on the upper level can acquire enough energy to bounce over the barrier and drop to the lower level. The balls then can be said to acquire enough **activation energy** to surmount the barrier. At the molecular level, the activation energy must be acquired either by collisions between molecules as the result of their thermal motions, or from some external agency, to permit the reactants to get over the barrier and be transformed into products. We shortly will discuss this more, but first we wish to illustrate another important concept with our mechanical analogy, that of **equilibrium** and **equilibration**.

With gentle shaking of our two-level box, all of the balls on the upper level are expected to wind up on the lower level. There will not be enough activation to have them go from the lower to the upper level. In this circumstance, we can say that the balls are not equilibrated between the lower and upper levels. However, if we shake the box *vigorously* and *continuously*, no matter whether we start with all of the balls on the lower or the upper level, an *equilibrium* will be set up with, on the average, most of the balls in the energetically more favorable lower level, but some in the upper level as well.



To maintain a constant average fraction of the balls at each level with vigorous and continued shaking, the *rate* at which balls go from the upper to the lower level must be equal to the *rate* that they go in the opposite direction. The balls now will be *equilibrated* between the two levels. At equilibrium, the fraction of the balls on each of the two levels is wholly independent of the height of the barrier, just as long as the activation (shaking) is sufficient to permit the balls to go *both* ways.

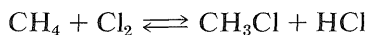
The diagrams of Figure 4-4 are to be interpreted in the same general way. If thermal agitation of the molecules is sufficient, then equilibrium can be expected to be established between the reactants and the products, whether the overall reaction is energetically favorable (left side of Figure 4-4) or energetically unfavorable (right side of Figure 4-4). But as with our analogy, when equilibrium is established we expect the major portion of the molecules to be in the more favorable energy state.

What happens when methane is mixed with chlorine? No measurable reaction occurs when the gases are mixed and kept in the dark at room temperature. Clearly, either the reaction is energetically unfavorable or the energy barrier is high. The answer as to which becomes clear when the mixture is heated to temperatures in excess of 300° or when exposed to strong violet or ultraviolet light, whereby a rapid or even explosive reaction takes place. Therefore the reaction is energetically favorable, but the activation energy is greater than can be attained by thermal agitation alone at room temperature. Heat or light therefore must initiate a pathway for the reactants to be converted to products that has a low barrier or activation energy.

Could we have predicted the results of this experiment ahead of time? First, we must recognize that there really are several questions here. Could we have decided whether the reaction was energetically favorable? That the dark reaction would be slow at room temperature? That light would cause the reaction to be fast? We consider these and some related questions in detail because they are *important* questions and the answers to them are relevant in one way or another to the study of *all* reactions in organic chemistry.

#### 4-4A The Question of the Equilibrium Constant

Presumably, methane could react with chlorine to give chloromethane and hydrogen chloride, or chloromethane could react with hydrogen chloride to give methane and chlorine. If conditions were found for which both reactions proceeded at a finite rate, equilibrium finally would be established when the rates of the reactions in each direction became equal:



At equilibrium, the relationship among the amounts of reactants and products is given by the equilibrium constant expression

$$K_{\text{eq}} = \frac{[\text{CH}_3\text{Cl}][\text{HCl}]}{[\text{CH}_4][\text{Cl}_2]} \quad (4-1)$$

in which  $K_{\text{eq}}$  is the equilibrium constant.

The quantities within the brackets of Equation 4-1 denote either concentrations for liquid reactants or partial pressures for gaseous substances. If the equilibrium constant  $K_{\text{eq}}$  is *greater than 1*, then on mixing equal volumes of each of the participant substances (all are gases above  $-24^\circ$ ), reaction to the *right* will be initially faster than reaction to the left, until equilibrium is established; at this point there will be more chloromethane and hydrogen chloride present than methane and chlorine. However, if the equilibrium constant were *less than 1*, the reaction initially would proceed faster to the *left* and, at equilibrium, there would be more methane and chlorine present than chloromethane and hydrogen chloride.<sup>4</sup> For methane chlorination, we know from experiment that the reaction goes to the right and that  $K_{\text{eq}}$  is much greater than unity. Naturally, it would be helpful in planning other organic preparations to be able to estimate  $K_{\text{eq}}$  in advance.

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**Exercise 4-9** Calculate the pressures of each of the participants at *equilibrium* in the reaction  $\text{CH}_4 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{HCl}$  when  $\text{CH}_4$  and  $\text{Cl}_2$  are mixed, each at one atmosphere pressure. Assume that  $K_{\text{eq}} = 10^{18}$ .

---

It is a common experience to associate chemical reactions with equilibrium constants greater than one with the evolution of heat, in other words, with negative  $\Delta H^0$  values. There are, in fact, many striking examples. Formation of chloromethane and hydrogen chloride from methane and chlorine has a  $K_{\text{eq}}$  of  $10^{18}$  and  $\Delta H^0$  of  $-24$  kcal per mole of  $\text{CH}_3\text{Cl}$  formed at  $25^\circ$ . Combustion of hydrogen with oxygen to give water has a  $K_{\text{eq}}$  of  $10^{40}$  and  $\Delta H^0 = -57$  kcal per mole of water formed at  $25^\circ$ . However, this correlation between  $K_{\text{eq}}$  and  $\Delta H^0$  is neither universal nor rigorous. Reactions are known that absorb heat (are endothermic) and yet have  $K_{\text{eq}} > 1$ . Other reactions have large  $\Delta H^0$  values and equilibrium constants much less than 1.

The problem is that the energy change that correlates with  $K_{\text{eq}}$  is not  $\Delta H^0$  but  $\Delta G^0$  (the so-called “Gibbs standard free energy”)<sup>5</sup>, and if we know  $\Delta G^0$ , we can calculate  $K_{\text{eq}}$  by the equation

$$\Delta G^0 = -2.303RT \log K_{\text{eq}} \quad (4-2)$$

<sup>4</sup>If calculations based on chemical equilibrium constants are unfamiliar to you, we suggest you study one of the general chemistry texts listed for supplemental reading at the end of Chapter 1.

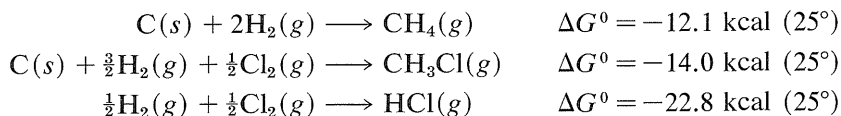
<sup>5</sup>Many books and references use  $\Delta F^0$  instead of  $\Delta G^0$ . The difference between standard free energy  $\Delta G^0$  and the free energy  $\Delta G$  is that  $\Delta G^0$  is defined as the value of the free energy when all of the participants are in standard states. The free energy for  $\Delta G$  for a reaction  $\text{A} + \text{B} + \dots \longrightarrow \text{X} + \text{Y} + \dots$  is equal to  $\Delta G^0 - 2.303RT \log \frac{[\text{X}][\text{Y}] \dots}{[\text{A}][\text{B}] \dots}$

where the products,  $[\text{X}]$ ,  $[\text{Y}] \dots$ , and the reactants,  $[\text{A}]$ ,  $[\text{B}] \dots$ , do not have to be in standard states. We shall use only  $\Delta G^0$  in this book.

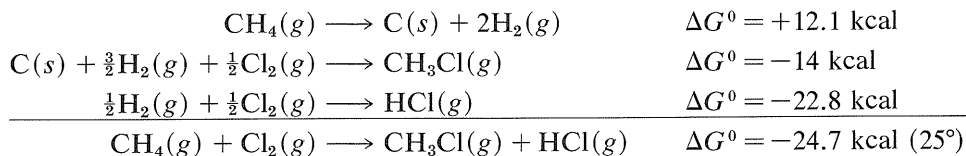


in which  $R$  is the gas constant and  $T$  is the absolute temperature in degrees Kelvin. For our calculations, we shall use  $R$  as  $1.987 \text{ cal deg}^{-1} \text{ mole}^{-1}$  and you should not forget to convert  $\Delta G^0$  to cal.

Tables of  $\Delta G^0$  values for formation of particular compounds (at various temperatures and states) from the elements are available in handbooks and the literature. With these, we can calculate equilibrium constants quite accurately. For example, handbooks give the following data, which are useful for methane chlorination:



Combining these with proper regard for sign gives



and  $\log K_{\text{eq}} = -(-24.7 \times 1000)/(2.303 \times 1.987 \times 298.2)$ , so  $K_{\text{eq}} = 1.3 \times 10^{18}$ . Unfortunately, insufficient  $\Delta G^0$  values for formation reactions are available to make this a widely applicable method of calculating  $K_{\text{eq}}$  values.

The situation is not wholly hopeless, because there is a relationship between  $\Delta G^0$  and  $\Delta H^0$  that also involves  $T$  and another quantity,  $\Delta S^0$ , the standard **entropy change** of the process:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4-3)$$

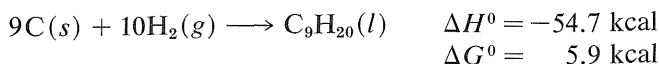
This equation shows that  $\Delta G^0$  and  $\Delta H^0$  are equal when  $\Delta S^0$  is zero. Therefore the sign and magnitude of  $T\Delta S^0$  determine how well  $K_{\text{eq}}$  correlates with  $\Delta H^0$ . Now, we have to give attention to whether we can estimate  $T\Delta S^0$  values well enough to decide whether the  $\Delta H^0$  of a given reaction (calculated from bond energies or other information) will give a good or poor measure of  $\Delta G^0$ .

## 4-4B Entropy and Molecular Disorder

To decide whether we need to worry about  $\Delta S^0$  with regard to any particular reaction, we have to have some idea what physical meaning entropy has. To be very detailed about this subject is beyond the scope of this book, but you should try to understand the physical basis of entropy, because if you do, then you will be able to predict at least qualitatively whether  $\Delta H^0$  will be about the same or very different from  $\Delta G^0$ . Essentially, the entropy of a chemical system is a measure of its *molecular disorder* or *randomness*. Other things being the same, the more random the system is, the more favorable the system is.

Different kinds of molecules have different degrees of translational, vibrational, and rotational freedom and, hence, different average degrees of molecular disorder or randomness. Now, if for a chemical reaction the degree of molecular disorder is different for the products than for the reactants, there will be a change in entropy and  $\Delta S^0 \neq 0$ .

A spectacular example of the effect of molecular disorder in contributing to the difference between  $\Delta H^0$  and  $\Delta G^0$  is afforded by the formation of liquid nonane,  $C_9H_{20}$ , from solid carbon and hydrogen gas at  $25^\circ$ :



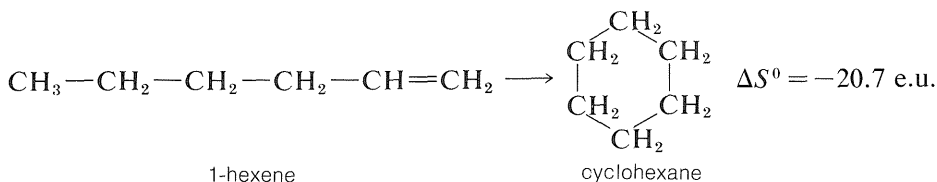
Equations 4-2 and 4-3 can be rearranged to calculate  $\Delta S^0$  and  $K_{eq}$  from  $\Delta H^0$  and  $\Delta G^0$ :

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{-54,700 - 5,900}{298.2} = -203.3 \text{ e.u.}^6$$

$$K_{eq} = 10^{-\Delta G^0/(2.303 RT)} = 10^{-5,900/(2.303 \times 1.987 \times 298.2)} = 4.7 \times 10^{-5}$$

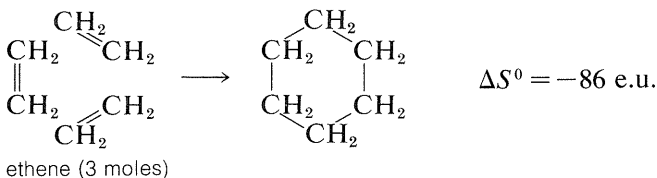
These  $\Delta H^0$ ,  $\Delta S^0$ , and  $K_{eq}$  values can be compared to those for  $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ , for which  $\Delta H^0$  is  $-57$  kcal,  $\Delta S^0$  is  $8.6$  e.u., and  $K_{eq}$  is  $10^{40}$ . Obviously, there is something *unfavorable* about the entropy change from carbon and hydrogen to nonane. The important thing is that there is a great *difference* in the constraints on the atoms on each side of the equation. In particular, hydrogen molecules in the gaseous state have great translational freedom and a high degree of disorder, the greater part of which is lost when the hydrogen atoms become attached to a chain of carbons. This makes for a large *negative*  $\Delta S^0$ , which corresponds to a *decrease* in  $K_{eq}$ . The differences in constraints of the carbons are less important. Solid carbon has an ordered, rigid structure with little freedom of motion of the individual carbon atoms. These carbons are less constrained in nonane, and this would tend to make  $\Delta S^0$  more positive and  $\Delta G^0$  more negative, corresponding to an increase in  $K_{eq}$  (see Equations 4-2 and 4-3). However, this is a *small* effect on  $\Delta S^0$  compared to the enormous difference in the degree of disorder of hydrogen between hydrogen gas and hydrogen bound to carbon in nonane.

Negative entropy effects usually are observed in ring-closure reactions such as the formation of cyclohexane from 1-hexene, which occur with substantial loss of rotational freedom (disorder) about the C-C bonds:



<sup>6</sup>The entropy unit e.u. has the dimensions cal per degree or cal deg<sup>-1</sup>.

There is an even greater loss in entropy on forming cyclohexane from ethene because substantially more freedom is lost in orienting three ethene molecules to form a ring:



For simple reactions, with the same number of molecules on each side of the equation, with no ring formation or other unusual changes in the constraints between the products and reactants,  $\Delta S^\circ$  usually is relatively small. In general, for such processes, we know from experience that  $K_{\text{eq}}$  usually is greater than 1 if  $\Delta H^\circ$  is more negative than  $-15 \text{ kcal}$  and usually is less than 1 for  $\Delta H^\circ$  more positive than  $+15 \text{ kcal}$ . We can use this as a “rule of thumb” to predict whether  $K_{\text{eq}}$  should be greater or less than unity for vapor-phase reactions involving simple molecules. Some idea of the degree of success to be expected from this rule may be inferred from the examples in Table 4-5, which also contains a further comparison of some experimental  $\Delta H^\circ$  values with those calculated from bond energies.

**Table 4-5**

Comparison of Calculated and Experimental  $\Delta H^\circ$  Values and Equilibrium Constants for Some Simple Reactions<sup>a,b</sup>

Reaction	Expt. $\Delta H^\circ$	Calc. $\Delta H^\circ$	$K_{\text{eq}}$
$\text{CH}_4 + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{HCl}$	-23.8	-25	$1 \times 10^{18}$
$\text{C(s)} + 2\text{H}_2 \longrightarrow \text{CH}_4$	-17.9	-15 <sup>c</sup>	$8.0 \times 10^8$
$3\text{C(s)} + 4\text{H}_2 \longrightarrow \text{C}_3\text{H}_8$ (propane)	-24.8	-24 <sup>c</sup>	$1.3 \times 10^4$
$6\text{C(s)} + 7\text{H}_2 \longrightarrow \text{C}_6\text{H}_{14}$ (hexane)	-40.0	-38 <sup>c</sup>	0.9
$9\text{C(s)} + 10\text{H}_2 \longrightarrow \text{C}_9\text{H}_{20}$ (nonane)	-54.7	-51 <sup>c</sup>	$4.7 \times 10^{-5}$
1-hexene $\longrightarrow$ cyclohexane	-19.5	-19.4	$6.0 \times 10^9$
$\frac{1}{2}\text{H}_2 + \frac{3}{2}\text{Cl}_2 \longrightarrow \text{HCl}$	-22.0	-22 <sup>d</sup>	$5.0 \times 10^{16}$
$\frac{3}{2}\text{H}_2 + \frac{1}{2}\text{N}_2 \longrightarrow \text{NH}_3$	-11.0	-11	$8.2 \times 10^2$
$\text{CO} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + \text{H}_2$	-9.9	-10	$1 \times 10^5$
$\text{CH}_3\text{OH} + \text{HCl} \longrightarrow \text{CH}_3\text{Cl} + \text{H}_2\text{O}$	-7.3	-3	$1.8 \times 10^5$

<sup>a</sup>All participants in the gaseous state at 298.2°K unless otherwise stated, and at constant pressure.

<sup>b</sup>Thermochemical values have been taken mostly from *Selected Values of Chemical Thermodynamic Properties* by F. D. Rossini, et al. (Circular of the National Bureau of Standards 500, Washington, D.C., 1952) and *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds* by F. D. Rossini, et al. (American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, 1953).

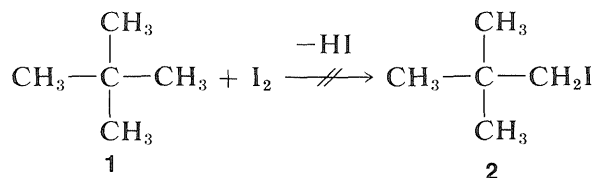
<sup>c</sup>Calculated using  $\Delta H^\circ = 171.3 \text{ kcal}$  per mole for  $\text{C(s)} \longrightarrow \text{C(g)}$ , at 25°.

<sup>d</sup>Not an independent value because the bond energy for product was calculated from the experimental  $\Delta H^\circ$ .

**Exercise 4-10 a.** Calculate  $\Delta H^\circ$  from bond energies for the conversion of 1-hexene to cyclohexane at 25° and from this, with  $\Delta S^\circ$  as  $-20.7$  e.u. per mole, calculate the equilibrium constant  $K_{\text{eq}}$  from Equation 4-2. For comparison, calculate the equilibrium constant that would be expected if the degrees of disorder of the reactants and the products were equal (i.e.,  $\Delta S^\circ = 0$ ). **b.** How large can  $\Delta S^\circ$  be at 25° for a reaction before our  $\pm 15$  kcal rule starts to give incorrect answers?

**Exercise 4-11** Knowing that the equilibrium constant  $K_{\text{eq}}$  for formation of nonane from solid carbon and hydrogen gas is  $4.7 \times 10^{-5}$ , explain why liquid nonane does not forthwith decompose into its elements.

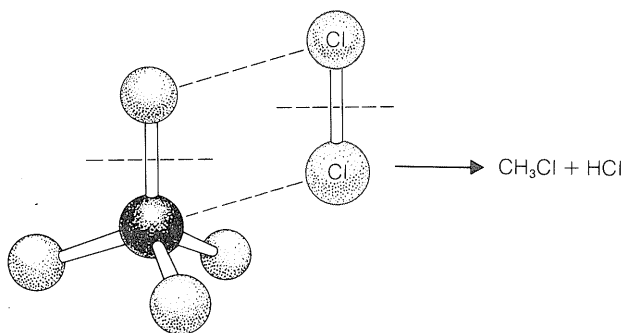
Suppose  $\Delta G^\circ$  is positive, what hope do we have of obtaining a useful conversion to a desired product? There is no simple straightforward and general answer to this question. When the reaction is reversible the classic procedure of removing one or more of the products to prevent equilibrium from being established has many applications in organic chemistry, as will be seen later. When this approach is inapplicable, a change in reagents is necessary. Thus, iodine does not give a useful conversion with 2,2-dimethylpropane, **1**, to give 1-iodo-2,2-dimethylpropane, **2**, because the position of equilibrium is too far to the left ( $K_{\text{eq}} \cong 10^{-5}$ ):



Alternative routes with favorable  $\Delta G^\circ$  values are required. Development of ways to make indirectly, by efficient processes, what cannot be made directly is one of the most interesting and challenging activities of organic chemists.

#### 4-4C Why Do Methane and Chlorine Fail to React in the Dark at 25°?

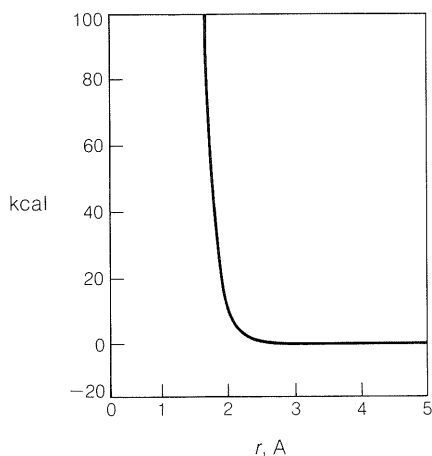
To reach an understanding of why methane and chlorine do not react in the dark, we must consider the details of *how* the reaction occurs—that is, the *reaction mechanism*. The simplest mechanism would be for a chlorine molecule to collide with a methane molecule in such a way as to have chloromethane and hydrogen chloride formed directly as the result of a *concerted* breaking of the Cl–Cl and C–H bonds and making of the C–Cl and H–Cl bonds (see Figure 4-5). The failure to react indicates that there must be an energy barrier too high for this mechanism to operate. Why should this be so?



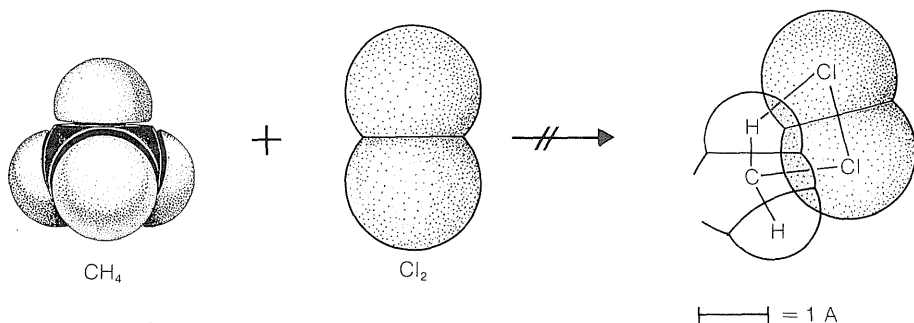
**Figure 4-5** Four-center collision of chlorine with methane as visualized with ball-and-stick models

First, this mechanism involves a very precisely oriented “four-center” collision between chlorine and methane that would have a low probability of occurrence (i.e., a large decrease in entropy because a precise orientation means high molecular ordering). Second, it requires pushing a chlorine molecule sufficiently deeply into a methane molecule so one of the chlorine atoms comes close enough to the carbon to form a bond and yield chloromethane.

Generally, to bring nonbonded atoms to near-bonding distances (1.2 Å to 1.8 Å) requires a large expenditure of energy, as can be seen in Figure 4-6. Interatomic repulsive forces increase rapidly at short distances, and pushing a chlorine molecule into a methane molecule to attain distances similar to the 1.77-Å carbon–chlorine bond distance in chloromethane would require a considerable amount of compression (see Figure 4-7). Valuable information



**Figure 4-6** Graph of the potential energy of pairs of neon atoms as a function of the internuclear distance. The energy values are per mole of neon atoms.

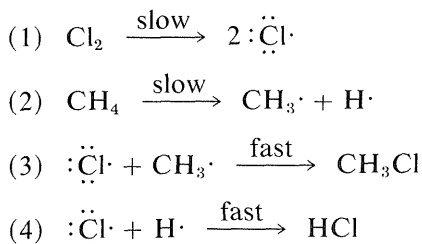


**Figure 4-7** Models showing the degree of atomic compression required to bring a chlorine molecule to within bonding distance of carbon and hydrogen of methane

about interatomic repulsions can be obtained with space-filling models of the CPK type (Section 2-2), which have radii scaled to correspond to actual atomic interference radii, that is, the interatomic distance at the point where curves of the type of Figure 4-6 start to rise steeply. With such models, the degree of atomic compression required to bring the nonbonded atoms to within near-bonding distance is more evident than with ball-and-stick models. It may be noted that four-center reactions of the type postulated in Figure 4-5 are encountered only rarely.

If the concerted four-center mechanism for formation of chloromethane and hydrogen chloride from chlorine and methane is discarded, all the remaining possibilities are *stepwise reaction mechanisms*. A slow stepwise reaction is dynamically analogous to the flow of sand through a succession of funnels with different stem diameters. The funnel with the smallest stem will be the most important bottleneck and, if its stem diameter is much smaller than the others, it alone will determine the flow rate. Generally, a multistep chemical reaction will have a slow *rate-determining step* (analogous to the funnel with the small stem) and other relatively *fast steps*, which may occur either before or after the slow step.

A possible set of steps for the chlorination of methane follows:



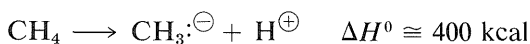
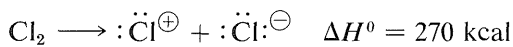
Reactions 1 and 2 involve dissociation of chlorine into chlorine atoms and the breaking of a C-H bond of methane to give a methyl radical and a hydrogen atom. The methyl radical, like chlorine and hydrogen atoms, has one electron not involved in bonding. Atoms and radicals usually are highly reactive, so

formation of chloromethane and hydrogen chloride should proceed readily by Reactions 3 and 4. The crux then will be whether Steps 1 and 2 are reasonable under the reaction conditions.

In the absence of some *external stimulus*, only collisions due to the usual thermal motions of the molecules can provide the energy needed to break the bonds. At temperatures below 100°, it is very rare indeed that thermal agitation alone can supply sufficient energy to break any significant number of bonds stronger than 30 to 35 kcal mole<sup>-1</sup>.

The Cl-Cl bond energy from Table 4-3 is 58.1 kcal, which is much too great to allow bond breaking from thermal agitation at 25° in accord with Reaction 1. For Reaction 2 it is not advisable to use the 98.7 kcal C-H bond energy from Table 4-3 because this is one fourth of the energy required to break all four C-H bonds (see Section 4-3). More specific **bond-dissociation energies** are given in Table 4-6, and it will be seen that to break one C-H bond of methane requires 104 kcal at 25°, which again is too much to be gained by thermal agitation. Therefore we can conclude that Reactions 1-4 can not be an important mechanism for chlorination of methane at room temperature.

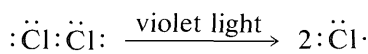
One might ask whether dissociation into ions would provide viable mechanisms for methane chlorination. Part of the answer certainly is: Not in the vapor phase, as the following thermochemical data show:



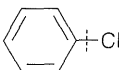
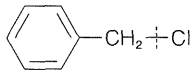
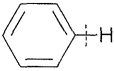
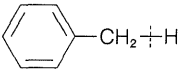
Ionic dissociation simply does not occur at ordinarily accessible temperatures by collisions between molecules in the vapor state. What is needed for formation of ions is either a highly energetic external stimulus, such as bombardment with fast-moving electrons, or an ionizing solvent that will assist ionization. Both of these processes will be discussed later. The point here is that ionic dissociation is not a viable step for the vapor-phase chlorination of methane.

#### 4-4D Why Does Light Induce the Chlorination of Methane?

First, we should make clear that the light does more than provide energy merely to lift the molecules of methane and chlorine over the barrier of Figure 4-4. This is evident from the fact that very little light is needed, far less than one light photon per molecule of chloromethane produced. The light could activate either methane or chlorine, or both. However, methane is colorless and chlorine is yellow-green. This indicates that chlorine, not methane, interacts with visible light. A photon of near-ultraviolet light, such as is absorbed by chlorine gas, provides more than enough energy to split the molecule into two chlorine atoms:



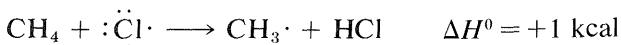
**Table 4-6**  
Bond-Dissociation Energies at 25°

Compound	Bond energy (kcal mole <sup>-1</sup> ) <sup>a</sup>	Compound	Bond energy (kcal mole <sup>-1</sup> ) <sup>a</sup>
CH <sub>3</sub> -H	104	H <sub>3</sub> C-CH <sub>3</sub>	88
CH <sub>3</sub> CH <sub>2</sub> -H	98	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{CH}_3 \end{array}$	77
(CH <sub>3</sub> ) <sub>2</sub> CH-H	95	H <sub>3</sub> C-F	109
(CH <sub>3</sub> ) <sub>3</sub> C-H	92	H <sub>3</sub> C-Cl	84
CH <sub>2</sub> =CH-H	108	CCl <sub>3</sub> -Cl	73
HC≡C-H	128	H <sub>2</sub> C=CH-Cl	89
$\begin{array}{c} \text{CH}_2 \\   \\ \text{CH}_2-\text{CH}-\text{H} \\   \\ \text{CH}_2 \end{array}$	101	H <sub>2</sub> C=CHCH <sub>2</sub> -Cl	71
$\begin{array}{c} \text{CH}_2 \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}-\text{H} \\ \backslash \quad / \\ \text{CH}_2 \end{array}$	97		95
$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad \backslash \\ \text{CH}_2-\text{CH}-\text{H} \\   \quad / \\ \text{CH}_2-\text{CH}_2 \end{array}$	95		69
$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\   \quad \backslash \\ \text{CH}_2-\text{CH}-\text{H} \\   \quad / \\ \text{CH}_2-\text{CH}_2 \end{array}$	96	H <sub>3</sub> C-Br	70
	110	CCl <sub>3</sub> -Br	54
CH <sub>2</sub> =CH-CH <sub>2</sub> -H	89	H <sub>3</sub> C-I	56
	85	HC≡CH → 2CH	230
Cl <sub>3</sub> C-H	96	H <sub>2</sub> C≡CH <sub>2</sub> → 2CH <sub>2</sub>	173
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{H} \end{array}$	86	HO-H	119
		CH <sub>3</sub> O-H	102
		HS-H	90
		CH <sub>3</sub> S-H	88
		HO-OH	51
		(CH <sub>3</sub> ) <sub>3</sub> CO-OC(CH <sub>3</sub> ) <sub>3</sub>	37

<sup>a</sup>These values are mostly from the compilations of K. W. Egger and A. T. Cocks, *Helv. chim. Acta* **56**, 1516 (1973), and J. A. Kerr, M. J. Parsonage, and A. F. Trotman-Dickenson, *Handbook of Chemistry and Physics*, 55th ed., CRC Publishing Co., 1975, F-213 to F-216.



Once produced, a chlorine atom can remove a hydrogen atom from a methane molecule and form a methyl radical and a hydrogen chloride molecule. The bond-dissociation energies of  $\text{CH}_4$  (104 kcal) and  $\text{HCl}$  (103.1 kcal) suggest that this reaction is endothermic by about 1 kcal:

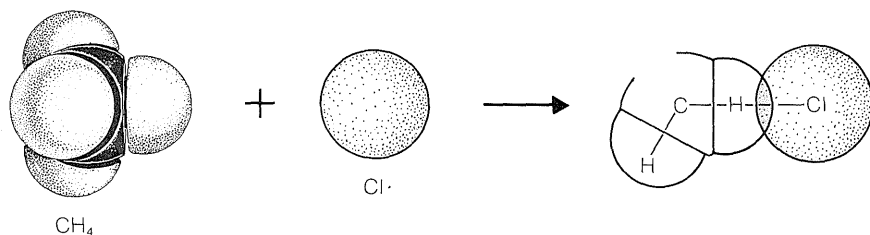


The attack of a chlorine atom on a methane hydrogen is not expected to require a precisely oriented collision. Moreover, the interatomic repulsions should be considerably smaller than in the four-center mechanism discussed previously for the reaction of molecular chlorine with methane because only two centers have to come close together (Figure 4-8). The methyl radical resulting from the attack of atomic chlorine on a hydrogen of methane then can remove a chlorine atom from molecular chlorine and form chloromethane and a new chlorine atom:



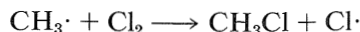
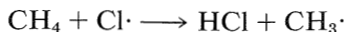
Use of bond-dissociation energies gives a calculated  $\Delta H^0$  of  $-26$  kcal for this reaction, which is certainly large enough, by our rule of thumb, to predict that  $K_{\text{eq}}$  will be greater than 1. Attack of a methyl radical on molecular chlorine is expected to require a somewhat more oriented collision than for a chlorine atom reacting with methane (the chlorine molecule probably should be endwise, not sideways, to the radical) but the interatomic repulsion probably should not be much different.

The net result of  $\text{CH}_4 + \text{Cl}\cdot \longrightarrow \text{CH}_3\cdot + \text{HCl}$  and  $\text{CH}_3\cdot + \text{Cl}_2 \longrightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$  is formation of chloromethane and hydrogen chloride from methane and chlorine. Notice that the chlorine atom consumed in the first step is replaced by another one in the second step. This kind of sequence of reactions is called a **chain reaction** because, in principle, one atom can induce the reaction of an infinite number of molecules through operation of a “chain” or cycle of reactions. In our example, chlorine atoms formed by the action of light on

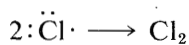
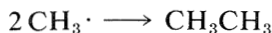
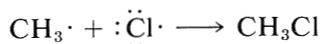


**Figure 4-8** Models showing the degree of atomic compression required to bring a chlorine atom to within bonding distance of a methane hydrogen. Compare with Figure 4-7.

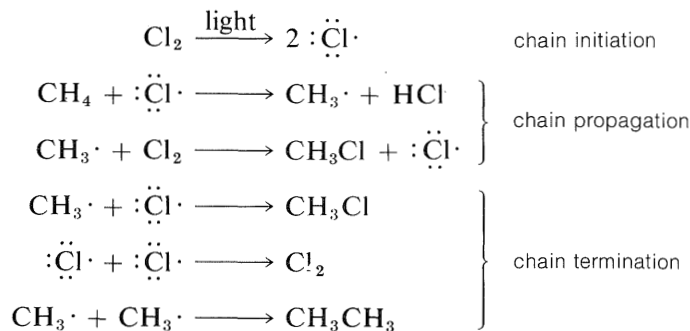
$\text{Cl}_2$  can induce the chlorination of methane by the **chain-propagating steps**:



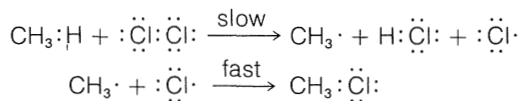
In practice, chain reactions are limited by so-called **termination** processes. In our example, chlorine atoms or methyl radicals are destroyed by reacting with one another, as shown in the following equations:



Chain reactions may be considered to involve three phases. First, **chain initiation** must occur, which for methane chlorination is activation and conversion of chlorine molecules to chlorine atoms by light. Second, **chain-propagation** steps convert reactants to products with no net consumption of atoms or radicals. The propagation reactions occur in competition with **chain-terminating** steps, which result in destruction of atoms or radicals. Putting everything together, we can write:

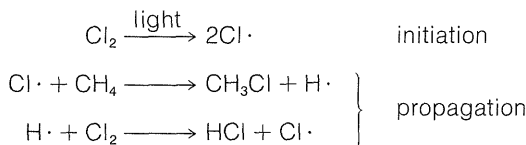


**Exercise 4-12** A possible mechanism for the reaction of chlorine with methane would be to have collisions by which a chlorine molecule removes a hydrogen according to the following scheme:



Use appropriate bond energies to assess the likelihood of this reaction mechanism. What about the possibility of a similar mechanism with elemental fluorine and methane?

**Exercise 4-13** Calculate  $\Delta H^\circ$  for each of the propagation steps of methane chlorination by a mechanism of the type

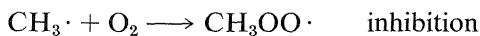


Compare the relative energetic feasibilities of these chain-propagation steps with those of other possible mechanisms.

The chain-termination reactions are expected to be exceedingly fast because atoms and radicals have electrons in unfilled shells that normally are bonding. As a result, bond formation can begin as soon as the atoms or radicals approach one another closely, without need for other bonds to begin to break. The evidence is strong that bond-forming reactions between atoms and radicals usually are **diffusion-controlled**, that there is almost no barrier or activation energy required, and the rates of combination are simply the rates at which encounters between radicals or atoms occur.

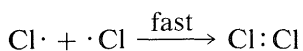
If the rates of combination of radicals or atoms are so fast, you might well wonder how chain propagation ever could compete. Of course, competition will be possible if the propagation reactions themselves are fast, but another important consideration is the fact that the *atom or radical concentrations are very low*. Suppose that the concentration of  $\text{Cl}\cdot$  is  $10^{-11}M$  and the  $\text{CH}_4$  concentration  $1M$ . The probability of encounters between two  $\text{Cl}\cdot$  atoms will be proportional to  $10^{-11} \times 10^{-11}$ , and between  $\text{CH}_4$  and  $\text{Cl}\cdot$  atoms it will be  $10^{-11} \times 1$ . Thus, other things being the same,  $\text{CH}_4 + \text{Cl}\cdot \longrightarrow \text{CH}_3\cdot + \text{HCl}$  (propagation) would be favored over  $2\text{Cl}\cdot \longrightarrow \text{Cl}_2$  (termination) by a factor of  $10^{11}$ . Under favorable conditions, the methane-chlorination chain may go through 100 to 10,000 cycles before termination occurs by radical or atom combination. Consequently the efficiency (or **quantum yield**) of the reaction is very high in terms of the amount of chlorination that occurs relative to the amount of the light absorbed.

The overall rates of chain reactions usually are slowed very much by substances that can combine with atoms or radicals and convert them into species incapable of participating in the chain-propagation steps. Such substances are called **radical traps**, or **inhibitors**. Oxygen acts as an inhibitor in the chlorination of methane by rapidly combining with a methyl radical to form the comparatively stable (less reactive) peroxyethyl radical,  $\text{CH}_3\text{OO}\cdot$ . This effectively terminates the chain:



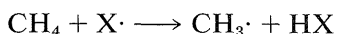
## 4-4E Can We Predict Whether Reactions Will Be Fast or Slow?

To a considerable degree, we can predict *relative* reactivities, provided we use common sense to limit our efforts to reasonable situations. In the preceding section, we argued that reactions in which atoms or radicals combine can well be expected to be extremely fast because each entity has a potentially bonding electron in an outer unfilled shell, and bringing these together to form a bond does not require that other bonds be broken:



For the reaction  $\text{CH}_4 + \text{Cl}\cdot \longrightarrow \text{CH}_3\cdot + \text{HCl}$ , the methane hydrogen and carbon valence shells are filled and, as  $\text{Cl}\cdot$  approaches, it can combine with a hydrogen only if a C–H bond is broken. This kind of process is associated with a barrier but is very different from a nonreactive encounter, such as two neon atoms coming together (see Figure 4-6). As  $\text{CH}_4$  and  $\text{Cl}\cdot$  get closer together, the new bond starts to form and the old bond starts to break. At the top of the barrier, the hydrogen will be bonded partly to chlorine and partly to carbon,  $[\text{Cl}\cdots\text{H}\cdots\text{CH}_3]$ , and this we call the **activated complex** or **transition state**. The concept of the transition state is an important one, which we will use repeatedly later in connection with many other kinds of reactions. The value of the concept lies in the fact that the reacting system, when it reaches the top of the barrier, can be thought of as a chemical entity with a particular, even if not a well-defined, structure and definite thermodynamic properties.

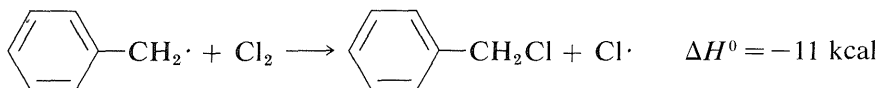
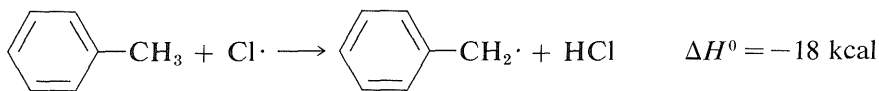
The difference between the average energy of the reactants and the energy of the transition state is called the *activation energy* (Figure 4-4). We expect this energy to be smaller (lower barrier) if a weak bond is being broken and a strong bond is being made. The perceptive reader will notice that we are suggesting a parallel between reaction rate and  $\Delta H^0$  because  $\Delta H^0$  depends on the difference in the strengths of the bonds broken and formed. Yet previously (Section 4-4A), we pointed out that the energy barrier for a reaction need bear no relationship to how energetically feasible the reaction is, and this is indeed true for complex reactions involving many steps. But our intuitive parallel between rate and  $\Delta H^0$  usually works quite well for the rates of *individual* steps. This is borne out by experimental data on rates of removal of a hydrogen atom from methane by atoms or radicals ( $\text{X}\cdot$ ), such as  $\text{F}\cdot$ ,  $\text{Cl}\cdot$ ,  $\text{Br}\cdot$ ,  $\text{HO}\cdot$ ,  $\text{H}_2\text{N}\cdot$ , which generally parallel the strength of the new bond formed:



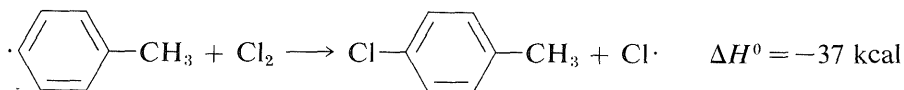
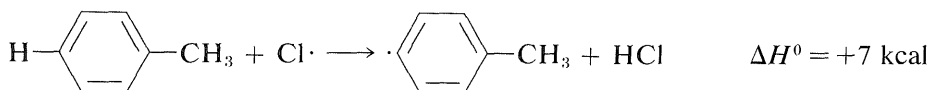
Similarly, if we look at the H–C bond-dissociation energies of the hydrocarbons shown in Table 4-6, we would infer that  $\text{Cl}\cdot$  would remove a hydrogen most rapidly from the carbon forming the weakest C–H bond and, again, this is very much in accord with experience. For example, the chlorination of methylbenzene (toluene) in sunlight leads to the substitution of a methyl hydro-

gen rather than a ring hydrogen for the reason that the methyl C–H bonds are weaker and are attacked more rapidly than the ring C–H bonds. This can be seen explicitly in the  $\Delta H^0$  values for the chain-propagation steps calculated from the bond-dissociation energies of Table 4-6.

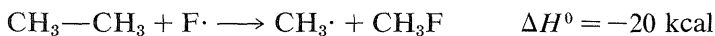
*Methyl substitution (observed):*



*Ring substitution (not observed):*



The  $\Delta H^0$  of ring-hydrogen abstraction is unfavorable by +7 kcal because of the high C–H bond energy (110 kcal). Thus this step is not observed. It is too slow in comparison with the more favorable reaction at the methyl group even though the second propagation step is energetically favorable by –37 kcal and presumably would occur very rapidly. Use of bond-dissociation energies to predict relative reaction rates becomes much less valid when we try to compare different kinds of reactions. To illustrate, ethane might react with  $\text{F}\cdot$  to give fluoromethane or hydrogen fluoride:



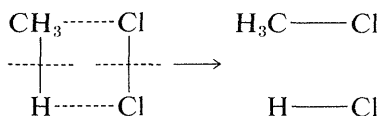
It is not a good idea to try to predict the relative rates of these two reactions on the basis of their overall  $\Delta H^0$  values because the nature of the bonds made and broken is too different.

**Exercise 4-14** Show how the data in Table 4-6 might be extrapolated to predict the principal product to be expected from the vapor-phase, light-induced monochlorination of 1,1-dimethylcyclopropane.

#### 4-4F How Should We Go about Formulating a Reaction Mechanism?

Faced with proposing a mechanism for a reaction that involves overall making or breaking of more than two bonds, the beginner almost invariably tries to concoct a process wherein, with a *single* step, all of the right bonds break and all of the right bonds form. Such mechanisms, called **concerted mechanisms**, have three disadvantages. First, they are almost impossible to prove correct. Second, prediction of the relative rates of reactions involving concerted mechanisms is especially difficult. Third, concerted mechanisms have a certain sterility in that one has no control over what happens while they are taking place, except an overall control of rate by regulating concentrations, temperature, pressure, choice of solvents, and so on.

To illustrate, suppose that methane chlorination appeared to proceed by way of a one-step concerted mechanism:



At the instant of reaction, the reactant molecules in effect would disappear into a dark closet and later emerge as product molecules. There is no way to prove experimentally that all of the bonds were made and formed simultaneously. All one could do would be to use the most searching possible tests to probe for the existence of discrete steps. If these tests fail, the reaction still would not be *proved* concerted because other, still more searching tests might be developed later that would give a different answer. The fact is, once you accept that a particular reaction is concerted, you, in effect, accept the proposition that further work on its *mechanism* is futile, no matter how important you might feel that other studies would be regarding the factors affecting the reaction rate.

The experienced practitioner in reaction mechanisms accepts a concerted mechanism for a reaction involving the breaking and making of more than two bonds as a last resort. He first will try to analyze the overall transformation in terms of discrete steps that are individually simple enough surely to be concerted and that also involve energetically reasonable intermediates.

Such an analysis of a reaction in terms of discrete mechanistic steps offers many possibilities for experimental studies, especially in development of procedures for detecting the existence, even if highly transitory, of the proposed intermediates. We shall give many examples of the fruitfulness of this kind of approach in subsequent discussions.

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#### 4-5 PRACTICAL HALOGENATIONS. PROBLEMS OF SELECTIVITY

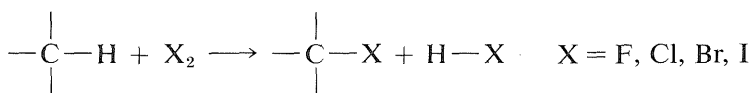
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Given the knowledge that a particular reaction will proceed at a suitable rate, a host of practical considerations are necessary for satisfactory operation.

These considerations include interference by possible side reactions that give products other than those desired, the ease of separation of the desired products from the reaction mixture, and costs of materials, apparatus, and labor. We shall consider these problems in connection with the important synthetic reactions discussed in this book.

The chlorination of saturated hydrocarbons can be induced by light, but also can be carried out at temperatures of about 300° in the dark. Under such circumstances the mechanism is similar to that of light-induced chlorination, except that the chlorine atoms are formed by thermal dissociation of chlorine molecules. Solid carbon surfaces catalyze thermal chlorination, possibly by aiding in the cleavage of the chlorine molecules.

Direct monohalogenation of saturated hydrocarbons works satisfactorily only with chlorine and bromine. For the general reaction



the calculated  $\Delta H^0$  value is negative and very large for fluorine, negative and moderate for chlorine and bromine, and positive for iodine (see Table 4-7). With fluorine, the reaction evolves so much heat that it may be difficult to control, and products from cleavage of carbon-carbon as well as of carbon-hydrogen bonds may be obtained. The only successful, direct fluorination procedure for hydrocarbons involves diffusion of minute amounts of fluorine mixed with helium into liquid or solid hydrocarbons at low temperatures, typically  $-78^\circ$  (Dry Ice temperature). As fluorination proceeds, the concentration of fluorine can be increased. The process is best suited for preparation of completely fluorinated compounds, and it has been possible to obtain in this way amounts of  $(\text{CF}_3)_4\text{C}$  and  $(\text{CF}_3)_3\text{C}-\text{C}(\text{CF}_3)_3$  from 2,2-dimethylpropane and 2,2,3,3-tetramethylbutane corresponding to 10–15% yields based on the fluorine used.

Bromine generally is much less reactive toward hydrocarbons than chlorine is, both at high temperatures and with activation by light. Nonetheless, it usually is possible to brominate saturated hydrocarbons successfully. Iodine is unreactive.

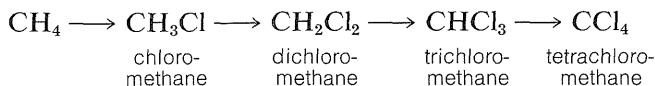
**Table 4-7**

Calculated Heats of Reaction for Halogenation of Hydrocarbons

X	$\Delta H^0$ (kcal mole <sup>-1</sup> ) <sup>a</sup>	
F	-116	$\begin{array}{c}   \\ -\text{C}-\text{H} \\   \end{array} + \text{X}_2 \longrightarrow \begin{array}{c}   \\ -\text{C}-\text{X} \\   \end{array} + \text{HX}$
Cl	-27	
Br	-10	
I	13	

<sup>a</sup>Calculated from the bond energies of Table 4-3.

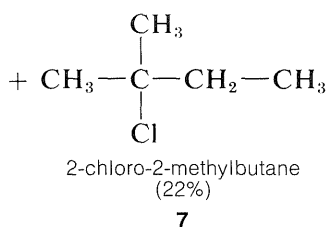
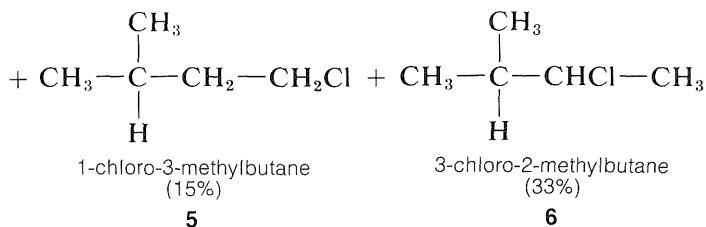
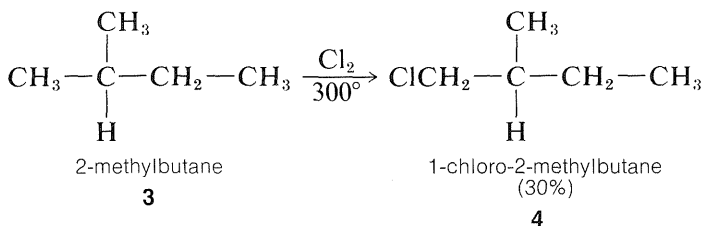
The chlorination of methane does not have to stop with the formation of chloromethane (methyl chloride). It is usual when chlorinating methane to obtain some of the higher chlorination products: dichloromethane (methylene chloride), trichloromethane (chloroform), and tetrachloromethane (carbon tetrachloride):



In practice, one can control the degree of substitution to a considerable extent by controlling the methane-chlorine ratio. For example, for monochlorination to predominate, a high methane-chlorine ratio is necessary such that the chlorine atoms react with  $\text{CH}_4$  and not with  $\text{CH}_3\text{Cl}$ .

#### 4-5A Selectivity in Alkane Halogenation

For propane and higher hydrocarbons for which more than one monosubstitution product is generally possible, difficult separation problems may arise when a particular product is desired. For example, the chlorination of 2-methylbutane **3** at  $300^\circ$  gives all four possible monosubstitution products, **4**, **5**, **6**, and **7**:





On a purely statistical basis, we may expect the ratio of products from **3** to correlate with the number of available hydrogens at the various positions of substitution. That is, **4**, **5**, **6**, and **7** would be formed in the ratio 6:3:2:1 (50%:25%:17%:8%). However, as can be seen from Table 4-6, the strengths of hydrogen bonds to primary, secondary, and tertiary carbons are not the same and, from the argument given in Section 4-4E we would expect the weaker C–H bonds to be preferentially attacked by Cl $\cdot$ . The proportion of **7** formed is about three times that expected on a statistical basis which is in accord with our expectation that the tertiary C–H bond of 2-methylbutane should be the weakest of the C–H bonds. (See Table 4-6.)

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**Exercise 4-15\*** Use the data given above for the percentages of the monochlorides formed in the vapor-phase chlorination of 2-methylbutane at 300° and take into account the statistical factors for the different numbers and kinds of hydrogens in answering the following:

- From the ratio of 1-chloro-2-methylbutane to 1-chloro-3-methylbutane formed, what can you say about the C–H bond strengths at the CH<sub>3</sub> carbons?
  - Calculate the ratio of rates of attack of Cl $\cdot$  on the *individual* hydrogens attached to primary (C1 and C4), secondary (C3), and tertiary (C2) carbons of 2-methylbutane. Check these ratios by showing they are consistent with the composition of the overall chlorination product.
  - Use your relative rate ratios from Part b to calculate the ratios of isomers to be expected in the thermal (300°) monochlorination of (a) propane, (b) 2-methylpropane, and (c) 2,2-dimethylbutane. Show your method in detail.
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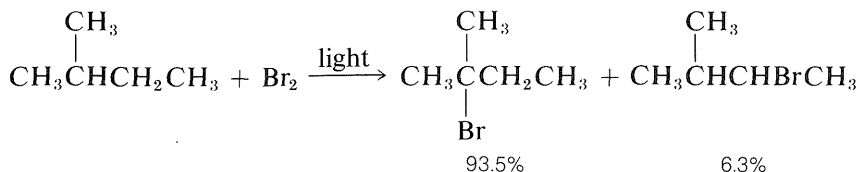
The factors governing selectivity in halogenation of alkanes follow:

- The rates at which the various C–H bonds of 2-methylbutane are broken by attack of chlorine atoms approach 1:1:1 as the temperature is raised above 300°. At higher temperatures both chlorine atoms and hydrocarbons become more reactive because of increases in their thermal energies. Ultimately, temperatures are attained where a chlorine atom essentially removes the first hydrogen with which it collides regardless of position on the hydrocarbon chain. In such circumstances, the composition of monochlorination products will correspond to that expected from simple statistics.

- Bromine atoms are far more selective than chlorine atoms. This is not unexpected because  $\begin{array}{c} | \\ \text{---C---H} \\ | \end{array} + \text{Br}\cdot \longrightarrow \begin{array}{c} | \\ \text{---C}\cdot \\ | \end{array} + \text{HBr}$  is endothermic,

whereas corresponding reactions with a chlorine atom usually are exothermic (data from Table 4-6). Bromine removes only those hydrogens that are relatively weakly bonded to a carbon atom. As predicted, attack of Br $\cdot$  on 2-methylbutane leads mostly to 2-bromo-2-methylbutane, some secondary bromide,

and essentially no primary bromides:



3. The selectivity of chlorination reactions carried on in *solution* is increased markedly in the presence of benzene or alkyl-substituted benzenes because benzene and other arenes form loose complexes with chlorine atoms. This substantially cuts down chlorine-atom reactivity, thereby making the chlorine atoms behave more like bromine atoms.

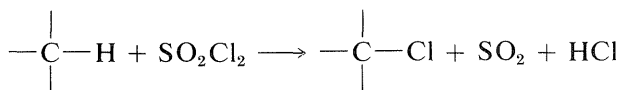
**Exercise 4-16 a.** Write equations to show reasonable radical-chain initiation, propagation, and termination steps in the monobromination of 2-methylbutane shown above. Explain clearly why the products of chain termination are obtained in trace amounts only.

**b.** Use bond energies of Tables 4-3 and 4-6 and bond-dissociation energies of 63 kcal for tertiary C–Br and 68 kcal for secondary C–Br bonds to estimate  $\Delta H^\circ$  for each of the propagation steps leading to the two observed products. Which propagation step in the formation of 2-bromo-2-methylbutane is expected to be the slow step?

**c.** Calculate the relative rates of attack of bromine atoms at the tertiary C–H *versus* the secondary C–H bonds from the product composition in the bromination of 2-methylbutane. Are the relative rates qualitatively consistent with what you would expect based on the  $\Delta H^\circ$  data?

## 4-5B Chemical Initiation of Radical-Chain Substitution

It is possible to achieve chlorination of alkanes using sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ , bp  $69^\circ$ ) in place of chlorine:

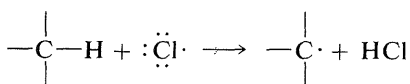
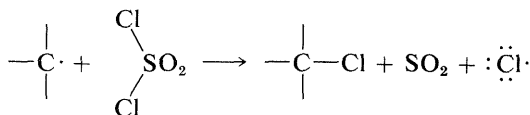


The reaction has a radical-chain mechanism and the chains can be initiated by light or by chemicals, usually peroxides, ROOR. Chemical initiation requires an *initiator* with a weak bond that dissociates at temperatures between  $40\text{--}80^\circ$ . Peroxides are good examples. The O–O bond is very weak (30–50 kcal) and on heating dissociates to alkoxy radicals,  $\text{RO}\cdot$ , which are reactive enough to generate the chain-propagating radicals from the reactants. The exact sequence

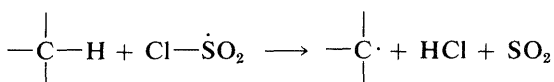
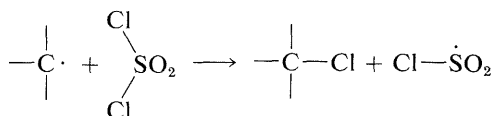
of chemical initiation is not always known, but a plausible route in the present case would have  $\text{RO}\cdot$  abstract hydrogen from the alkane:



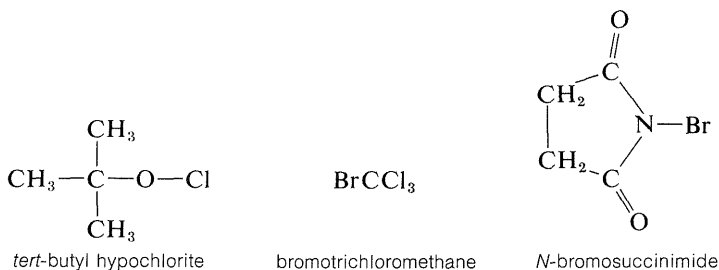
The propagation steps that would follow are



Chlorination with sulfonyl chloride of alkanes with more than one kind of hydrogen gives a mixture of alkyl chlorides resembling that obtained with chlorine itself. However, in some circumstances the mixture of chlorides is not the same mixture obtained with chlorine itself and when this is true, the hydrogen-abstraction step probably involves  $\cdot\text{SO}_2\text{Cl}$  rather than  $\text{Cl}\cdot$ . The alternative propagation steps then are

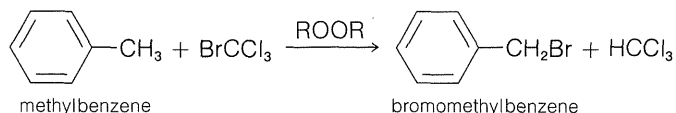


Different product ratios are expected from  $\text{Cl}\cdot$  and  $\text{ClSO}_2\cdot$  for the same reason that  $\text{Cl}\cdot$  and  $\text{Br}\cdot$  lead to different product ratios (Section 4-5A). Other reagents that sometimes are useful halogenating agents in radical-chain reactions include



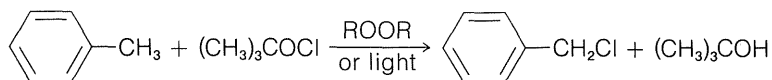
How these substances are employed is illustrated by Exercises 4-17 through 4-19 and 4-36.

**Exercise 4-17\*** The peroxide-induced bromination of methylbenzene with bromotrichloromethane gives bromomethylbenzene and trichloromethane:



Write initiation, propagation, and termination steps for this radical-chain reaction. Estimate a  $\Delta H^\circ$  for the overall reaction using the bond-dissociation energies of Table 4-6. Would you expect bromotrichloromethane to be a selective or nonselective brominating agent? Explain.

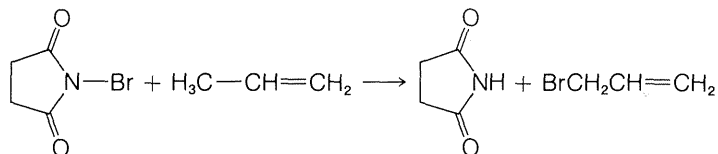
**Exercise 4-18\*** *tert*-Butyl hypochlorite is a useful chlorinating agent. On irradiation, or with chemical initiators, this reagent with methylbenzene gives chloromethylbenzene:



Write a possible mechanism for the reaction, showing the propagation steps with  $(\text{CH}_3)_3\text{CO}\cdot$  as the chain-propagating radical. Use the bond-dissociation energies of Table 4-6 to determine whether your mechanism is energetically and kinetically feasible. Assume the O–Cl bond-dissociation energy of *tert*-butyl hypochlorite is 61 kcal mole<sup>-1</sup>.

**Exercise 4-19\***

**a.** *N*-Bromosuccinimide (NBS) is an excellent brominating reagent and is used widely to prepare bromalkenes from alkenes (Wohl-Ziegler reaction):



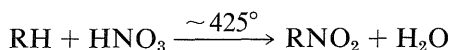
The reaction is initiated with chemical initiators (peroxides) and is as selective as bromination with molecular bromine. Write plausible propagation steps (three of them) for this reaction, given the fact that the actual brominating agent appears to be molecular bromine that is generated from NBS by HBr.

**b.** What products would you expect to be formed on bromination of 2-methylbutane with *N*-bromosuccinimide?

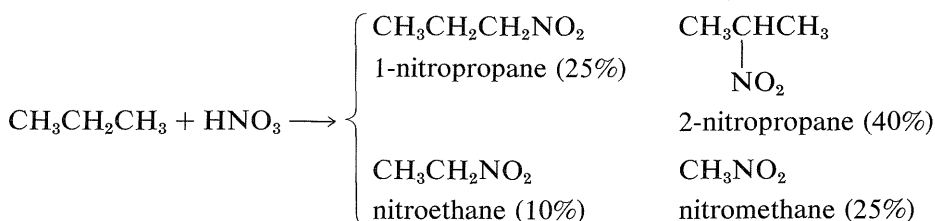
## 4-6 NITRATION OF ALKANES

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Another reaction of commercial importance is the nitration of alkanes to give nitroparaffins. Such reactions usually are carried out in the vapor phase at elevated temperatures using nitric acid ( $\text{HNO}_3$ ) or nitrogen tetroxide ( $\text{N}_2\text{O}_4$ ) as the nitrating agent:



All available evidence points to a radical mechanism for nitration, but many aspects of the reaction are not fully understood. Mixtures are obtained; nitration of propane gives not only 1- and 2-nitropropanes but nitroethane and nitromethane:



In commercial practice, the yield and product distribution in nitration of alkanes is controlled as far as possible by the judicious addition of catalysts (e.g., oxygen and halogens), which are believed to raise the concentration of alkyl radicals. The products are separated from the mixtures by fractional distillation.

### Additional Reading

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S. W. Benson, "Bond Energies," *J. Chem. Educ.* **42**, 502 (1965).

E. S. Huyser, *Free-Radical Chain Reactions*, Wiley-Interscience, New York, 1970.

A very useful procedure for calculating heats of formation and entropies of organic molecules is available that sums contributions of specific groups rather than summing bond energies. The tables required are rather large, but the answers are more precise because second-order effects associated with particular groups are taken into account. See "Additivity Rules for Estimation of Thermochemical Properties," by S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chemical Reviews* **69**, 279 (1969).

D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, John Wiley and Sons, Inc., New York, 1969. Summarizes  $\Delta H^\circ$  of formation of some 4500 organic compounds and  $\Delta G^\circ$  values for about half that many. Includes many valuable descriptions of the use of thermodynamic data in the planning of industrial processes.

J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, New York, 1970. A very authoritative compilation of  $\Delta H^\circ$  values in which all of the data for a given compound are listed and a selected value given. No  $\Delta G^\circ$  values are given.

### Supplementary Exercises

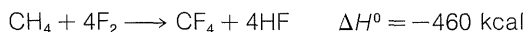
**4-20** Calculate  $\Delta H^\circ$  for the following reactions in the vapor state at  $25^\circ$ , using the bond energies of Table 4-3:

- $2\text{CH}_4 + 7\text{Cl}_2 \longrightarrow \text{CCl}_3\text{—CCl}_3 + 8\text{HCl}$
- $\text{CH}_3\text{CH}_3 + \frac{7}{2}\text{O}_2 \longrightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$
- $\text{CH}_3\text{CH}_3 + \text{H}_2 \longrightarrow 2\text{CH}_4$
- $\text{CH}_3\text{CH}_3 + \text{Br}_2 \longrightarrow 2\text{CH}_3\text{Br}$
- $\text{CH}_4 + 2\text{Cl}_2 \longrightarrow \text{C}(g) + 4\text{HCl}$

**4-21 a.** Would  $\Delta H^\circ$  for Exercise 4-20e be greater, or less, if C (solid) were the reaction product? Explain.

**b.** What are the implications of the heats of reaction determined in Exercise 4-20c and d with regard to the "saturated" character of ethane?

**4-22** A C–F bond energy can be computed from thermochemical studies of the vapor-phase reaction



Show how the  $\Delta H^\circ$  value for this reaction may be used to calculate the energy of the C–F bond if all the other required bond energies are known.

**4-23** The heat of combustion of liquid benzene to give carbon dioxide and liquid water is  $780.96 \text{ kcal mole}^{-1}$ . The heat required to vaporize one mole of benzene is  $8.2 \text{ kcal}$  and one mole of water  $10.5 \text{ kcal}$ . Calculate the heat of combustion of benzene from the bond energies given in Table 4-3 and determine the extent to which benzene is *more*, or *less*, *stable* than expected from bond energies shown.

**4-24\*** Suppose we assume the following bond energies (kcal):

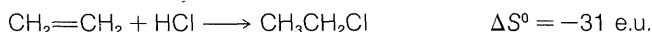
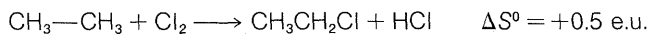
$\equiv\text{C—H}$	120	$\text{C}\equiv\text{C}$	230
$=\text{C—H}$	104	$\text{C}=\text{C}$	167
$-\text{C—H}$	98.0	$\text{C—C}$	88

What corresponding values would we have to assign to C–Br bonds if the  $\Delta H^\circ$  values calculated for the reactions  $\text{HC}\equiv\text{CH} + \text{Br}_2 \longrightarrow \text{BrHC}=\text{CHBr}$  and  $\text{BrHC}=\text{CHBr} + \text{Br}_2 \longrightarrow \text{CHBr}_2\text{CHBr}_2$  are to be exactly the same as those calculated using only the bond energies from Table 4-3? Show your reasoning.

**4-25** Explain why there is an increasingly poor correlation between  $\Delta H^\circ$  and the equilibrium constant  $K_{\text{eq}}$  for the formation of methane, propane, hexane, and nonane from solid carbon and hydrogen gas (Table 4-5).

**4-26** The  $\Delta H^\circ$  values for formation of cyclohexane from 1-hexene and of hydrogen chloride from hydrogen and chlorine differ by less than 3 kcal mole<sup>-1</sup> but the respective equilibrium constants are different by a factor of 10<sup>7</sup>. Explain.

**4-27\*** The entropy change  $\Delta S^\circ$  for the formation of chloroethane by chlorination of ethane is +0.5 e.u., and for the formation of chloroethane by combination of hydrogen chloride with ethene  $\Delta S^\circ$  is -31 e.u. Explain.

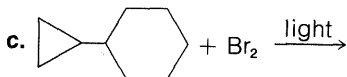
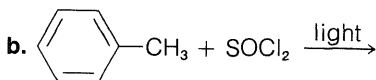
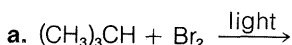


**4-28** Investigate the energies ( $\Delta H^\circ$ ) of possible chain mechanisms for the light-induced monobromination of methane and compare with those for chlorination. What are the prospects for iodination of methane?

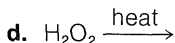
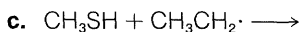
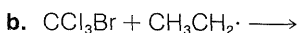
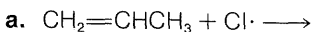
**4-29** The heat of combustion of cyclopropane, (CH<sub>2</sub>)<sub>3</sub>, to give carbon dioxide and liquid water is 499.8 kcal mole<sup>-1</sup>. Show how this value, assuming normal C-H bond strengths, can be used to calculate the average C-C bond energy of cyclopropane.

**4-30** Write a mechanism analogous to that usually written for methane chlorination that would lead to production of hexachloroethane as in Exercise 4-20a. (This reaction is used for commercial production of hexachloroethane.)

**4-31** With reference to the data in Table 4-6, draw the structure(s) of the *major* organic product(s) to be expected from hydrogen abstraction in the following reactions:



**4-32** Use the data in Table 4-6 to predict the products of the following reactions. Indicate any ambiguities that you encounter as the result of insufficient data.



**4-33\*** The oxidation of hydrocarbons by atmospheric oxygen to give hydroperoxides is called **autoxidation**:



It is a detrimental reaction because it leads to the deterioration of organic compounds exposed to air (e.g., rubber cracking). Furthermore, the product, ROOH, in common with virtually all organic compounds with —O—O— bonds, has the potential of undergoing rapid decomposition on heating, which in fact may occur with explosive violence.

The mechanism of autoxidation is a radical-chain process that is initiated by formation of a hydrocarbon radical, R·.

**a.** Write the propagation steps for this reaction, using R· or ROO· as the chain-propagating radical. How do you expect that **antioxidants** added to materials such as rubber act to help protect them from autoxidation (see Section 4-4D).

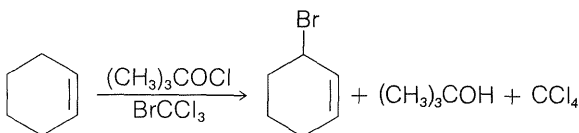
**b.** Use the data of Table 4-6 to determine the most favorable products of autoxidation of cyclohexene and methylbenzene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>).

**c.** It is extremely hazardous to store some organic chemicals for long periods of time in unsealed containers exposed to air and light. Aldehydes and ethers are particularly dangerous chemicals to store in this way. Explain why this should be so.

**4-34\*** The first step in preparing the very useful elastomer Hypalon involves treating a mixture of long-chain alkanes, H(CH<sub>2</sub>)<sub>n</sub>H, where  $n = 50\text{--}200$ , with sulfuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>) in the presence of substances that can initiate radical-chain chlorination, as described in Section 4-5B. The product molecules contain many C—Cl bonds and a few C—SO<sub>2</sub>—Cl bonds, the latter of which are subsequently used in a curing step to improve the physical properties. How can the chain mechanism for chlorination with SO<sub>2</sub>Cl<sub>2</sub> be modified to account for the formation of C—SO<sub>2</sub>—Cl bonds?

**4-35\*** Explain why the product distribution in the chlorination of propane by sulfuryl chloride is expected to differ according to whether the hydrogen-abstraction step is accomplished by Cl· or ·SO<sub>2</sub>Cl.

**4-36\*** *tert*-Butyl hypobromite is a radical brominating agent that is similar to *tert*-butyl hypochlorite (Exercise 4-18\*), but it is less easily prepared than the hypochlorite. A good substitute, provided radical bromination is possible, is a mixture of BrCCl<sub>3</sub> and (CH<sub>3</sub>)<sub>3</sub>COCl. Thus, bromination of cyclohexene results if a high ratio of bromotrichloromethane to hypochlorite is used.



Suggest how this reaction is initiated and propagated, and explain why it is necessary to have an excess of bromotrichloromethane.



**4-37\*** Use the data of Table 4-6 and tin–hydrogen and tin–chlorine bond energies of 80 kcal and 120 kcal, respectively, to determine the overall feasibility of the following reaction:



- Assume the reaction proceeds by a radical-chain mechanism and work out energetically feasible initiation and propagation steps.
- Draw energy diagrams like those shown in Figure 4-4 that correspond to each of the propagation steps. Indicate clearly on your diagrams which step would be expected to have the highest activation energy (that is, be the slower step), which point on your curves corresponds to the transition state, and which energy differences correspond to the energy change ( $\Delta G^\circ$ ) in that step of the reaction (assume  $T\Delta S^\circ = 0$ ).