Chapter 1

Structure and Properties

1.1 Organic chemistry

Organic chemistry is the chemistry of the **compounds of carbon.**

The misleading name "organic" is a relic of the days when chemical compounds were divided into two classes, inorganic and organic, depending upon where they had come from. Inorganic compounds were those obtained from minerals; organic compounds were those obtained from vegetable or animal sources, that is, from material produced by living organisms. Indeed, until about 1850 many chemists believed that organic compounds *must* have their origin in living organisms, and consequently could never be synthesized from inorganic material.

These compounds from organic sources had this in common: they all contained the element carbon. Even after it had become clear that these compounds did not have to come from living sources but could be made in the laboratory, it was convenient to keep the name *organic* to describe them and compounds like them. The division between inorganic and organic compounds has been retained to this day.

Today, although many compounds of carbon are still most conveniently isolated from plant and animal sources, most of them are synthesized. They are sometimes synthesized from inorganic substances like carbonates or cyanides, but more often from other organic compounds. There are two large reservoirs of organic material from which simple organic compounds can be obtained: *petroleum* and *coal.* (Both of these are "organic" in the old sense, being products of the decay of plants and animals.) These simple compounds are used as building blocks from which larger and more complicated compounds can be made.

We recognize petroleum and coal as the *fossil fuels*, laid down over millenia and nonreplaceable, that are being consumed at an alarming rate to meet our constantly increasing demands for power. There *is*, fortunately, an alternative source of power—nuclear energy—but where are we to find an alternative reservoir of organic raw material?

What is so special about the compounds of carbon that they should be separated from compounds of all the other hundred-odd elements of the Periodic Table? In part, at least, the answer seems to be this: there are so very many compounds of carbon, and their molecules can be so large and complex.

The number of compounds that contain carbon is many times greater than the number of compounds that do not contain carbon. These organic compounds have been divided into families, which generally have no counterparts among the inorganic compounds.

Organic molecules containing thousands of atoms are known, and the arrangement of atoms in even relatively small molecules can be very complicated. One of the major problems in organic chemistry is to find out how the atoms are arranged in molecules, that is, to determine the structures of compounds.

There are many ways in which these complicated molecules can break apart, or rearrange themselves, to form new molecules; there are many ways in which atoms can be added to these molecules, or new atoms substituted for old ones. Much of organic chemistry is devoted to finding out what these reactions are, how they take place, and how they can be used to synthesize compounds we want.

What is so special about carbon that it should form so many compounds? The answer to this question came to August Kekulé in 1854 during a London bus ride.

> "One fine summer evening, I was returning by the last omnibus, 'outside' as usual, through the deserted streets of the metropolis, which are at other times so full of life. I fell into a reverie and lo! the atoms were gambolling before my eyes. . . . I saw how, frequently, two smaller atoms united to form a pair, how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain. . . . I spent part of the night putting on paper at least sketches of these dream forms."—August Kekulé, 1890.

Carbon atoms can attach themselves to one another to an extent not possible for atoms of any other element. Carbon atoms can form chains thousands of atoms long, or rings of all sizes; the chains and rings can have branches and cross-links. To the carbon atoms of these chains and rings there are attached other atoms, chiefly hydrogen, but also fluorine, chlorine, bromine, iodine, oxygen, nitrogen, sulfur, phosphorus, and many others. (Look, for example, at cellulose on page 1126, chlorophyll on page 1004, and oxytocin on page 1143.)

Each different arrangement of atoms corresponds to a different compound, and each compound has its own characteristic set of chemical and physical properties. It is not surprising that close to a million compounds of carbon are known today and that thousands of new ones are being made each year. It is not surprising that the study of their chemistry is a special field.

Organic chemistry is a field of immense importance to technology: it is the chemistry of dyes and drugs, paper and ink, paints and plastics, gasoline and rubber tires; it is the chemistry of the food we eat and the clothing we wear.

Organic chemistry is fundamental to biology and medicine. Aside from water, living organisms are made up chiefly of organic compounds; the molecules of "molecular biology" are organic molecules. Ultimately, biological processes are a matter of organic chemistry.

1.2 The structural theory

> "Organic chemistry nowadays almost drives me mad. To me it appears like a primeval tropical forest full of the most remarkable things, a dreadful endless jungle into which one does not dare enter for there seems to be no way out."—Friedrich Wohler, 1835.

How can we even begin to study a subject of such enormous complexity? Is organic chemistry today as Wöhler saw it a century and a half ago? The jungle is still there—largely unexplored—and in it are more remarkable things than Wöhler ever dreamed of. But, so long as we do not wander too far too fast, we can enter without fear of losing our way, for we have a chart: the **structural theory**.

The structural theory is the basis upon which millions of facts about hundreds of thousands of individual compounds have been brought together and arranged in a systematic way. It is the basis upon which these facts can best be accounted for and understood.

The structural theory is the framework of ideas about how atoms are put together to make molecules. The structural theory has to do with the order in which atoms are attached to each other, and with the electrons that hold them together. It has to do with the shapes and sizes of the molecules that these atoms form, and with the way that electrons are distributed over them.

A molecule is often represented by a picture or a model—sometimes by several pictures or several models. The atomic nuclei are represented by letters or wooden balls, and the electrons that join them by lines or dots or wooden pegs. These crude pictures and models are useful to us only if we understand what they are intended to mean. Interpreted in terms of the structural theory, they tell us a good deal about the compound whose molecules they represent: how to go about making it; what physical properties to expect of it—melting point, boiling point, specific gravity, the kind of solvents the compound will dissolve in, even whether it will be colored or not; what kind of chemical behavior to expect—the kind of reagents the compound will react with and the kind of products that will be formed, whether it will react rapidly or slowly. We would know all this about a compound that we had never encountered before, simply on the basis of its structural formula and what we understand its structural formula to mean.

1.3 The chemical bond before 1926

Any consideration of the structure of molecules must begin with a discussion of *chemical bonds*, the forces that hold atoms together in a molecule.

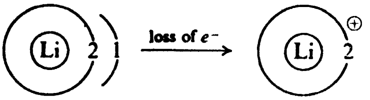
We shall discuss chemical bonds first in terms of the theory as it had developed prior to 1926, and then in terms of the theory of today. The introduction of quantum mechanics in 1926 caused a tremendous change in ideas about how molecules are formed. For convenience, the older, simpler language and pictorial representations are often still used, although the words and pictures are given a modern interpretation.

In 1916 two kinds of chemical bond were described: the *ionic bond* by Walther Kossel (in Germany) and the *covalent bond* by G. N. Lewis (of the University of

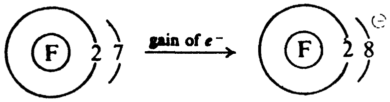
California). Both Kossel and Lewis based their ideas on the following concept the atom.

A positively charged nucleus is surrounded by electrons arranged in concentric shells or energy levels. There is a maximum number of electrons that can be accommodated in each shell: two in the first shell, eight in the second shell, eight or eighteen in the third shell, and so on. The greatest stability is reached when the outer shell is full, as in the noble gases. Both ionic and covalent bonds arise from the tendency of atoms to attain this stable configuration of electrons.

The **ionic bond** results from **transfer of electrons**, as, for example, in the formation of lithium fluoride. A lithium atom has two electrons in its inner shell and one electron in its outer or valence shell; the loss of one electron would leave lithium with a full outer shell of two electrons. A fluorine atom has two electrons in its inner shell and seven electrons in its valence shell; the gain of one electron would give fluorine a full outer shell of eight. Lithium fluoride is formed by the transfer of one electron from lithium to fluorine; lithium now bears a positive charge and fluorine bears a negative charge. The electrostatic attraction between the oppositely charged ions is called an ionic bond. Such ionic bonds are typical of the salts formed by combination of the metallic elements (electropositive elements) on the far left side of the Periodic Table with the non-metallic elements (electronegative elements) on the far right side.

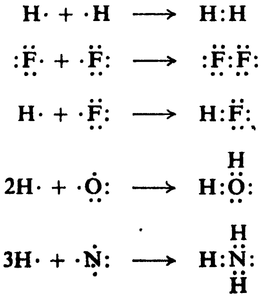


$Li \longrightarrow Li^+ + e^-$



$F + e^- \longrightarrow F^-$

The **covalent bond** results from **sharing of electrons**, as, for example, in the formation of the hydrogen molecule. Each hydrogen atom has a single electron; by sharing a pair of electrons, both hydrogens can complete their shells of two. Two fluorine atoms, each with seven electrons in the valence shell, can complete their octets by sharing a pair of electrons. In a similar way we can visualize the formation of HF, H_2O, NH_3, CH_4, and CF_4. Here, too, the bonding force is electrostatic attraction: this time between each electron and *both* nuclei.



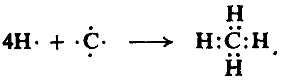
$$H\cdot + \cdot H \longrightarrow H:H$$

$$:\underset{\cdot\cdot}{\ddot{F}}\cdot + \cdot\underset{\cdot\cdot}{\ddot{F}}: \longrightarrow :\underset{\cdot\cdot}{\ddot{F}}:\underset{\cdot\cdot}{\ddot{F}}:$$

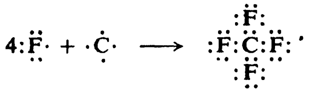
$$H\cdot + \cdot\underset{\cdot\cdot}{\ddot{F}}: \longrightarrow H:\underset{\cdot\cdot}{\ddot{F}}:$$

$$2H\cdot + \cdot\underset{\cdot\cdot}{\dot{O}}: \longrightarrow H:\underset{\cdot\cdot}{\overset{H}{\ddot{O}}}:$$

$$3H\cdot + \cdot\underset{\cdot}{\dot{N}}: \longrightarrow H:\underset{H}{\underset{\cdot\cdot}{\overset{H}{\ddot{N}}}}:$$



$$4H\cdot + \cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot \longrightarrow H:\overset{H}{\underset{H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}}:H$$



$$4:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}\cdot + \cdot\overset{\cdot}{\underset{\cdot}{C}}\cdot \longrightarrow :\overset{:\overset{\cdot\cdot}{F}:}{\underset{:\underset{\cdot\cdot}{F}:}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{F}}}}:$$

The covalent bond is typical of the compounds of carbon; it is the bond of chief importance in the study of organic chemistry.

Problem 1.1 Which of the following would you expect to be ionic, and which non-ionic? Give a simple electronic structure for each, showing only valence shell electrons.

(a) KBr	(c) NF_3	(e) $CaSO_4$	(g) PH_3
(b) H_2S	(d) $CHCl_3$	(f) NH_4Cl	(h) CH_3OH

Problem 1.2 Give a likely simple electronic structure for each of the following, assuming them to be completely covalent. Assume that every atom (except hydrogen, of course) has a complete octet, and that two atoms may share more than one pair of electrons.

(a) H_2O_2	(c) $HONO_2$	(e) HCN	(g) H_2CO_3
(b) N_2	(d) NO_3^-	(f) CO_2	(h) C_2H_6

1.4 Quantum mechanics

In 1926 there emerged the theory known as *quantum mechanics*, developed, in the form most useful to chemists, by Erwin Schrödinger (of the University of Zurich). He worked out mathematical expressions to describe the motion of an electron in terms of its energy. These mathematical expressions are called *wave equations*, since they are based upon the concept that electrons show properties not only of particles but also of waves.

A wave equation has a series of solutions, called *wave functions*, each corresponding to a different energy level for the electron. For all but the simplest of systems, doing the mathematics is so time-consuming that at present—and super-high-speed computers will some day change this—only approximate solutions can be obtained. Even so, quantum mechanics gives answers agreeing so well with the facts that it is accepted today as the most fruitful approach to an understanding of atomic and molecular structure.

> "Wave mechanics has shown us what is going on, and at the deepest possible level . . . it has taken the concepts of the experimental chemist—the imaginative perception that came to those who had lived in their laboratories and allowed their minds to dwell creatively upon the facts that they had found—and it has shown how they all fit together; how, if you wish, they all have one single rationale; and how this hidden relationship to each other can be brought out."—C. A. Coulson, London, 1951.

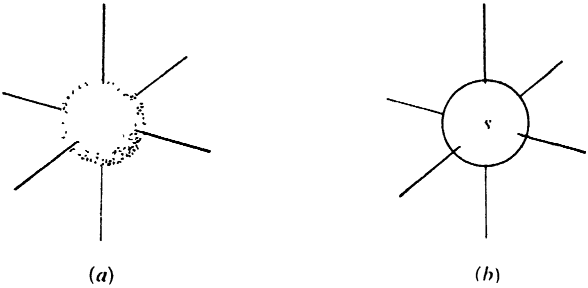
1.5 Atomic orbitals

A wave equation cannot tell us exactly where an electron is at any particular moment, or how fast it is moving; it does not permit us to plot a precise orbit about the nucleus. Instead, it tells us the *probability* of finding the electron at any particular place.

The region in space where an electron is likely to be found is called an **orbital.** There are different kinds of orbitals, which have different sizes and different shapes, and which are disposed about the nucleus in specific ways. The particular kind of orbital that an electron occupies depends upon the energy of the electron. It is the shapes of these orbitals and their disposition with respect to each other that we are particularly interested in, since these determine—or, more precisely, can conveniently be *thought of* as determining—the arrangement in space of the atoms of a molecule, and even help determine its chemical behavior.

It is convenient to picture an electron as being smeared out to form a cloud. We might think of this cloud as a sort of blurred photograph of the rapidly moving electron. The shape of the cloud is the shape of the orbital. The cloud is not uniform, but is densest in those regions where the probability of finding the electron is highest, that is, in those regions where the average negative charge, or *electron density*, is greatest.

Let us see what the shapes of some of the atomic orbitals are. The orbital at the lowest energy level is called the 1*s* orbital. It is a sphere with its center at the nucleus of the atom, as represented in Fig. 1.1. An orbital has no definite boundary since there is a probability, although a very small one, of finding the electron essentially separated from the atom—or even on some other atom! However, the probability decreases very rapidly beyond a certain distance from the nucleus, so that the distribution of charge is fairly well represented by the electron cloud in Fig. 1.1*a*. For simplicity, we may even represent an orbital as in Fig. 1.1*b*, where the solid line encloses the region where the electron spends most (say 95%) of its time.



(*a*) (*b*)

Figure 1.1. Atomic orbitals: *s* orbital. Nucleus at center.

At the next higher energy level there is the 2*s* orbital. This, too, is a sphere with its center at the atomic nucleus. It is—*naturally*—larger than the 1*s* orbital: the higher energy (lower stability) is due to the greater average distance between electron and nucleus, with the resulting decrease in electrostatic attraction. (Consider the work that must be done—the energy put into the system—to move an electron away from the oppositely charged nucleus.)

Next there are three orbitals of equal energy called 2*p* orbitals, shown in

Fig. 1.2. Each $2p$ orbital is dumbbell-shaped. It consists of two lobes with the atomic nucleus lying between them. The axis of each $2p$ orbital is perpendicular to the axes of the other two. They are differentiated by the names $2p_x$, $2p_y$, and $2p_z$, where the x, y, and z refer to the corresponding axes.

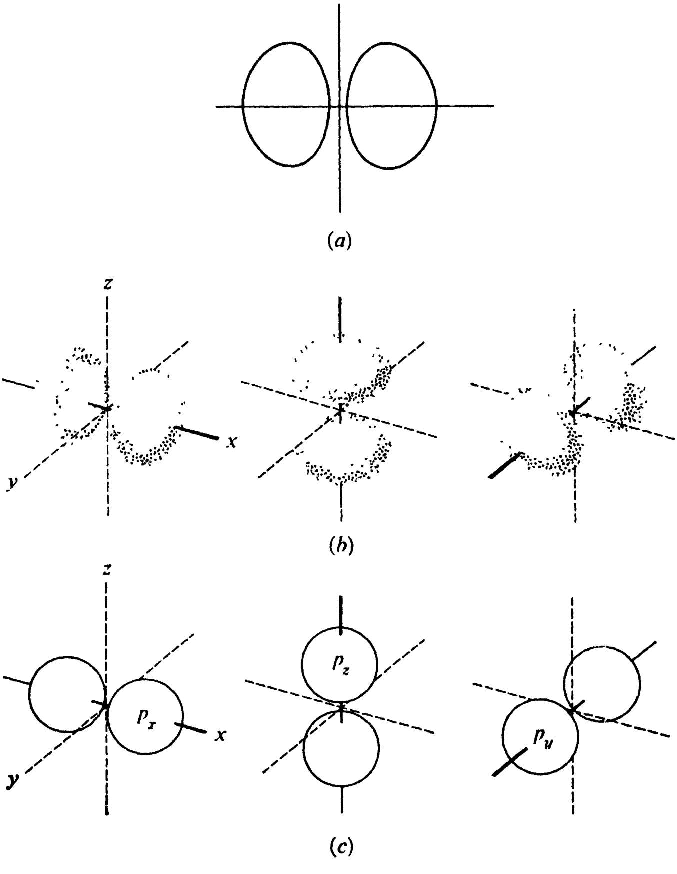


Figure 1.2. Atomic orbitals: p orbitals. Axes mutually perpendicular. (*a*) Cross-section showing the two lobes of a single orbital. (*b*) Approximate shape as pairs of distorted ellipsoids. (*c*) Representation as pairs of not-quite-touching spheres.

1.6 Electronic configuration. Pauli exclusion principle

There are a number of "rules" that determine the way in which the electrons of an atom may be distributed, that is, that determine the *electronic configuration* of an atom.

The most fundamental of these rules is the **Pauli exclusion principle**: *only two electrons can occupy any atomic orbital, and to do so these two must have* **opposite** *spins.* These electrons of opposite spins are said to be *paired. Electrons of* **like** *spin tend to get as far from each other as possible.* This tendency is the most important of all the factors that determine the shapes and properties of molecules.

The exclusion principle, advanced in 1925 by Wolfgang Pauli, Jr. (of the Institute for Theoretical Physics, Hamburg, Germany), has been called the cornerstone of chemistry.

The first ten elements of the Periodic Table have the electronic configurations shown in Table 1.1. We see that an orbital becomes occupied only if the orbitals of lower energy are filled (e.g., 2*s* after 1*s*, 2*p* after 2*s*). We see that an orbital is not occupied by a pair of electrons until other orbitals of equal energy are each occupied by one electron (e.g., the 2*p* orbitals). The 1*s* electrons make up the first shell of two, and the 2*s* and 2*p* electrons make up the second shell of eight. For elements beyond the first ten, there is a third shell containing a 3*s* orbital, 3*p* orbitals, and so on.

Table 1.1 ELECTRONIC CONFIGURATIONS

	1*s*	2*s*	2*p*		
H	⊙				
He	(··)				
Li	(··)	⊙	○	○	○
Be	(··)	(··)	○	○	○
B	(··)	(··)	⊙	○	○
C	(··)	(··)	⊙	⊙	○
N	(··)	(··)	⊙	⊙	⊙
O	(··)	(··)	(··)	⊙	⊙
F	(··)	(··)	(··)	(··)	⊙
Ne	(··)	(··)	(··)	(··)	(··)

Problem 1.3 (a) Show the electronic configurations for the next eight elements in the Periodic Table (from sodium through argon). (b) What relationship is there between electronic configuration and periodic family? (c) Between electronic configuration and chemical properties of the elements?

1.7 Molecular orbitals

In molecules, as in isolated atoms, electrons occupy orbitals, and in accordance with much the same "rules." These *molecular orbitals* are considered to be centered about many nuclei, perhaps covering the entire molecule; the distribution of nuclei and electrons is simply the one that results in the most stable molecule.

To make the enormously complicated mathematics more workable, two simplifying assumptions are commonly made: (a) that each pair of electrons is essentially localized near just two nuclei, and (b) that the shapes of these localized molecular orbitals and their disposition with respect to each other are related in a simple way to the shapes and disposition of atomic orbitals in the component atoms.

The idea of localized molecular orbitals—or what we might call *bond orbitals*—is evidently not a bad one, since mathematically this method of approximation is successful with most (although *not all*) molecules. Furthermore, this idea closely parallels the chemist's classical concept of a bond as a force acting between two atoms and pretty much independent of the rest of the molecule; it can hardly be accidental that this concept has worked amazingly well for a hundred years. Significantly, the exceptional molecules for which classical formulas do not work are just those for which the localized molecular orbital approach does not work, either. (Even these cases, we shall find, can be handled by a rather simple adaptation of classical formulas, an adaptation which again parallels a method of mathematical approximation.)

The second assumption, of a relationship between atomic and molecular orbitals, is a highly reasonable one, as discussed in the following section. It has proven so useful that, when necessary, atomic orbitals of certain kinds have been *invented* just so that the assumption can be retained.

1.8 The covalent bond

Now let us consider the formation of a molecule. For convenience we shall picture this as happening by the coming together of the individual atoms, although most molecules are not actually made this way. We make physical models of molecules out of wooden or plastic balls that represent the various atoms; the location of holes or snap fasteners tells us how to put them together. In the same way, we shall make *mental* models of molecules out of mental atoms; the location of atomic orbitals—some of them imaginary—will tell us how to put these together.

For a covalent bond to form, two atoms must be located so that an orbital of one *overlaps* an orbital of the other; each orbital must contain a single electron. When this happens, the two atomic orbitals merge to form a single *bond orbital* which is occupied by both electrons. The two electrons that occupy a bond orbital must have opposite spins, that is, must be paired. Each electron has available to it the entire bond orbital, and thus may be considered to "belong to" both atomic nuclei.

This arrangement of electrons and nuclei contains less energy—that is, is more stable—than the arrangement in the isolated atoms; as a result, formation of a bond is accompanied by evolution of energy. The amount of energy (per mole) that is given off when a bond is formed (or the amount that must be put in to break the bond) is called the *bond dissociation energy*. For a given pair of atoms, the greater the overlap of atomic orbitals, the stronger the bond.

What gives the covalent bond its strength? It is the increase in electrostatic attraction. In the isolated atoms, each electron is attracted by—and attracts—one positive nucleus; in the molecule, each electron is attracted by *two* positive nuclei.

It is the concept of "overlap" that provides the mental bridge between atomic orbitals and bond orbitals. Overlap of atomic orbitals means that the bond orbital occupies much of the same region in space that was occupied by *both* atomic orbitals. Consequently, an electron from one atom can, to a considerable extent, remain in its original, favorable location with respect to "its" nucleus, and at the same time occupy a similarly favorable location with respect to the second nucleus; the same holds, of course, for the other electron.

The principle of *maximum overlap*, first stated in 1931 by Linus Pauling (at the California Institute of Technology), has been ranked only slightly below the exclusion principle in importance to the understanding of molecular structure.

As our first example, let us consider the formation of the hydrogen molecule, H_2, from two hydrogen atoms. Each hydrogen atom has one electron, which occupies the 1*s* orbital. As we have seen, this 1*s* orbital is a sphere with its center at the atomic nucleus. For a bond to form, the two nuclei must be brought closely enough together for overlap of the atomic orbitals to occur (Fig. 1.3). For hydrogen, the system is most stable when the distance between the nuclei is 0.74 A; this distance is called the **bond length**. At this distance the stabilizing effect of overlap is exactly balanced by repulsion between the similarly charged nuclei. The resulting hydrogen molecule contains 104 kcal/mole less energy than the hydrogen atoms from which it was made. We say that the hydrogen–hydrogen bond has a length of 0.74 A and a strength of 104 kcal.

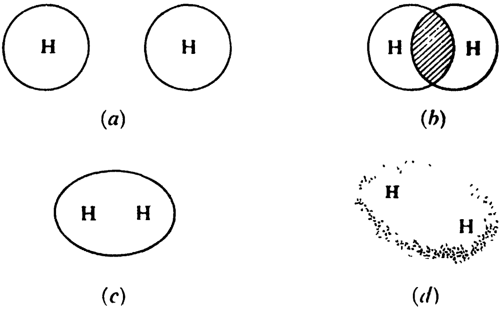


Figure 1.3. Bond formation: H_2 molecule. (*a*) Separate *s* orbitals. (*b*) Overlap of *s* orbitals. (*c*) and (*d*) The σ bond orbital.

This bond orbital has roughly the shape we would expect from the merging of two *s* orbitals. As shown in Fig. 1.3, it is sausage-shaped, with its long axis lying along the line joining the nuclei. It is cylindrically symmetrical about this long axis; that is, a slice of the sausage is circular. Bond orbitals having this shape are called *σ orbitals* (*sigma orbitals*) and the bonds are called *σ bonds*. We may visualize the hydrogen molecule as two nuclei embedded in a single sausage-shaped electron cloud. This cloud is densest in the region between the two nuclei, where the negative charge is attracted most strongly by the two positive charges.

The size of the hydrogen molecule—as measured, say, by the volume inside the 95% probability surface—is considerably *smaller* than that of a single hydrogen atom. Although surprising at first, this shrinking of the electron cloud is actually what would be expected. It is the powerful attraction of the electrons by *two* nuclei that gives the molecule greater stability than the isolated hydrogen atoms; this must mean that the electrons are held tighter, *closer*, than in the atoms.

Next, let us consider the formation of the fluorine molecule, F_2, from two fluorine atoms. As we can see from our table of electronic configurations (Table 1.1), a fluorine atom has two electrons in the 1*s* orbital, two electrons in the 2*s* orbital, and two electrons in each of two 2*p* orbitals. In the third 2*p* orbital there is a single electron which is unpaired and available for bond formation. Overlap of this *p* orbital with a similar *p* orbital of another fluorine atom permits electrons to pair and the bond to form (Fig. 1.4). The electronic charge is concentrated between the two nuclei, so that the back lobe of each of the overlapping orbitals shrinks to a comparatively small size. Although formed by overlap of atomic orbitals of a different kind, the fluorine–fluorine bond has the same general shape as the hydrogen–hydrogen bond, being cylindrically symmetrical about a line joining the nuclei; it, too, is given the designation of σ bond. The fluorine–fluorine bond has a length of 1.42 A and a strength of about 38 kcal.

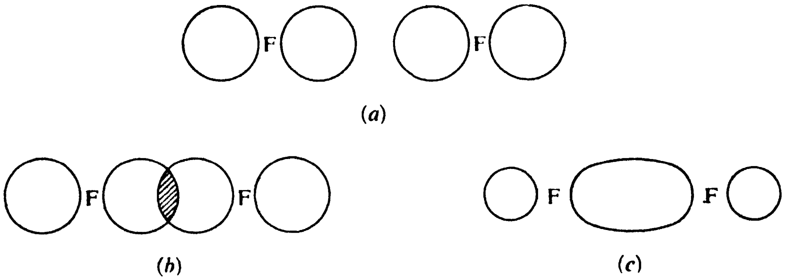


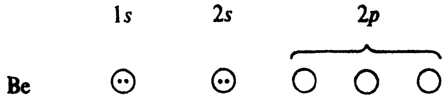
Figure 1.4. Bond formation: F_2 molecule. (*a*) Separate *p* orbitals. (*b*) Overlap of *p* orbitals. (*c*) The σ bond orbital.

As the examples show, a covalent bond results from the overlap of two atomic orbitals to form a bond orbital occupied by a pair of electrons. *Each kind of covalent bond has a characteristic length and strength.*

1.9 Hybrid orbitals: *sp*

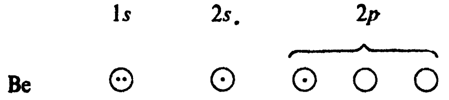
Let us next consider beryllium chloride, $BeCl_2$.

Beryllium (Table 1.1) has no unpaired electrons.



How are we to account for its combining with two chlorine atoms? Bond formation is an energy-releasing (stabilizing) process, and the tendency is to form bonds—and as many as possible—even if this results in bond orbitals that bear little resemblance to the atomic orbitals we have talked about. If our method of mental molecule-building is to be applied here, it must be modified. We must invent an imaginary kind of beryllium atom, one that is about to become bonded to two chlorine atoms.

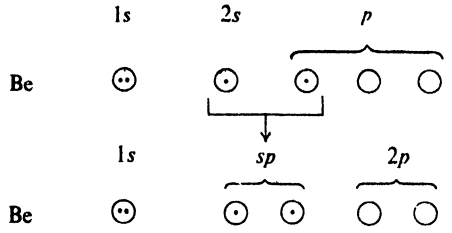
To arrive at this divalent beryllium atom, let us do a little electronic bookkeeping. First, we "promote" one of the 2*s* electrons to an empty *p* orbital:



One electron promoted: two unpaired electrons

This provides two unpaired electrons, which are needed for bonding to two chlorine atoms. We might now expect beryllium to form one bond of one kind, using the *p* orbital, and one bond of another kind, using the *s* orbital. Again, this is contrary to fact: the two bonds in beryllium chloride are known to be equivalent.

Next, then, we *hybridize* the orbitals. Various combinations of one *s* and one *p* orbitals are taken mathematically, and the mixed (*hybrid*) orbitals with the greatest degree of *directional character* are found (Fig. 1.5). The more an atomic orbital is concentrated in the direction of the bond, the greater the overlap and the stronger the bond it can form. Three highly significant results emerge from the



***sp* Hybridization**

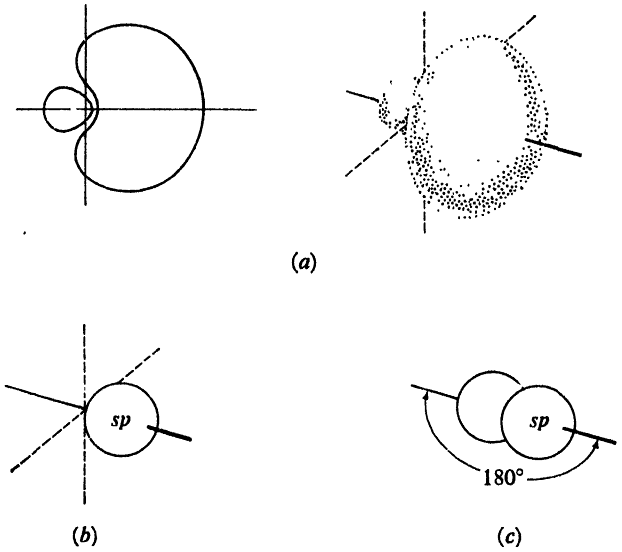


Figure 1.5. Atomic orbitals: hybrid *sp* orbitals. (*a*) Cross-section and approximate shape of a single orbital. Strongly directed along one axis. (*b*) Representation as a sphere, with small back lobe omitted. (*c*) Two orbitals, with axes lying along a straight line.

These hybrid orbitals are called sp^2 orbitals, since they are considered to arise from the mixing of *one s* orbital and *two p* orbitals. They lie in a plane, which includes the atomic nucleus, and are directed to the corners of an equilateral triangle; the angle between any two orbitals is thus 120°. Again we see the geometry that permits the orbitals to be as far apart as possible: here, a *trigonal* (three-cornered) arrangement.

When we arrange the atoms for maximum overlap of each of the sp^2 orbitals of boron with a *p* orbital of fluorine, we obtain the structure shown in Fig. 1.8: a *flat* molecule, with the boron atom at the center of a triangle and the three fluorine atoms at the corners. Every bond angle is 120°.

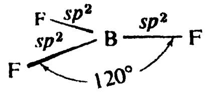


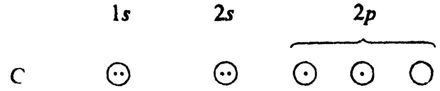
Figure 1.8. BF_3 molecule.

Experiment has shown that boron fluoride has exactly this flat, symmetrical structure calculated by quantum mechanics.

1.11 Hybrid orbitals: sp^3

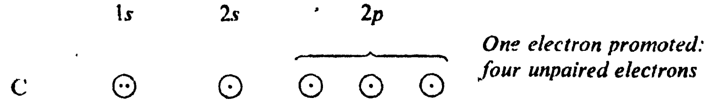
Now, let us turn to one of the simplest of organic molecules, *methane*, CH_4.

Carbon (Table 1.1) has an unpaired electron in each of the two *p* orbitals, and on this basis might be expected to form a compound CH_2. (It *does*, but

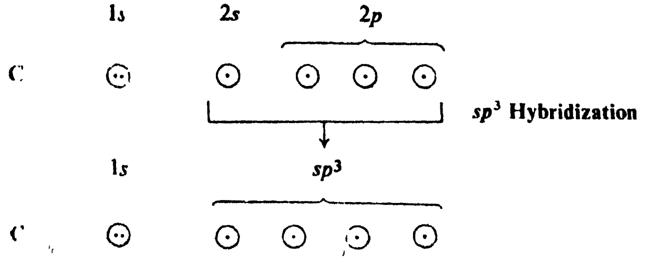


CH_2 is a highly reactive molecule whose properties center about the need to provide carbon with two more bonds.) Again, we see the tendency to form as many bonds as possible: in this case, to combine with *four* hydrogen atoms.

To provide four unpaired electrons, we promote one of the 2*s* electrons to the empty *p* orbital:



Once more the most strongly directed orbitals are hybrid orbitals: this time, sp^3 orbitals, from the mixing of *one s* orbital and *three p* orbitals. Each one has the



shape shown in Fig. 1.9; as with sp and sp^2 orbitals, we shall back lobe and represent the front lobe as a sphere.

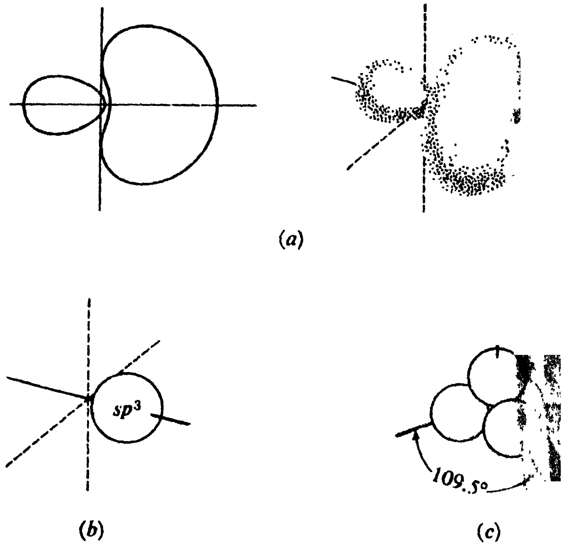


Figure 1 9. Atomic orbitals: hybrid sp^3 orbitals. (*a*) Cross-[illegible] approximate shape of a single orbital. Strongly directed along [illegible] (*b*) Representation as a sphere, with small back lobe omitted. (*c* [illegible] orbitals, with axes directed toward corners of tetrahedron.

Now, how are sp^3 orbitals arranged in space? The answer [illegible] us: in the way that lets them get as far away from each other as possible. [illegible] are directed to the corners of a regular tetrahedron. The angle between any [illegible] orbitals is the tetrahedral angle 109.5° (Fig. 1.9). Just as mutual repulsion among orbitals gives two linear bonds or three trigonal bonds, so it gives [illegible] tetrahedral bonds.

Overlap of each of the sp^3 orbitals of carbon with an s orbital of hydrogen results in methane: carbon at the center of a regular tetrahedron and the four hydrogens at the corners (Fig. 1.10).

Experimentally, methane has been found to have the highly symmetrical tetrahedral structure we have assembled. Each carbon–hydrogen bond has exactly the same length, 1.10 A; the angle between any pair of bonds is the tetrahedral angle 109.5°. It takes 104 kcal/mole to break one of the bonds of methane.

Thus, in these last three sections, we have seen that there are associated with covalent bonds not only characteristic bond lengths and bond dissociation energies but also characteristic bond *angles*. These bond angles can be [illegible] related to the arrangement of atomic orbitals—including hybrid [illegible] involved in bond formation; they ultimately go back to the Pauli exclusion principle and the tendency for unpaired electrons to get as far from each other as possible.

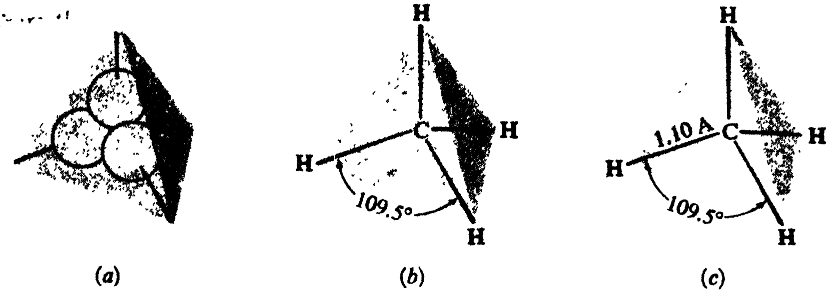


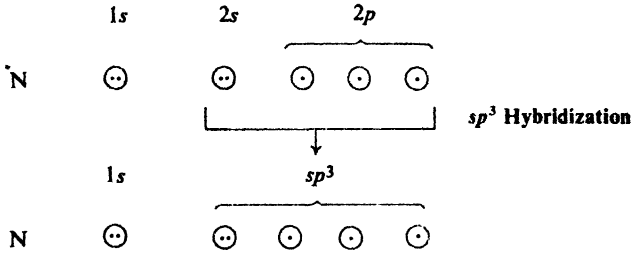
Figure 1.10. Bond formation: CH_4 molecule. (*a*) Tetrahedral sp^3 orbitals. (*b*) Predicted shape: H nuclei located for maximum overlap. (*c*) Shape and size.

Unlike the ionic bond, which is equally strong in all directions, *the covalent nd is a directed bond.* We can begin to see why the chemistry of the covalent ond is so much concerned with molecular size and shape.

1.12 Unshared pairs of electrons

Two familiar compounds, ammonia (NH_3) and water (H_2O), show how *unshared pairs of electrons* can affect molecular structure.

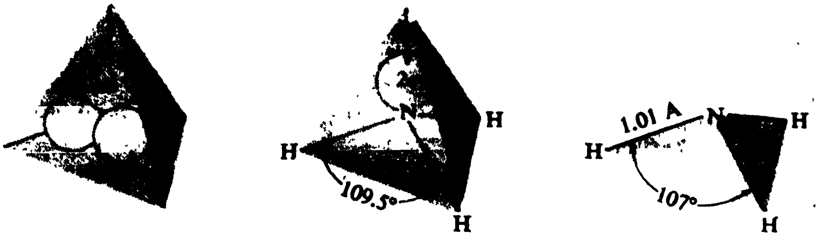
In ammonia, nitrogen resembles the carbon of methane. Nitrogen is sp^3-hybridized, but (Table 1.1) has only three unpaired electrons; they occupy three



of the sp^3 orbitals. Overlap of each of these orbitals with the s orbital of a hydrogen atom results in ammonia (Fig. 1.11). The fourth sp^3 orbital of nitrogen contains a pair of electrons.

If there is to be maximum overlap and hence maximum bond strength, the hydrogen nuclei must be located at three corners of a tetrahedron; the fourth corner is occupied by an unshared pair of electrons. Considering only atomic nuclei, we would expect ammonia to be shaped like a pyramid with nitrogen at the apex and hydrogen at the corners of a triangular base. Each bond angle should be the tetrahedral angle 109.5°.

Experimentally, ammonia is found to have the pyramidal shape calculated by quantum mechanics. The bond angles are 107°, slightly smaller than the predicted value; it has been suggested that the unshared pair of electrons occupies more space than any of the hydrogen atoms, and hence tends to compress the bond



(a) (b) (c)

Figure 1.11. Bond formation: NH_3 molecule. (*a*) Tetrahedral *sp*^{3} orbitals. (*b*) Predicted shape, showing unshared pair: H nuclei located for maximum overlap. (*c*) Shape and size.

angles slightly. The nitrogen–hydrogen bond length is 1.01 A; it takes 103 kcal/mole to break one of the bonds of ammonia.

The *sp*^{3} orbital occupied by the unshared pair of electrons is a region of high electron density. This region is a source of electrons for electron-seeking atoms and molecules, and thus gives ammonia its basic properties (Sec. 1.22).

There are two other conceivable electronic configurations for ammonia, but neither fits the facts.

(a) Since nitrogen is bonded to three other atoms, we might have pictured it as using *sp*^{2} orbitals, as boron does in boron trifluoride. But ammonia is *not* a flat molecule, and so we must reject this possibility. It is the unshared pair of electrons on nitrogen that makes the difference between NH_3 and BF_3—these electrons need to stay away from those in the carbon–hydrogen bonds, and the tetrahedral shape makes this possible.

(b) We might have pictured nitrogen as simply using the *p* orbitals for overlap, since they would provide the necessary three unpaired electrons. But this would give bond angles of 90°—remember, the *p* orbitals are at right angles to each other—in contrast to the observed angles of 107°. More importantly, the unshared pair would be buried in an *s* orbital, and there is evidence from dipole moments (Sec. 1.16) that this is not so. Evidently the stability gained by using the highly directed *sp*^{3} orbitals for bond formation more than makes up for raising the unshared pair from an *s* orbital to the higher-energy *sp*^{3} orbital.

One further fact about ammonia: spectroscopy reveals that the molecule undergoes *inversion*, that is, turns inside-out (Fig. 1.12). There is an energy barrier

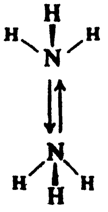
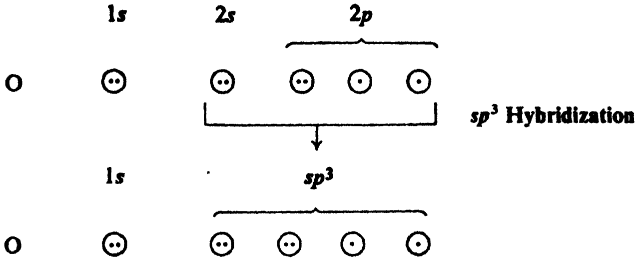


Figure 1.12. Inversion of ammonia.

of only 6 kcal/mole between one pyramidal arrangement and the other, equivalent one. This energy is provided by molecular collisions, and even at room temperature the fraction of collisions hard enough to do the job is so large that a rapid transformation between pyramidal arrangements occurs.

Compare ammonia with methane, which does *not* undergo inversion. The unshared pair plays the role of a carbon–hydrogen bond in determining the most stable shape of the molecule, tetrahedral. But, unlike a carbon–hydrogen bond, the unshared pair cannot maintain a *particular* tetrahedral arrangement; the pair points now in one direction, and the next instant in the opposite direction.

Finally, let us consider water, H_2O. The situation is similar to that for ammonia, except that oxygen has only two unpaired electrons, and hence it bonds



with only two hydrogen atoms, which occupy two corners of a tetrahedron. The other two corners of the tetrahedron are occupied by unshared pairs of electrons (Fig. 1.13).

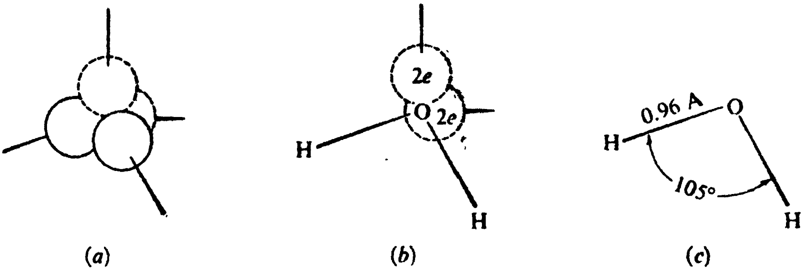


Figure 1.13. Bond formation: H_2O molecule. (*a*) Tetrahedral sp^3 orbitals. (*b*) Predicted shape, showing unshared pairs: H nuclei located for maximum overlap. (*c*) Shape and size.

As actually measured, the H—O—H angle is 105°, smaller than the calculated tetrahedral angle, and even smaller than the angle in ammonia. Here there are two bulky unshared pairs of electrons compressing the bond angles. The oxygen–hydrogen bond length is 0.96 A; it takes 118 kcal/mole to break one of the bonds of water.

Because of the unshared pairs of electrons on oxygen, water is basic, although less strongly so than ammonia (Sec. 1.22).

Problem 1.4 Predict the shape of each of the following molecules, and tell how you arrived at your prediction: (a) the ammonium ion, NH_4^+; (b) the hydronium ion, H_3O^+; (c) methyl alcohol, CH_3OH; (d) methylamine, CH_3NH_2.

1.13 Intramolecular forces

We must remember that the particular method of mentally building molecules that we are learning to use is artificial: it is a purely intellectual process involving imaginary overlap of imaginary orbitals. There are other, equally artificial ways that use different mental or physical models. Our method is the one.that so far has seemed to work out best for the organic chemist. Our kit of mental atomic models will contain just three "kinds" of carbon: *tetrahedral* (sp^3-hybridized), *trigonal* (sp^2-hybridized), and *digonal* (sp-hybridized). By use of this kit, we shall find, one can do an amazingly good job of building hundreds of thousands of organic molecules.

But, however we arrive at it, we see the actual structure of a molecule to be the net result of a combination of *repulsive* and *attractive* forces, which are related to *charge* and *electron spin.*

(a) *Repulsive forces.* Electrons tend to stay as far apart as possible because they have the same charge and also, if they are unpaired, because they have the same spin (Pauli exclusion principle). The like-charged atomic nuclei, too, repel each other.

(b) *Attractive forces.* Electrons are attracted by atomic nuclei—as are the nuclei by the electrons—because of their opposite charge, and hence tend to occupy the region between two nuclei. Opposite spin *permits* (although, in itself, probably does not actually *encourage*) two electrons to occupy the same region.

In methane, for example, the four hydrogen nuclei are as widely separated as they can be. The distribution of the eight bonding electrons is such that each one occupies the desirable region near two nuclei—the bond orbital—and yet, except for its partner, is as far as possible from the other electrons. We can picture each electron accepting—perhaps reluctantly because of their similar charges—one orbital-mate of opposite spin, but staying as far as possible from all other electrons and even, as it wanders within the loose confines of its orbital, doing its best to avoid the vicinity of its restless partner.

1.14 Bond dissociation energy. Homolysis and heterolysis

We have seen that energy is liberated when atoms combine to form a molecule. For a molecule to break into atoms, an equivalent amount of energy must be consumed. *The amount of energy consumed or liberated when a bond is broken or formed is known as the* **bond dissociation energy, D.** It is characteristic of the particular bond. Table 1.2 lists bond dissociation energies that have been measured for a number of bonds. As can be seen, they vary widely, from weak bonds like I—I (36 kcal/mole) to very strong bonds like H—F (136 kcal/mole). Although the accepted values may change as experimental methods improve, certain trends are clear.

We must not confuse *bond dissociation energy* (D) with another measure of bond strength called *bond energy* (E). If one begins with methane, for example, and breaks, successively, four carbon-hydrogen bonds, one finds four different bond dissociation energies:

$$CH_4 \longrightarrow CH_3 + H\cdot \qquad D(CH_3{-}H) = 104\ \text{kcal/mole}$$

$$CH_3 \longrightarrow CH_2 + H\cdot \qquad D(CH_2{-}H) = 106$$

$$CH_2 \longrightarrow CH + H\cdot \qquad D(CH{-}H) = 106$$

$$CH \longrightarrow C + H\cdot \qquad D(C{-}H) = 81$$

The carbon-hydrogen bond energy in methane, E(C—H), on the other hand, is a single average value:

$$CH_4 \longrightarrow C + 4H\cdot \qquad \Delta H = 397 \text{ kcal/mole}, \quad E(C{-}H) = 397/4 = 99 \text{ kcal/mole}$$

We shall generally find bond dissociation energies more useful for our purposes.

Table 1.2 Bond Dissociation Energies, Kcal/Mole

$$A{:}B \longrightarrow A\cdot + \cdot B \qquad \Delta H = \text{Bond Dissociation Energy or } D(A{-}B)$$

H—H	104			CH_3—H	104		
H—F	136	F—F	38	CH_3—F	108		
H—Cl	103	Cl—Cl	58	CH_3—Cl	84		
H—Br	88	Br—Br	46	CH_3—Br	70		
H—I	71	I—I	36	CH_3—I	56		
CH_3—H	104	CH_3—CH_3	88	CH_3—Cl	84	CH_3—Br	70
C_2H_5—H	98	C_2H_5—CH_3	85	C_2H_5—Cl	81	C_2H_5—Br	69
n-C_3H_7—H	98	n-C_3H_7—CH_3	85	n-C_3H_7—Cl	82	n-C_3H_7—Br	69
i-C_3H_7—H	95	i-C_3H_7—CH_3	84	i-C_3H_7—Cl	81	i-C_3H_7—Br	68
t-C_4H_9—H	91	t-C_4H_9—CH_3	80	t-C_4H_9—Cl	79	t-C_4H_9—Br	63
H_2C=CH—H	104	H_2C=CH—CH_3	92	H_2C=CH—Cl	84		
H_2C=$CHCH_2$—H	88	H_2C=$CHCH_2$—CH_3	72	H_2C=$CHCH_2$—Cl	60	H_2C=$CHCH_2$—Br	47
C_6H_5—H	112	C_6H_5—CH_3	93	C_6H_5—Cl	86	C_6H_5—Br	72
$C_6H_5CH_2$—H	85	$C_6H_5CH_2$—CH_3	70	$C_6H_5CH_2$—Cl	68	$C_6H_5CH_2$—Br	51

So far, we have spoken of breaking a molecule into two atoms or into an atom and a group of atoms. Thus, of the two electrons making up the covalent bond, one goes to each fragment; such bond-breaking is called *homolysis*. We shall also encounter reactions involving bond-breaking of a different kind: *heterolysis*, in which both bonding electrons go to the same fragment.

$$A{:}B \longrightarrow A\cdot + B\cdot$$

Homolysis:
one electron to each fragment

$$A{:}B \longrightarrow A + {:}B$$

Heterolysis:
both electrons to one fragment

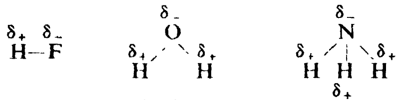
(These words are taken from the Greek: *homo* and *hetero*, the same and different; and *lysis*, a loosing. To a chemist *lysis* means "cleavage" as in, for example, *hydro-lysis*, "cleavage by water.")

Simple heterolysis of a neutral molecule yields, of course, a positive ion and a negative ion. Separation of these oppositely charged particles takes a great deal of energy: 100 kcal/mole or so *more* than separation of neutral particles. In the gas phase, therefore, bond dissociation generally takes place by the easier route, homolysis. In an ionizing solvent (Sec. 1.21), on the other hand, heterolysis is the preferred kind of cleavage

1.15 Polarity of bonds

Besides the properties already described, certain covalent bonds have another property: **polarity**. Two atoms joined by a covalent bond share electrons; their nuclei are held by the same electron cloud. But in most cases the two nuclei do not share the electrons equally; the electron cloud is denser about one atom than the other. One end of the bond is thus relatively negative and the other end is relatively positive; that is, there is a *negative pole* and a *positive pole*. Such a bond is said to be a **polar bond**, or to *possess polarity*.

We can indicate polarity by using the symbols δ_+ and δ_-, which indicate *partial* + and − charges. For example:



Polar bonds

We can expect a covalent bond to be polar if it joins atoms that differ in their tendency to attract electrons, that is, atoms that differ in *electronegativity*. Furthermore, the greater the difference in electronegativity, the more polar the bond will be.

The most electronegative elements are those located in the upper right-hand corner of the Periodic Table. Of the elements we are likely to encounter in organic chemistry, fluorine has the highest electronegativity, then oxygen, then nitrogen and chlorine, then bromine, and finally carbon. Hydrogen does not differ very much from carbon in electronegativity; it is not certain whether it is more or less electronegative.

Electronegativity $F > O > Cl, N > Br > C, H$

Bond polarities are intimately concerned with both physical and chemical properties. The polarity of bonds can lead to polarity of molecules, and thus profoundly affect melting point, boiling point, and solubility. The polarity of a bond determines the kind of reaction that can take place at that bond, and even affects reactivity at nearby bonds.

1.16 Polarity of molecules

A molecule is polar if the center of negative charge does not coincide with the center of positive charge. Such a molecule constitutes a *dipole*: two equal and opposite charges separated in space. A dipole is often symbolized by $+\!\!\!\rightarrow$, where the arrow points from positive to negative. The molecule possesses a dipole moment, μ, which is equal to the magnitude of the charge, e, multiplied by the distance, d, between the centers of charge:

$$\underset{\substack{\text{in}\\ \text{Debye}\\ \text{units, D}}}{\mu} = \underset{\substack{\text{in}\\ \text{e.s.u.}}}{e} \times \underset{\substack{\text{in}\\ \text{Angstroms}}}{d}$$

In a way that cannot be gone into here, it is possible to measure the dipole moments of molecules; some of the values obtained are listed in Table 1.3. We shall be interested in the values of dipole moments as indications of the relative polarities of different molecules.

Table 1.3 Dipole Moments, D

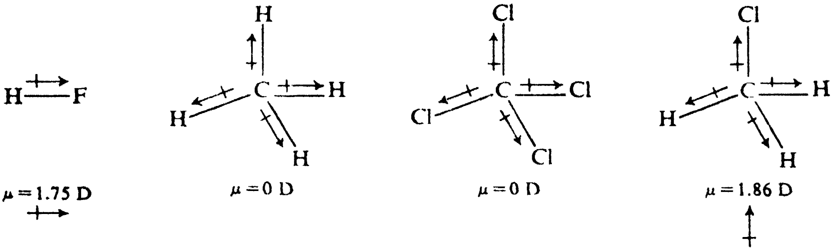
H_2	0	HF	1.75	CH_4	0
O_2	0	H_2O	1.84	CH_3Cl	1.86
N_2	0	NH_3	1.46	CCl_4	0
Cl_2	0	NF_3	0.24	CO_2	0
Br_2	0	BF_3	0		

It is the *fact* that some molecules are polar which has given rise to the *speculation* that some bonds are polar. We have taken up bond polarity first simply because it is convenient to consider that the polarity of a molecule is a composite of the polarities of the individual bonds.

Molecules like H_2, O_2, N_2, Cl_2, and Br_2 have zero dipole moments, that is, are non-polar. The two identical atoms of each of these molecules have, of course, the same electronegativity and share electrons equally; e is zero and hence μ is zero, too.

A molecule like hydrogen fluoride has the large dipole moment of 1.75 D. Although hydrogen fluoride is a small molecule, the very high electronegative fluorine pulls the electrons strongly; although d is small, e is large, and hence μ is large, too.

Methane and carbon tetrachloride, CCl_4, have zero dipole moments. We certainly would expect the individual bonds—of carbon tetrachloride at least—to be polar; because of the very symmetrical tetrahedral arrangement, however, they exactly cancel each other out (Fig. 1.14). In methyl chloride, CH_3Cl, the polarity

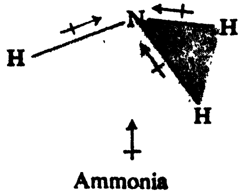


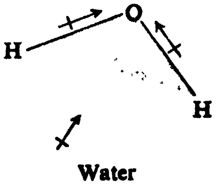
Hydrogen fluoride Methane Carbon tetrachloride Methyl chloride

Figure 1.14. Dipole moments of some molecules. Polarity of bonds and of molecules.

of the carbon-chlorine bond is not canceled, however, and methyl chloride has a dipole moment of 1.86 D. Thus the polarity of a molecule depends not only upon the polarity of its individual bonds but also upon the way the bonds are directed, that is, upon the shape of the molecule.

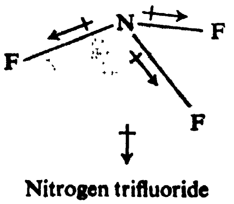
Ammonia has a dipole moment of 1.46 D. This could be accounted for as a net dipole moment (*a vector sum*) resulting from the three individual bond moments, and would be in the direction shown in the diagram. In a similar way, we could account for water's dipole moment of 1.84 D.





Dipole moments expected from bond moments alone

Now, what kind of dipole moment would we expect for nitrogen trifluoride, NF_3, which, like ammonia, is pyramidal? Fluorine is the most electronegative element of all and should certainly pull electrons strongly from nitrogen; the N—F bonds should be highly polar, and their vector sum should be large—far larger than for ammonia with its modestly polar N—H bonds.



Large dipole moment expected from bond moments alone

What are the facts? Nitrogen trifluoride has a dipole moment of only 0.24 D. It is not larger than the moment for ammonia, but rather is *much smaller.*

How are we to account for this? We have forgotten the *unshared pair of electrons.* In NF_3 (as in NH_3) this pair occupies an sp^3 orbital and must contribute a dipole moment in the direction opposite to that of the net moment of the N—F bonds (Fig. 1.15); these opposing moments are evidently of about the same size,

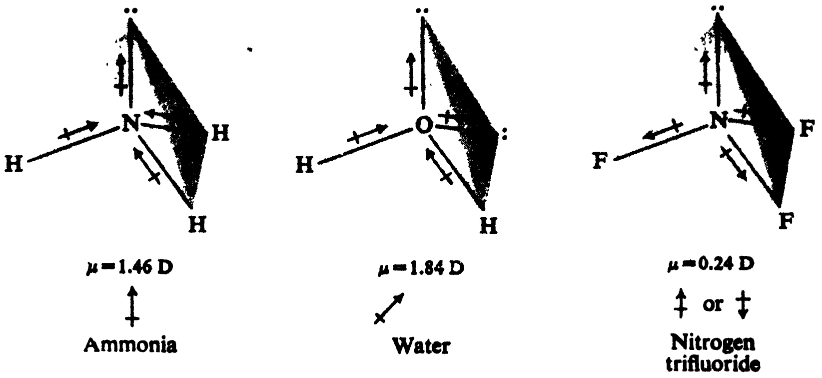


Figure 1.15. Dipole moments of some molecules. Contribution from unshared pairs. In NF_3, moment due to unshared pair opposes vector sum of bond moments.

and the result is a small moment, in which direction we cannot say. In ammonia the observed moment is probably due chiefly to the unshared pair, augmented by the sum of the bond moments. In a similar way, unshared pairs of electrons must contribute to the dipole moments of water and, indeed, of any molecules in which they appear.

Dipole moments can give valuable information about the structure of molecules. For example, any structure for carbon tetrachloride that would result in a polar molecule can be ruled out on the basis of dipole moment alone. The evidence of dipole moment thus supports the tetrahedral structure for carbon tetrachloride. (However, it does not prove this structure, since there are other conceivable structures that would also result in a non-polar molecule.)

Problem 1.5 Which of the following conceivable structures of CCl_4 would also have a zero dipole moment? (a) Carbon at the center of a square with a chlorine at each corner. (b) Carbon at the apex of a pyramid with a chlorine at each corner of a square base.

Problem 1.6 Suggest a shape for the CO_2 molecule that would account for its zero dipole moment.

Problem 1.7 In Sec. 1.12 we rejected two conceivable electronic configurations for ammonia. (a) If nitrogen were sp^2-hybridized, what dipole moment would you expect for ammonia? What *is* the dipole moment of ammonia? (b) If nitrogen used p orbitals for bonding, how would you expect the dipole moments of ammonia and nitrogen trifluoride to compare? How *do* they compare?

The dipole moments of most compounds have never been measured. For these substances we must predict polarity from structure. From our knowledge of electronegativity, we can estimate the polarity of bonds; from our knowledge of bond angles, we can then estimate the polarity of molecules, taking into account any unshared pairs of electrons.

1.17 Structure and physical properties

We have just discussed one physical property of compounds: dipole moment. Other physical properties—like melting point, boiling point, or solubility in a particular solvent—are also of concern to us. The physical properties of a new compound give valuable clues about its structure. Conversely, the structure of a compound often tells us what physical properties to expect of it.

In attempting to synthesize a new compound, for example, we must plan a series of reactions to convert a compound that we have into the compound that we want. In addition, we must work out a method of separating our product from all the other compounds making up the reaction mixture: unconsumed reactants, solvent, catalyst, by-products. Usually the *isolation* and *purification* of a product take much more time and effort than the actual making of it. The feasibility of isolating the product by distillation depends upon its boiling point and the boiling points of the contaminants; isolation by recrystallization depends upon its solubility in various solvents and the solubility of the contaminants. Success in the laboratory often depends upon making a good prediction of physical properties from structure.

We have seen that there are two extreme kinds of chemical bonds: ionic bonds, formed by the transfer of electrons, and covalent bonds, formed by the sharing of electrons. The physical properties of a compound depend largely upon which kind of bonds hold its atoms together in the molecule.

1.18 Melting point

In a crystalline solid the particles acting as structural units—ions or molecules—are arranged in some very regular, symmetrical way; there is a geometric pattern repeated over and over within a crystal.

Melting is the change from the highly ordered arrangement of particles in the crystalline lattice to the more random arrangement that characterizes a liquid (see Figs. 1.16 and 1.17). Melting occurs when a temperature is reached at which the thermal energy of the particles is great enough to overcome the intracrystalline forces that hold them in position.

An **ionic compound** forms crystals in which the structural units are *ions*. Solid sodium chloride, for example, is made up of positive sodium ions and negative chloride ions alternating in a very regular way. Surrounding each positive ion and equidistant from it are six negative ions: one on each side of it, one above and one below, one in front and one in back. Each negative ion is surrounded in a similar way by six positive ions. There is nothing that we can properly call a *molecule* of sodium chloride. A particular sodium ion does not "belong" to any one chloride ion; it is equally attracted to six chloride ions. The crystal is an extremely strong, rigid structure, since the electrostatic forces holding each ion in position are powerful. These powerful *interionic* forces are overcome only at a very high temperature; sodium chloride has a melting point of 801°.

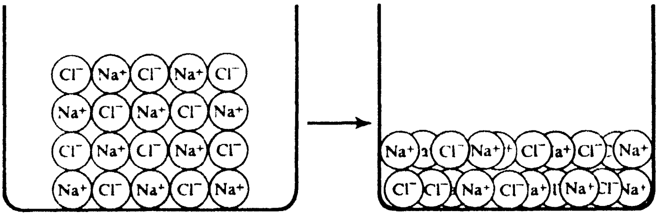


Figure 1.16. Melting of an ionic crystal. Units are ions.

Crystals of other ionic compounds resemble crystals of sodium chloride in having an ionic lattice, although the exact geometric arrangement may be different. As a result, these other ionic compounds, too, have high melting points. Many molecules contain both ionic and covalent bonds. Potassium nitrate, KNO_3, for example, is made up of K^+ ions and NO_3^- ions; the oxygen and nitrogen atoms of the NO_3^- ion are held to each other by covalent bonds. The physical properties of compounds like these are largely determined by the ionic bonds; potassium nitrate has very much the same sort of physical properties as sodium chloride.

A **non-ionic compound**, one whose atoms are held to each other entirely by covalent bonds, forms crystals in which the structural units are *molecules*. It is the forces holding these molecules to each other that must be overcome for melting to occur. In general, these *intermolecular* forces are very weak compared with the

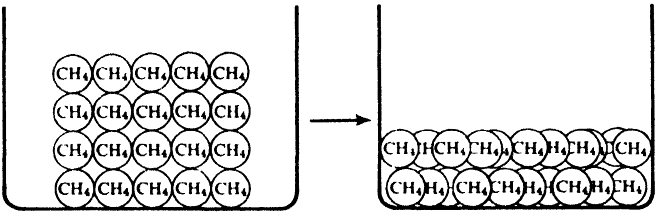


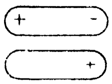
Figure 1.17. Melting of a non-ionic crystal. Units are molecules.

forces holding ions to each other. To melt sodium chloride we must supply enough energy to break ionic bonds between Na^+ and Cl^-. To melt methane, CH_4, we do not need to supply enough energy to break covalent bonds between carbon and hydrogen; we need only supply enough energy to break CH_4 molecules away from each other. In contrast to sodium chloride, methane melts at −183°.

1.19 Intermolecular forces

What kind of forces hold neutral molecules to each other? Like interionic forces, these forces seem to be electrostatic in nature, involving attraction of positive charge for negative charge. There are two kinds of intermolecular forces: *dipole-dipole interactions* and *van der Waals forces.*

Dipole-dipole interaction is the attraction of the positive end of one polar molecule for the negative end of another polar molecule. In hydrogen chloride, for example, the relatively positive hydrogen of one molecule is attracted to the relatively negative chlorine of another:

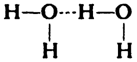


As a result of dipole-dipole interaction, polar molecules are generally held to each other more strongly than are non-polar molecules of comparable molecular weight; this difference in strength of intermolecular forces is reflected in the physical properties of the compounds concerned.

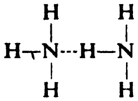
An especially strong kind of dipole dipole attraction is **hydrogen bonding,** in which *a hydrogen atom serves as a bridge between two electronegative atoms, holding one by a covalent bond and the other by purely electrostatic forces.* When hydrogen is attached to a highly electronegative atom, the electron cloud is greatly distorted toward the electronegative atom, exposing the hydrogen nucleus. The strong positive charge of the thinly shielded hydrogen nucleus is strongly attracted by the negative charge of the electronegative atom of a second molecule. This attraction has a strength of about 5 kcal/mole, and is thus much weaker than the covalent bond—about 50–100 kcal/mole—that holds it to the first electronegative atom. It is, however, much stronger than other dipole-dipole attractions.

Hydrogen bonding is generally indicated in formulas by a broken line:

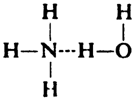
$\mathrm{H{-}F\cdots H{-}F}$



$$\mathrm{H{-}\underset{H}{\underset{|}{O}}\cdots H{-}\underset{H}{\underset{|}{O}}}$$



$$\mathrm{H{-}\overset{H}{\overset{|}{\underset{H}{\underset{|}{N}}}}\cdots H{-}\overset{H}{\overset{|}{\underset{H}{\underset{|}{N}}}}}$$

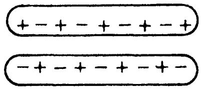


$$\mathrm{H{-}\overset{H}{\overset{|}{\underset{H}{\underset{|}{N}}}}\cdots H{-}\overset{H}{\overset{|}{O}}}$$

For hydrogen bonding to be important, both electronegative atoms must come from the group: **F**, **O**, **N**. Only hydrogen bonded to one of these three elements is positive enough, and only these three elements are negative enough, for the necessary attraction to exist. These three elements owe their special effectiveness to the concentrated negative charge on their small atoms.

Hydrogen bonding, we shall find, not only exerts profound effects on the boiling point and solubility properties of compounds, but also plays a key role in determining the *shapes* of large molecules like proteins and nucleic acids, shapes that in a very direct way determine, in turn, their biological properties: the size of the "pockets" in the hemoglobin molecule, just big enough to hold heme groups with their oxygen-carrying iron atoms (p. 1152); the helical shape of α-keratin and collagen molecules that makes wool and hair strong, and tendons and skin tough (p. 1158). It is hydrogen bonding that makes the double helix of DNA *double*—and thus permits the self-duplication of molecules that is the basis of heredity (p. 1179).

There must be forces between the molecules of a non-polar compound, since even such compounds can solidify. Such attractions are called **van der Waals forces**. The existence of these forces is accounted for by quantum mechanics. We can roughly visualize them arising in the following way. The average distribution of charge about, say, a methane molecule is symmetrical, so that there is no net dipole moment. However, the electrons move about, so that at any instant of time the distribution will probably be distorted, and a small dipole will exist. This momentary dipole will affect the electron distribution in a second methane molecule nearby. The negative end of the dipole tends to repel electrons, and the positive end tends to attract electrons; the dipole thus *induces* an oppositely oriented dipole in the neighboring molecule:



Although the momentary dipoles and induced dipoles are constantly changing, the net result is attraction between the two molecules. These van der Waals forces have a very short range; they act only between the portions of different molecules that are in close contact, that is, between the surfaces of molecules. As we shall see, the relationship between the strength of van der Waals forces and the surface areas of molecules (Sec. 3.12) will help us to understand the effect of molecular size and shape on physical properties. We must not underestimate the power of these weakest intermolecular forces; acting between non-polar chains of phospholipids, for example, they are the mortar in the walls of living cells.

With respect to other atoms to which it is not bonded—whether in another molecule or in another part of the same molecule—every atom has an effective "size," called its

van der Waals radius. As two non-bonded atoms are brought together the attraction between them steadily increases, and reaches a maximum when they are just "touching"—that is to say, when the distance between the nuclei is equal to the sum of the van der Waals radii. Now, if the atoms are forced still closer together, van der Waals attraction is very rapidly replaced by van der Waals *repulsion*. Thus, non-bonded atoms welcome each other's touch, but strongly resist crowding.

We shall find both attractive and repulsive van der Waals forces important to our understanding of molecular structure.

1.20 Boiling point

Although the particles in a liquid are arranged less regularly and are freer to move about than in a crystal, each particle is attracted by a number of other particles. Boiling involves the breaking away from the liquid of individual molecules or pairs of oppositely charged ions (see Figs. 1.18 and 1.19). This occurs when a temperature is reached at which the thermal energy of the particles is great enough to overcome the cohesive forces that hold them in the liquid.

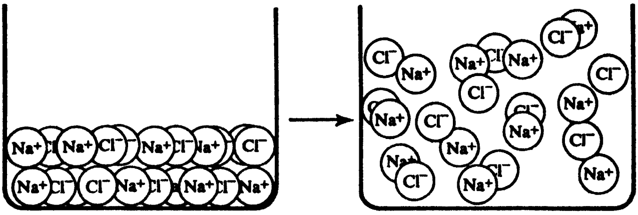


Figure 1.18. Boiling of an ionic liquid. Units are ions and ion pairs.

In the liquid state the unit of an ionic compound is again the ion. Each ion is still held strongly by a number of oppositely charged ions. Again there is nothing we could properly call a molecule. A great deal of energy is required for a pair of oppositely charged ions to break away from the liquid; boiling occurs only at a very high temperature. The boiling point of sodium chloride, for example, is 1413°. In the gaseous state we have an *ion pair*, which can be considered a sodium chloride molecule.

In the liquid state the unit of a non-ionic compound is again the molecule. The weak intermolecular forces here—dipole–dipole interactions and van der Waals forces—are more readily overcome than the strong interionic forces of ionic compounds, and boiling occurs at a very much lower temperature. Non-polar methane boils at −161.5°, and even polar hydrogen chloride boils at only −85°.

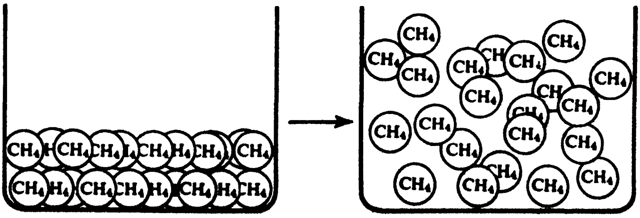


Figure 1.19. Boiling of a non-ionic liquid. Units are molecules.

Liquids whose molecules are held together by hydrogen bonds are called *associated liquids.* Breaking these hydrogen bonds takes considerable energy, and so an associated liquid has a boiling point that is abnormally high for a compound of its molecular weight and dipole moment. Hydrogen fluoride, for example, boils 100 degrees higher than the heavier, non-associated hydrogen chloride; water boils 160 degrees higher than hydrogen sulfide.

The bigger the molecules, the stronger the van der Waals forces. Other things being equal—polarity, hydrogen bonding—boiling point rises with increasing molecular size. Boiling points of organic compounds range upward from that of tiny, non-polar methane, but we seldom encounter boiling points much above 350°; at higher temperatures, covalent bonds *within* the molecules start to break, and decomposition competes with boiling. It is to lower the boiling point and thus minimize decomposition that distillation of organic compounds is often carried out under reduced pressure.

Problem 1.8 Which of the following organic compounds would you predict to be *associated* liquids? Draw structures to show the hydrogen bonding you would expect. (a) CH_3OH; (b) CH_3OCH_3; (c) CH_3F; (d) CH_3Cl; (e) CH_3NH_2; (f) $(CH_3)_2NH$; (g) $(CH_3)_3N$.

1.21 Solubility

When a solid or liquid dissolves, the structural units—ions or molecules—become separated from each other, and the spaces in between become occupied by solvent molecules. In dissolution, as in melting and boiling, energy must be supplied to overcome the interionic or intermolecular forces. Where does the necessary energy come from? The energy required to break the bonds between solute particles is supplied by the formation of bonds between the solute particles and the solvent molecules: the old attractive forces are replaced by new ones.

A great deal of energy is necessary to overcome the powerful electrostatic forces holding together an ionic lattice. Only water or other highly polar solvents are able to dissolve ionic compounds appreciably. What kind of bonds are formed between ions and a polar solvent? By definition, a polar molecule has a positive end and a negative end. Consequently, there is electrostatic attraction between a positive ion and the negative end of the solvent molecule, and between a negative ion and the positive end of the solvent molecule. These attractions are called **ion–dipole** bonds. Each ion–dipole bond is relatively weak, but in the aggregate they supply enough energy to overcome the interionic forces in the crystal. In solution each ion is surrounded by a cluster of solvent molecules, and is said to be *solvated*; if the solvent happens to be water, the ion is said to be *hydrated.* In solution, as in the solid and liquid states, the unit of a substance like sodium chloride is the ion, although in this case it is a solvated ion (see Fig. 1.20).

To dissolve ionic compounds a solvent must also have a high *dielectric constant,* that is, have high insulating properties to lower the attraction between oppositely charged ions once they are solvated.

Water owes its superiority as a solvent for ionic substances not only to its polarity and its high dielectric constant, but to another factor as well: it contains the —OH group and thus can form hydrogen bonds. Water solvates both cations

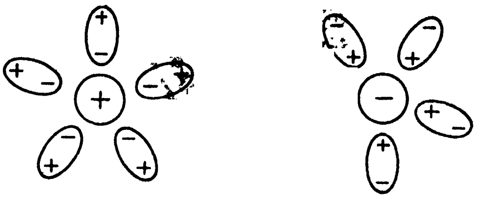


Figure 1.20. Ion–dipole interactions: solvated cation and anion.

and anions: cations, at its negative pole (its unshared electrons, essentially); anions, through hydrogen bonding.

The solubility characteristics of non-ionic compounds are determined chiefly by their polarity. Non-polar or weakly polar compounds dissolve in non-polar or weakly polar solvents; highly polar compounds dissolve in highly polar solvents. "Like dissolves like" is an extremely useful rule of thumb. Methane dissolves in carbon tetrachloride because the forces holding methane molecules to each other and carbon tetrachloride molecules to each other are replaced by very similar forces holding methane molecules to carbon tetrachloride molecules.

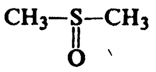
Neither methane nor carbon tetrachloride is readily soluble in water. The highly polar water molecules are held to each other by very strong dipole–dipole interactions—hydrogen bonds; there could be only very weak attractive forces between water molecules on the one hand and the non-polar methane or carbon tetrachloride molecules on the other.

In contrast, the highly polar organic compound methanol, CH_3OH, is quite soluble in water. Hydrogen bonds between water and methanol molecules can readily replace the very similar hydrogen bonds between different methanol molecules and different water molecules.

As we shall see, much of organic chemistry is concerned with reactions between non-ionic compounds (generally organic) and ionic compounds (inorganic and organic), and it is necessary to select a solvent in which both the reagents will dissolve. Water is a poor solvent for most organic compounds, but this difficulty can be overcome by addition of a second solvent like methanol.

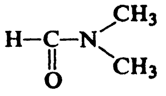
Solvents like water or methanol are called *protic solvents*: solvents containing hydrogen that is attached to oxygen or nitrogen, and hence is appreciably acidic (Sec. 1.22). Through hydrogen bonding such solvents tend to solvate anions particularly strongly; and anions, as it turns out, are usually the important half of an ionic reagent. Thus, although protic solvents dissolve the reagent and bring it into contact with the organic molecule, at the same time they stabilize the anions and lower their reactivity drastically; their basicity is weakened and, with it, the related property, *nucleophilic* power (Sec. 14.5).

Recent years have seen the development and widespread use of *aprotic solvents*: polar solvents of moderately high dielectric constants, which do not contain acidic hydrogen. For example:

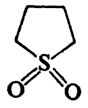


$CH_3-\underset{\overset{\|}{O}}{S}-CH_3$

Dimethyl sulfoxide
DMSO



N,N-Dimethylformamide
DMF



Sulfolane

These solvents dissolve both organic and inorganic reagents but, in dissolving ionic compounds, solvate *cations* most strongly, and leave the anions relatively unencumbered and highly reactive; anions are more basic and more nucleophilic.

Since about 1958, reports of dramatic solvent effects on a wide variety of reactions have appeared, first about dimethylformamide (DMF) and more recently about dimethyl sulfoxide (DMSO): reactions that, in most solvents, proceed slowly at high temperatures to give low yields may be found, in an aprotic solvent, to proceed rapidly—often at room temperature—to give high yields. A change of solvent may cause a million-fold change in reaction rate. A solvent is not simply a place—a kind of gymnasium—where solute molecules may gambol about and occasionally collide; the solvent is intimately *involved* in any reaction that takes place in it, and we are just beginning to find out how much it is involved, and in what way.

Individual molecules may have both polar and non-polar parts and, if the molecules are big enough, these parts display their individual solubility properties. The polar parts dissolve in water; the non-polar parts dissolve in a non-polar solvent or, if there is none about, cluster together—in effect, dissolve in each other. Such dual solubility behavior gives soaps and detergents their cleansing power, and controls the alignment of molecules in cell membranes; a globular protein molecule—an enzyme, say—coils up to expose its polar parts to the surrounding water and to hide its non-polar parts, and in doing this takes on the particular shape needed for its characteristic biological properties.

1.22 Acids and bases

Turning from physical to chemical properties, let us review briefly one familiar topic that is fundamental to the understanding of organic chemistry: acidity and basicity.

The terms *acid* and *base* have been defined in a number of ways, each definition corresponding to a particular way of looking at the properties of acidity and basicity. We shall find it useful to look at acids and bases from two of these viewpoints; the one we select will depend upon the problem at hand.

According to the **Lowry-Brønsted** definition, *an acid is a substance that gives up a proton*, and *a base is a substance that accepts a proton*. When sulfuric acid dissolves in water, the acid H_2SO_4 gives up a proton (hydrogen nucleus) to the base H_2O to form a new acid H_3O^+ and a new base HSO_4^-. When hydrogen chloride reacts with ammonia, the acid HCl gives up a proton to the base NH_3 to form the new acid NH_4^+ and the new base Cl^-.

$$\underset{\substack{\text{Stronger}\\\text{acid}}}{H_2SO_4} + \underset{\substack{\text{Stronger}\\\text{base}}}{H_2O} \rightleftarrows \underset{\substack{\text{Weaker}\\\text{acid}}}{H_3O^+} + \underset{\substack{\text{Weaker}\\\text{base}}}{HSO_4^-}$$

$$\underset{\substack{\text{Stronger}\\\text{acid}}}{HCl} + \underset{\substack{\text{Stronger}\\\text{base}}}{NH_3} \rightleftarrows \underset{\substack{\text{Weaker}\\\text{acid}}}{NH_4^+} + \underset{\substack{\text{Weaker}\\\text{base}}}{Cl^-}$$

According to the Lowry-Brønsted definition, the strength of an acid depends upon its tendency to give up a proton, and the strength of a base depends upon its tendency to accept a proton. Sulfuric acid and hydrogen chloride are strong acids since they tend to give up a proton very readily; conversely, bisulfate ion, HSO_4^-, and chloride ion must necessarily be weak bases since they have little tendency to hold on to protons. In each of the reactions just described, the equilibrium favors the formation of the weaker acid and the weaker base.

If aqueous H_2SO_4 is mixed with aqueous NaOH, the acid H_3O^+ (hydronium ion) gives up a proton to the base OH^- to form the new acid H_2O and the new base H_2O. When aqueous NH_4Cl is mixed with aqueous NaOH, the acid NH_4^+ (ammonium ion) gives up a proton to the base OH^- to form the new acid H_2O and the new base NH_3. In each case the strong base, hydroxide ion, has accepted a proton to form the weak acid H_2O. If we arrange these acids in the order shown, we must necessarily arrange the corresponding (conjugate) bases in the opposite order.

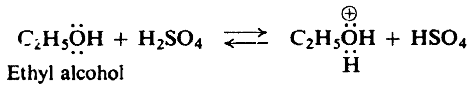
$$\begin{array}{ccccccc} H_3O^+ & + & OH^- & \rightleftharpoons & H_2O & + & H_2O \\ \text{Stronger} & & \text{Stronger} & & \text{Weaker} & & \text{Weaker} \\ \text{acid} & & \text{base} & & \text{acid} & & \text{base} \end{array}$$

$$\begin{array}{ccccccc} NH_4^+ & + & OH^- & \rightleftharpoons & H_2O & + & NH_3 \\ \text{Stronger} & & \text{Stronger} & & \text{Weaker} & & \text{Weaker} \\ \text{acid} & & \text{base} & & \text{acid} & & \text{base} \end{array}$$

Acid strength $\begin{matrix} H_2SO_4 \\ HCl \end{matrix} > H_3O^+ > NH_4^+ > H_2O$

Base strength $\begin{matrix} HSO_4^- \\ Cl^- \end{matrix} < H_2O < NH_3 < OH^-$

Like water, many organic compounds that contain oxygen can act as bases and accept protons; ethyl alcohol and ethyl ether, for example, form the *oxonium ions* I and II. For convenience, we shall often refer to a structure like I as a *protonated alcohol* and a structure like II as a *protonated ether.*

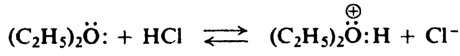


$$C_2H_5\ddot{\underset{\cdot\cdot}{O}}H + H_2SO_4 \rightleftharpoons C_2H_5\overset{\oplus}{\ddot{\underset{\underset{H}{|}}{O}}}H + HSO_4$$

Ethyl alcohol

I

An oxonium ion
Protonated ethyl alcohol



$$(C_2H_5)_2\ddot{O}: + HCl \rightleftharpoons (C_2H_5)_2\overset{\oplus}{\ddot{O}}:H + Cl^-$$

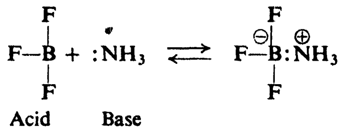
Ethyl ether

II

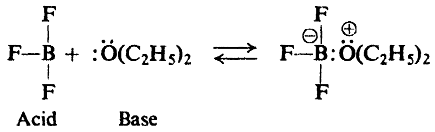
An oxonium ion
Protonated ethyl ether

According to the **Lewis** definition, *a base is a substance that can furnish an electron pair to form a covalent bond,* and *an acid is a substance that can take up an electron pair to form a covalent bond.* Thus **an acid is an electron-pair acceptor and a base is an electron-pair donor.** This is the most fundamental of the acid-base concepts, and the most general; it includes all the other concepts.

A proton is an acid because it is deficient in electrons, and needs an electron pair to complete its valence shell. Hydroxide ion, ammonia, and water are bases because they contain electron pairs available for sharing. In boron trifluoride, BF_3, boron has only six electrons in its outer shell and hence tends to accept another pair to complete its octet. Boron trifluoride is an acid and combines with



$$F\text{—}\underset{F}{\overset{F}{B}} + :NH_3 \rightleftharpoons F\text{—}\underset{F}{\overset{F}{\overset{\ominus}{B}}}:\overset{\oplus}{N}H_3$$



$$F\text{—}\underset{F}{\overset{F}{B}} + :\ddot{O}(C_2H_5)_2 \rightleftharpoons F\text{—}\underset{F}{\overset{F}{\overset{\ominus}{B}}}:\overset{\oplus}{\ddot{O}}(C_2H_5)_2$$

such bases as ammonia or ethyl ether. Aluminum chloride, $AlCl_3$, is an acid, and for the same reason. In stannic chloride, $SnCl_4$, tin has a complete octet, but can accept additional pairs of electrons (e.g., in $SnCl_6^{--}$) and hence it is an acid, too.

We write a formal negative charge on boron in these formulas because it has one more electron—half-interest in the pair shared with nitrogen or oxygen—than is balanced by the nuclear charge; correspondingly, nitrogen or oxygen is shown with a formal positive charge.

We shall find the Lewis concept of acidity and basicity fundamental to our understanding of organic chemistry. To make it clear that we are talking about this kind of acid or base, we shall often use the expression *Lewis acid* (or *base*), or sometimes *acid* (or *base*) *in the Lewis sense*.

Chemical properties, like physical properties, depend upon molecular structure. Just what features in a molecule's structure tell us what to expect about its acidity or basicity? We can try to answer this question in a general way now, although we shall return to it many times later.

To be acidic in the Lowry-Brønsted sense, a molecule must, of course, contain hydrogen. The degree of acidity is determined largely by the kind of atom that holds the hydrogen and, in particular, by that atom's ability to accommodate the electron pair left behind by the departing hydrogen ion. This ability to accommodate the electron pair seems to depend upon several factors, including (a) the atom's *electronegativity*, and (b) its *size*. Thus, within a given row of the Periodic Table, acidity increases as electronegativity increases:

Acidity

$$H\text{—}CH_3 < H\text{—}NH_2 < H\text{—}OH < H\text{—}F$$

$$H\text{—}SH < H\text{—}Cl$$

And within a given family, acidity increases as the size increases:

Acidity

$$H\text{—}F < H\text{—}Cl < H\text{—}Br < H\text{—}I$$

$$H\text{—}OH < H\text{—}SH < H\text{—}SeH$$

Among organic compounds, we can expect appreciable Lowry-Brønsted acidity from those containing O—H, N—H, and S—H groups.

To be acidic in the Lewis sense, a molecule must be electron-deficient; in particular, we would look for an atom bearing only a sextet of electrons.

Problem 1.9 Predict the relative acidity of: (a) methyl alcohol (CH_3OH) and methylamine (CH_3NH_2); (b) methyl alcohol (CH_3OH) and methanethiol (CH_3SH); (c) H_3O^+ and NH_4^+.

Problem 1.10 Which is the stronger acid of each pair: (a) H_3O^+ or H_2O; (b) NH_4^+ or NH_3; (c) H_2S or HS^-; (d) H_2O or OH^-? (e) What relationship is there between *charge* and acidity?

To be basic in either the Lowry-Brønsted or the Lewis sense, a molecule must have an electron pair available for sharing. The availability of these unshared electrons is determined largely by the atom that holds them: its electronegativity, its size, its charge. The operation of these factors here is necessarily opposite to what we observed for acidity; the better an atom accommodates the electron pair, the less available the pair is for sharing.

Problem 1.11 Arrange the members of each group in order of basicity: (a) F^-, OH^-, NH_2^-, CH_3^-; (b) HF, H_2O, NH_3; (c) Cl^-, SH^-; (d) F^-, Cl^-, Br^-, I^-; (e) OH^-, SH^-, SeH^-.

Problem 1.12 Predict the relative basicity of methyl fluoride (CH_3F), methyl alcohol (CH_3OH), and methylamine (CH_3NH_2).

Problem 1.13 Arrange the members of each group in order of basicity: (a) H_3O^+, H_2O, OH^-; (b) NH_3, NH_2^-; (c) H_2S, HS^-, S^{--}. (d) What relationship is there between charge and basicity?

1.23 Electronic and steric effects

Like acidity and basicity, other chemical properties, too, depend upon molecular structure. Indeed, most of this book will be concerned with finding out what this relationship is.

A particular compound is found to undergo a particular reaction. Not surprisingly, other compounds of similar structure are also found to undergo the same reaction—but faster or slower, or with the equilibrium lying farther to the right or left. We shall, first of all, try to see how it is that a particular kind of structure predisposes a compound to a particular reaction. Then—and much of our time will be spent with this—we shall try to see how it is that variations in molecular structure give rise to variations in reactivity: to differences in rate of reaction or in position of equilibrium.

To do all this is a complicated business, and to help us we shall mentally analyze the molecule: we shall consider that a molecule consists of a reaction center to which are attached various substituents. The nature of the reaction center determines what reaction occurs. The nature of the substituents determines the reactivity.

A substituent affects reactivity in two general ways: (a) by its *electronic effect*, that is, by its effect on the availability of electrons at the reaction center; and (b) by its *steric effect*, that is, by its effect on crowding in the molecule. Since hydrogen is the element most commonly attached to carbon, it is used as the standard of reference. We consider a substituent G, which may be an atom or a group of atoms, to be attached to a carbon in place of a hydrogen, and we ask the question: How does G—C~ compare with H—C~?

Let us look first at **electronic effects.** At some stage of most reactions, a positive or negative charge develops in the reacting molecule. Reactivity usually depends upon how easily the molecule can accommodate that charge. Accommodation of charge depends, in turn, on the electronic effects of the substituents. Compared with hydrogen, a substituent may tend either to *withdraw electrons* (G←C~) or to *release electrons* (G→C~). An electron-withdrawing substituent will help to accept the surplus of electrons that constitutes a negative charge; an electron-releasing substituent will help offset the deficit of electrons that constitutes a positive charge.

Just how does a substituent exert its electronic effect? Despite the vast amount of work that has been done—and is still being done—on this problem, there is no general agreement, except that at least two factors must be at work. We shall consider electron withdrawal and release to result from the operation of two factors: the *inductive effect* and the *resonance effect.*

The **inductive effect** depends upon the "intrinsic" tendency of a substituent to withdraw electrons—by definition, its electronegativity—acting either through the molecular chain or through space. The effect weakens steadily with increasing distance from the substituent. Most elements likely to be substituted for hydrogen in an organic molecule are more electronegative than hydrogen, so that most substituents exert electron-withdrawing inductive effects: for example, —F, —Cl, —Br, —I, —OH, $—NH_2$, $—NO_2$.

The **resonance effect** involves *delocalization* of electrons—typically, those called π (pi) electrons. It depends upon the overlap of certain orbitals, and therefore can operate only when the substituent is located in certain special ways relative to the charge center. By its very nature, as we shall see (Sec. 6.25), the resonance effect is a stabilizing effect, and so it amounts to electron withdrawal from a negatively charged center, and electron release to a positively charged center.

A substituent can influence reactivity not only by its electronic effect (inductive and/or resonance), but also, in some cases, by its **steric effect**: an effect due to crowding at some stage of the reaction, and dependent therefore on the *size* of the substituent.

Problem 1.14 Predict the relative basicity of NH_3 and NF_3.

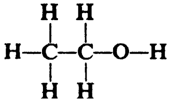
1.24 Isomerism

Before we start our systematic study of the different kinds of organic compounds, let us look at one further concept which illustrates especially well the fundamental importance of molecular structure: the concept of **isomerism.**

The compound *ethyl alcohol* is a liquid boiling at 78°. Analysis (by the methods described later, Sec. 2.26) shows that it contains carbon, hydrogen, and oxygen in the proportions 2C:6H:1O. Measurement of its mass spectrum shows that it has a molecular weight of 46. The molecular formula of ethyl alcohol must therefore be C_2H_6O. Ethyl alcohol is a quite reactive compound. For example, if a piece of sodium metal is dropped into a test tube containing ethyl alcohol, there is a vigorous bubbling and the sodium metal is consumed; hydrogen gas is evolved and there is left behind a compound of formula C_2H_5ONa. Ethyl alcohol reacts with hydriodic acid to form water and a compound of formula C_2H_5I.

The compound *methyl ether* is a gas with a boiling point of −24°. It is clearly a different substance from ethyl alcohol, differing not only in its physical properties but also in its chemical properties. It does not react at all with sodium metal. Like ethyl alcohol, it reacts with hydriodic acid, but it yields a compound of formula CH_3I. Analysis of methyl ether shows that it contains carbon, hydrogen, and oxygen in the same proportions as ethyl alcohol, 2C:6H:1O. It has the same molecular weight as ethyl alcohol, 46. We conclude that it has the same molecular formula, C_2H_6O.

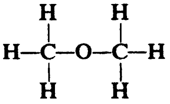
Here we have two substances, ethyl alcohol and methyl ether, which have the same molecular formula, C_2H_6O, and yet quite clearly are different compounds. How can we account for the existence of these two compounds? The answer is: *they differ in molecular structure.* Ethyl alcohol has the structure represented by I, and methyl ether the structure represented by II. As we shall see, the differences in physical and chemical properties of these two compounds can readily be accounted for on the basis of the difference in structure.



$$H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}O{-}H$$

I

Ethyl alcohol



$$H{-}\overset{H}{\underset{H}{C}}{-}O{-}\overset{H}{\underset{H}{C}}{-}H$$

II

Methyl ether

Different compounds that have the same molecular formula are called **isomers** (Gr.: *isos*, equal; *meros*, part). They contain the same numbers of the same kinds of atoms, but the atoms are attached to one another in different ways. Isomers are different compounds because they have different molecular structures.

This difference in molecular structure gives rise to a difference in properties; it is the difference in properties which tells us that we are dealing with different compounds. In some cases, the difference in structure—and hence the difference in properties—is so marked that the isomers are assigned to different chemical families, as, for example, ethyl *alcohol* and methyl *ether*. In other cases the difference in structure is so subtle that it can be described only in terms of three-dimensional models. Other kinds of isomerism fall between these two extremes.

PROBLEMS

1. Which of the following would you expect to be ionic, and which non-ionic? Give a simple electronic structure (Sec. 1.3) for each, showing only valence shell electrons.

(a) $MgCl_2$
(b) CH_2Cl_2
(c) ICl
(d) NaOCl
(e) $KClO_4$
(f) $SiCl_4$
(g) $BaSO_4$
(h) CH_3NH_2

2. Give a likely simple electronic structure (Sec. 1.3) for each of the following, assuming them to be completely covalent. Assume that every atom (except hydrogen, of course) has a complete octet, and that two atoms may share more than one pair of electrons.

(a) N_2H_4
(b) H_2SO_4
(c) HSO_4^-
(d) $COCl_2$
(e) HONO
(f) NO_2^-
(g) CO_3^{--}
(h) C_2H_4
(i) C_2H_2
(j) CH_2O
(k) CH_2O_2
(l) C_3H_8

3. What shape would you expect each of the following to have?

(a) $(CH_3)_3B$
(b) the methyl anion, $CH_3{:}^-$
(c) the methyl cation, CH_3^+
(d) H_2S
(e) the amide ion, NH_2^-
(f) methyl ether
(g) the fluoborate ion, BF_4^-
(h) $(CH_3)_3N$

4. In many complex ions, e.g., $Co(NH_3)_6^{+++}$, the bonds to the central atom can be pictured as utilizing six equivalent sp^3d^2 (or d^2sp^3) hybrid orbitals. On the basis of maximum separation of orbitals, what geometry would you expect these complexes to have?

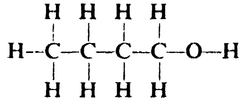
5. Indicate the direction of the dipole moment, *if any*, that you would expect for each of the following:

(a) HBr	(d) CH_2Cl_2	(g) methyl ether
(b) ICl	(e) $CHCl_3$	(h) $(CH_3)_3N$
(c) I_2	(f) CH_3OH	(i) CF_2Cl_2

6. (a) Although HCl (1.27 A) is a longer molecule than HF (0.92 A), it has a *smaller* dipole moment (1.03 D compared to 1.75 D). How do you account for this fact? (b) The dipole moment of CH_3F is 1.847 D, and of CD_3F, 1.858 D. (D is ^2H, deuterium.) Compared with the C—H bond, what is the direction of the C—D dipole?

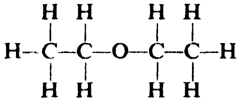
7. What do the differences in properties between lithium acetylacetonate (m.p. very high, insoluble in chloroform) and beryllium acetylacetonate (m.p. 108°, b.p. 270°, soluble in chloroform) suggest about their structures?

8. *n*-Butyl alcohol (b.p. 118°) has a much higher boiling point than its isomer ethyl ether (b.p. 35°), yet both compounds show the same solubility (8 g per 100 g) in water.



$$H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}O{-}H$$

n-Butyl alcohol



$$H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}O{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}H$$

Ethyl ether

How do you account for these facts?

9. Rewrite the following equations to show the Lowry-Brønsted acids and bases actually involved. Label each as stronger or weaker, as in Sec. 1.22.

(a) $HCl(aq) + NaHCO_3(aq) \rightleftarrows H_2CO_3 + NaCl$

(b) $NaOH(aq) + NaHCO_3(aq) \rightleftarrows Na_2CO_3 + H_2O$

(c) $NH_3(aq) + HNO_3(aq) \rightleftarrows NH_4NO_3(aq)$

(d) $NaCN(aq) \leftrightarrows HCN(aq) + NaOH(aq)$

(e) $NaH + H_2O \longrightarrow H_2 + NaOH$

(f) $CaC_2 + H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

Calcium carbide Acetylene

10. What is the Lowry-Brønsted acid in (a) HCl dissolved in water; (b) HCl (unionized) dissolved in benzene? (c) Which solution is the more strongly acidic?

11. Account for the fact that nearly every organic compound containing oxygen dissolves in cold concentrated sulfuric acid to yield a solution from which the compound can be recovered by dilution with water.

12. For each of the following molecular formulas, draw structures like those in Sec. 1.24 (a line for each shared pair of electrons) for all the isomers you can think of. Assume that every atom (except hydrogen) has a complete octet, and that two atoms may share more than one pair of electrons.

(a) C_2H_7N	(c) C_4H_{10}	(e) C_3H_8O
(b) C_3H_8	(d) C_3H_7Cl	(f) C_2H_4O

13. In ordinary distillation, a liquid is placed in a flask and heated, at ordinary or reduced pressure, until distillation is complete. In the modification called *flash distillation*, the liquid is dripped into a heated flask at the same rate that it distills out, so that there is little liquid in the flask at any time. What advantage might flash distillation have, and under what conditions might you use it?

About Working Problems

Working problems is a necessary part of your work for two reasons: it will guide your study in the right direction, and, after you have studied a particular chapter, it will show whether or not you have reached your destination.

You should work all the problems that you can; you should get help with the ones you cannot work yourself. The first problems in each set are easy, but provide the drill in drawing formulas, naming compounds, and using reactions that even the best student needs. The later problems in each set are the kind encountered by practicing chemists, and test your ability to *use* what you have learned.

You can check your answers to many of the problems in the answer section in the back of the book, and by use of the index.

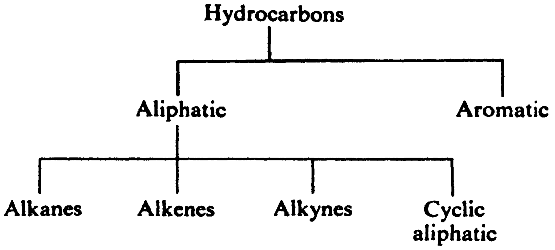
Chapter 2

Methane

Energy of Activation. Transition State

2.1 Hydrocarbons

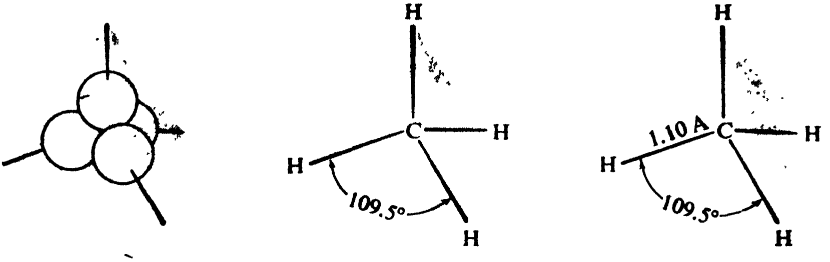
Certain organic compounds contain only two elements, hydrogen and carbon, and hence are known as **hydrocarbons**. On the basis of structure, hydrocarbons are divided into two main classes, **aliphatic** and **aromatic**. Aliphatic hydrocarbons are further divided into families: alkanes, alkenes, alkynes, and their cyclic **analogs** (cycloalkanes, etc.). We shall take up these families in the order given.



The simplest member of the alkane family and, indeed, one of the simplest of all organic compounds is **methane**, CH_4. We shall study this single compound at some length, since most of what we learn about it can be carried over with minor modifications to any alkane.

2.2 Structure of methane

As we discussed in the previous chapter (Sec. 1.11), each of the four hydrogen atoms is bonded to the carbon atom by a covalent bond, that is, by the sharing of a pair of electrons. When carbon is bonded to four other atoms, its bonding orbitals (sp^3 orbitals, formed by the mixing of one s and three p orbitals) are directed to the corners of a tetrahedron (Fig. 2.1a). This tetrahedral arrangement is the one that permits the orbitals to be as far apart as possible. For each of these orbitals to overlap most effectively the spherical *s* orbital of a hydrogen atom, and thus to form the strongest bond, each hydrogen nucleus must be located at a corner of this tetrahedron (Fig. 2.1*b*).

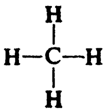


(*a*) (*b*) (*c*)

Figure 2.1. Methane molecule. (*a*) Tetrahedral sp^3 orbitals. (*b*) Predicted shape: H nuclei located for maximum overlap. (*c*) Shape and size.

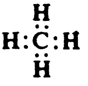
The tetrahedral structure of methane has been verified by electron diffraction (Fig. 2.1*c*), which shows beyond question the arrangement of atoms in such simple molecules. Later on, we shall examine some of the evidence that led chemists to accept this tetrahedral structure long before quantum mechanics or electron diffraction was known.

We shall ordinarily write methane with a dash to represent each pair of electrons shared by carbon and hydrogen (I). To focus our attention on individual electrons, we may sometimes indicate a pair of electrons by a pair of dots (II). Finally, when we wish to consider the actual shape of the molecule, we shall use a simple three-dimensional picture (III).



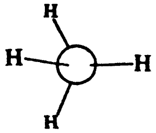
$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

I



$$\begin{array}{c} H \\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}:H \\ H \end{array}$$

II



III

2.3 Physical properties

As we discussed in the previous chapter (Sec. 1.18), the unit of such a non-ionic compound, whether solid, liquid, or gas, is the molecule. Because the methane molecule is highly symmetrical, the polarities of the individual carbon–hydrogen bonds cancel out; as a result, the molecule itself is non-polar.

Attraction between such non-polar molecules is limited to van der Waals forces; for such small molecules, these attractive forces must be tiny compared with the enormous forces between, say, sodium and chloride ions. It is not surprising, then, that these attractive forces are easily overcome by thermal energy, so that melting and boiling occur at very low temperatures: m.p −183°, b.p. −161.5°. (Compare these values with the corresponding ones for sodium chloride: m.p. 801°. b.p. 1413°.) As a consequence, methane is a gas at ordinary temperatures.

Methane is colorless and, when liquefied, is less dense than water (sp.gr. 0.4). In agreement with the rule of thumb that "like dissolves like," it is only slightly soluble in water, but very soluble in organic liquids such as gasoline, ether, and alcohol. In its physical properties methane sets the pattern for the other members of the alkane family.

2.4 Source

Methane is an end product of the anaerobic ("without air") decay of plants, that is, of the breakdown of certain very complicated molecules. As such, it is the major constituent (up to 97%) of **natural gas**. It is the dangerous *firedamp* of the coal mine, and can be seen as *marsh gas* bubbling to the surface of swamps.

If methane is wanted in very pure form, it can be separated from the other constituents of natural gas (mostly other alkanes) by fractional distillation. Most of it, of course, is consumed as fuel without purification.

According to one theory, the origins of life go back to a primitive earth surrounded by an atmosphere of methane, water, ammonia, and hydrogen. Energy—radiation from the sun, lightning discharges--broke these simple molecules into reactive fragments (free radicals, Sec. 2.12); these combined to form larger molecules which eventually yielded the enormously complicated organic compounds that make up living organisms. (Recent detection of organic molecules in space has even led to the speculation that "organic seeds for life could have existed in interstellar clouds.")

Evidence that this *could* have happened was found in 1953 by the Nobel Prize winner Harold C. Urey and his student Stanley Miller at the University of Chicago. They showed that an electric discharge converts a mixture of methane, water, ammonia, and hydrogen into a large number of organic compounds, including amino acids, the building blocks from which proteins, the "stuff of life" (Chap. 36), are made. (It is perhaps appropriate that we begin this study of organic chemistry with methane and its conversion into free radicals.)

The methane generated in the final decay of a once-living organism may well be the very substance from which—in the final analysis—the organism was derived. "*. . . earth to earth, ashes to ashes, dust to dust. . . .*"

2.5 Reactions

In its chemical properties as in its physical properties, methane sets the pattern for the alkane family (Sec. 3.18). Typically, it reacts only with highly reactive substances—or under very vigorous conditions, which, as we shall see, amounts to the same thing. At this point we shall take up only its oxidation: by oxygen, by halogens, and even by water.

2.6 Oxidation. Heat of combustion

Combustion to carbon dioxide and water is characteristic of organic compounds; under special conditions it is used to determine their content of carbon and hydrogen (Sec. 2.26).

Combustion of methane is the principal reaction taking place during the

REACTIONS OF METHANE

1. Oxidation

$CH_4 + 2O_2 \xrightarrow{\text{flame}} CO_2 + 2H_2O + \text{heat (213 kcal/mole)}$ *Combustion*

$6CH_4 + O_2 \xrightarrow{1500^\circ} \underset{\text{Acetylene}}{2HC{\equiv}CH} + 2CO + 10H_2$ Discussed in Sec. 8.5.

$CH_4 + H_2O \xrightarrow[Ni]{850^\circ} CO + 3H_2$

2. Halogenation

$$CH_4 \xrightarrow{X_2} \overset{\substack{HX\\+}}{CH_3X} \xrightarrow{X_2} \overset{\substack{HX\\+}}{CH_2X_2} \xrightarrow{X_2} \overset{\substack{HX\\+}}{CHX_3} \xrightarrow{X_2} \overset{\substack{HX\\+}}{CX_4}$$

Heat or light required

Reactivity of X_2 $F_2 > Cl_2 > Br_2\ (> \underset{\textit{Unreactive}}{I_2})$

burning of natural gas. It is hardly necessary to emphasize its importance in the areas where natural gas is available; the important product is not carbon dioxide or water but *heat.*

Burning of hydrocarbons takes place only at high temperatures, as provided, for example, by a flame or a spark. Once started, however, the reaction gives off heat which is often sufficient to maintain the high temperature and to permit burning to continue. *The quantity of heat evolved when one mole of a hydrocarbon is burned to carbon dioxide and water is called the* **heat of combustion**; for methane its value is 213 kcal.

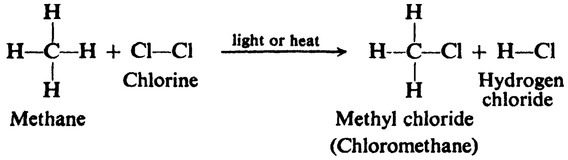
Through controlled *partial* oxidation of methane and the high-temperature catalytic reaction with water, methane is an increasingly important source of products other than heat: of hydrogen, used in the manufacture of ammonia; of mixtures of carbon monoxide and hydrogen, used in the manufacture of *methanol* and other alcohols; and of *acetylene* (Sec. 8.5), itself the starting point of large-scale production of many organic compounds.

Oxidation by halogens is of particular interest to us—partly because we know more about it than the other reactions of methane—and, in one way or another, is the topic of discussion throughout the remainder of this chapter.

2.7 Chlorination: a substitution reaction

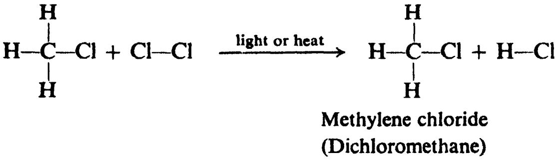
Under the influence of ultraviolet light or at a temperature of 250–400° a mixture of the two gases, methane and chlorine, reacts vigorously to yield hydrogen chloride and a compound of formula CH_3Cl. We say that methane has undergone **chlorination**, and we call the product, CH_3Cl, *chloromethane* or *methyl chloride* (CH_3 = **methyl**).

Chlorination is a typical example of a broad class of organic reactions known as **substitution**. A chlorine atom has been substituted for a hydrogen atom of methane, and the hydrogen atom thus replaced is found combined with a second atom of chlorine.



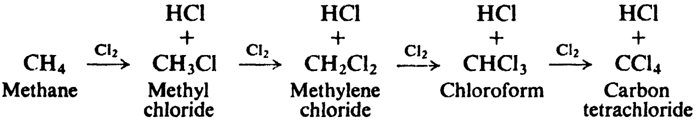
$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H + Cl{-}Cl \xrightarrow{\text{light or heat}} H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}Cl + H{-}Cl}$$

The methyl chloride can itself undergo further substitution to form more hydrogen chloride and CH_2Cl_2, *dichloromethane* or *methylene chloride* (CH_2 = **methylene**).



$$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}Cl + Cl{-}Cl \xrightarrow{\text{light or heat}} H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}Cl + H{-}Cl}$$

In a similar way, chlorination may continue to yield $CHCl_3$, *trichloromethane* or *chloroform*, and CCl_4, *tetrachloromethane* or *carbon tetrachloride.* These last two compounds are already familiar to us, chloroform as an anesthetic, and carbon tetrachloride as a non-flammable cleaning agent and the fluid in certain fire extinguishers.



$$\mathrm{CH_4 \xrightarrow{Cl_2} \overset{\substack{HCl\\+}}{CH_3Cl} \xrightarrow{Cl_2} \overset{\substack{HCl\\+}}{CH_2Cl_2} \xrightarrow{Cl_2} \overset{\substack{HCl\\+}}{CHCl_3} \xrightarrow{Cl_2} \overset{\substack{HCl\\+}}{CCl_4}}$$

Heat or light required

2.8 Control of chlorination

Chlorination of methane may yield any one of four organic products, depending upon the stage to which the reaction is carried. Can we control this reaction so that methyl chloride is the principal organic product? That is, can we limit the reaction to the first stage, *mono*chlorination?

We might at first expect—naïvely, as it turns out—to accomplish this by providing only one mole of chlorine for each mole of methane. But let us see what happens if we do so. At the beginning of the reaction there is only methane for the chlorine to react with, and consequently only the first stage of chlorination takes place. This reaction, however, yields methyl chloride, so that as the reaction proceeds methane disappears and methyl chloride takes its place.

As the proportion of methyl chloride grows, it competes with the methane for the available chlorine. By the time the concentration of methyl chloride exceeds that of methane, chlorine is more likely to attack methyl chloride than methane, and the second stage of chlorination becomes more important than the first. A large amount of methylene chloride is formed, which in a similar way is chlorinated to chloroform and this, in turn, is chlorinated to carbon tetrachloride. When we finally work up the reaction product, we find that it is a mixture of all four chlorinated methanes together with some unreacted methane.

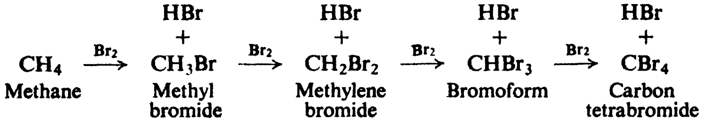
The reaction may, however, be limited almost entirely to monochlorination if we use a large excess of methane. In this case, even at the very end of the reaction unreacted methane greatly exceeds methyl chloride. Chlorine is more likely to attack methane than methyl chloride, and thus the first stage of chlorination is the principal reaction.

Because of the great difference in their boiling points, it is easy to separate the excess methane (b.p. −161.5°) from the methyl chloride (b.p. −24°) so that the methane can be mixed with more chlorine and put through the process again. While there is a low **conversion** of methane into methyl chloride in each cycle, the **yield** of methyl chloride based on the chlorine consumed is quite high.

The use of a large excess of one reactant is a common device of the organic chemist when he wishes to limit reaction to only one of a number of reactive sites in the molecule of that reactant.

2.9 Reaction with other halogens: halogenation

Methane reacts with bromine, again at high temperatures or under the influence of ultraviolet light, to yield the corresponding bromomethanes: methyl bromide, methylene bromide, bromoform, and carbon tetrabromide.



$$\underset{\text{Methane}}{CH_4} \xrightarrow{Br_2} \overset{\begin{matrix}HBr\\+\end{matrix}}{\underset{\begin{matrix}\text{Methyl}\\\text{bromide}\end{matrix}}{CH_3Br}} \xrightarrow{Br_2} \overset{\begin{matrix}HBr\\+\end{matrix}}{\underset{\begin{matrix}\text{Methylene}\\\text{bromide}\end{matrix}}{CH_2Br_2}} \xrightarrow{Br_2} \overset{\begin{matrix}HBr\\+\end{matrix}}{\underset{\text{Bromoform}}{CHBr_3}} \xrightarrow{Br_2} \overset{\begin{matrix}HBr\\+\end{matrix}}{\underset{\begin{matrix}\text{Carbon}\\\text{tetrabromide}\end{matrix}}{CBr_4}}$$

Heat or light required

Bromination takes place somewhat less readily than chlorination.

Methane does not react with iodine at all. With fluorine it reacts so vigorously that, even in the dark and at room temperature, the reaction must be carefully controlled: the reactants, diluted with an inert gas, are mixed at low pressure.

We can, therefore, arrange the halogens in order of reactivity.

Reactivity of halogens $F_2 > Cl_2 > Br_2 (> I_2)$

This same order of reactivity holds for the reaction of the halogens with other alkanes and, indeed, with most other organic compounds. The spread of reactivities is so great that only chlorination and bromination proceed at such rates as to be generally useful.

2.10 Relative reactivity

Throughout our study of organic chemistry, we shall constantly be interested in *relative reactivities*. We shall compare the reactivities of various reagents toward the same organic compound, the reactivities of different organic compounds toward the same reagent, and even the reactivities of different sites in an organic molecule toward the same reagent.

It should be understood that when we compare reactivities we compare rates of reaction. When we say that chlorine is *more reactive* than bromine toward methane, we mean that under the same conditions (same concentration, same temperature, etc.) chlorine reacts with methane *faster* than does bromine. From another point of view, we mean that the bromine reaction must be carried out under more vigorous conditions (higher concentration or higher temperature) if it is to take place as fast as the chlorine reaction. When we say that methane and iodine do not react at all, we mean that the reaction is too slow to be significant.

We shall want to know not only what these relative reactivities are, but also, whenever possible, how to account for them. To see what factors cause one reaction to be faster than another, we shall take up in more detail this matter of the different reactivities of the halogens toward methane. Before we can do this, however, we must understand a little more about the reaction itself.

2.11 Reaction mechanisms

It is important for us to know not only *what* happens in a chemical reaction but also *how* it happens, that is, to know not only the *facts* but also the *theory.*

For example, we know that methane and chlorine under the influence of heat or light form methyl chloride and hydrogen chloride. Just how is a molecule of methane converted into a molecule of methyl chloride? Does this transformation involve more than one step, and, if so, what are these steps? Just what is the function of heat or light?

The answer to questions like these, that is, *the detailed, step-by-step description of a chemical reaction, is called a* **mechanism**. It is only a hypothesis; it is advanced to account for the facts. As more facts are discovered, the mechanism must also account for them, or else be modified so that it does account for them; it may even be necessary to discard a mechanism and to propose a new one.

It would be difficult to say that a mechanism had ever been *proved.* If, however, a mechanism accounts satisfactorily for a wide variety of facts; if we make predictions based upon this mechanism and find these predictions borne out; if the mechanism is consistent with mechanisms for other, related reactions; then the mechanism is said to be *well established,* and it becomes part of the theory of organic chemistry.

Why are we interested in the mechanisms of reactions? As an important part of the theory of organic chemistry, they help make up the framework on which we hang the facts we learn. An understanding of mechanisms will help us to see a pattern in the complicated and confusing multitude of organic reactions. We shall find that many apparently unrelated reactions proceed by the same or similar mechanisms, so that most of what we have already learned about one reaction may be applied directly to many new ones.

By knowing how a reaction takes place, we can make changes in the experimental conditions—not by trial and error, but logically—that will improve the yield of the product we want, or that will even alter the course of the reaction completely and give us an entirely different product. As our understanding of reactions grows, so does our power to control them.

2.12 Mechanism of chlorination. Free radicals

It will be worthwhile to examine the mechanism of chlorination of methane in some detail. The same mechanism holds for bromination as well as chlorination, and for other alkanes as well as methane; it even holds for many compounds which, while not alkanes, contain alkane-like portions in their molecules. Closely related mechanisms are involved in oxidation (combustion) and other reactions of alkanes. More important, this mechanism illustrates certain general principles that can be carried over to a wide range of chemical reactions. Finally, by studying the evidence that supports the mechanism, we can learn something of how a chemist finds out what goes on during a chemical reaction.

Among the facts that must be accounted for are these: (a) Methane and chlorine do not react in the dark at room temperature. (b) Reaction takes place readily, however, in the dark at temperatures over 250°, or (c) under the influence of ultraviolet light at room temperature. (d) When the reaction is induced by light, many (several thousand) molecules of methyl chloride are obtained for each photon of light that is absorbed by the system. (e) The presence of a small amount of oxygen slows down the reaction for a period of time, after which the reaction proceeds normally; the length of this period depends upon how much oxygen is present.

The mechanism that accounts for these facts most satisfactorily, and hence is generally accepted, is shown in the following equation:

$$(1) \qquad \mathrm{Cl_2} \xrightarrow{\text{heat or light}} 2\mathrm{Cl}\cdot$$

$$(2) \qquad \mathrm{Cl}\cdot + \mathrm{CH_4} \xrightarrow{\qquad\qquad} \mathrm{HCl} + \mathrm{CH_3}\cdot$$

$$(3) \qquad \mathrm{CH_3}\cdot + \mathrm{Cl_2} \xrightarrow{\qquad\qquad} \mathrm{CH_3Cl} + \mathrm{Cl}\cdot$$

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

The first step is the breaking of a chlorine molecule into two chlorine atoms. Like the breaking of any bond, this requires energy, the *bond dissociation energy*, and in Table 1.2 (p. 21) we find that in this case the value is 58 kcal/mole. The energy is supplied as either heat or light.

$$\text{energy} + :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Cl}}}:$$

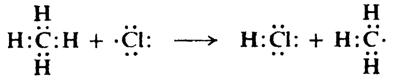
The chlorine molecule undergoes *homolysis* (Sec. 1.14): that is, cleavage of the chlorine–chlorine bond takes place in a symmetrical way, so that each atom retains one electron of the pair that formed the covalent bond. This **odd electron** is not *paired* as are all the other electrons of the chlorine atom; that is, it does not have a partner of opposite spin (Sec. 1.6). *An atom or group of atoms possessing an odd (unpaired) electron is called a* **free radical**. In writing the symbol for a free radical, we generally include a dot to represent the odd electron just as we include a plus or minus sign in the symbol of an ion.

Once formed, what is a chlorine atom most likely to do? Like most free radicals, it is extremely reactive because of its tendency to gain an additional electron and thus have a complete octet; from another point of view, energy was supplied to each chlorine atom during the cleavage of the chlorine molecule, and this energy-rich particle tends strongly to lose energy by the formation of a new chemical bond.

To form a new chemical bond, that is, to react, the chlorine atom must collide with some other molecule or atom. What is it most likely to collide with? Obviously, it is most likely to collide with the particles that are present in the highest concentration: chlorine molecules and methane molecules. Collision with another chlorine atom is quite unlikely simply because there are very few of these reactive, short-lived particles around at any time. Of the likely collisions, that with a chlorine molecule causes no net change; reaction may occur, but it can result only in the exchange of one chlorine atom for another:

$$:\underset{..}{\ddot{Cl}}\cdot + :\underset{..}{\ddot{Cl}}.\underset{..}{\ddot{Cl}}: \longrightarrow :\underset{..}{\ddot{Cl}}:\underset{..}{\ddot{Cl}}: + :\underset{..}{\ddot{Cl}}\cdot \qquad \textit{Collision probable but not productive}$$

Collision of a chlorine atom with a methane molecule is both *probable* and *productive*. The chlorine atom abstracts a hydrogen atom, with one electron, to form a molecule of hydrogen chloride:

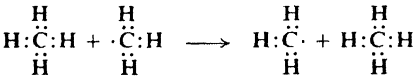


$$H:\overset{H}{\underset{H}{C}}:H + \cdot\underset{..}{\ddot{Cl}}: \longrightarrow H:\underset{..}{\ddot{Cl}}: + H:\overset{H}{\underset{H}{C}}\cdot \qquad \textit{Collision probable and productive}$$

Methane Methyl radical

Now the methyl group is left with an odd, unpaired electron; the carbon atom has only seven electrons in its valence shell. One free radical, the chlorine atom, has been consumed, and a new one, the methyl radical, $CH_3\cdot$, has been formed in its place. This is step (2) in the mechanism.

Now, what is this methyl radical most likely to do? Like the chlorine atom, it is extremely reactive, and for the same reason: the tendency to complete its octet, to lose energy by forming a new bond. Again, collisions with chlorine molecules or methane molecules are the probable ones, not collisions with the relatively scarce chlorine atoms or methyl radicals. But collision with a methane molecule could at most result only in the exchange of one methyl radical for another:



$$H:\overset{H}{\underset{H}{C}}:H + \cdot\overset{H}{\underset{H}{C}}:H \longrightarrow H:\overset{H}{\underset{H}{C}}\cdot + H:\overset{H}{\underset{H}{C}}:H \qquad \textit{Collision probable but not productive}$$

The collision of a methyl radical with a chlorine molecule is, then, the important one. The methyl radical abstracts a chlorine atom, with one of the bonding electrons, to form a molecule of methyl chloride:

$$H:\overset{H}{\underset{H}{C}}\cdot + :\underset{..}{\ddot{Cl}}:\underset{..}{\ddot{Cl}}: \longrightarrow H:\overset{H}{\underset{H}{C}}:\underset{..}{\ddot{Cl}}: + :\underset{..}{\ddot{Cl}}\cdot \qquad \textit{Collision probable and productive}$$

Methyl radical Methyl chloride

The other product is a chlorine atom. This is step (3) in the mechanism.

Here again the consumption of one reactive particle has been accompanied by the formation of another. The new chlorine atom attacks methane to form a methyl radical, which attacks a chlorine molecule to form a chlorine atom, and so the sequence is repeated over and over. Each step produces not only a new reactive particle but also a molecule of product: methyl chloride or hydrogen chloride.

This process cannot, however, go on forever. As we saw earlier, union of two short-lived, relatively scarce particles is not likely: but every so often it does happen and when it does, this particular sequence of reactions stops. Reactive particles are consumed but not generated.

$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \longrightarrow :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

$$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3:CH_3$$

$$CH_3\cdot + \cdot\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: \longrightarrow CH_3:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:$$

It is clear, then, how the mechanism accounts for facts (a), (b), (c), and (d) on page 47: either light or heat is required to cleave the chlorine molecule and form the initial chlorine atoms; once formed, each atom may eventually bring about the formation of many molecules of methyl chloride.

2.13 Chain reactions

The chlorination of methane is an example of a **chain reaction,** *a reaction that involves a series of steps, each of which generates a reactive substance that brings about the next step.* While chain reactions may vary widely in their details, they all have certain fundamental characteristics in common.

(1) $Cl_2 \xrightarrow{\text{heat or light}} 2Cl\cdot$ **Chain-initiating step**

(2) $Cl\cdot + CH_4 \longrightarrow HCl + CH_3\cdot$
(3) $CH_3\cdot + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$
Chain-propagating steps

then (2), (3), (2), (3), etc., *until finally*:

(4) $Cl\cdot + \cdot Cl \longrightarrow Cl_2$
or
(5) $CH_3\cdot + \cdot CH_3 \longrightarrow CH_3CH_3$
or
(6) $CH_3\cdot + \cdot Cl \longrightarrow CH_3Cl$
Chain-terminating steps

First in the chain of reactions is a **chain-initiating step,** in which energy is absorbed and a reactive particle generated; in the present reaction it is the cleavage of chlorine into atoms (step 1).

There are one or more **chain-propagating steps,** each of which consumes a reactive particle and generates another; here they are the reaction of chlorine atoms with methane (step 2), and of methyl radicals with chlorine (step 3).

Finally, there are **chain-terminating steps,** in which reactive particles are consumed but not generated; in the chlorination of methane these would involve the union of two of the reactive particles, or the capture of one of them by the walls of the reaction vessel.

Under one set of conditions, about 10,000 molecules of methyl chloride are formed for every quantum (photon) of light absorbed. Each photon cleaves one chlorine molecule to form two chlorine atoms, each of which starts a chain. On the average, each chain consists of 5000 repetitions of the chain-propagating cycle before it is finally stopped.

2.14 Inhibitors

Finally, how does the mechanism of chlorination account for fact (e), that a small amount of oxygen slows down the reaction for a period of time, which depends upon the amount of oxygen, after which the reaction proceeds normally?

Oxygen is believed to react with a methyl radical to form a new free radical:

$$CH_3\cdot + O_2 \longrightarrow CH_3{-}O{-}O\cdot$$

The $CH_3OO\cdot$ radical is much less reactive than the $CH_3\cdot$ radical, and can do little to continue the chain. By combining with a methyl radical, one oxygen molecule breaks a chain, and thus prevents the formation of thousands of molecules of methyl chloride; this, of course, slows down the reaction tremendously. After all the oxygen molecules present have combined with methyl radicals, the reaction is free to proceed at its normal rate.

A substance that slows down or stops a reaction even though present in small amount is called an **inhibitor**. *The period of time during which inhibition lasts, and after which the reaction proceeds normally, is called the inhibition period.* Inhibition by a relatively small amount of an added material is quite characteristic of chain reactions of any type, and is often one of the clues that first leads us to suspect that we are dealing with a chain reaction. It is hard to see how else a few molecules could prevent the reaction of so many. (We shall frequently encounter the use of oxygen to inhibit free-radical reactions.)

2.15 Heat of reaction

In our consideration of the chlorination of methane, we have so far been concerned chiefly with the particles involved—molecules and atoms—and the changes that they undergo. As with any reaction, however, it is important to consider also the energy changes involved, since these changes determine to a large extent how fast the reaction will go, and, in fact, whether it will take place at all.

By using the values of bond dissociation energies given in Table 1.2 (p. 21), we can calculate the energy changes that take place in a great number of reactions. In the conversion of methane into methyl chloride, two bonds are broken, $CH_3{-}H$ and Cl—Cl, consuming 104 + 58, or a total of 162 kcal/mole. At the same time two new bonds are formed, $CH_3{-}Cl$ and H—Cl, liberating 84 + 103, or a total of 187 kcal/mole. The result is the liberation of 25 kcal of heat for every mole of methane that is converted into methyl chloride; this is, then, an **exothermic reaction**. (This calculation, we note, does not depend on our knowing the mechanism of the reaction.)

$$\begin{array}{ccccc} CH_3{-}H + Cl{-}Cl & \longrightarrow & CH_3{-}Cl + H{-}Cl & & \\ \underline{104 \qquad 58} & & \underline{84 \qquad 103} & & \\ 162 & & 187 & & \Delta H = -25 \text{ kcal} \end{array}$$

When heat is liberated, the heat content (enthalpy), H, of the molecules themselves must decrease; the change in heat content, ΔH, is therefore given a negative sign. (In the case of an endothermic reaction, where heat is absorbed, the increase in heat content of the molecules is indicated by a positive ΔH.)

Problem 2.1 Calculate ΔH for the corresponding reaction of methane with: (a) bromine, (b) iodine, (c) fluorine.

The value of -25 kcal that we have just calculated is the *net* ΔH for the overall reaction. A more useful picture of the reaction is given by the ΔH's of the individual steps. These are calculated below:

$$(1) \qquad \underset{(58)}{\text{Cl—Cl}} \longrightarrow 2\text{Cl}\cdot \qquad \Delta H = +58 \text{ kcal}$$

$$(2) \qquad \text{Cl}\cdot + \underset{(104)}{\text{CH}_3\text{—H}} \longrightarrow \text{CH}_3\cdot + \underset{(103)}{\text{H—Cl}} \qquad \Delta H = +1$$

$$(3) \qquad \text{CH}_3\cdot + \underset{(58)}{\text{Cl—Cl}} \longrightarrow \underset{(84)}{\text{CH}_3\text{—Cl}} + \text{Cl}\cdot \qquad \Delta H = -26$$

It is clear why this reaction, even though exothermic, occurs only at a high temperature (in the absence of light). The chain-initiating step, without which reaction cannot occur, is highly *endothermic*, and takes place (at a significant rate) only at a high temperature. Once the chlorine atoms are formed, the two exothermic chain-propagating steps occur readily many times before the chain is broken. The difficult cleavage of chlorine is the barrier that must be surmounted before the subsequent easy steps can be taken.

Problem 2.2 Calculate ΔH for the corresponding steps in the reaction of methane with: (a) bromine, (b) iodine, (c) fluorine.

We have assumed so far that exothermic reactions proceed readily, that is, are reasonably fast at ordinary temperatures, whereas endothermic reactions proceed with difficulty, that is, are slow except at very high temperatures. This assumed relationship between ΔH and rate of reaction is a useful rule of thumb when other information is not available; it is *not*, however, a *necessary* relationship, and there are many exceptions to the rule. We shall go on, then, to a discussion of another energy quantity, the *energy of activation*, which is related in a more exact way to rate of reaction.

2.16 Energy of activation

To see what actually happens during a chemical reaction, let us look more closely at a specific example, the attack of chlorine atoms on methane:

$$\text{Cl}\cdot + \underset{(104)}{\text{CH}_3\text{—H}} \longrightarrow \underset{(103)}{\text{H—Cl}} + \text{CH}_3\cdot \qquad \Delta H = +1 \text{ kcal} \quad E_{\text{act}} = 4 \text{ kcal}$$

This reaction is comparatively simple: it occurs in the gas phase, and is thus not complicated by the presence of a solvent; it involves the interaction of a single atom and the simplest of organic molecules. Yet from it we can learn certain principles that apply to any reaction.

Just what must happen if this reaction is to occur? First of all, a chlorine atom and a methane molecule must **collide**. Since chemical forces are of extremely short range, a hydrogen–chlorine bond can form only when the atoms are in close contact.

Next, to be *effective*, the collision must provide a certain *minimum amount of energy*. Formation of the H—Cl bond liberates 103 kcal/mole; breaking the

CH_3—H bond requires 104 kcal/mole. We might have expected that only 1 kcal/mole additional energy would be needed for reaction to occur; however, this is not so. Bond-breaking and bond-making evidently are not perfectly synchronized, and the energy liberated by the one process is not completely available for the other. Experiment has shown that if reaction is to occur, an additional 4 kcal/mole of energy must be supplied.

The minimum amount of energy that must be provided by a collision for reaction to occur is called the **energy of activation**, E_{act}. Its source is the kinetic energy of the moving particles. Most collisions provide less than this minimum quantity and are fruitless, the original particles simply bouncing apart. Only solid collisions between particles one or both of which are moving unusually fast are energetic enough to bring about reaction. In the present example, at 275°, only about one collision in 40 is sufficiently energetic.

Finally, in addition to being sufficiently energetic, the collisions must occur when the particles are properly **oriented**. At the instant of collision, the methane molecule must be turned in such a way as to present a hydrogen atom to the full force of the impact. In the present example, only about one collision in eight is properly oriented.

In general, then, *a chemical reaction requires collisions of sufficient energy* (E_{act}) *and of proper orientation.* There is an energy of activation for nearly every reaction where bonds are broken, even for exothermic reactions, in which bond-making liberates more energy than is consumed by bond-breaking.

The attack of bromine atoms on methane is more highly endothermic, with a ΔH of +16 kcal.

$$\underset{}{Br\cdot} + \underset{(104)}{CH_3{-}H} \longrightarrow \underset{(88)}{H{-}Br} + CH_3\cdot \qquad \Delta H = +16\text{ kcal} \quad E_{act} = 18\text{ kcal}$$

Breaking the CH_3—H bond, as before, requires 104 kcal/mole, of which only 88 kcal is provided by formation of the H—Br bond. It is evident that, even if this 88 kcal were completely available for bond-breaking, at least an additional 16 kcal/mole would have to be supplied by the collision. In other words, the E_{act} of an endothermic reaction must be at least as large as the ΔH. As is generally true, the E_{act} of the present reaction (18 kcal) is actually somewhat larger than the ΔH.

2.17 Progress of reaction: energy changes

These energy relationships can be seen more clearly in diagrams like Figs. 2.2 and 2.3. Progress of reaction is represented by horizontal movement from reactants on the left to products on the right. Potential energy (that is, all energy except kinetic) at any stage of reaction is indicated by the height of the curve.

Let us follow the course of reaction in Fig. 2.2. We start in a potential energy valley with a methane molecule and a chlorine atom. These particles are moving, and hence possess kinetic energy in addition to the potential energy shown. The exact amount of kinetic energy varies with the particular pair of particles, since some move faster than others. They collide, and kinetic energy is converted into potential energy. With this increase in potential energy, reaction begins, and we move up the energy hill. If enough kinetic energy is converted, we reach the top of the hill and start down the far side.

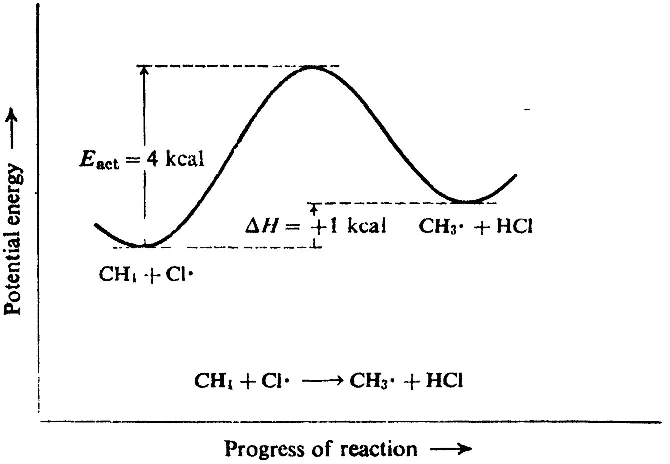


Figure 2.2. Potential energy changes during progress of reaction: the methane-chlorine atom reaction.

During the descent, potential energy is converted back into kinetic energy, until we reach the level of the products. The products contain a little more potential energy than did the reactants, and we find ourselves in a slightly higher valley than the one we left. With this net increase in potential energy there must be a corresponding decrease in kinetic energy. The new particles break apart, and sin they are moving more slowly than the particles from which they were for

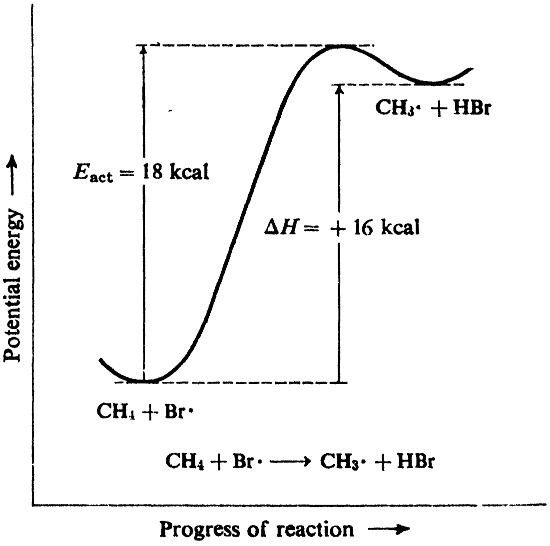


Figure 2.3. Potential energy changes during progress of reaction: the methane-bromine atom reaction.

we observe a drop in temperature. Heat will be *taken up* from the surroundings.

In the bromine reaction, shown in Fig. 2.3, we climb a much higher hill and end up in a much higher valley. The increase in potential energy—and the corresponding decrease in kinetic energy—is much larger than in the chlorine reaction; more heat will be taken up from the surroundings.

An exothermic reaction follows much the same course. (Take, for example, the reverse of the bromine reaction: that is, read from right to left in Fig. 2.3.) In this case, however, the products contain less potential energy than did the reactants so that we end up in a lower valley than the one we left. Since this time the new particles contain more kinetic energy than the particles from which they were formed, and hence move faster, we observe a rise in temperature. Heat will be *given off* to the surroundings.

In any reaction there are many collisions that provide too little energy for us to reach the top of the hill. These collisions are fruitless, and we slide back to our original valley. Many collisions provide sufficient energy, but take place when the molecules are improperly oriented. We then climb an energy hill, but we are off the road; we may climb very high without finding the pass that leads over into the next valley.

The difference in level between the two valleys is, of course, the ΔH; the difference in level between the reactant valley and the top of the hill is the E_{act}. We are concerned only with these differences, and not with the absolute height at any stage of the reaction. We are not even concerned with the relative levels of the reactant valleys in the chlorine and bromine reactions. We need only to know that in the chlorine reaction we climb a hill 4 kcal high and end up in a valley 1 kcal higher than our starting point; and that in the bromine reaction we climb a hill 18 kcal hign and end up in a valley 16 kcal higher than our starting point.

As we shall see, it is the height of the hill, the E_{act} that determines the rate of reaction, and not the difference in level of the two valleys, ΔH. In going to a lower valley, the hill might be very high, but *could* be very low—or even non-existent. In climbing to a higher valley, however, the hill can be no lower than the valley to which we are going; that is to say, *in an endothermic reaction the E_{act} must be at least as large as the ΔH.*

An energy diagram of the sort shown in Figs. 2.2 and 2.3 is particularly useful because it tells us not only about the reaction we are considering, but also about the reverse reaction. Let us move from right to left in Fig. 2.2, for example. We see that the reaction

$$\underset{}{CH_3\cdot} + \underset{(103)}{H{-}Cl} \longrightarrow \underset{(104)}{CH_3{-}H} + Cl\cdot \qquad \Delta H = -1, \quad E_{act} = 3$$

has an energy of activation of 3 kcal, since in this case we climb the hill from the higher valley. This is, of course, an exothermic reaction with a ΔH of -1 kcal.

In the same way we can see from Fig. 2.3 that the reaction

$$CH_3\cdot + \underset{(88)}{H{-}Br} \longrightarrow \underset{(104)}{CH_3{-}H} + Br\cdot \qquad \Delta H = -16, \quad E_{act} = 2$$

has an energy of activation of 2 kcal, and is exothermic with a ΔH of -16 kcal. (We notice that, even though exothermic, these last two reactions have energies of activation.)

Reactions like the cleavage of chlorine into atoms fall into a special category:

$$\underset{(58)}{\mathrm{Cl{-}Cl}} \longrightarrow \mathrm{Cl}\cdot + \cdot\mathrm{Cl} \qquad \Delta H = +58, \quad E_{act} = 58$$

a bond is broken but no bonds are formed. The reverse of this reaction, the union of chlorine atoms, involves no bond-breaking and hence would be expected to

$$\mathrm{Cl}\cdot + \cdot\mathrm{Cl} \longrightarrow \underset{(58)}{\mathrm{Cl{-}Cl}} \qquad \Delta H = -58, \quad E_{act} = 0$$

take place very easily, in fact, with no energy of activation at all. This is considered to be generally true for reactions involving the union of two free radicals.

If there is no hill to climb in going from chlorine atoms to a chlorine molecule, but simply a slope to descend, the cleavage of a chlorine molecule must involve simply the ascent of a slope as shown in Fig. 2.4. The E_{act} for the cleavage of a chlorine molecule, then, must equal the ΔH, that is, 58 kcal. This equality of E_{act} and ΔH is believed to hold generally for reactions in which molecules dissociate into radicals.

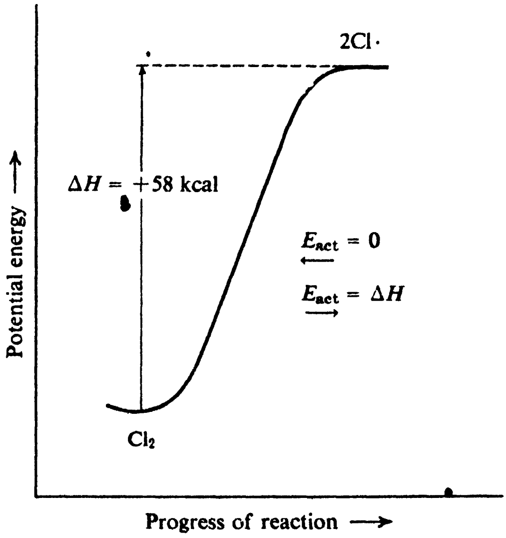


Figure 2.4. Potential energy changes during progress of reaction: simple dissociation.

2.18 Rate of reaction

A chemical reaction is the result of collisions of sufficient energy and proper orientation. The rate of reaction, therefore, must be the rate at which these effective collisions occur, the number of effective collisions, let us say, that occur during each second within each cc of reaction space. We can then express the rate as the product of three factors. (The number expressing the probability that a collision will have the proper orientation is commonly called the **probability factor.**) Anything that affects any one of these factors affects the rate of reaction.

$$\begin{array}{lclclcl} \begin{array}{l}\text{number of}\\ \text{effective}\\ \text{collisions}\\ \text{per cc per sec}\end{array} & = & \begin{array}{l}\text{total number}\\ \text{of collisions.}\\ \text{per cc per sec}\end{array} & \times & \begin{array}{l}\text{fraction of}\\ \text{collisions}\\ \text{that have}\\ \text{sufficient}\\ \text{energy}\end{array} & \times & \begin{array}{l}\text{fraction of}\\ \text{collisions}\\ \text{that have}\\ \text{proper}\\ \text{orientation}\end{array} \\ \\ \text{rate} & = & \begin{array}{l}\text{collision}\\ \text{frequency}\end{array} & \times & \begin{array}{l}\text{energy}\\ \text{factor}\end{array} & \times & \begin{array}{l}\text{probability}\\ \text{factor}\\ \text{(orientation}\\ \text{factor)}\end{array} \end{array}$$

The **collision frequency** depends upon (a) how closely the particles are crowded together, that is, concentration or pressure; (b) how large they are; and (c) how fast they are moving, which in turn depends upon their weight and the temperature.

We can change the concentration and temperature, and thus change the rate. We are familiar with the fact that an increase in concentration causes an increase in rate; it does so, of course, by increasing the collision frequency. A rise in temperature increases the collision frequency; as we shall see, it also increases the energy factor, and this latter effect is so great that the effect of temperature on collision frequency is by comparison unimportant.

The size and weight of the particles are characteristic of each reaction and cannot be changed. Although they vary widely from reaction to reaction, this variation does not affect the collision frequency greatly. A heavier weight makes the particle move more slowly at a given temperature, and hence tends to decrease the collision frequency. A heavier particle is, however, generally a larger particle, and the larger size tends to increase the collision frequency. These two factors thus tend to cancel out.

The **probability factor** depends upon the geometry of the particles and the kind of reaction that is taking place. For closely related reactions it does not vary widely.

Kinetic energy of the moving molecules is not the only source of the energy needed for reaction; energy can also be provided, for example, from vibrations among the various atoms within the molecule. Thus the probability factor has to do not only with what atoms in the molecule suffer the collision, but also with the alignment of the other atoms in the molecule at the time of collision.

By far the most important factor determining rate is the **energy factor**: the fraction of collisions that are sufficiently energetic. This factor depends upon the temperature, which we can control, and upon the energy of activation, which is characteristic of each reaction.

At a given temperature the molecules of a particular compound have an average velocity and hence an average kinetic energy that is characteristic of this system; in fact, the temperature is a measure of this average kinetic energy. But the individual molecules do not all travel with the same velocity, some moving faster than the average and some slower. The distribution of velocities is shown in Fig. 2.5 by the familiar bell-shaped curve that describes the distribution among individuals of so many qualities, for example, height, intelligence, income, or even life expectancy. The number of molecules with a particular velocity is greatest

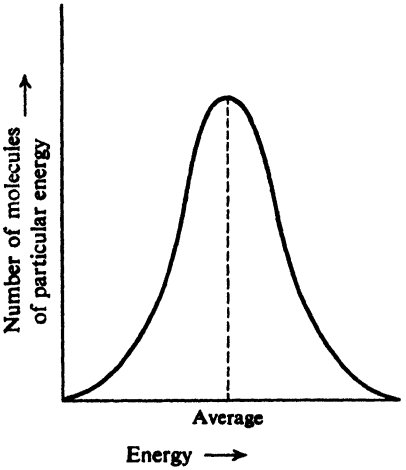


Figure 2.5. Distribution of kinetic energy among molecules.

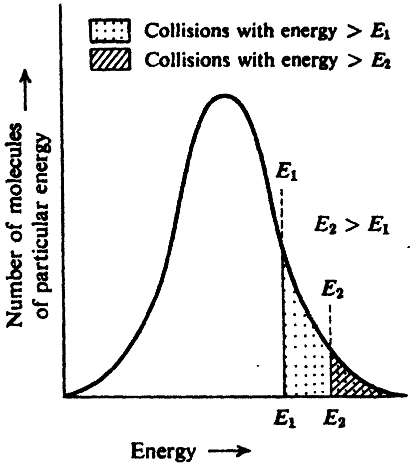


Figure 2.6. Distribution of kinetic energy among collisions.

for a velocity near the average and decreases as the velocity becomes larger or smaller than the average.

The distribution of collision energies, as we might expect, is described by a similar curve, Fig. 2.6. Let us indicate collisions of a particular energy, E_{act}, by a vertical line. The number of collisions with energy equal to or greater than E_{act} is indicated by the shaded area under the curve to the right of the vertical line. The fraction of the total number of collisions that have this minimum energy, E_{act}, is then the fraction of the total area that is shaded. It is evident that *the greater the value of E_{act}, the smaller the fraction of collisions that possess that energy.*

The exact relationship between energy of activation and fraction of collisions with that energy is:

$$e^{-E_{act}/RT} = \text{fraction of collisions with energy greater than } E_{act}$$

where

e = 2.718 (base of natural logarithms)
R = 1.986 (gas constant)
T = absolute temperature.

Using P for the probability factor and Z for the collision frequency, we arrive at the rate equation:

$$\text{rate} = PZe^{-E_{act}/RT}$$

This exponential relationship is important to us in that it indicates that a small difference in E_{act} has a large effect on the fraction of sufficiently energetic collisions, and hence on the rate of reaction. For example, at 275°, out of every million collisions, 10,000 provide sufficient energy if E_{act} = 5 kcal, 100 provide sufficient energy if E_{act} = 10 kcal, and only one provides sufficient energy if E_{act} = 15 kcal. This means that (all other things being equal) a reaction with E_{act} = 5 kcal will go 100 times as fast as one with E_{act} = 10 kcal, and 10,000 times as fast as one with E_{act} = 15 kcal.

We have so far considered a system held at a given temperature. A rise in temperature, of course, increases the average kinetic energy and average velocities, and hence shifts the entire curve to the right, as shown in Fig. 2.7. For a given energy of activation, then, a rise in temperature increases the fraction of sufficiently energetic collisions, and hence increases the rate, as we already know.

The exponential relationship again leads to a large change in rate, this time for a small change in temperature. For example, a rise from 250° to 300°, which is only a 10% increase in absolute temperature, increases the rate by 50% if $E_{act} =$ 5 kcal, doubles the rate if $E_{act} = 10$ kcal, and trebles the rate if $E_{act} = 15$ kcal. As this example shows, the greater the E_{act}, the greater the effect of a given change in temperature; this follows from the $e^{-E_{act}/RT}$ relationship. Indeed, it is from the relationship between rate and temperature that the E_{act} of a reaction is determined: the rate is measured at different temperatures, and from the results E_{act} is calculated.

We have examined the factors that determine rate of reaction. What we have learned may be used in many ways. To speed up a particular reaction, for example, we know that we might raise the temperature, or increase the concentration of reactants, or even (in ways that we shall take up later) lower the E_{act}.

Of immediate interest, however, is the matter of relative reactivities. Let us see, therefore, how our knowledge of reaction rates can help us to account for the fact that one reaction proceeds faster than another, even though conditions for the two reactions are identical.

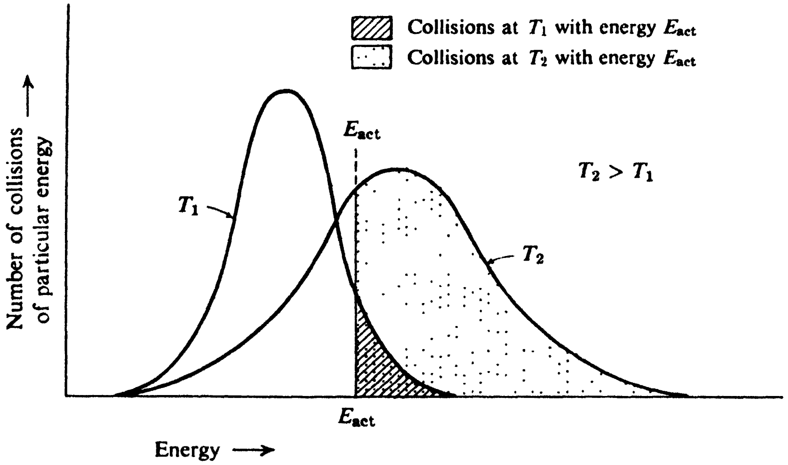


Figure 2.7. Change in collision energies with change in temperature.

2.19 Relative rates of reaction

We have seen that the rate of a reaction can be expressed as a product of three factors:

rate = collision frequency × energy factor × probability factor

Two reactions could proceed at different rates because of differences in any or all these factors. To account for a difference in rate, we must first see in which of these factors the difference lies.

As an example, let us compare the reactivities of chlorine and bromine atoms toward methane; that is, let us compare the rates, under the same conditions, of the two reactions:

$$Cl\cdot + CH_3{-}H \longrightarrow H{-}Cl + CH_3\cdot \qquad \Delta H = +1, \quad E_{act} = 4$$

$$Br\cdot + CH_3{-}H \longrightarrow H{-}Br + CH_3\cdot \qquad \Delta H = +16, \quad E_{act} = 18$$

Since temperature and concentration must be the same for the two reactions if we are to compare them under the same conditions, any difference in **collision frequency** would have to arise from differences in particle weight or size. A bromine atom is heavier than a chlorine atom, and it is also larger; as we have seen, the effects of these two properties tend to cancel out. In actuality, the collision frequencies differ by only a few per cent. It is generally true that for the same temperature and concentration, two closely related reactions differ but little in collision frequency. A difference in collision frequency therefore cannot be the cause of a large difference in reactivity.

The nature of the **probability factor** is very poorly understood. Since our two reactions are quite similar, however, we might expect them to have similar probability factors. Experiment has shown this to be true: whether chlorine or bromine atoms are involved, about one in every eight collisions with methane has the proper orientation for reaction. In general, where closely related reactions are concerned, we may assume that a difference in probability factor is *not likely* to be the cause of a large difference in reactivity.

We are left with a consideration of the **energy factor**. At a given temperature, the fraction of collisions that possess the amount of energy required for reaction depends upon how large that amount is, that is, depends upon the E_{act}. In our example E_{act} is 4 kcal for the chlorine reaction, 18 kcal for the bromine reaction. As we have seen, a difference of this size in the E_{act} causes an enormous difference in the energy factor, and hence in the rate. At 275°, of every 10 million collisions, 250,000 are sufficiently energetic when chlorine atoms are involved, and only *one* when bromine atoms are involved. Because of the difference in E_{act} alone, then, chlorine atoms are 250,000 times as reactive as bromine atoms toward methane.

As we encounter, again and again, differences in reactivity, we shall in general attribute them to differences in E_{act}; in many cases we shall be able to account for these differences in E_{act} on the basis of differences in molecular structure. *It must be understood that we are justified in doing this only when the reactions being compared are so closely related that differences in collision frequency and in probability factor are comparatively insignificant.*

2.20 Relative reactivities of halogens toward methane

With this background, let us return to the reaction between methane and the various halogens, and see if we can account for the order of reactivity given before, $F_2 > Cl_2 > Br_2 > I_2$, and in particular for the fact that iodine does not react at all.

From the table of bond dissociation energies (Table 1.2, p. 21) we can calculate for each of the four halogens the ΔH for each of the three steps of halogenation. Since E_{act} has been measured for only a few of these reactions, let us see what tentative conclusions we can reach using only ΔH.

		X =	F	Cl	Br	I
(1)	$X_2 \longrightarrow 2X\cdot$	$\Delta H =$	+38	+58	+46	+36
(2)	$X\cdot + CH_4 \longrightarrow HX + CH_3\cdot$		−32	+1	+16	+33
(3)	$CH_3\cdot + X_2 \longrightarrow CH_3X + X\cdot$		−70	−26	−24	−20

Since step (1) involves simply dissociation of molecules into atoms, we may quite confidently assume (Sec. 2.17 and Fig. 2.4) that ΔH in this case is equal to E_{act}. Chlorine has the largest E_{act}, and should dissociate most slowly; iodine has the smallest E_{act}, and should dissociate most rapidly. Yet this does not agree with the observed order of reactivity. Thus, except possibly for fluorine, dissociation of the halogen into atoms cannot be the step that determines the observed reactivities.

Step (3), attack of methyl radicals on halogen, is exothermic for all four halogens, and for chlorine, bromine, and iodine it has very nearly the same ΔH. For these reactions, E_{act} *could* be very small, and does indeed seem to be so; probably only a fraction of a kcal. Even iodine has been found to react readily with methyl radicals generated in another way, e.g., by the heating of tetramethyllead. In fact, iodine is sometimes employed as a free-radical "trap" or "scavenger" in the study of reaction mechanisms. The third step, then, cannot be the cause of the observed relative reactivities.

This leaves step (2), abstraction of hydrogen from methane by a halogen atom. Here we see a wide spread of ΔH's, from the highly exothermic reaction with the fluorine atom to the highly endothermic reaction with the iodine atom. The endothermic bromine atom reaction must have an E_{act} of at least 16 kcal; as we have seen, it is actually 18 kcal. The slightly endothermic chlorine atom reaction could have a very small E_{act}; it is actually 4 kcal. At a given temperature, then, the fraction of collisions of sufficient energy is much larger for methane and chlorine atoms than for methane and bromine atoms. To be specific, at 275° the fraction is about 1 in 40 for chlorine and 1 in 10 million for bromine.

A bromine atom, on the average, collides with many methane molecules before it succeeds in abstracting hydrogen; a chlorine atom collides with relatively few. During its longer search for the proper methane molecule, a bromine atom is more likely to encounter another scarce particle—a second halogen atom or a methyl radical—or be captured by the vessel wall; the chains should therefore be much shorter than in chlorination. Experiment has shown this to be so: where the average chain length is several thousand for chlorination, it is less than 100 for bromination. Even though bromine atoms are formed more rapidly than chlorine atoms at a given temperature because of the lower E_{act} of step (1), overall bromination is slower than chlorination because of the shorter chain length.

For the endothermic reaction of an iodine atom with methane, E_{act} can be no less than 33 kcal, and is probably somewhat larger. Even for this minimum value of 33 kcal, an iodine atom must collide with an enormous number of methane molecules (10^{12} or a million million at 275°) before reaction is likely to occur. Virtually no iodine atoms last this long, but instead recombine to form iodine molecules; the reaction therefore proceeds at a negligible rate. Iodine atoms are easy to form; it is their inability to abstract hydrogen from methane that prevents iodination from occurring.

We cannot predict the E_{act} for the highly exothermic attack of fluorine atoms on methane, but we would certainly not expect it to be any larger than for the attack of chlorine atoms on methane. It appears actually to be smaller (about 1 kcal), thus permitting even longer chains. Because of the surprising weakness of the fluorine-fluorine bond, fluorine atoms should be formed faster than chlorine atoms; thus there should be not only longer chains in fluorination but also *more* chains. The overall reaction is extremely exothermic, with a ΔH of -102 kcal, and the difficulty of removing this heat is one cause of the difficulty of control of fluorination.

Of the two chain-propagating steps, then, step (2) is more difficult than step (3) (see Fig. 2.8). Once formed, methyl radicals react easily with any of the halogens; it is how fast methyl radicals are formed that limits the rate of overall reaction. Fluorination is fast because fluorine atoms rapidly abstract hydrogen atoms from methane; E_{act} is only 1 kcal. Iodination does not take place because iodine atoms find it virtually impossible to abstract hydrogen from methane; E_{act} is more than 33 kcal.

Values of E_{act} for step (2), we notice, parallel the values of ΔH. Since the same bond, CH_3—H, is being broken in every case, the differences in ΔH reflect differences in bond dissociation energy among the various hydrogen-halogen bonds. Ultimately, it appears, the reactivity of a halogen toward methane depends upon the strength of the bond which that halogen forms with hydrogen.

One further point requires clarification. We have said that an E_{act} of 33 kcal is too great for the reaction between iodine atoms and methane to proceed at a significant rate; yet the initial step in each of these halogenations requires an even

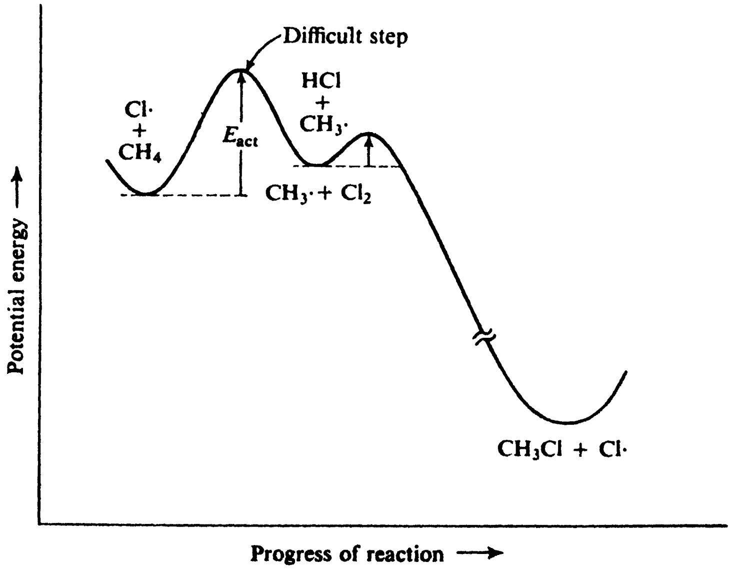


Figure 2.8. Potential energy changes during progress of reaction: chlorination of methane. Formation of radical is difficult step.

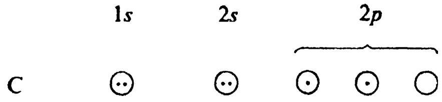
greater E_{act}. The difference is this: since halogenation is a chain reaction, dissociation of each molecule of halogen gives rise ultimately to many molecules of methyl halide; hence, even though dissociation is very slow, the overall reaction can be fast. The attack of iodine atoms on methane, however, is a chain-carrying step and if it is slow the entire reaction must be slow; under these circumstances chain-terminating steps (e.g., union of two iodine atoms) become so important that effectively there is *no* chain.

2.21 Structure of the methyl radical. *sp*² Hybridization

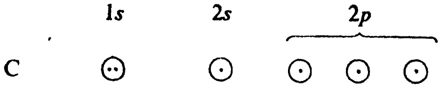
We have spent a good part of this chapter discussing the formation and reactions of the methyl free radical $CH_3\cdot$. Just what is this molecule like? What is its shape? How are the electrons distributed and, in particular, where is the odd electron?

These are important questions, for the answers apply not only to this simple radical but to any free radical, however complicated, that we shall encounter. The *shape*, naturally, underlies the three-dimensional chemistry—the stereochemistry—of free radicals. The *location of the odd electron* is intimately involved with the stabilization of free radicals by substituent groups.

As we did when we "made" methane (Sec. 1.11), let us start with the electronic configuration of carbon,

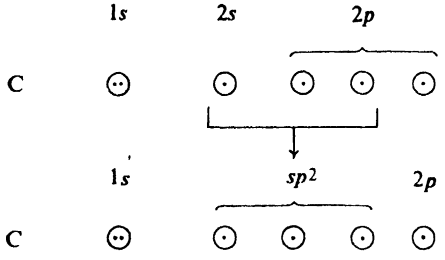


and, to provide more than two unpaired electrons for bonding, promote a 2*s* electron to the empty 2*p* orbital:



One electron promoted: four unpaired electrons

Like boron in boron trifluoride (Sec. 1.10), carbon here is bonded to three other atoms. Hybridization of the 2*s* orbital and two of the *p* orbitals provides the



*sp*² Hybridization

necessary orbitals: three strongly directed *sp*² orbitals which, as we saw before, lie in a plane that includes the carbon nucleus, and are directed to the corners of an equilateral triangle.

If we arrange the carbon and three hydrogens of a methyl radical to permit maximum overlap of orbitals, we obtain the structure shown in Fig. 2.9*a*. It is

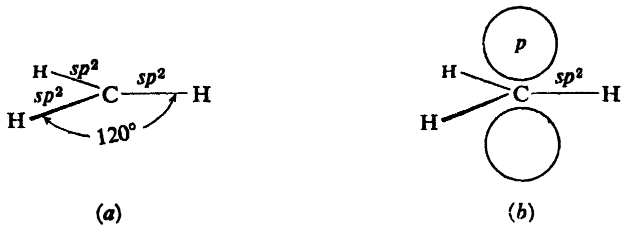


Figure 2.9. Methyl radical. (*a*) Only σ bonds shown. (*b*) Odd electron in *p* orbital above and below plane of σ bonds.

flat, with the carbon atom at the center of a triangle and the three hydrogen atoms at the corners. Every bond angle is 120°.

Now where is the odd electron? In forming the sp^2 orbitals, the carbon atom has used only two of its three *p* orbitals. The remaining *p* orbital consists of two equal lobes, one lying above and the other lying below the plane of the three sp^2 orbitals (Fig. 2.9*b*); it is occupied by the odd electron.

This is not the only conceivable electronic configuration for the methyl radical: an alternative treatment would lead to a pyramidal molecule like that of ammonia, except that the fourth sp^3 orbital contains the odd electron instead of an electron pair (Sec. 1.12). Quantum mechanical calculations do not offer a clear-cut decision between the two configurations. Spectroscopic studies indicate that the methyl radical is actually flat, or nearly so. Carbon is trigonal, or not far from it; the odd electron occupies a *p* orbital, or at least an orbital with much *p* character.

Compare the shapes of three molecules in which the central atom is bonded to three other atoms: (a) boron trifluoride, with no unshared electrons, trigonal; (b) ammonia, with an unshared *pair*, tetrahedral; and (c) the methyl radical, with a *single* unshared electron, trigonal or intermediate between trigonal and tetrahedral.

There is stereochemical evidence (for example, Sec. 7.10) that most other free radicals are either flat or, if pyramidal, undergo rapid *inversion* like that of the ammonia molecule (Sec. 1.12).

Problem 2.3 Besides free radicals, we shall encounter two other kinds of reactive particles, carbonium ions (positive charge on carbon) and carbanions (negative charge on carbon). Suggest an electronic configuration, and from this predict the shape, of the methyl cation, CH_3^+; of the methyl anion, $CH_3{:}^-$.

2.22 Transition state

Clearly, the concept of E_{act} is to be our key to the understanding of chemical reactivity. To make it *useful*, we need a further concept: *transition state.*

A chemical reaction is presumably a continuous process involving a gradual transition from reactants to products. It has been found extremely helpful, however, to consider the arrangement of atoms at an intermediate stage of reaction as though it were an actual molecule. This intermediate structure is called the **transition state**; its energy content corresponds to the top of the energy hill (Fig. 2.10).

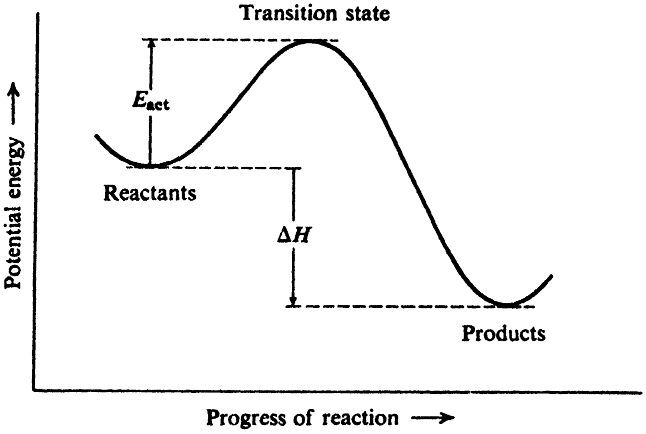


Figure 2.10. Potential energy changes during progress of reaction: transition state at top of energy hump.

The reaction sequence is now:

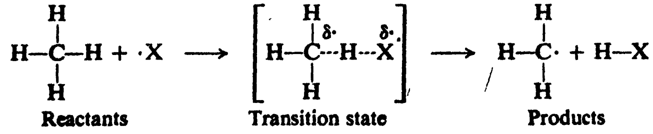
$$\text{reactants} \longrightarrow \text{transition state} \longrightarrow \text{products}$$

Just as ΔH is the difference in energy content between reactants and products, so E_{act} *is the difference in energy content between reactants and transition state.*

The transition state concept is useful for this reason: we can analyze the structure of the transition state very much as though it were a molecule, and attempt to estimate its stability. Any factor that stabilizes the transition state relative to the reactants tends to lower the energy of activation; that is to say, any factor that lowers the top of the energy hill more than it lowers the reactant valley reduces the net height we must climb during reaction. Transition state stability will be the basis—whether explicit or implicit—of almost every discussion of reactivity in this book.

But the transition state is only a fleeting arrangement of atoms which, by its very nature—lying at the top of an energy hill—cannot be isolated and examined. How can we possibly know anything about its structure? Well, let us take as an example the transition state for the abstraction of hydrogen from methane by a halogen atom, and see where a little thinking will lead us.

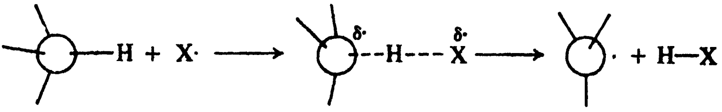
To start with, we can certainly say this: the carbon–hydrogen bond is stretched but not entirely broken, and the hydrogen–halogen bond has started to form but is not yet complete. This condition could be represented as



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}H} + \cdot\mathrm{X} \longrightarrow \left[\mathrm{H{-}\underset{H}{\overset{H}{C}}\overset{\delta\cdot}{\cdots}H\cdots\overset{\delta\cdot}{X}}\right] \longrightarrow \mathrm{H{-}\underset{H}{\overset{H}{C}}\cdot} + \mathrm{H{-}X}$$

where the dashed lines indicate partly broken or partly formed bonds.

Now, what can we say about the shape of the methyl group in this transition state? In the reactant, where methyl holds the hydrogen, carbon is tetrahedral (sp^3-hybridized); in the product, where methyl has lost the hydrogen, carbon is trigonal (sp^2-hybridized). In the transition state, where the carbon–hydrogen bond is partly broken, hybridization of carbon is somewhere between sp^3 and sp^2. The methyl group is partly but not completely flattened; bond angles are greater than 109.5° but less than 120°.



Reactant
Tetrahedral

Transition state
Becoming trigonal

Product
Trigonal

Finally, where is the odd electron? It is on chlorine in the reactants, on the methyl group in the products, and divided between the two in the transition state. (Each atom's share is represented by the symbol δ·.) The methyl group *partly* carries the odd electron it will have in the product, and to this extent has taken on some of the character of the free radical it will become.

Thus, in a straightforward way, we have drawn a picture of the transition state that shows the bond-making and bond-breaking, the spatial arrangement of the atoms, and the distribution of the electrons.

(This particular transition state is intermediate between reactants and products not only in the time sequence but also in structure. Not *all* transition states are intermediate in structure: as shown on page 462, reactant and product in S_N2 reactions are tetrahedral, whereas the transition state contains pentavalent carbon.)

In Sec. 2.18, we looked at the matter of reaction rates from the standpoint of the *collision theory*. An alternative, more generally useful approach is the *transition state* (or *thermodynamic*) *theory* of reaction rates. An equilibrium is considered to exist between the reactants and the transition state, and this is handled in the same way as true equilibria of reversible reactions (Sec. 18.11). Energy of activation (E_{act}) and probability factor are replaced by, respectively, *heat* (*enthalpy*) *of activation* ($\Delta H^\ddagger$) and *entropy of activation* ($\Delta S^\ddagger$), which together make up *free energy of activation* ($\Delta G^\ddagger$).

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

The smaller (the less positive) the $\Delta H^\ddagger$ and the larger (the more positive) the $\Delta S^\ddagger$, the smaller $\Delta G^\ddagger$ will be, and the faster the reaction.

Entropy corresponds, roughly, to the randomness of a system; equilibrium tends to favor the side in which fewer restrictions are placed on the atoms and molecules. Entropy of activation, then, is a measure of the relative randomness of reactants and transition state; the fewer the restrictions that are placed on the arrangement of atoms in the transition state—relative to the reactants—the faster the reaction will go. We can see, in a general way, how probability factor and entropy of activation measure much the same thing. A low probability factor means that a rather special orientation of atoms is required on collision. In the other language, an unfavorable (low) entropy of activation means that rather severe restrictions are placed on the positions of atoms in the transition state.

2.23 Reactivity and development of the transition state

For the abstraction of hydrogen from methane by a halogen atom, we have just seen that the transition state differs from the reactants—and this difference is, of course, what we are looking for—chiefly in being like the products. This is generally true for reactions in which free radicals (or, for that matter, carbonium ions or carbanions) are formed.

But just *how much* does this particular transition state resemble the products? How far have bond-breaking and bond-making gone? How flat has the methyl group become, and to what extent does it carry the odd electron?

Surprisingly, we can answer even questions like these, at least in a relative way. **In a set of similar reactions, the higher the E_{act}, the later the transition state is reached in the reaction process.** Of the theoretical considerations underlying this postulate, we shall mention only this: the difference in electronic distribution that we call a difference in structure corresponds to a difference in energy; the greater the difference in structure, the greater the difference in energy. If E_{act} is high, the transition state differs greatly from the reactants in energy and, presumably, also in electronic structure; if E_{act} is low, the transition state differs little from the reactants in energy and, presumably, also in electronic structure (see Fig. 2.11).

Practically, this postulate has been found extremely useful in the interpretation of experimental results; among other things, as we shall see, it enables us to account for the relationship between reactivity and selectivity (Sec. 3.28).

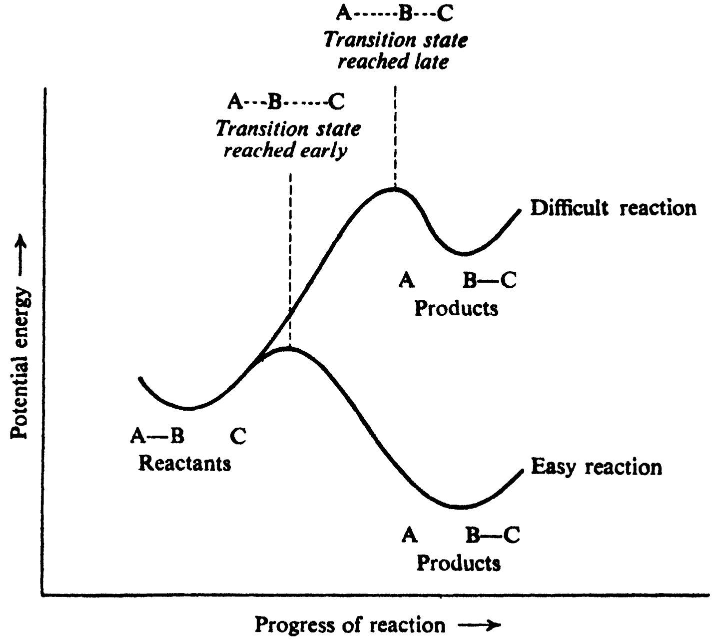


Figure 2.11. Potential energy changes during progress of reaction: reactivity and development of the transition state. Difficult reaction: transition state reached late, resembles products. Easy reaction: transition state reached early, resembles reactants.

Abstraction of hydrogen by the highly reactive chlorine atom has a low E_{act}. According to the postulate, then, the transition state is reached before the reaction has proceeded very far, and when the carbon–hydrogen bond is only slightly stretched. Atoms and electrons are still distributed much as they were in the reactants; carbon is still nearly tetrahedral. The methyl group has developed little free-radical character.

Abstraction of hydrogen by the less reactive bromine atom, in contrast, has a very high E_{act}. The transition state is reached only after reaction is well along toward completion and when the carbon–hydrogen bond is more nearly broken. The geometry and electron distribution has begun to approach that of the products, and carbon may well be almost trigonal. The methyl group has developed much free-radical character.

Thus, *in the attack by a reagent of high reactivity, the transition state tends to resemble the reactant; in the attack by a reagent of low reactivity, the transition state tends to resemble the products.*

2.24 Molecular formula: its fundamental importance

In this chapter we have been concerned with the structure of methane: the way in which atoms are put together to form a molecule of methane. But first we had to know what kinds of atoms these are and how many of them make up the molecule; we had to know that methane is CH_4. Before we can assign a structural formula to a compound, we must first know its molecular formula.

Much of the chapter has been spent in discussing the substitution of chlorine for the hydrogen of methane. But first we had to know that there *is* substitution, that each step of the reaction yields a product that contains one less hydrogen atom and one more chlorine atom than the reactant; we had to know that CH_4 is converted successively into CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Before we can discuss the reactions of an organic compound, we must first know the molecular formulas of the products.

Let us review a little of what we know about the assigning of a molecular formula to a compound. We must carry out:

(a) a *qualitative elemental analysis*, to find out what kinds of atoms are present in the molecule;

(b) a *quantitative elemental analysis*, to find out the relative numbers of the different kinds of atoms, that is, to determine the *empirical formula*;

(c) a *molecular weight determination*, which (combined with the empirical formula) shows the actual numbers of the different kinds of atoms, that is, gives us the *molecular formula.*

Most of this should be familiar to the student from previous courses in chemistry. What we shall concentrate on here will be the application of these principles to organic analysis.

2.25 Qualitative elemental analysis

The presence of carbon or hydrogen in a compound is detected by **combustion**: heating with copper oxide, which converts carbon into carbon dioxide and hydrogen into water. (*Problem:* How could each of these products be identified?)

$$(C,H) + CuO \xrightarrow{heat} Cu + CO_2 + H_2O$$

Covalently bonded halogen, nitrogen, and sulfur must be converted into inorganic ions, which can then be detected in already familiar ways. This conversion is accomplished in either of two ways: (a) through **sodium fusion**, treatment with hot molten sodium metal;

$$(C,H,X,N,S) + Na \xrightarrow{heat} Na^+X^- + Na^+CN^- + Na^+S^{--}Na^+$$

or (b) through **Schöniger oxidation** by oxygen gas.

$$(C,H,X,N,S) + O_2 \xrightarrow{NaOH} Na^+X^- + Na^+NO_2^- + Na^+SO_3^{--}Na^+$$

(A simpler method of detecting halogen in *some* organic compounds is discussed in Sec. 14.24.)

By these methods, we could show, for example, that methane contains carbon and hydrogen, or that methyl chloride contains carbon, hydrogen, and chlorine.

Further tests would show the absence of any other element in these compounds, except possibly oxygen, for which there is no simple chemical test; presence or absence of oxygen would be shown by a quantitative analysis.

Problem 2.4 (a) How would you detect halide ion as a product of sodium fusion or oxidation? (b) If sulfur and/or nitrogen is also present in an organic molecule, this test cannot be carried out on a sodium fusion mixture until it has been acidified and boiled. Why is this so?

Problem 2.5 Only carbon and hydrogen were detected by a qualitative elemental analysis of the compound ethyl alcohol; quantitative analysis gave 52.1% carbon and 13.1% hydrogen. (a) Why would it be assumed that ethyl alcohol contains oxygen? (b) What percentage of oxygen would be assumed?

2.26 Quantitative elemental analysis: carbon, hydrogen, and halogen

Knowing what elements make up a compound, we must next determine the proportions in which they are present. To do this, we carry out very much the same analysis as before, only this time on a quantitative basis. To find out the relative amounts of carbon and hydrogen in methane, for example, we would completely oxidize a measured amount of methane and weigh the carbon dioxide and water formed.

In a quantitative combustion, a weighed sample of the organic compound is passed through a *combustion train*: a tube packed with copper oxide heated to 600–800°, followed by a tube containing a drying agent (usually Dehydrite, magnesium perchlorate) and a tube containing a strong base (usually Ascarite, sodium hydroxide on asbestos). The water formed is absorbed by the drying agent, and the carbon dioxide is absorbed by the base; the increase in weight of each tube gives the weight of product formed.

For example, we might find that a sample of methane weighing 9.67 mg produced 26.53 mg of CO_2 and 21.56 mg of H_2O. Now, only the fraction $C/CO_2 = 12.01/44.01$ of the carbon dioxide is carbon, and only the fraction $2H/H_2O = 2.016/18.02$ of the water is hydrogen. Therefore

$$\text{wt. C} = 26.53 \times 12.01/44.01 \qquad \text{wt. H} = 21.56 \times 2.016/18.02$$

wt. C (in sample) = 7.24 mg   wt. H (in sample) = 2.41 mg

and the percentage composition is

$\% \text{ C} = 7.24/9.67 \times 100$ $\% \text{ H} = 2.41/9.67 \times 100$

$\% \text{ C (in sample)} = 74.9$ $\% \text{ H (in sample)} = 24.9$

Since the total of carbon and hydrogen is 100%, within the limits of error of the analysis, oxygen (or any other element) must be absent.

In quantitative, as in qualitative, analysis, covalently bonded halogen must be converted into halide ion. The organic compound is heated either (a) in a bomb with sodium peroxide or (b) in a sealed tube with nitric acid (*Carius method*). The halide ion thus formed is converted into silver halide, which can be weighed.

Problem 2.6 When 7.36 mg of methyl chloride was heated in a bomb with sodium peroxide, the chloride ion liberated yielded 20.68 mg of silver chloride. (a) What percentage of chlorine is indicated by this analysis? (b) What percentage of chlorine would be expected from a compound of formula CH_3Cl? (c) What weight of silver chloride would you expect from 7.36 mg of methylene chloride? (d) Of chloroform? (e) Of carbon tetrachloride?

(We shall take up other quantitative analytical methods when we need them: nitrogen and sulfur analysis, Sec. 10.12; methoxyl determination, Sec. 17.16; neutralization equivalent, Sec. 18.21; saponification equivalent, Sec. 20.24.)

2.27 Empirical formula

Knowing the percentage composition of a compound, we can now calculate the **empirical formula**: *the simplest formula that shows the relative numbers of the different kinds of atoms in a molecule*. For example, in 100 g (taken for convenience) of methane there are 74.9 g of carbon and 24.9 g of hydrogen, according to our quantitative analysis. Dividing each quantity by the proper atomic weight gives the number of gram-atoms of each element.

$$\text{C: } \frac{74.9}{12.01} = 6.24 \text{ gram-atoms}$$

$$\text{H: } \frac{24.9}{1.008} = 24.7 \text{ gram-atoms}$$

Since a gram-atom of one element contains the same number of atoms as a gram-atom of any other element, we now know the relative number of carbon and hydrogen atoms in methane: $C_{6.24}H_{24.7}$. Conversion to smallest whole numbers gives the empirical formula CH_4 for methane.

$$\text{C: } 6.24/6.24 = 1$$

$$\text{H: } 24.7/6.24 = 3.96, \text{ approximately } 4$$

Problem 2.7 Calculate the percentage composition and then the empirical formula for each of the following compounds: (a) Combustion of a 3.02-mg sample of a compound gave 8.86 mg of carbon dioxide and 5.43 mg of water. (b) Combustion of an 8.23-mg sample of a compound gave 9.62 mg of carbon dioxide and 3.94 mg of water. Analysis of a 5.32-mg sample of the same compound by the Carius method gave 13.49 mg of silver chloride.

2.28√ Molecular weight. Molecular formula

At this stage we know what kinds of atoms make up the molecule we are studying, and in what ratio they are present. This knowledge is summarized in the empirical formula.

But this is not enough. On the basis of just the empirical formula, a molecule of methane, for example, might contain one carbon and four hydrogens, or two carbons and eight hydrogens, or *any* multiple of CH_4. We still have to find the **molecular formula**: *the formula that shows the actual number of each kind of atom in a molecule.*

To find the molecular formula, we must determine the molecular weight: today, almost certainly by mass spectrometry, which gives an exact value (Sec. 13.2). *Ethane*, for example, has an empirical formula of CH_3. A molecular weight of 30 is found, indicating that, of the possible molecular formulas, C_2H_6 must be the correct one.

Problem 2.8 Quantitative elemental analysis shows that the empirical formula of a compound is CH. The molecular weight is found to be 78. What is the molecular formula?

Problem 2.9 Combustion of a 5.17-mg sample of a compound gives 10.32 mg of carbon dioxide and 4.23 mg of water. The molecular weight is 88. What is the molecular formula of the compound?

PROBLEMS

1. Calculate the percentage composition of A, B, and C from the following analytical data:

	wt. sample	wt. CO_2	wt. H_2O	wt. AgCl
A	4.37 mg	15.02 mg	2.48 mg	—
B	5.95 mg	13.97 mg	2.39 mg	7.55 mg
C	4.02 mg	9.14 mg	3.71 mg	—

2. What is the percentage composition of:

(a) C_3H_7Cl
(b) C_2H_6O
(c) $C_4H_8O_2$
(d) $C_6H_8O_2N_2S$
(e) CH_4ON_2
(f) C_6H_8NCl

3. What is the empirical formula of an organic compound whose percentage composition is:

(a) 85.6% C, 14.4% H
(b) 92.2% C, 7.8% H
(c) 40.0% C, 6.7% H
(d) 29.8% C, 6.3% H, 44.0% Cl
(e) 48.7% C, 13.6% H, 37.8% N
(f) 25.2% C, 2.8% H, 49.6% Cl

(*Note:* remember that oxygen often is not determined directly.)

4. A qualitative analysis of *papaverine*, one of the alkaloids in opium, showed carbon, hydrogen, and nitrogen. A quantitative analysis gave 70.8% carbon, 6.2% hydrogen, and 4.1% nitrogen. Calculate the empirical formula of papaverine.

5. *Methyl orange*, an acid-base indicator, is the sodium salt of an acid that contains carbon, hydrogen, nitrogen, sulfur, and oxygen. Quantitative analysis gave 51.4% carbon, 4.3% hydrogen, 12.8% nitrogen, 9.8% sulfur, and 7.0% sodium. What is the empirical formula of methyl orange?

6. Combustion of 6.51 mg of a compound gave 20.47 mg of carbon dioxide and

8.36 mg of water. The molecular weight was found to be 84. Calculate: (a) percentage composition; (b) empirical formula; and (c) molecular formula of the compound.

7. A liquid of molecular weight 60 was found to contain 40.0% carbon and 6.7% hydrogen. What is the molecular formula of the compound?

8. A gas of the same empirical formula as the compound in Problem 7 has a molecular weight of 30. What is its molecular formula?

9. *Indigo*, an important dyestuff, gave an analysis of 73.3% carbon, 3.8% hydrogen, and 10.7% nitrogen. Molecular weight determination gave a value of 262. What is the molecular formula of indigo?

10. The hormone *insulin* contains 3.4% sulfur. (a) What is the minimum molecular weight of insulin? (b) The actual molecular weight is 5734; how many sulfur atoms are probably present per molecule?

11. Calculate ΔH for:

(a)-(d) $H_2 + X_2 \longrightarrow 2HX$, where X = F, Cl, Br, I
(e) $C_2H_6 + Br_2 \longrightarrow C_2H_5Br + HBr$
(f) $C_6H_5CH_3 + Br_2 \longrightarrow C_6H_5CH_2Br + HBr$
(g) $H_2C{=}CHCH_3 + Br_2 \longrightarrow H_2C{=}CHCH_2Br + HBr$
(h) Reactions (e), (f), and (g) proceed by the same free radical mechanism as halogenation of methane. Calculate ΔH for each step in these three reactions.

12. A conceivable mechanism for the chlorination of methane involves the following steps:

(1) $Cl_2 \longrightarrow 2Cl\cdot$

(2) $Cl\cdot + CH_4 \longrightarrow CH_3Cl + H\cdot$

(3) $H\cdot + Cl_2 \longrightarrow HCl + Cl\cdot$

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

(a) Calculate ΔH for each of these steps. (b) Why does this mechanism seem less likely than the accepted one given in Sec. 2.12? (Additional, conclusive evidence against this alternative mechanism will be presented in Sec. 7.10.)

13. (a) Free methyl radicals react with methane as follows:

$$(i)\quad CH_3\cdot + CH_4 \longrightarrow CH_4 + CH_3\cdot$$

On the basis of the bond strengths involved, show why the above reaction takes place rather than the following:

$$(ii)\quad CH_3\cdot + CH_4 \longrightarrow CH_3{-}CH_3 + H\cdot$$

(b) Reaction (*i*) has an E_{act} of 13 kcal. In Sec. 2.12 it was listed as probable (but unproductive) on grounds of collision probability. In actuality, how probable is reaction (*i*) in, say, a 50:50 mixture of CH_4 and Cl_2? (*Hint:* See Secs. 2.20 and 2.18.)

14. Bromination of methane is slowed down by addition of fairly large amounts of HBr. (a) Suggest a possible explanation for this. (*Hint:* See Sec. 2.17.) (b) Account for the fact that HCl does not have a similar effect upon chlorination. (c) Any reaction tends to slow down as reactants are used up and their concentrations decrease. How do you account for the fact that bromination of methane slows down to an unusually great extent, more than, say, chlorination of methane?

15. A mixture of H_2 and Cl_2 does not react in the dark at room temperature. At high temperatures or under the influence of light (of a wavelength absorbed by chlorine) a violent reaction occurs and HCl is formed. The photochemical reaction yields as many as a million molecules of HCl for each photon absorbed. The presence of a small amount of oxygen slows down the reaction markedly. (a) Outline a possible mechanism to account for these facts. (b) Account for the fact that a mixture of H_2 and I_2 does not behave in the same way. (Hydrogen iodide is actually formed, but by an entirely different mechanism.)

16. A stream of tetramethyllead vapor, $(CH_3)_4Pb$, was passed through a quartz tube which was heated at one spot; a mirror of metallic lead was deposited at the hot point, and the gas escaping from the tube was found to be chiefly ethane. The tube was next heated upstream of the lead mirror while more tetramethyllead was passed through; a new mirror appeared at the hot point, the old mirror disappeared, and the gas escaping from the tube was now found to be chiefly tetramethyllead. Experiments like this, done by Fritz Paneth at the University of Berlin, were considered the first good evidence for the existence of short-lived free radicals like methyl. (a) Show how these experimental results can be accounted for in terms of intermediate free radicals. (b) The farther upstream the tube was heated, the more slowly the old mirror disappeared. Account for this.

17. When a small amount (0.02%) of tetraethyllead, $(C_2H_5)_4Pb$, is added to a mixture of methane and chlorine, chlorination takes place at only 140° instead of the usual minimum of 250°. In light of Problem 16, show how this fact strengthens the mechanism of Sec. 2.12.

Chapter 3

Alkanes

Free-Radical Substitution

3.1 Classification by structure: the family

The basis of organic chemistry, we have said, is the structural theory. We separate all organic compounds into a number of families on the basis of structure. Having done this, we find that we have at the same time classified the compounds as to their physical and chemical properties. A particular set of properties is thus characteristic of a particular kind of structure.

Within a family there are variations in properties. All members of the family may, for example, react with a particular reagent, but some may react more readily than others. Within a single compound there may be variations in properties, one part of a molecule being more reactive than another part. These variations in properties correspond to variations in structure.

As we take up each family of organic compounds, we shall first see what structure and properties are characteristic of the family. Next we shall see how structure and properties vary within the family. We shall not simply memorize these facts, but, whenever possible, shall try to understand properties in terms of structure, and to understand variations in properties in terms of variations in structure.

Having studied methane in some detail, let us now look at the more complicated members of the alkane family. These hydrocarbons have been assigned to the same family as methane on the basis of their structure, and on the whole their properties follow the pattern laid down by methane. However, certain new points will arise simply because of the greater size and complexity of these compounds.

3.2 Structure of ethane

Next in size after methane is **ethane**, C_2H_6. If we connect the atoms of this molecule by covalent bonds, following the rule of one bond (one pair of electrons for each hydrogen and four bonds (four pairs of electrons) for each carbon, we arrive at the structure

$$\begin{array}{ccc}\text{H}\,\text{H} & & \text{H}\quad\text{H}\\ \text{H}:\ddot{\text{C}}:\ddot{\text{C}}:\text{H} & \qquad & \text{H}-\text{C}-\text{C}-\text{H}\\ \ddot{\text{H}}\,\ddot{\text{H}} & & \text{H}\quad\text{H}\end{array}$$

Ethane

Each carbon is bonded to three hydrogens and to the other carbon.

Since each carbon atom is bonded to four other atoms, its bonding orbitals (sp^3 orbitals) are directed toward the corners of a tetrahedron. As in the case of methane, the carbon-hydrogen bonds result from overlap of these sp^3 orbitals with the s orbitals of the hydrogens. The carbon-carbon bond arises from overlap of two sp^3 orbitals.

The carbon-hydrogen and carbon-carbon bonds have the same general electron distribution, being cylindrically symmetrical about a line joining the atomic nuclei (see Fig. 3.1); because of this similarity in shape, the bonds are given the same name, *σ bonds* (*sigma bonds*).

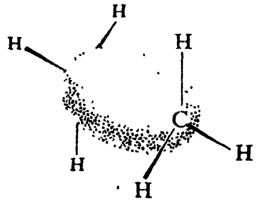


Figure 3.1. Ethane molecule. Carbon-carbon single bond: σ bond.

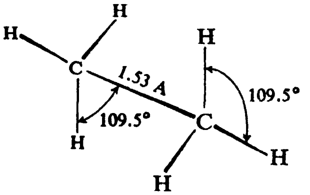


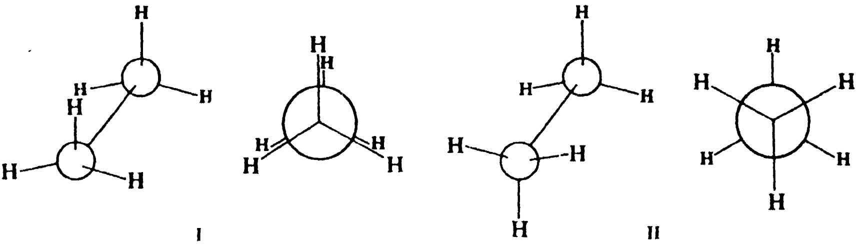
Figure 3.2. Ethane molecule: shape and size.

In ethane, then, the bond angles and carbon-hydrogen bond lengths should be very much the same as in methane, that is, about 109.5° and about 1.10 A, respectively. Electron diffraction and spectroscopic studies have verified this structure in all respects, giving (Fig. 3.2) the following measurements for the molecule: bond angles, 109.5°; C—H length, 1.10 A; C—C length, 1.53 A. Similar studies have shown that, with only slight variations, these values are quite characteristic of carbon-hydrogen and carbon-carbon bonds and of carbon bond angles in alkanes.

3.3 Free rotation about the carbon-carbon single bond. Conformations. Torsional strain

This particular set of bond angles and bond lengths still does not limit us to a single arrangement of atoms for the ethane molecule, since the relationship between the hydrogens of one carbon and the hydrogens of the other carbon is not specified. We could have an arrangement like I in which the hydrogens exactly oppose each other, an arrangement like II in which the hydrogens are perfectly staggered, or an infinity of intermediate arrangements. Which of these is the actual structure of ethane? The answer is: *all of them.*

We have seen that the σ bond joining the carbon atoms is cylindrically symmetrical about a line joining the two carbon nuclei; overlap and hence bond



I
Eclipsed conformation

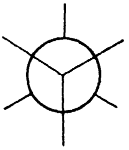
II
Staggered conformation

Ethane

strength should be the same for all these possible arrangements. If the various arrangements do not differ in energy, then the molecule is not restricted to any one of them, but can change freely from one to another. Since the change from one to another involves rotation about the carbon–carbon bond, we describe this freedom to change by saying that *there is free rotation about the carbon–carbon single bond.*

Different arrangements of atoms that can be converted into one another by rotation about single bonds are called **conformations.** I is called the *eclipsed conformation;* II is called the *staggered conformation.* (The infinity of intermediate conformations are called *skew conformations.*)

The highly useful representations of the kind



are called *Newman projections,* after M. S. Newman, of The Ohio State University, who first proposed their use.

The picture is not yet complete. Certain physical properties show that rotation is *not quite free*: there is an energy barrier of about 3 kcal/mole. The potential energy of the molecule is at a minimum for the staggered conformation, increases with rotation, and reaches a maximum at the eclipsed conformation (Fig. 3.3). Most ethane molecules, naturally, exist in the most stable, staggered conformation; or, put differently, any molecule spends most of its time in the most stable conformation.

How free are ethane molecules to rotate from one staggered arrangement to another? The 3-kcal barrier is not a very high one; even at room temperature the fraction of collisions with sufficient energy is large enough that a rapid interconversion between staggered arrangements occurs. For most practical purposes, we may still consider that the carbon–carbon single bond permits free rotation.

The nature of the rotational barrier in ethane is not understood or—what is not exactly the same thing—is not readily explained. It is too high to be due merely to van der Waals forces (Sec. 1.19): although thrown closer together in the eclipsed conformation than in the staggered conformation, the hydrogens on opposite carbons are not big enough for this to cause appreciable crowding. The barrier is considered to arise in some way from interaction among the electron clouds of the carbon–hydrogen bonds. Quantum

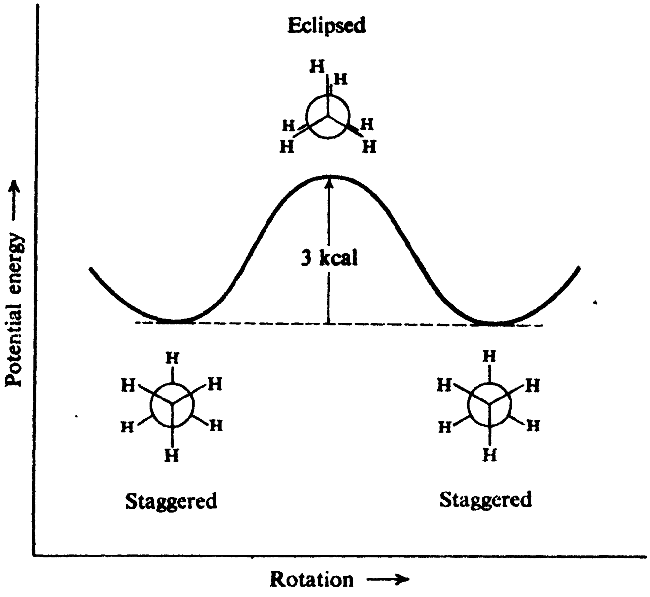


Figure 3.3. Potential energy changes during rotation about carbon–carbon single bond of ethane.

mechanical calculations show that the barrier should exist, and so perhaps "lack of understanding" amounts to difficulty in paraphrasing the mathematics in physical terms. Like the bond orbitals in methane, the two sets of orbitals in ethane tend to be as far apart as possible—to be *staggered*.

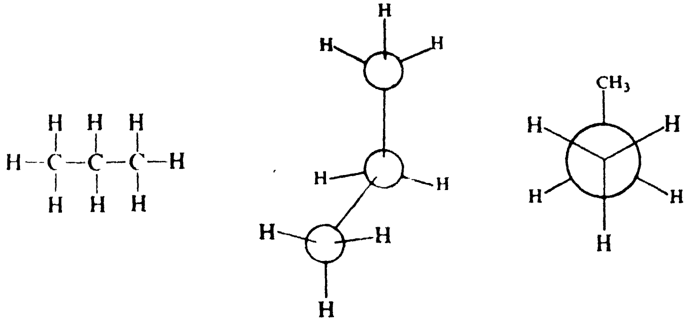
The energy required to rotate the ethane molecule about the carbon–carbon bond is called *torsional energy*. We speak of the relative instability of the eclipsed conformation—or any of the intermediate skew conformations—as being due to *torsional strain*.

As the hydrogens of ethane are replaced by other atoms or groups of atoms, other factors affecting the relative stability of conformations appear: van der Waals forces, dipole–dipole interactions, hydrogen bonding. But the tendency for the bond orbitals on adjacent carbons to be staggered remains, and any rotation away from the staggered conformation is accompanied by torsional strain.

3.4 Propane and the butanes

The next member of the alkane family is **propane**, C_3H_8. Again following the rule of one bond per hydrogen and four bonds per carbon, we arrive at structure I.

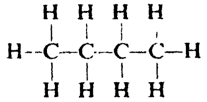
Here, rotation can occur about two carbon–carbon bonds, and again is essentially free. Although the methyl group is considerably larger than hydrogen, the rotational barrier (3.3 kcal/mole) is only a little higher than for ethane. Evidently there is still not significant crowding in the eclipsed conformation, and the rotational barrier is due chiefly to the same factor as the barrier in ethane: *torsional strain.*



I

Propane

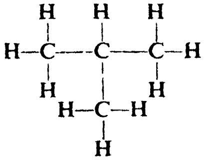
When we consider **butane**, C_4H_{10}, we find that there are two possible structures, II and III. II has a four-carbon chain and III has a three-carbon chain with a one-carbon branch. There can be no doubt that these represent different structures, since no amount of moving, twisting, or rotating about carbon–carbon bonds will cause these structures to coincide. We can see that in the *straight-chain* structure (II) each carbon possesses at least two hydrogens, whereas in the *branched-chain* structure (III) one carbon possesses only a single hydrogen; or we may notice that in the branched-chain structure (III) one carbon is bonded to three other carbons, whereas in the straight-chain structure (II) no carbon is bonded to more than two other carbons.



$$\begin{array}{ccccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & \vert & & \vert & & \vert & & \vert & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & \vert & & \vert & & \vert & & \vert & & \\ & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

II

n-Butane



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & \vert & & \vert & & \vert & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{H} \\ & & \vert & & \vert & & \vert & & \\ & & \mathrm{H} & & \vert & & \mathrm{H} & & \\ & & & \mathrm{H}- & \mathrm{C} & -\mathrm{H} & & & \\ & & & & \vert & & & & \\ & & & & \mathrm{H} & & & & \end{array}$$

III

Isobutane

In agreement with this prediction, we find that two compounds of the same formula, C_4H_{10}, have been isolated. There can be no doubt that these two substances are different compounds, since they show definite differences in their physical and chemical properties (see Table 3.1); for example one boils at 0° and the other at −12°. By definition, they are *isomers* (Sec. 1.24).

Table 3.1 PHYSICAL CONSTANTS OF THE ISOMERIC BUTANES

	n-Butane	Isobutane
b.p.	0°	−12°
m.p.	−138°	−159°
sp.gr. at −20°	0.622	0.604
solub. in 100 ml alcohol	1813 ml	1320 ml

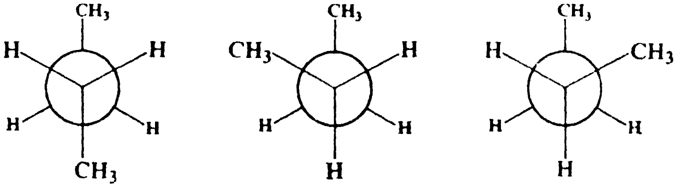
Two compounds of formula C_4H_{10} are known and we have drawn two structures to represent them. The next question is: which structure represents which compound? For the answer we turn to the evidence of **isomer number**. Like methane, the butanes can be chlorinated; the chlorination can be allowed to proceed until there are two chlorine atoms per molecule. From the butane of b.p. 0°, *six* isomeric products of formula $C_4H_8Cl_2$ are obtained, from the butane of b.p. −12°, only *three*. We find that we can draw just six dichlorobutanes containing a straight chain of carbon atoms, and just three containing a branched chain. Therefore, the butane of b.p. 0° must have the straight chain, and the butane of b.p. −12° must have the branched chain. To distinguish between these two isomers, the straight-chain structure is called ***n*-butane** (spoken "normal butane") and the branched-chain structure is called **isobutane**.

Problem 3.1 Draw the structures of all possible dichloro derivatives of: (a) *n*-butane; (b) isobutane.

Problem 3.2 Could we assign structures to the isomeric butanes on the basis of the number of isomeric *mono*chloro derivatives?

3.5 Conformations of *n*-butane. Van der Waals repulsion

Let us look more closely at the *n*-butane molecule and the conformations in which it exists. Focusing our attention on the middle C—C bond, we see a molecule



I
Anti conformation

II III
Gauche conformations

n-Butane

similar to ethane, but with a methyl group replacing one hydrogen on each carbon. As with ethane, staggered conformations have lower torsional energies and hence are more stable than eclipsed conformations. But, due to the presence of the methyl groups, two new points are encountered here: first, there are several *different* staggered conformations; and second, a factor besides torsional strain comes into play to affect conformational stabilities.

There is the *anti* conformation, I, in which the methyl groups are as far apart as they can be (dihedral angle 180°). There are two *gauche* conformations, II and III, in which the methyl groups are only 60° apart. (Conformations II and III are mirror images of each other, and are of the same stability; nevertheless, they *are* different. Make models and convince yourself that this is so.)

The *anti* conformation, it has been found, is more stable (by 0.8 kcal/mole) than the *gauche* (Fig. 3.4). Both are free of torsional strain. But in a *gauche* conformation, the methyl groups are crowded together, that is, are thrown together closer than the sum of their van der Waals radii; under these conditions, van der Waals forces are *repulsive* (Sec. 1.19) and raise the energy of the conformation. We say that there is ***van der Waals repulsion*** (or ***steric repulsion***) between the

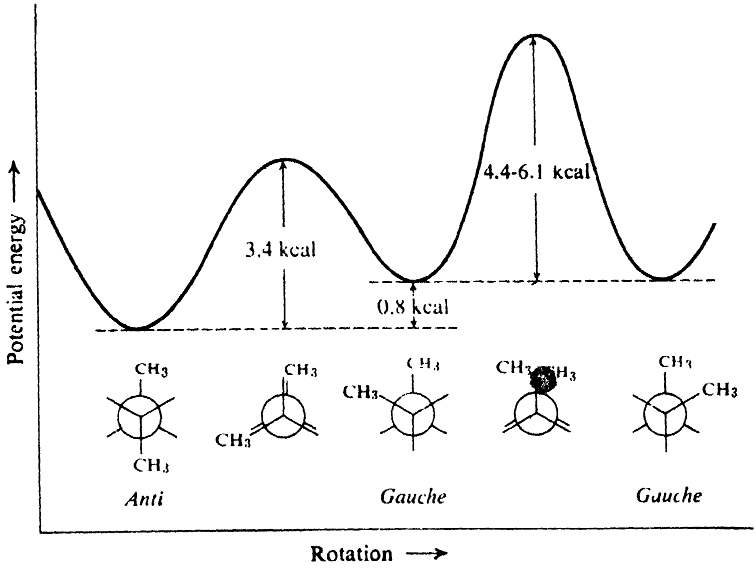


Figure 3.4. Potential energy changes during rotation about $C_2—C_3$ bond of *n*-butane.

methyl groups, and that the molecule is less stable because of *van der Waals strain* (or *steric strain*).

Van der Waals strain can affect not only the relative stabilities of various staggered conformations, but also the heights of the barriers between them. The energy maximum reached when two methyl groups swing past each other—rather than past hydrogens—is the highest rotational barrier of all, and has been estimated at 4.4–6.1 kcal/mole. Even so, it is low enough that—at ordinary temperatures, at least—the energy of molecular collisions causes rapid rotation; a given molecule exists now in a *gauche* conformation, and the next instant in the *anti* conformation.

We shall return to the relationships among conformations like these of *n*-butane in Sec. 4.20.

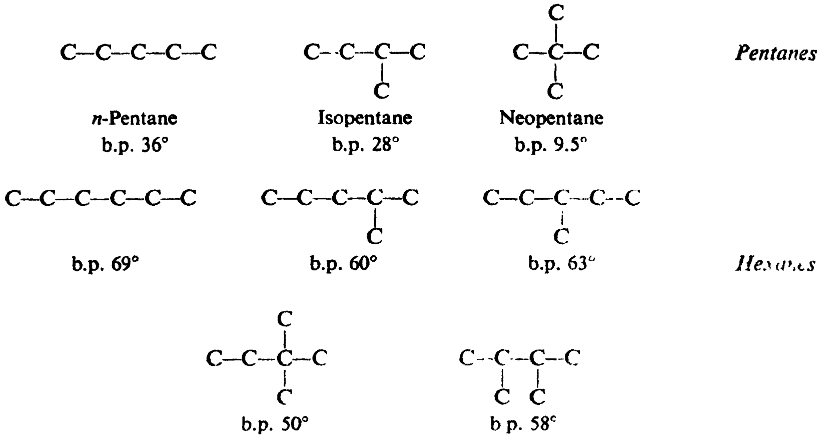
Problem 3.3 Both calculations and experimental evidence indicate that the dihedral angle between the methyl groups in the *gauche* conformation of *n*-butane is actually somewhat *larger* than 60°. How would you account for this?

Problem 3.4 Considering only rotation about the bond shown, draw a potential energy *vs.* rotation curve like Fig. 3.4 for: (a) $(CH_3)_2CH—CH(CH_3)_2$; (b) $(CH_3)_2CH—CH_2CH_3$; (c) $(CH_3)_3C—C(CH_3)_3$. (d) Compare the heights of the various energy barriers with each other and with those in Fig. 3.4.

3.6 Higher alkanes. The homologous series

If we examine the molecular formulas of the alkanes we have so far considered, we see that butane contains one carbon and two hydrogens more than propane, which in turn contains one carbon and two hydrogens more than ethane, and so on. *A series of compounds in which each member differs from the next member by a constant amount is called a* **homologous series,** *and the members of the series are called* **homologs.** The family of alkanes forms such a homologous series, the constant difference between successive members being CH_2. We also notice that in each of these alkanes the number of hydrogen atoms equals two more than twice the number of carbon atoms, so that we may write as a *general formula* for members of this series, C_nH_{2n+2}. As we shall see later, other homologous series have their own characteristic general formulas.

In agreement with this general formula, we find that the next alkane, *pentane*, has the formula C_5H_{12}, followed by *hexane*, C_6H_{14}, *heptane*, C_7H_{16}, and so on. We would expect that, as the number of atoms increases, so does the number of possible arrangements of those atoms. As we go up the series of alkanes, we find that this is true: the number of isomers of successive homologs increases at a surprising rate. There are 3 isomeric pentanes, 5 hexanes, 9 heptanes, and 75 decanes (C_{10}); for the twenty-carbon eicosane, there are 366,319 possible isomeric structures! The carbon skeletons of the isomeric pentanes and hexanes are shown below.



n-Pentane b.p. 36°

Isopentane b.p. 28°

Neopentane b.p. 9.5°

b.p. 69°

b.p. 60°

b.p. 63°

b.p. 50°

b.p. 58°

It is important to practice drawing the possible isomeric structures that correspond to a single molecular formula. In doing this, a set of molecular models is especially helpful since it will show that many structures which appear to be different when drawn on paper are actually identical.

Problem 3.5 Draw the structures of: (a) the nine isomeric heptanes (C_7H_{16}); (b) the eight chloropentanes ($C_5H_{11}Cl$); (c) the nine dibromobutanes ($C_4H_8Br_2$).

3.7 Nomenclature

We have seen that the names *methane, ethane, propane, butane,* and *pentane* are used for alkanes containing respectively one, two, three, four, and five carbon atoms. Table 3.2 gives the names of many larger alkanes. Except for the first

Table 3.2 NAMES OF ALKANES

CH_4	methane	C_9H_{20}	nonane
C_2H_6	ethane	$C_{10}H_{22}$	decane
C_3H_8	propane	$C_{11}H_{24}$	undecane
C_4H_{10}	butane	$C_{12}H_{26}$	dodecane
C_5H_{12}	pentane	$C_{14}H_{30}$	tetradecane
C_6H_{14}	hexane	$C_{16}H_{34}$	hexadecane
C_7H_{16}	heptane	$C_{18}H_{38}$	octadecane
C_8H_{18}	octane	$C_{20}H_{42}$	eicosane

four members of the family, the name is simply derived from the Greek (or Latin) prefix for the particular number of carbons in the alkane; thus **pent**ane for five, **hex**ane for six, **hept**ane for seven, **oct**ane for eight, and so on.

The student should certainly memorize the names of at least the first ten alkanes. Having done this, he has at the same time essentially learned the names of the first ten alkenes, alkynes, alcohols, etc., since the names of many families of compounds are closely related. Compare, for example, the names *propane*, *propene*, and *propyne* for the three-carbon alkane, alkene, and alkyne.

But nearly every alkane can have a number of isomeric structures, and there must be an unambiguous name for each of these isomers. The butanes and pentanes are distinguished by the use of prefixes: *n*-butane and **iso**butane; *n*-pentane, **iso**pentane, and **neo**pentane. But there are 5 hexanes, 9 heptanes, and 75 decanes; it would be difficult to devise, and even more difficult to remember, a different prefix for each of these isomers. It is obvious that some systematic method of naming is needed.

As organic chemistry has developed, several different methods have been devised to name the members of nearly every class of organic compounds; each method was devised when the previously used system had been found inadequate for the growing number of increasingly complex organic compounds. Unfortunately for the student, perhaps, several systems have survived and are in current use. Even if we are content ourselves to use only one system, we still have to understand the names used by other chemists; hence it is necessary for us to learn more than one system of nomenclature. But before we can do this, we must first learn the names of certain organic groups.

3.8 Alkyl groups

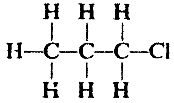
In our study of inorganic chemistry, we found it useful to have names for certain groups of atoms that compose only part of a molecule and yet appear many times as a unit. For example, NH_4^+ is called *ammonium*; NO_3^-, *nitrate*; SO_3^{--}, *sulfite*; and so on.

In a similar way names are given to certain groups that constantly appear as structural units of organic molecules. We have seen that chloromethane, CH_3Cl, is also known as *methyl chloride*. The CH_3 group is called **methyl** wherever it appears, CH_3Br being *methyl* bromide, CH_3I, *methyl* iodide, and CH_3OH, *methyl* alcohol. In an analogous way, the C_2H_5 group is **ethyl**; C_3H_7, **propyl**; C_4H_9, **butyl**; and so on.

These groups are named simply by dropping *-ane* from the name of the corresponding alkane and replacing it by *-yl*. They are known collectively as

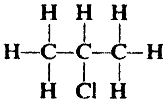
alkyl groups. The general formula for an alkyl group is C_nH_{2n+1}, since it contains one less hydrogen than the parent alkane, C_nH_{2n+2}.

Among the alkyl groups we again encounter the problem of isomerism. There is only one methyl chloride or ethyl chloride, and correspondingly only one methyl group or ethyl group. We can see, however, that there are two propyl chlorides, I and II, and hence that there must be two propyl groups. These groups



I

n-Propyl chloride



II

Isopropyl chloride

both contain the propane chain, but differ in the point of attachment of the chlorine; they are called ***n*-propyl** and **isopropyl**. We can distinguish the two

$CH_3CH_2CH_2—$

n-Propyl

CH_3CHCH_3

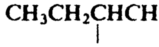
Isopropyl

chlorides by the names *n-propyl chloride* and *isopropyl chloride*; we distinguish the two propyl bromides, iodides, alcohols, and so on in the same way.

We find that there are four butyl groups, two derived from the straight-chain *n*-butane, and two derived from the branched-chain isobutane. These are given the designations ***n*-** (*normal*), ***sec*-** (*secondary*), ***iso*-**, and ***tert*-** (*tertiary*), as shown below. Again the difference between *n*-butyl and *sec*-butyl and between isobutyl and *tert*-butyl lies in the point of attachment of the alkyl group to the rest of the molecule.

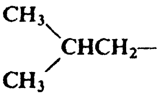
$CH_3CH_2CH_2CH_2—$

n-Butyl

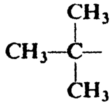


$CH_3CH_2\underset{|}{C}HCH_3$

sec-Butyl



Isobutyl



$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—$

tert-Butyl

Beyond butyl the number of isomeric groups derived from each alkane becomes so great that it is impracticable to designate them all by various prefixes. Even though limited, this system is so useful for the small groups just described that it is widely used; a student must therefore memorize these names and learn to recognize these groups at a glance in whatever way they happen to be represented.

However large the group concerned, one of its many possible arrangements can still be designated by this simple system. The prefix *n*- is used to designate any alkyl group in which all carbons form a single continuous chain and in which the point of attachment is the very end carbon. For example:

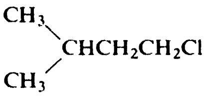
$CH_3CH_2CH_2CH_2CH_2Cl$

n-Pentyl chloride

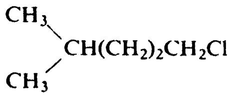
$CH_3(CH_2)_4CH_2Cl$

n-Hexyl chloride

The prefix *iso*- is used to designate any alkyl group (of six carbons or less) that has a single one-carbon branch on the next-to-last carbon of a chain and has the point of attachment at the opposite end of the chain. For example:



Isopentyl chloride



Isohexyl chloride

If the branching occurs at any other position, or if the point of attachment is at any other position, this name does not apply.

Now that we have learned the names of certain alkyl groups, let us return to the original problem: the naming of alkanes.

3.9 Common names of alkanes

As we have seen, the prefixes *n*-, *iso*-, and *neo*- are adequate to differentiate the various butanes and pentanes, but beyond this point an impracticable number of prefixes would be required. However, the prefix *n*- has been retained for any alkane, no matter how large, in which all carbons form a continuous chain with no branching:

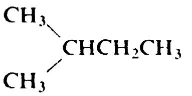
$CH_3CH_2CH_2CH_2CH_3$

n-Pentane

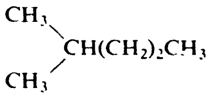
$CH_3(CH_2)_4CH_3$

n-Hexane

An *isoalkane* is a compound of six carbons or less in which all carbons except one form a continuous chain and that one carbon is attached to the next-to-end carbon:



Isopentane



Isohexane

In naming any other of the higher alkanes, we make use of the IUPAC system, outlined in the following section.

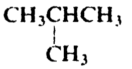
(It is sometimes convenient to name alkanes as derivatives of methane; see, for example, I on p. 129.)

3.10 IUPAC names of alkanes

To devise a system of nomenclature that could be used for even the most complicated compounds, various committees and commissions representing the chemists of the world have met periodically since 1892. In its present modification, the system so devised is known as the **IUPAC system** (International Union of Pure and Applied Chemistry). Since this system follows much the same pattern for all families of organic compounds, we shall consider it in some detail as applied to the alkanes.

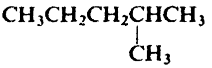
Essentially the rules of the IUPAC system are:

1. Select as the parent structure the longest continuous chain, and then consider the compound to have been derived from this structure by the replacement of hydrogen by various alkyl groups. Isobutane (I) can be considered to arise from propane by the replacement of a hydrogen atom by a methyl group, and thus may be named *methylpropane.*


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

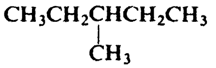
I

Methylpropane
(Isobutane)


$CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{C}HCH_3$

II

2-Methylpentane


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

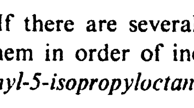
III

3-Methylpentane

2. Where necessary, as in the isomeric methylpentanes (II and III), indicate by a number the carbon to which the alkyl group is attached.

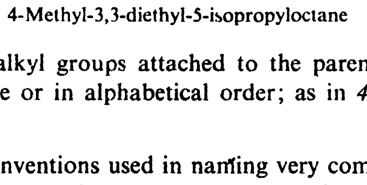
3. In numbering the parent carbon chain, start at whichever end results in the use of the lowest numbers; thus II is called *2-methylpentane* rather than 4-methylpentane.

4. If the same alkyl group occurs more than once as a side chain, indicate this by the prefix *di-*, *tri-*, *tetra-*, etc., to show how many of these alkyl groups there are, and indicate by various numbers the positions of *each* group, as in *2,2,4-trimethylpentane* (IV).


$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_3$

IV

2.2,4-Trimethylpentane



V

4-Methyl-3,3-diethyl-5-isopropyloctane

5. If there are several different alkyl groups attached to the parent chain, name them in order of increasing size or in alphabetical order; as in *4-methyl-3,3-diethyl-5-isopropyloctane* (V).

There are additional rules and conventions used in naming very complicated alkanes, but the five fundamental rules mentioned here will suffice for the compounds we are likely to encounter.

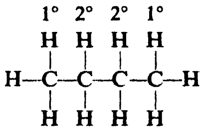
Problem 3.6 Give the IUPAC names for: (a) the isomeric hexanes shown on page 80; (b) the nine isomeric heptanes (see Problem 3.5, p. 80).

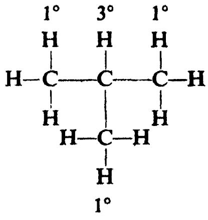
Problem 3.7 The IUPAC names for *n*-propyl and isopropyl chlorides are *1-chloropropane* and *2-chloropropane*. On this basis name: (a) the eight isomeric chloropentanes; (b) the nine isomeric dibromobutanes (see Problem 3.5, p. 80).

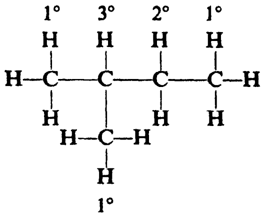
3.11 Classes of carbon atoms and hydrogen atoms

It has been found extremely useful to classify each carbon atom of an alkane with respect to the number of other carbon atoms to which it is attached.

A **primary** *(1°) carbon atom is attached to only one other carbon atom; a* **secondary** *(2°) is attached to two others; and a* **tertiary** *(3°) to three others.* For example:







Each hydrogen atom is similarly classified, being given the same designation of *primary*, *secondary*, or *tertiary* as the carbon atom to which it is attached.

We shall make constant use of these designations in our consideration of the relative reactivities of various parts of an alkane molecule.

3.12 Physical properties

The physical properties of the alkanes follow the pattern laid down by methane, and are consistent with the alkane structure. An alkane molecule is held together entirely by covalent bonds. These bonds either join two atoms of the same kind and hence are non-polar, or join two atoms that differ very little in electronegativity and hence are only slightly polar. Furthermore, these bonds are directed in a very symmetrical way, so that the slight bond polarities tend to cancel out. As a result an alkane molecule is either non-polar or very weakly polar.

As we have seen (Sec. 1.19), the forces holding non-polar molecules together (van der Waals forces) are weak and of very short range; they act only between the portions of different molecules that are in close contact, that is, between the surfaces of molecules. Within a family, therefore, we would expect that the larger the molecule—and hence the larger its surface area—the stronger the intermolecular forces.

Table 3.3 lists certain physical constants for a number of the *n*-alkanes. As we can see, the boiling points and melting points rise as the number of carbons increases. The processes of boiling and melting require overcoming the intermolecular forces of a liquid and a solid; the boiling points and melting points rise because these intermolecular forces increase as the molecules get larger.

Except for the very small alkanes, *the boiling point rises 20 to 30 degrees for each carbon that is added to the chain*; we shall find that this increment of 20–30° per carbon holds not only for the alkanes but also for each of the homologous series that we shall study.

The increase in melting point is not quite so regular, since the intermolecular forces in a crystal depend not only upon the size of the molecules but also upon how well they fit into a crystal lattice.

The first four *n*-alkanes are gases, but, as a result of the rise in boiling point and melting point with increasing chain length, the next 13 (C_5—C_{17}) are liquids, and those containing 18 carbons or more are solids.

Table 3.3 ALKANES

Name	Formula	M.p., °C	B.p., °C	Density (at 20°)
Methane	CH_4	−183	−162	
Ethane	CH_3CH_3	−172	− 88.5	
Propane	$CH_3CH_2CH_3$	−187	− 42	
n-Butane	$CH_3(CH_2)_2CH_3$	−138	0	
n-Pentane	$CH_3(CH_2)_3CH_3$	−130	36	0.626
n-Hexane	$CH_3(CH_2)_4CH_3$	− 95	69	.659
n-Heptane	$CH_3(CH_2)_5CH_3$	− 90.5	98	.684
n-Octane	$CH_3(CH_2)_6CH_3$	− 57	126	.703
n-Nonane	$CH_3(CH_2)_7CH_3$	− 54	151	.718
n-Decane	$CH_3(CH_2)_8CH_3$	− 30	174	.730
n-Undecane	$CH_3(CH_2)_9CH_3$	− 26	196	.740
n-Dodecane	$CH_3(CH_2)_{10}CH_3$	− 10	216	.749
n-Tridecane	$CH_3(CH_2)_{11}CH_3$	− 6	234	.757
n-Tetradecane	$CH_3(CH_2)_{12}CH_3$	5.5	252	.764
n-Pentadecane	$CH_3(CH_2)_{13}CH_3$	10	266	.769
n-Hexadecane	$CH_3(CH_2)_{14}CH_3$	18	280	.775
n-Heptadecane	$CH_3(CH_2)_{15}CH_3$	22	292	
n-Octadecane	$CH_3(CH_2)_{16}CH_3$	28	308	
n-Nonadecane	$CH_3(CH_2)_{17}CH_3$	32	320	
n-Eicosane	$CH_3(CH_2)_{18}CH_3$	36		
Isobutane	$(CH_3)_2CHCH_3$	−159	− 12	
Isopentane	$(CH_3)_2CHCH_2CH_3$	−160	28	.620
Neopentane	$(CH_3)_4C$	− 17	9.5	
Isohexane	$(CH_3)_2CH(CH_2)_2CH_3$	−154	60	.654
3-Methylpentane	$CH_3CH_2CH(CH_3)CH_2CH_3$	−118	63	.676
2,2-Dimethylbutane	$(CH_3)_3CCH_2CH_3$	− 98	50	.649
2,3-Dimethylbutane	$(CH_3)_2CHCH(CH_3)_2$	−129	58	.668

Problem 3.8 Using the data of Table 3.3, make a graph of: (a) b.p. *vs.* carbon number for the *n*-alkanes; (b) m.p. *vs.* carbon number; (c) density *vs.* carbon number.

There are somewhat smaller differences among the boiling points of alkanes that have the same carbon number but different structures. On pages 77 and 80 the boiling points of the isomeric butanes, pentanes, and hexanes are given. We see that in every case ***a branched-chain isomer has a lower boiling point than a straight-chain isomer***, and further, that the more numerous the branches, the lower the boiling point. Thus *n*-butane has a boiling point of 0° and isobutane −12°. *n*-Pentane has a boiling point of 36°, isopentane with a single branch 28°, and neopentane with two branches 9.5°. This effect of branching on boiling point is observed within all families of organic compounds. That branching should lower the boiling point is reasonable: with branching the shape of the molecule tends to approach that of a sphere; and as this happens the surface area decreases, with the result that the intermolecular forces become weaker and are overcome at a lower temperature.

In agreement with the rule of thumb, "like dissolves like," the alkanes are soluble in non-polar solvents such as benzene, ether, and chloroform, and are insoluble in water and other highly polar solvents. Considered themselves as solvents, the liquid alkanes dissolve compounds of low polarity and do not dissolve compounds of high polarity.

The density increases with size of the alkanes, but tends to level off at about 0.8; thus all alkanes are less dense than water. It is not surprising that nearly all organic compounds are less dense than water since, like the alkanes, they consist chiefly of carbon and hydrogen. In general, to be denser than water a compound must contain a heavy atom like bromine or iodine, or several atoms like chlorine.

3.13 Industrial source

The principal source of alkanes is **petroleum**, together with the accompanying **natural gas**. Decay and millions of years of geological stresses have transformed the complicated organic compounds that once made up living plants or animals into a mixture of alkanes ranging in size from one carbon to 30 or 40 carbons. Formed along with the alkanes, and particularly abundant in California petroleum, are *cycloalkanes* (Chap. 9), known to the petroleum industry as *naphthenes.*

The other fossil fuel, coal, is a potential second source of alkanes: processes are being developed to convert coal, through hydrogenation, into gasoline and fuel oil, and into synthetic gas to offset anticipated shortages of natural gas.

Natural gas contains, of course, only the more volatile alkanes, that is, those of low molecular weight; it consists chiefly of methane and progressively smaller amounts of ethane, propane, and higher alkanes. For example, a sample taken from a pipeline supplied by a large number of Pennsylvania wells contained methane, ethane, and propane in the ratio of 12:2:1, with higher alkanes making up only 3% of the total. The propane–butane fraction is separated from the more volatile components by liquefaction, compressed into cylinders, and sold as *bottled gas* in areas not served by a gas utility.

Petroleum is separated by distillation into the various fractions listed in Table 3.4; because of the relationship between boiling point and molecular weight, this amounts to a rough separation according to carbon number. Each fraction is still a very complicated mixture, however, since it contains alkanes of a range of carbon numbers, and since each carbon number is represented by numerous isomers. The use that each fraction is put to depends chiefly upon its volatility or viscosity, and it matters very little whether it is a complicated mixture or a

Table 3.4 PETROLEUM CONSTITUENTS

Fraction	Distillation Temperature, °C	Carbon Number
Gas	Below 20°	C_1–C_4
Petroleum ether	20–60°	C_5–C_6
Ligroin (light naphtha)	60–100°	C_6–C_7
Natural gasoline	40–205°	C_5–C_{10}, and cycloalkanes
Kerosene	175–325°	C_{12}–C_{18}, and aromatics
Gas oil	Above 275°	C_{12} and higher
Lubricating oil	Non-volatile liquids	Probably long chains attached to cyclic structures
Asphalt or petroleum coke	Non-volatile solids	Polycyclic structures

single pure compound. (In gasoline, as we shall see in Sec. 3.30, the structures of the components are of key importance.)

The chief use of all but the non-volatile fractions is as fuel. The gas fraction, like natural gas, is used chiefly for heating. Gasoline is used in those internal combustion engines that require a fairly volatile fuel, kerosene is used in tractor and jet engines, and gas oil is used in Diesel engines. Kerosene and gas oil are also used for heating purposes, the latter being the familiar "furnace oil."

The lubricating oil fraction, especially that from Pennsylvania crude oil (*paraffin-base petroleum*), often contains large amounts of long-chain alkanes (C_{20}–C_{34}) that have fairly high melting points. If these remained in the oil, they might crystallize to waxy solids in an oil line in cold weather. To prevent this, the oil is chilled and the wax is removed by filtration. After purification this is sold as solid *paraffin wax* (m.p. 50–55°) or used in *petrolatum jelly* (Vaseline). Asphalt is used in roofing and road building. The coke that is obtained from paraffin-base crude oil consists of complex hydrocarbons having a high carbon-to-hydrogen ratio; it is used as a fuel or in the manufacture of carbon electrodes for the electrochemical industries. Petroleum ether and ligroin are useful solvents for many organic materials of low polarity.

In addition to being used directly as just described, certain petroleum fractions are converted into other kinds of chemical compounds. Catalytic **isomerization** changes straight-chain alkanes into branched-chain ones. The **cracking** process (Sec. 3.31) converts higher alkanes into smaller alkanes and alkenes, and thus increases the gasoline yield; it can even be used for the production of "natural" gas. In addition, the alkenes thus formed are perhaps the most important raw materials for the large-scale synthesis of aliphatic compounds. The process of **catalytic reforming** (Sec. 12.4) converts alkanes and cycloalkanes into aromatic hydrocarbons and thus helps provide the raw material for the large-scale synthesis of another broad class of compounds.

3.14 Industrial source *vs.* laboratory preparation

We shall generally divide the methods of obtaining a particular kind of organic compound into two categories: *industrial source* and *laboratory preparation.* We may contrast the two in the following way, although it must be realized that there are many exceptions to these generalizations.

An industrial source must provide large amounts of the desired material at the lowest possible cost. A laboratory preparation may be required to produce only a few hundred grams or even a few grams; cost is usually of less importance than the time of the investigator.

For many industrial purposes a mixture may be just as suitable as a pure compound; even when a single compound is required, it may be economically feasible to separate it from a mixture, particularly when the other components may also be marketed. In the laboratory a chemist nearly always wants a single pure compound. Separation of a single compound from a mixture of related substances is very time-consuming and frequently does not yield material of the required purity. Furthermore, the raw material for a particular preparation may well be the hard-won product of a previous preparation or even series of preparations, and hence he wishes to convert it as completely as possible into his desired compound. On an industrial scale, if a compound cannot be isolated from naturally occurring material, it may be synthesized along with a number of related compounds by some inexpensive reaction. In the laboratory, whenever possible, a reaction is selected that forms a single compound in high yield.

In industry it is frequently worth while to work out a procedure and design apparatus that may be used in the synthesis of only one member of a chemical family. In the laboratory a chemist is seldom interested in preparing the same compound over and over again, and hence he makes use of methods that are applicable to many or all members of a particular family.

In our study of organic chemistry, we shall concentrate our attention on versatile laboratory preparations rather than on limited industrial methods. In learning these we may, for the sake of simplicity, use as examples the preparation of compounds that may actually never be made by the method shown. We may discuss the synthesis of ethane by the hydrogenation of ethylene, even though we can buy all the ethane we need from the petroleum industry. However, if we know how to convert ethylene into ethane, then, when the need arises, we also know how to convert 2-methyl-1-hexene into 2-methylhexane, or cholesterol into cholestanol, or, for that matter, cottonseed oil into oleomargarine.

3.15 Preparation

Each of the smaller alkanes, from methane through *n*-pentane and isopentane, can be obtained in pure form by fractional distillation of petroleum and natural gas; neopentane does not occur naturally. Above the pentanes the number of isomers of each homolog becomes so large and the boiling point differences become so small that it is no longer feasible to isolate individual, pure compounds; these alkanes must be synthesized by one of the methods outlined below.

In some of these equations, the symbol **R** is used to represent **any alkyl group.** This convenient device helps to summarize reactions that are typical of an entire family, and emphasizes the essential similarity of the various members.

In writing these generalized equations, however, we must not lose sight of one important point. An equation involving RCl, to take a specific example, has meaning only in terms of a reaction that we can carry out in the laboratory using a real compound, like methyl chloride or *tert*-butyl chloride. Although *typical* of alkyl halides, a reaction may differ widely in rate or yield depending upon the particular alkyl group actually concerned. We may use quite different experimental conditions for methyl chloride than for *tert*-butyl chloride; in an extreme case, a reaction that goes well for methyl chloride might go so slowly or give so many side products as to be completely useless for *tert*-butyl chloride.

PREPARATION OF ALKANES

1. **Hydrogenation of alkenes.** Discussed in Sec. 6.3.

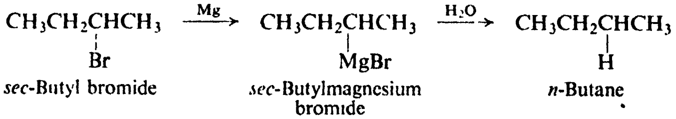
$$\underset{\text{Alkene}}{C_nH_{2n}} \xrightarrow{H_2 + \text{Pt, Pd, or Ni}} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

2. **Reduction of alkyl halides**

(a) **Hydrolysis of Grignard reagent.** Discussed in Sec. 3.16.

$$RX + Mg \longrightarrow \underset{\text{Grignard reagent}}{RMgX} \xrightarrow{H_2O} RH$$

Example:

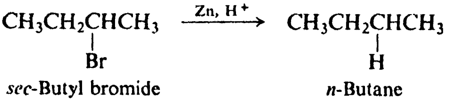


$$\underset{\textit{sec}\text{-Butyl bromide}}{\underset{Br}{CH_3CH_2CHCH_3}} \xrightarrow{Mg} \underset{\textit{sec}\text{-Butylmagnesium bromide}}{\underset{MgBr}{CH_3CH_2CHCH_3}} \xrightarrow{H_2O} \underset{n\text{-Butane}}{\underset{H}{CH_3CH_2CHCH_3}}$$

(b) **Reduction by metal and acid.** Discussed in Sec. 3.15.

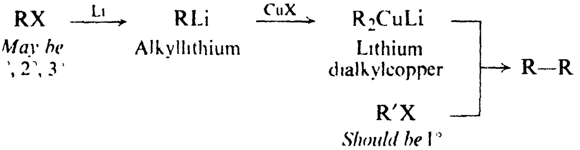
$$RX + Zn + H^+ \longrightarrow RH + Zn^{++} + X^-$$

Example:



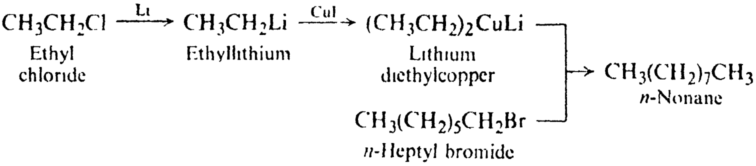
$$\underset{\textit{sec}\text{-Butyl bromide}}{\underset{Br}{CH_3CH_2CHCH_3}} \xrightarrow{Zn,\ H^+} \underset{n\text{-Butane}}{\underset{H}{CH_3CH_2CHCH_3}}$$

3. **Coupling of alkyl halides with organometallic compounds.** Discussed in Sec. 3.17.

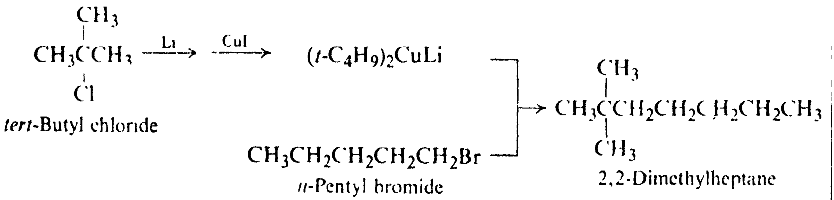


$$\underset{\substack{\textit{May be}\\ 1°,\ 2°,\ 3°}}{RX} \xrightarrow{Li} \underset{\text{Alkyllithium}}{RLi} \xrightarrow{CuX} \underset{\substack{\text{Lithium}\\ \text{dialkylcopper}}}{R_2CuLi} \quad + \quad \underset{\textit{Should be } 1°}{R'X} \longrightarrow R{-}R$$

Examples:



$$\underset{\substack{\text{Ethyl}\\ \text{chloride}}}{CH_3CH_2Cl} \xrightarrow{Li} \underset{\text{Ethyllithium}}{CH_3CH_2Li} \xrightarrow{CuI} \underset{\substack{\text{Lithium}\\ \text{diethylcopper}}}{(CH_3CH_2)_2CuLi} \quad + \quad \underset{n\text{-Heptyl bromide}}{CH_3(CH_2)_5CH_2Br} \longrightarrow \underset{n\text{-Nonane}}{CH_3(CH_2)_7CH_3}$$



$$\underset{\textit{tert}\text{-Butyl chloride}}{\overset{CH_3}{\underset{Cl}{CH_3CCH_3}}} \xrightarrow{Li} \xrightarrow{CuI} (t\text{-}C_4H_9)_2CuLi \quad + \quad \underset{n\text{-Pentyl bromide}}{CH_3CH_2CH_2CH_2CH_2Br} \longrightarrow \underset{2,2\text{-Dimethylheptane}}{\overset{CH_3}{\underset{CH_3}{CH_3CCH_2CH_2CH_2CH_2CH_3}}}$$

By far the most important of these methods is the hydrogenation of alkenes. When shaken under a slight pressure of hydrogen gas in the presence of a small amount of catalyst, alkenes are converted smoothly and quantitatively into alkanes of the same carbon skeleton. The method is limited only by the availability of the proper alkene. This is not a very serious limitation; as we shall see (Sec. 5.11), alkenes are readily prepared, chiefly from alcohols, which in turn can be readily synthesized (Sec. 15.7) in a wide variety of sizes and shapes.

Reduction of an alkyl halide, either via the Grignard reagent or directly with metal and acid, involves simply the replacement of a halogen atom by a hydrogen atom; the carbon skeleton remains intact. This method has about the same applicability as the previous method, since, like alkenes, alkyl halides are generally prepared from alcohols. Where either method could be used, the hydrogenation of alkenes would probably be preferred because of its simplicity and higher yield.

The coupling of alkyl halides with organometallic compounds is the only one of these methods in which carbon–carbon bonds are formed and a new, bigger carbon skeleton is generated.

3.16 The Grignard reagent: an organometallic compound

When a solution of an alkyl halide in dry ethyl ether, $(C_2H_5)_2O$, is allowed to stand over turnings of metallic magnesium, a vigorous reaction takes place: the solution turns cloudy, begins to boil, and the magnesium metal gradually disappears. The resulting solution is known as a **Grignard reagent**, after Victor Grignard (of the University of Lyons) who received the Nobel prize in 1912 for its discovery. It is one of the most useful and versatile reagents known to the organic chemist.

$$CH_3I + Mg \xrightarrow{\text{ether}} CH_3MgI$$

Methyl iodide — Methylmagnesium iodide

$$CH_3CH_2Br + Mg \xrightarrow{\text{ether}} CH_3CH_2MgBr$$

Ethyl bromide — Ethylmagnesium bromide

The Grignard reagent has the general formula RMgX, and the general name **alkylmagnesium halide**. The carbon–magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium–halogen bond is essentially ionic.

$$R{:}Mg^{+}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}{:}^{-}$$

Since magnesium becomes bonded to the same carbon that previously held halogen, the alkyl group remains intact during the preparation of the reagent. Thus *n*-propyl chloride yields *n*-propylmagnesium chloride, and isopropyl chloride yields isopropylmagnesium chloride.

$$CH_3CH_2CH_2Cl + Mg \xrightarrow{\text{ether}} CH_3CH_2CH_2MgCl$$

n-Propyl chloride — *n*-Propylmagnesium chloride

$$CH_3CHClCH_3 + Mg \xrightarrow{\text{ether}} CH_3CHMgClCH_3$$

Isopropyl chloride — Isopropylmagnesium chloride

The Grignard reagent is the best-known member of a broad class of substances, called **organometallic** compounds, in which carbon is bonded to a metal: lithium, potassium, sodium, zinc, mercury, lead, thallium—almost any metal known. Each kind of organometallic compound has, of course, its own set of properties, and its particular uses depend on these. But, whatever the metal, it is less electronegative than carbon, and the carbon–metal bond—like the one in the

$$\overset{\delta-}{R}-\overset{\delta+}{M}$$

Grignard reagent—is highly polar. Although the organic group is not a full-fledged *carbanion*—an anion in which carbon carries negative charge—it nevertheless has considerable carbanion character. As we shall see, organometallic compounds owe their enormous usefulness chiefly to one common quality: they can serve as a source from which carbon is readily transferred *with its electrons*.

The Grignard reagent is highly reactive. It reacts with numerous inorganic compounds including water, carbon dioxide, and oxygen, and with most kinds of organic compounds; in many of these cases the reaction provides the best way to make a particular class of organic compound.

The reaction with water to form an alkane is typical of the behavior of the Grignard reagent—and many of the more reactive organometallic compounds—toward acids. In view of the marked carbanion character of the alkyl group, we may consider the Grignard reagent to be the magnesium salt, RMgX, of the extremely weak acid, R—H. The reaction

$$\mathrm{RMgX} + \underset{\substack{\text{Stronger}\\\text{acid}}}{\mathrm{HOH}} \longrightarrow \underset{\substack{\text{Weaker}\\\text{acid}}}{\mathrm{R{-}H}} + \mathrm{Mg(OH)X}$$

is simply the displacement of the weaker acid, R—H, from its salt by the stronger acid, HOH.

An alkane is such a weak acid that it is displaced from the Grignard reagent by compounds that we might ordinarily consider to be very weak acids themselves, or possibly not acids at all. Any compound containing hydrogen attached to oxygen or nitrogen is tremendously more acidic than an alkane, and therefore can decompose the Grignard reagent: for example, ammonia or methyl alcohol.

$$\mathrm{RMgX} + \underset{\substack{\text{Stronger}\\\text{acid}}}{\mathrm{NH_3}} \longrightarrow \underset{\substack{\text{Weaker}\\\text{acid}}}{\mathrm{R{-}H}} + \mathrm{Mg(NH_2)X}$$

$$\mathrm{RMgX} + \underset{\substack{\text{Stronger}\\\text{acid}}}{\mathrm{CH_3OH}} \longrightarrow \underset{\substack{\text{Weaker}\\\text{acid}}}{\mathrm{R{-}H}} + \mathrm{Mg(OCH_3)X}$$

For the preparation of an alkane, one acid is as good as another, so we naturally choose water as the most available and convenient.

Problem 3.9 (a) Which alkane would you expect to get by the action of water on *n*-propylmagnesium chloride? (b) On isopropylmagnesium chloride? (c) Answer (a) and (b) for the action of deuterium oxide ("heavy water," D_2O).

Problem 3.10 On conversion into the Grignard reagent followed by treatment with water, how many alkyl bromides would yield: (a) *n*-pentane; (b) 2-methylbutane; (c) 2,3-dimethylbutane; (d) neopentane? Draw the structures in each case.

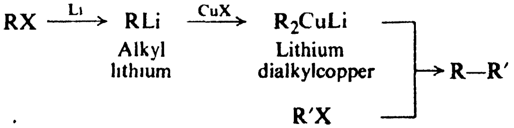
3.17 Coupling of alkyl halides with organometallic compounds

To make an alkane of higher carbon number than the starting material requires formation of carbon–carbon bonds, most directly by the coupling together of two alkyl groups. The most versatile method of doing this is through a synthesis developed during the late 1960s by E. J. Corey and Herbert House, working independently at Harvard University and Massachusetts Institute of Technology.

Coupling takes place in the reaction between a *lithium dialkylcopper*, R_2CuLi, and an alkyl halide, R'X. (R' stands for an alkyl group that may be the same as, or different from, R.)

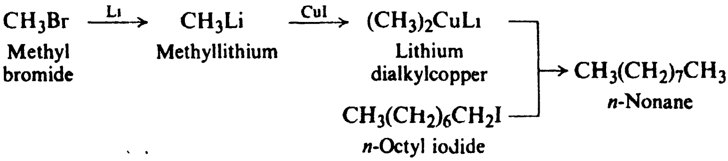
$$\underset{\text{Lithium dialkylcopper}}{R_2CuLi} + \underset{\text{Alkyl halide}}{R'X} \longrightarrow \underset{\text{Alkane}}{R{-}R'} + RCu + LiX$$

An alkyllithium, RLi, is prepared from an alkyl halide, RX, in much the same way as a Grignard reagent. To it is added cuprous halide, CuX, and then, finally, the second alkyl halide, R'X. Ultimately, the alkane is synthesized from the two alkyl halides, RX and R'X.

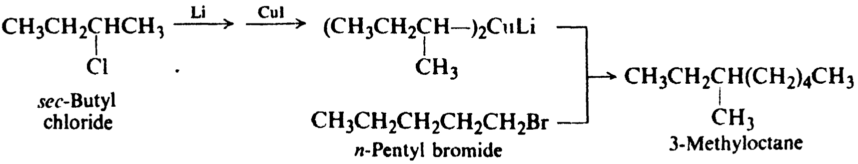


$$RX \xrightarrow{Li} \underset{\text{Alkyl lithium}}{RLi} \xrightarrow{CuX} \underset{\text{Lithium dialkylcopper}}{R_2CuLi} \;\; + \;\; R'X \longrightarrow R{-}R'$$

For good yields, R'X should be a *primary* halide; the alkyl group R in the organometallic may be primary, secondary, or tertiary. For example:



$$\underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow{Li} \underset{\text{Methyllithium}}{CH_3Li} \xrightarrow{CuI} \underset{\text{Lithium dialkylcopper}}{(CH_3)_2CuLi} \;\; + \;\; \underset{n\text{-Octyl iodide}}{CH_3(CH_2)_6CH_2I} \longrightarrow \underset{n\text{-Nonane}}{CH_3(CH_2)_7CH_3}$$



$$\underset{sec\text{-Butyl chloride}}{CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3} \xrightarrow{Li} \xrightarrow{CuI} (CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H{-})_2CuLi \;\; + \;\; \underset{n\text{-Pentyl bromide}}{CH_3CH_2CH_2CH_2CH_2Br} \longrightarrow \underset{\text{3-Methyloctane}}{CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_4CH_3}$$

The choice of organometallic reagent is crucial. Grignard reagents or organolithium compounds, for example, couple with only a few unusually reactive organic halides. Organosodium compounds couple, but are so reactive that they couple, as they are being formed, with their parent alkyl halide; the reaction of sodium with alkyl halides (*Wurtz reaction*) is thus limited to the synthesis of symmetrical alkanes, R—R.

Organocopper compounds were long known to be particularly good at the formation of carbon–carbon bonds, but are unstable. Here, they are generated *in situ* from the organolithium, and then combine with more of it to form these relatively stable organometallics. They exist as complex aggregates but are believed to correspond roughly to $R_2Cu^-Li^+$. The anion here is an example of an *ate* complex, the negative counterpart of an *onium* complex (ammo*nium*, ox*onium*).

Although the mechanism is not understood, evidence strongly suggests this much: the alkyl group R is transferred from copper, taking a pair of electrons with it, and attaches itself to the alkyl group R' by pushing out halide ion (*nucleophilic aliphatic substitution*, Sec. 14.9).

Problem 3.11 (a) Outline two conceivable syntheses of 2-methylpentane from three-carbon compounds. (b) Which of the two would you actually use? Why?

3.18 Reactions

The alkanes are sometimes referred to by the old-fashioned name of *paraffins.* This name (Latin: *parum affinis*, not enough affinity) was given to describe what appeared to be the low reactivity of these hydrocarbons.

But reactivity depends upon the choice of reagent. If alkanes are inert toward hydrochloric and sulfuric acids, they react readily with acids like $HF\text{-}SbF_5$ and $FSO_3H\text{-}SbF_5$ ("magic acid") to yield a variety of products. If alkanes are inert toward oxidizing agents like potassium permanganate or sodium dichromate, most of this chapter is devoted to their oxidation by halogens. Certain yeasts feed happily on alkanes to produce proteins—certainly a chemical reaction. As Professor M. S. Kharasch (p. 189) used to put it, consider the "inertness" of a room containing natural gas, air, and a lighted match.

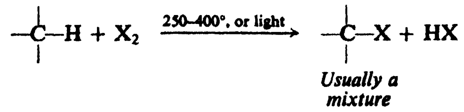
Still, on a comparative basis, reactivity *is* limited. "Magic acid" is, after all, one of the strongest acids known; halogenation requires heat or light; combustion needs a flame or spark to get it started.

Much of the chemistry of alkanes involves free-radical chain reactions, which take place under vigorous conditions and usually yield mixtures of products. A reactive particle—typically an atom or free radical—is needed to begin the attack on an alkane molecule. It is the generation of this reactive particle that requires the vigorous conditions: the dissociation of a halogen molecule into atoms, for example, or even (as in pyrolysis) dissociation of the alkane molecule itself.

In its attack, the reactive particle abstracts hydrogen from the alkane; the alkane itself is thus converted into a reactive particle which continues the reaction sequence, that is, carries on the chain. But an alkane molecule contains many hydrogen atoms and the particular product eventually obtained depends upon *which* of these hydrogen atoms is abstracted. Although an attacking particle may show a certain selectivity, it can abstract a hydrogen from any part of the molecule, and thus bring about the formation of many isomeric products.

REACTIONS OF ALKANES

1. Halogenation. Discussed in Secs. 3.19–3.22.



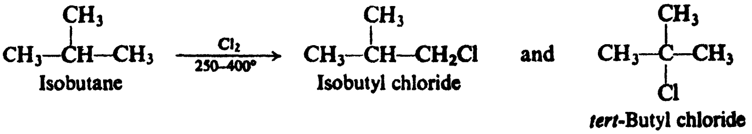
$$-\overset{|}{\underset{|}{C}}-H + X_2 \xrightarrow{250\text{–}400^\circ\text{, or light}} -\overset{|}{\underset{|}{C}}-X + HX$$

Usually a mixture

Reactivity X_2: $Cl_2 > Br_2$

H: $3^\circ > 2^\circ > 1^\circ > CH_3\text{—}H$

Example:



$$\underset{\text{Isobutane}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3} \xrightarrow[250\text{–}400^\circ]{Cl_2} \underset{\text{Isobutyl chloride}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2Cl} \quad \text{and} \quad \underset{tert\text{-Butyl chloride}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3}$$

2. Combustion. Discussed in Sec. 3.30.

$$C_nH_{2n+2} + \text{excess } O_2 \xrightarrow{\text{flame}} nCO_2 + (n+1)H_2O \qquad \Delta H = \text{heat of combustion}$$

Example:

$$n\text{-}C_5H_{12} + 8\,O_2 \xrightarrow{\text{flame}} 5CO_2 + 6H_2O \qquad \Delta H = -845 \text{ kcal}$$

3. Pyrolysis (cracking). Discussed in Sec. 3.31.

$$\text{alkane} \xrightarrow[\text{without catalysts}]{400\text{–}600^\circ\text{; with or}} H_2 + \text{smaller alkanes} + \text{alkenes}$$

3.19 Halogenation

As we might expect, halogenation of the higher alkanes is essentially the same as the halogenation of methane. It can be complicated, however, by the formation of mixtures of isomers.

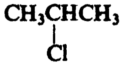
Under the influence of ultraviolet light, or at 250–400°, chlorine or bromine converts alkanes into chloroalkanes (alkyl chlorides) or bromoalkanes (alkyl bromides); an equivalent amount of hydrogen chloride or hydrogen bromide is formed at the same time. When diluted with an inert gas, and in an apparatus designed to carry away the heat produced, fluorine has recently been found to give analogous results. As with methane, iodination does not take place at all.

Depending upon which nydrogen atom is replaced, any of a number of isomeric products can be formed from a single alkane. Ethane can yield only one haloethane; propane, *n*-butane, and isobutane can yield two isomers each; *n*-pentane can yield three isomers, and isopentane, four isomers. Experiment has shown that on halogenation an alkane yields a mixture of all possible isomeric products, indicating that all hydrogen atoms are susceptible to replacement. For example, for chlorination:

$$\underset{\text{Ethane}}{CH_3CH_3} \xrightarrow[\text{light, }25^\circ]{Cl_2} CH_3CH_2\text{—}Cl$$

b.p. 13°
Chloroethane
Ethyl chloride

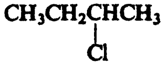
$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow[\text{light, }25^\circ]{Cl_2} CH_3CH_2CH_2\text{—}Cl \quad \text{and} \quad CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$$



b.p. 47°
1-Chloropropane
***n*-Propyl chloride**
45%

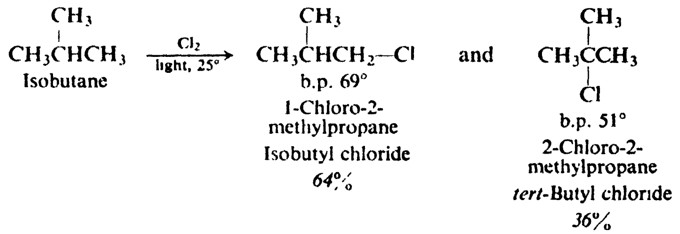
b.p. 36°
2-Chloropropane
Isopropyl chloride
55%

$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{light, }25^\circ]{Cl_2} CH_3CH_2CH_2CH_2\text{—}Cl \quad \text{and} \quad CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$$



b.p. 78.5°
1-Chlorobutane
***n*-Butyl chloride**
28%

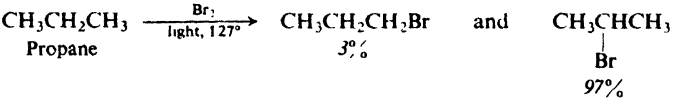
b.p. 68°
2-Chlorobutane
***sec*-Butyl chloride**



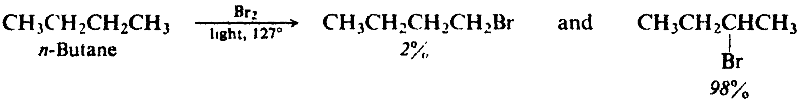
$$\begin{array}{c}CH_3\\|\\CH_3CHCH_3\\\text{Isobutane}\end{array}\xrightarrow[\text{light, }25^\circ]{Cl_2}\begin{array}{c}CH_3\\|\\CH_3CHCH_2{-}Cl\\\text{b.p. }69^\circ\\\text{1-Chloro-2-}\\\text{methylpropane}\\\text{Isobutyl chloride}\\64\%\end{array}\quad\text{and}\quad\begin{array}{c}CH_3\\|\\CH_3CCH_3\\|\\Cl\\\text{b.p. }51^\circ\\\text{2-Chloro-2-}\\\text{methylpropane}\\\textit{tert}\text{-Butyl chloride}\\36\%\end{array}$$

Bromination gives the corresponding bromides but in different proportions:

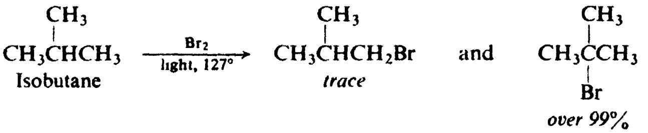
$$\underset{\text{Ethane}}{CH_3CH_3}\xrightarrow[\text{light, }127^\circ]{Br_2}CH_3CH_2Br$$



$$\underset{\text{Propane}}{CH_3CH_2CH_3}\xrightarrow[\text{light, }127^\circ]{Br_2}\underset{3\%}{CH_3CH_2CH_2Br}\quad\text{and}\quad\begin{array}{c}CH_3CHCH_3\\|\\Br\\97\%\end{array}$$



$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3}\xrightarrow[\text{light, }127^\circ]{Br_2}\underset{2\%}{CH_3CH_2CH_2CH_2Br}\quad\text{and}\quad\begin{array}{c}CH_3CH_2CHCH_3\\|\\Br\\98\%\end{array}$$



$$\begin{array}{c}CH_3\\|\\CH_3CHCH_3\\\text{Isobutane}\end{array}\xrightarrow[\text{light, }127^\circ]{Br_2}\begin{array}{c}CH_3\\|\\CH_3CHCH_2Br\\\textit{trace}\end{array}\quad\text{and}\quad\begin{array}{c}CH_3\\|\\CH_3CCH_3\\|\\Br\\\textit{over }99\%\end{array}$$

Problem 3.12 Draw the structures of: (a) the three monochloro derivatives of *n*-pentane; (b) the four monochloro derivatives of isopentane.

Although both chlorination and bromination yield mixtures of isomers, the results given above show that the *relative amounts* of the various isomers differ markedly depending upon the halogen used. Chlorination gives mixtures in which no isomer greatly predominates; in bromination, by contrast, one isomer may predominate to such an extent as to be almost the only product, making up 97–99% of the total mixture. In bromination, there is a high degree of *selectivity* as to which hydrogen atoms are to be replaced. (As we shall see in Sec. 3.28, this characteristic of bromination is due to the relatively low reactivity of bromine atoms, and is an example of a general relationship between *reactivity* and *selectivity*.)

Chlorination of an alkane is not usually suitable for the laboratory preparation of an alkyl chloride; any one product is necessarily formed in low yield, and is difficult to separate from its isomers, whose boiling points are seldom far from its own. Bromination, on the other hand, often gives a nearly pure alkyl bromide in high yield. As we shall see, it is possible to predict just which isomer will predominate; if this product is the one desired, direct bromination could be a feasible synthetic route.

On an industrial scale, chlorination of alkanes is important. For many purposes, for example, use as a solvent, a mixture of isomers is just as suitable as, and much cheaper than, a pure compound. It may be even worthwhile, when necessary, to separate a mixture of isomers if each isomer can then be marketed.

Problem 3.13 How do you account for the fact that not only bromination but also chlorination is a feasible laboratory route to a neopentyl halide, $(CH_3)_3CCH_2X$?

3.20 Mechanism of halogenation

Halogenation of alkanes proceeds by the same mechanism as halogenation of methane:

(1) $X_2 \xrightarrow[\text{or ultraviolet light}]{250-400^\circ} 2X\cdot$ **Chain-initiating step**

(2) $X\cdot + RH \longrightarrow HX + R\cdot$

(3) $R\cdot + X_2 \longrightarrow RX + X\cdot$

Chain-propagating steps

then (2), (3), (2), (3), *etc., until finally a chain is terminated* (Sec. 2.13)

A halogen atom abstracts hydrogen from the alkane (RH) to form an alkyl radical (R·). The radical in turn abstracts a halogen atom from a halogen molecule to yield the alkyl halide (RX).

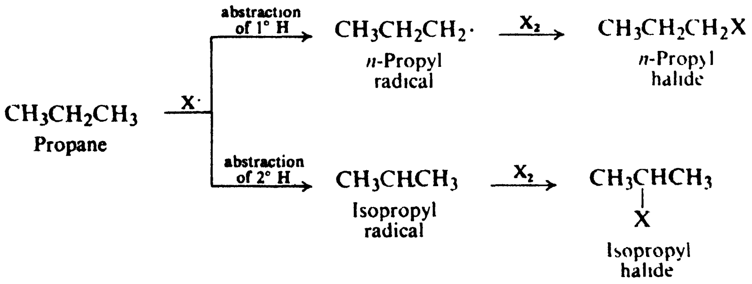
Which alkyl halide is obtained depends upon which alkyl radical is formed.

$$CH_4 \xrightarrow{X\cdot} CH_3\cdot \xrightarrow{X_2} CH_3X$$

Methane — Methyl radical — Methyl halide

$$CH_3CH_3 \xrightarrow{X\cdot} CH_3CH_2\cdot \xrightarrow{X_2} CH_3CH_2X$$

Ethane — Ethyl radical — Ethyl halide



This in turn depends upon the alkane and which hydrogen atom is abstracted from it. For example, *n*-propyl halide is obtained from a *n*-propyl radical, formed from propane by abstraction of a primary hydrogen; isopropyl halide is obtained from an isopropyl radical, formed by abstraction of a secondary hydrogen.

How fast an alkyl halide is formed depends upon how fast the alkyl radical is formed. Here also, as was the case with methane (Sec. 2.20), of the two chain-propagating steps, step (2) is more difficult than step (3), and hence controls the rate of overall reaction. Formation of the alkyl radical is difficult, but once formed the radical is readily converted into the alkyl halide (see Fig. 3.5).

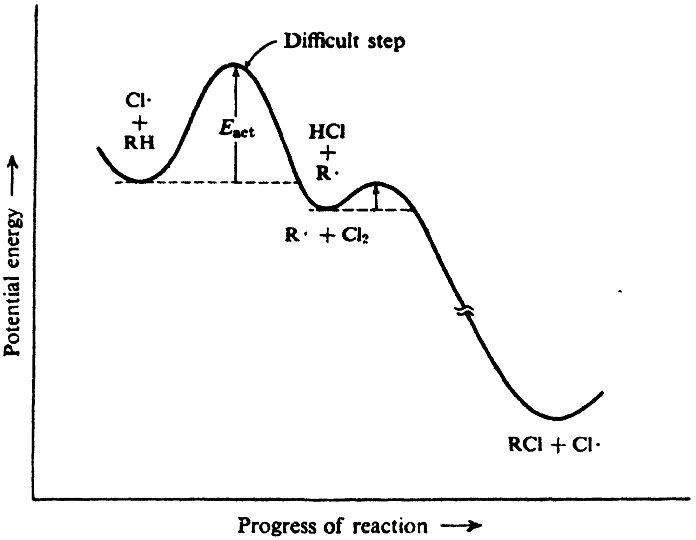
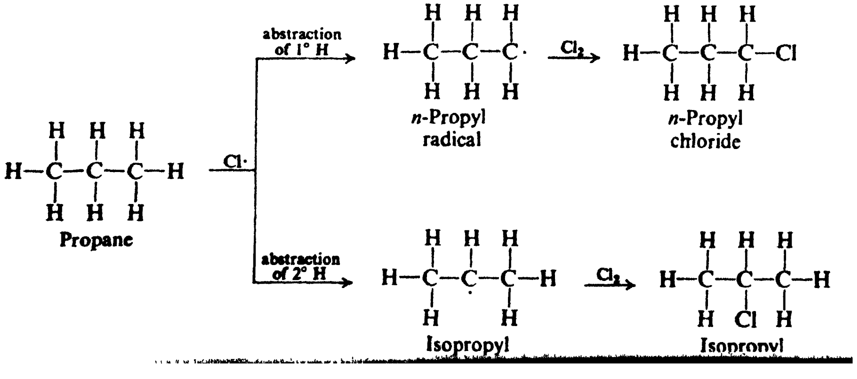


Figure 3.5. Potential energy changes during progress of reaction: chlorination of an alkane. Formation of radical is rate-controlling step.

3.21 Orientation of halogenation

With this background let us turn to the problem of **orientation**; that is, let us examine the factors that determine *where* in a molecule reaction is most likely to occur. It is a problem that we shall encounter again and again, whenever we study a compound that offers more than one reactive site to attack by a reagent. It is an important problem, because orientation determines what product we obtain.

As an example let us take chlorination of propane. The relative amounts of *n*-propyl chloride and isopropyl chloride obtained depend upon the relative rates at which *n*-propyl radicals and isopropyl radicals are formed. If, say, isopropyl radicals are formed faster, then isopropyl chloride will be formed faster, and will make up a larger fraction of the product. As we can see, *n*-propyl radicals are formed by abstraction of primary hydrogens, and isopropyl radicals by abstraction of secondary hydrogens.



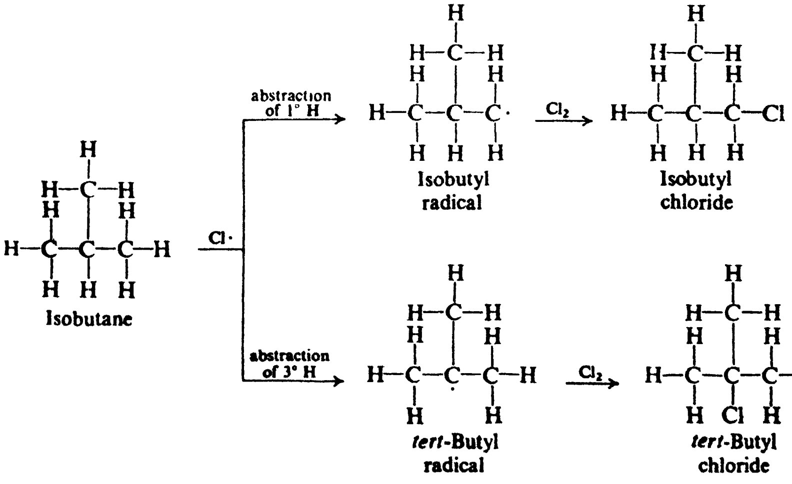
Thus *orientation is determined by the relative rates of competing reactions.* In this case we are comparing the rate of abstraction of primary hydrogens with the rate of abstraction of secondary hydrogens. What are the factors that determine the rates of these two reactions, and in which of these factors may the two reactions differ?

First of all, there is the collision frequency. This must be the same for the two reactions, since both involve collisions of the same particles: a propane molecule and a chlorine atom.

Next, there is the probability factor. If a primary hydrogen is to be abstracted, the propane molecule must be so oriented at the time of collision that the chlorine atom strikes a primary hydrogen; if a secondary hydrogen is to be abstracted, the propane must be so oriented that the chlorine collides with a secondary hydrogen. Since there are six primary hydrogens and only two secondary hydrogens in each molecule, we might estimate that the probability factor favors abstraction of primary hydrogens by the ratio of 6:2, or 3:1.

Considering only collision frequency and our guess about probability factors, we predict that chlorination of propane would yield *n*-propyl chloride and isopropyl chloride in the ratio of 3:1. As shown on page 95, however, the two chlorides are formed in roughly equal amounts, that is, in the ratio of about 1:1, or 3:3. The proportion of isopropyl chloride is about three times as great as predicted. Evidently, about three times as many collisions with secondary hydrogens are successful as collisions with primary hydrogens. If our assumption about the probability factor is correct, this means that E_{act} is less for abstraction of a secondary hydrogen than for abstraction of a primary hydrogen.

Chlorination of isobutane presents a similar problem. In this case, abstraction of one of the nine primary hydrogen leads to the formation of isobutyl chloride, whereas abstraction of the single tertiary hydrogen leads to the formation of *tert*-butyl chloride. We would estimate, then, that the probability factor favors formation of isobutyl chloride by the ratio of 9:1. The experimental results given on page 96 show that the ratio is roughly 2:1, or 9:4.5. Evidently, about 4.5 times as many collisions with the tertiary hydrogen are successful as collisions wi



the primary hydrogens. This, in turn, probably means that E_{act} is less for abstraction of a tertiary hydrogen than for abstraction of a primary hydrogen, and, in fact, even less than for abstraction of a secondary hydrogen.

Study of the chlorination of a great many alkanes has shown that these are typical results. After allowance is made for differences in the probability factor, the rate of abstraction of hydrogen atoms is always found to follow the sequence 3° > 2° > 1°. At room temperature, for example, the relative rates *per hydrogen atom* are 5.0:3.8:1.0. Using these values we can predict quite well the ratio of isomeric chlorination products from a given alkane. For example:

$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[\text{light, }25^\circ]{Cl_2} \underset{n\text{-Butyl chloride}}{CH_3CH_2CH_2CH_2Cl} \quad \text{and} \quad \underset{sec\text{-Butyl chloride}}{CH_3CH_2CHClCH_3}$$

$$\frac{n\text{-butyl chloride}}{sec\text{-butyl chloride}} = \frac{\text{no. of } 1^\circ \text{ H}}{\text{no. of } 2^\circ \text{ H}} \times \frac{\text{reactivity of } 1^\circ \text{ H}}{\text{reactivity of } 2^\circ \text{ H}}$$

$$= \frac{6}{4} \times \frac{1.0}{3.8}$$

$$= \frac{6}{15.2} \quad \textit{equivalent to} \quad \frac{28\%}{72\%}$$

In spite of these differences in reactivity, chlorination rarely yields a great preponderance of any single isomer. In nearly every alkane, as in the examples we have studied, the less reactive hydrogens are the more numerous; their lower reactivity is compensated for by a higher probability factor, with the result that appreciable amounts of every isomer are obtained.

Problem 3.14 Predict the proportions of isomeric products from chlorination at room temperature of: (a) propane; (b) isobutane; (c) 2,3-dimethylbutane, (d) *n*-pentane (*Note*: There are *three* isomeric products); (e) isopentane; (f) 2,2,3-trimethylbutane; (g) 2,2,4-trimethylpentane. For (a) and (b) check your calculations against the experimental values given on pages 95 and 96.

The same sequence of reactivity, 3° > 2° > 1°, is found in bromination, but with enormously larger reactivity ratios. At 127°, for example, the relative rates per hydrogen atom are 1600:82:1. Here, differences in reactivity are so marked as vastly to outweigh probability factors.

Problem 3.15 Answer Problem 3.14 for bromination at 127°.

3.22 Relative reactivities of alkanes toward halogenation

The best way to measure the relative reactivities of different compounds toward the same reagent is by the **method of competition**, since this permits an exact quantitative comparison under identical reaction conditions. Equimolar amounts of two compounds to be compared are mixed together and allowed to react with a limited amount of a particular reagent. Since there is not enough reagent for both compounds, the two compete with each other. Analysis of the reaction products shows which compound has consumed more of the reagent and hence is more reactive.

For example, if equimolar amounts of methane and ethane are allowed to react with a small amount of chlorine, about 400 times as much ethyl chloride as methyl chloride is obtained, showing that ethane is 400 times as reactive as methane. When allowance is made for the relative numbers of hydrogens in the two kinds of molecules, we see that each hydrogen of ethane is about 270 times as reactive as each hydrogen of methane.

$$\begin{array}{ccccc} CH_3Cl & \xleftarrow{CH_4} & Cl_2 & \xrightarrow{C_2H_6} & C_2H_5Cl \\ 1 & & \text{light, } 25^\circ & & 400 \end{array}$$

Problem 3.16 Because of the rather large difference in reactivity between ethane and methane, competition experiments have actually used mixtures containing more methane than ethane. If the molar ratio of methane to ethane were 10:1, what ratio of ethyl chloride to methyl chloride would you expect to obtain? What practical advantage would this experiment have over one involving a 1:1 ratio?

Data obtained from similar studies of other compounds are consistent with this simple generalization: *the reactivity of a hydrogen depends chiefly upon its class, and not upon the alkane to which it is attached.* Each primary hydrogen of propane, for example, is about as easily abstracted as each primary hydrogen in *n*-butane or isobutane; each secondary hydrogen of propane, about as easily as each secondary hydrogen of *n*-butane or *n*-pentane; and so on.

The hydrogen atoms of methane, which fall into a special class, are even less reactive than primary hydrogens, as shown by the above competition with ethane.

Problem 3.17 On chlorination, an equimolar mixture of ethane and neopentane yields neopentyl chloride and ethyl chloride in the ratio of 2.3:1. How does the reactivity of a primary hydrogen in neopentane compare with that of a primary hydrogen in ethane?

3.23 Ease of abstraction of hydrogen atoms. Energy of activation

At this stage we can summarize the effect of structure on halogenation of alkanes in the following way. The controlling step in halogenation is abstraction of hydrogen by a halogen atom:

$$R{-}H + X\cdot \longrightarrow H{-}X + R\cdot$$

The relative ease with which the different classes of hydrogen atoms are abstracted is:

Ease of abstraction of hydrogen atoms	$3^\circ > 2^\circ > 1^\circ > CH_4$

This sequence applies (a) to the various hydrogens within a single alkane and hence governs **orientation** of reaction, and (b) to the hydrogens of different alkanes and hence governs **relative reactivities**.

Earlier, we concluded that these differences in ease of abstraction—like most differences in rate between closely related reactions (Sec. 2.19)—are probably due to differences in E_{act}. By study of halogenation at a series of temperatures (Sec. 2.18), the values of E_{act} listed in Table 3.5 were measured. In agreement with our tentative conclusions, the increasing rate of reaction along the series, methyl, 1°,

Table 3.5 ENERGIES OF ACTIVATION, KCAL/MOLE

$$R{-}H + X\cdot \longrightarrow R\cdot + H{-}X$$

R	X = Cl	X = Br
CH_3	4	18
1°	1	13
2°	0.5	10
3°	0.1	7.5

2°, 3°, is paralleled by a decreasing E_{act}. In chlorination the differences in E_{act}, like the differences in rate, are small; in bromination both differences are large.

We have seen (Sec. 2.18) that the larger the E_{act} of a reaction, the larger the increase in rate brought about by a given rise in temperature. We have just found that the differences in rate of abstraction among primary, secondary, and tertiary hydrogens are due to differences in E_{act}. We predict, therefore, that a rise in temperature should speed up abstraction of primary hydrogens (with the largest E_{act}) most, and abstraction of tertiary hydrogens (with the smallest E_{act}) least; the three classes of hydrogen should then display more nearly the same reactivity.

This leveling-out effect has indeed been observed: as the temperature is raised, the relative rates per hydrogen atom change from 5.0:3.8:1.0 toward 1:1:1. At very high temperatures virtually every collision has enough energy for abstraction of even primary hydrogens. It is generally true that *as the temperature is raised a given reagent becomes less selective in the position of its attack*; conversely, as the temperature is lowered it becomes more selective.

How can we account for the effect of structure on ease of abstraction of hydrogen atoms? Since this is a matter of E_{act}, we must look for our answer, as always, in the transition state. To do this, however, we must first shift our focus from the hydrogen atom being abstracted to the radical being formed.

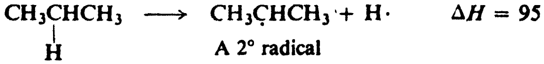
3.24 Stability of free radicals

In Table 1.2 (p. 21) we find the dissociation energies of the bonds that hold hydrogen atoms to a number of groups. These values are the ΔH's of the following reactions:

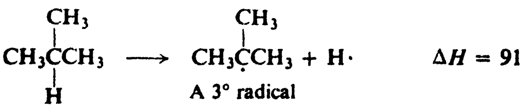
$$CH_3{-}H \longrightarrow CH_3\cdot + H\cdot \qquad \Delta H = 104 \text{ kcal}$$

$$CH_3CH_2{-}H \longrightarrow \underset{\text{A 1° radical}}{CH_3CH_2\cdot} + H\cdot \qquad \Delta H = 98$$

$$CH_3CH_2CH_2{-}H \longrightarrow \underset{\text{A 1° radical}}{CH_3CH_2CH_2\cdot} + H\cdot \qquad \Delta H = 98$$



$$CH_3\underset{H}{\underset{|}{C}}HCH_3 \longrightarrow \underset{\text{A 2° radical}}{CH_3\dot{C}HCH_3} + H\cdot \qquad \Delta H = 95$$



$$CH_3\overset{CH_3}{\overset{|}{\underset{H}{\underset{|}{C}}}}CH_3 \longrightarrow \underset{\text{A 3° radical}}{CH_3\overset{CH_3}{\overset{|}{\dot{C}}}CH_3} + H\cdot \qquad \Delta H = 91$$

By definition, bond dissociation energy is the amount of energy that must be supplied to convert a mole of alkane into radicals and hydrogen atoms. As we can see, the amount of energy needed to form the various classes of radicals decreases in the order: $CH_3\cdot > 1° > 2° > 3°$.

$$R{-}H \longrightarrow R\cdot + H\cdot \qquad \Delta H = \text{bond dissociation energy}$$

If less energy is needed to form one radical than another, it can only mean that, *relative to the alkane from which it is formed*, the one radical contains less energy than the other, that is to say, is *more stable* (see Fig. 3.6).

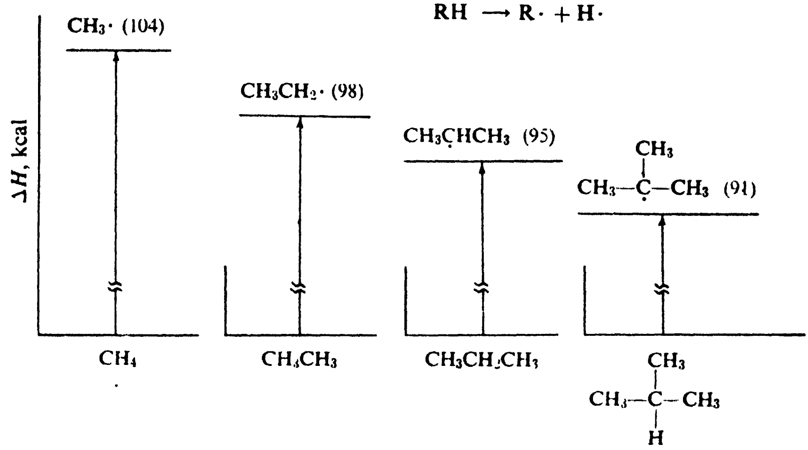


Figure 3.6. Relative stabilities of free radicals. (Plots aligned with each other for easy comparison.)

We are not attempting to compare the absolute energy contents of, say, methyl and ethyl radicals; we are simply saying that the difference in energy between methane and methyl radicals is greater than the difference between ethane and ethyl radicals. *When we compare stabilities of free radicals, it must be understood that our standard for each radical is the alkane from which it is formed.* As we shall see, this is precisely the kind of stability that we are interested in.

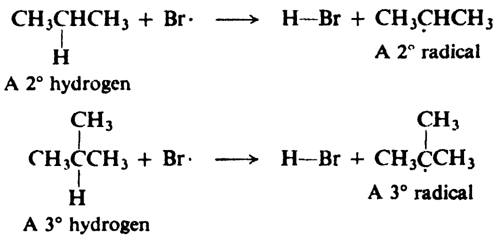
Relative to the alkane from which each is formed, then, the order of stability of free radicals is:

Stability of free radicals $3° > 2° > 1° > CH_3\cdot$

3.25 Ease of formation of free radicals

Let us return to the halogenation of alkanes. Orientation and reactivity, we have seen (Sec. 3.23), are governed by the relative ease with which the different classes of hydrogen atoms are abstracted. But by definition, the hydrogen being abstracted and the radical being formed belong to the same class. Abstraction of a primary hydrogen yields a primary radical, abstraction of a secondary hydrogen yields a secondary radical, and so on. For example:

$$\underset{\text{A 1° hydrogen}}{CH_3CH_2CH_2{-}H} + Br\cdot \longrightarrow H{-}Br + \underset{\text{A 1° radical}}{CH_3CH_2CH_2\cdot}$$



$$\underset{\text{A 2° hydrogen}}{CH_3\underset{\underset{H}{|}}{C}HCH_3} + Br\cdot \longrightarrow H{-}Br + \underset{\text{A 2° radical}}{CH_3\dot{C}HCH_3}$$

$$\underset{\text{A 3° hydrogen}}{CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}CH_3} + Br\cdot \longrightarrow H{-}Br + \underset{\text{A 3° radical}}{CH_3\overset{\overset{CH_3}{|}}{\dot{C}}CH_3}$$

If the ease of abstraction of hydrogen atoms follows the sequence $3° > 2° > 1° > CH_4$, then the ease of formation of free radicals must follow the same sequence:

Ease of formation of free radicals $3° > 2° > 1° > CH_3\cdot$

In listing free radicals in order of their ease of formation, we find that we have at the same time listed them in order of their stability. **The more stable the free radical, the more easily it is formed.**

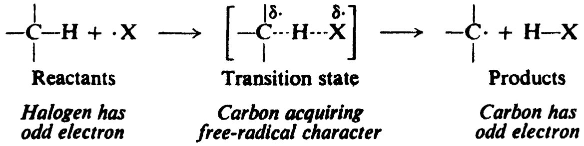
This is an extremely useful generalization. *Radical stability seems to govern orientation and reactivity in many reactions where radicals are formed.* The addition of bromine atoms to alkenes (Sec. 6.17), for example, is a quite different sort of reaction from the one we have just studied; yet, there too, orientation and reactivity are governed by radical stability. (Even in those cases where other factors—steric hindrance, polar effects—are significant or even dominant, it is convenient to use radical stability as a point of departure.)

3.26 Transition state for halogenation

Is it reasonable that the more stable radical should be formed more easily?

We have already seen that the differences in reactivity toward halogen atoms are due chiefly to differences in E_{act}: the more stable the radical, then, the lower the E_{act} for its formation. This, in turn, means that the more stable the radical, the more stable the transition state leading to its formation—both stabilities being measured, as they must be, against the same standard, the reactants. (*Remember*: E_{act} is the difference in energy content between reactants and transition state.)

Examination of the transition state shows that this is exactly what we would expect. As we saw before (Sec. 2.22), the hydrogen–halogen bond is partly formed and the carbon–hydrogen bond is partly broken. To the extent that the bond is broken, the alkyl group possesses character of the free radical it will become. *Factors that tend to stabilize the free radical tend to stabilize the incipient free radical in the transition state.*



$$-\underset{|}{\overset{|}{C}}{-}H + \cdot X \longrightarrow \left[-\underset{|}{\overset{|\delta\cdot}{C}}\cdots H\cdots \overset{\delta\cdot}{X}\right] \longrightarrow -\underset{|}{\overset{|}{C}}\cdot + H{-}X$$

We have seen that the stabilities of free radicals follow the sequence $3° > 2° > 1° > CH_3\cdot$. A certain factor (*delocalization of the odd electron*, Sec. 6.28) causes the energy difference between isobutane and the *tert*-butyl radical, for example, to be smaller than between propane and the isopropyl radical. It is not unreasonable that this same factor should cause the energy difference between isobutane and the *incipient tert*-butyl radical in the transition state to be smaller than between propane and the *incipient* isopropyl radical in its transition state (Fig. 3.7).

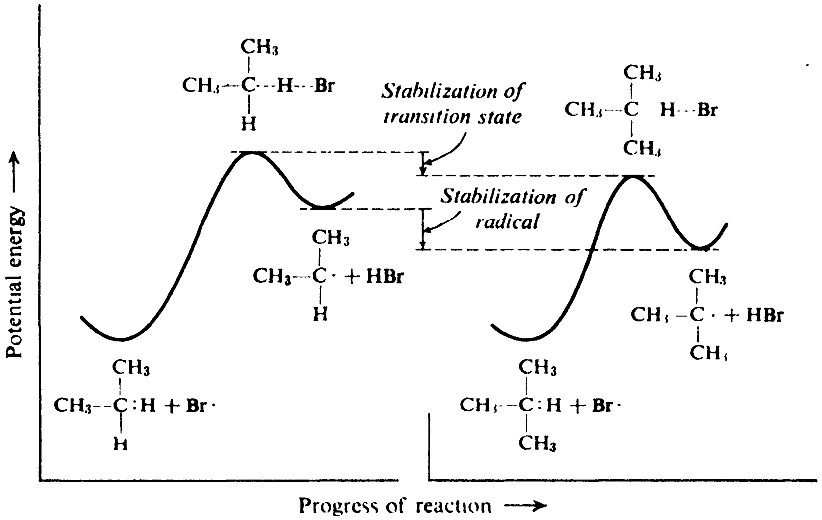


Figure 3.7. Molecular structure and rate of reaction. Stability of transition state parallels stability of radical: more stable radical formed faster. (Plots aligned with each other for easy comparison.)

3.27 Orientation and reactivity

Throughout our study of organic chemistry, we shall approach the problems of orientation and reactivity in the following way.

Both problems involve comparing the rates of closely related reactions: in the case of orientation, reactions at different sites in the same compound; in the case of reactivity, reactions with different compounds. For such closely related reactions, variations in rate are due mostly to differences in E_{act}; by definition, E_{act} is the difference in energy content between reactants and transition state.

We shall examine the most likely structure for the transition state, then, to see what structural features affect its stability without at the same time affecting by an equal amount the stability of the reactants; that is, we shall look for factors that tend to increase or decrease the energy difference between reactants and transition state. Having decided what structural features affect the E_{act}, we shall compare the transition states for the reactions whose rates we wish to compare: the more stable the transition state, the faster the reaction.

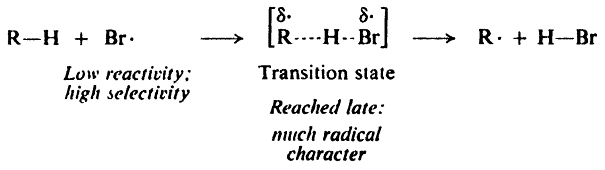
In many, if not most, reactions where a free radical is formed, as in the present case, the transition state differs from the reactants chiefly in being like the product. It is reasonable, then, that the factor most affecting the E_{act} should be the ***radical character*** of the transition state. Hence we find that the more stable the radical the more stable the transition state leading to its formation, and the faster the radical is formed.

3.28 Reactivity and selectivity

In its attack on alkanes, the bromine atom is much more selective than the chlorine atom (with relative rate factors of 1600:82:1 as compared with 5.0:3.8:1). It is also much less reactive than the chlorine atom (only 1/250,000 as reactive toward methane, for example, as we saw in Sec. 2.19). This is just one example of a general relationship: in a set of similar reactions, the *less reactive* the reagent, the *more selective* it is in its attack.

To account for this relationship, we must recall what we learned in Sec. 2.23. In the attack by the comparatively unreactive bromine atom, the transition state is reached late in the reaction process, after the alkyl group has developed considerable radical character. In the attack by the highly reactive chlorine atom, the transition state is reached early, when the alkyl group has gained very little radical character.

Bromination



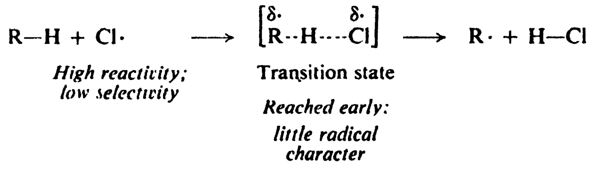
$$\mathrm{R{-}H + Br\cdot \longrightarrow \left[\overset{\delta\cdot}{R}\cdots\cdots H\cdot\cdot\overset{\delta\cdot}{Br}\right] \longrightarrow R\cdot + H{-}Br}$$

Low reactivity; high selectivity

Transition state

Reached late: much radical character

Chlorination



$$\mathrm{R{-}H + Cl\cdot \longrightarrow \left[\overset{\delta\cdot}{R}\cdot\cdot H\cdots\cdots\overset{\delta\cdot}{Cl}\right] \longrightarrow R\cdot + H{-}Cl}$$

High reactivity; low selectivity

Transition state

Reached early: little radical character

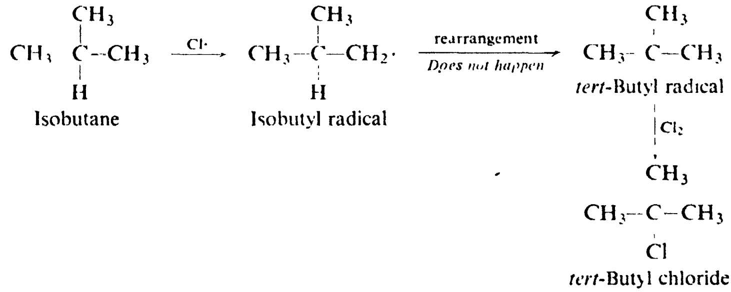
Now, by "selectivity" we mean here the differences in rate at which the various classes of free radicals are formed; a more stable free radical is formed faster, we said, because the factor that stabilizes it—delocalization of the odd electron (Sec. 6.28)—also stabilizes the incipient radical in the transition state. If this is so, then the more fully developed the radical character in the transition state, the more effective delocalization will be in stabilizing the transition state. The isopropyl radical, for example, is 3 kcal more stable than the *n*-propyl radical; if the radicals were *completely* formed in the transition state, the difference in E_{act} would be 3 kcal. Actually, in bromination the difference in E_{act} is 3 kcal: equal, within the limits of experimental error, to the maximum potential stabilization, indicating, as we expected, a great deal of radical character. In chlorination, by contrast, the difference in E_{act} is only 0.5 kcal, indicating only very slight radical character.

A similar situation exists for reactions of other kinds. Whatever the factor responsible for differences in stability among a set of transition states—whether it is delocalization of an odd electron, or accommodation of a positive or negative charge, or perhaps a change in crowding of the atoms—the factor will operate more effectively when the transition state is more fully developed, that is, when the reagent is less reactive.

3.29 Non-rearrangement of free radicals. Isotopic tracers

Our interpretation of orientation (Sec. 3.21) was based on an assumption that we have not yet justified: that the relative amounts of isomeric halides we find in the product reflect the relative rates at which various free radicals were formed from the alkane. From isobutane, for example, we obtain twice as much isobutyl chloride as *tert*-butyl chloride, and we assume from this that, by abstraction of hydrogen, isobutyl radicals are formed twice as fast as *tert*-butyl radicals.

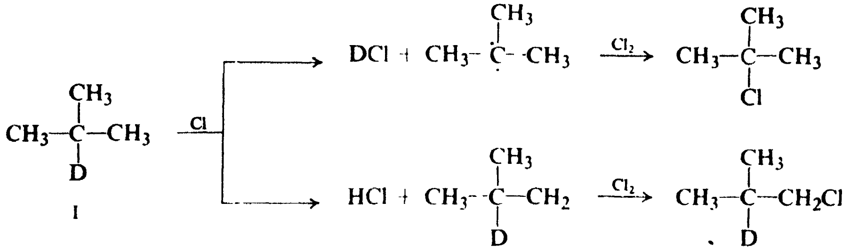
Yet how do we know, in this case, that every isobutyl radical that is formed ultimately yields a molecule of isobutyl chloride? Suppose some isobutyl radicals were to change– by *rearrangement* of atoms—into *tert*-butyl radicals, which then react with chlorine to yield *tert*-butyl chloride. This supposition is not so far-fetched as we, in our present innocence, might think; the doubt it raises is a very real one. We shall shortly see that another kind of reactive intermediate particle, the carbonium ion, is very prone to rearrange, with less stable ions readily changing into more stable ones (Sec. 5.22).



H. C. Brown (of Purdue University) and Glen Russell (now of Iowa State University) decided to test the possibility that free radicals, like carbonium ions, might rearrange, and chose the chlorination of isobutane as a good test case, because of the large difference in stability between *tert*-butyl and isobutyl radicals. If rearrangement of alkyl radicals can indeed take place, it should certainly happen here.

What the problem comes down to is this: does every abstraction of primary hydrogen lead to isobutyl chloride, and every abstraction of tertiary hydrogen lead to *tert*-butyl chloride? This, we might say, we could never know, because all hydrogen atoms are exactly alike. But are they? Actually, three isotopes of hydrogen exist: ^{1}H, *protium*, ordinary hydrogen; ^{2}H or D, *deuterium*, heavy hydrogen; and ^{3}H or T, *tritium*. Protium and deuterium are distributed in nature in the ratio of 5000:1. (Tritium, the unstable, radioactive isotope, is present in traces, but can be made by neutron bombardment of ^{6}Li.) Modern methods of separation of isotopes have made very pure deuterium available, at moderate prices, in the form of deuterium oxide, D_2O, heavy water.

Brown and Russell prepared the deuterium-labeled isobutane I,

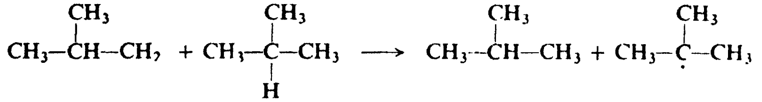


I

photochemically chlorinated it, and analyzed the products. The DCl : HCl ratio (determined by the mass spectrometer) was found to be equal (within experimental error) to the *tert*-butyl chloride : isobutyl chloride ratio. Clearly, every abstraction of a tertiary hydrogen (*deuterium*) gave a molecule of *tert*-butyl chloride, and every abstraction of a primary hydrogen (*protium*) gave a molecule of isobutyl chloride. *Rearrangement of the intermediate free radicals did not occur.*

All the existing evidence indicates quite strongly that, although rearrangement of free radicals occasionally happens, it is not very common and does not involve simple alkyl radicals.

Problem 3.18 (a) What results would have been obtained if some isobutyl radicals *had* rearranged to *tert*-butyl radicals? (b) Suppose that, instead of rearranging, isobutyl radicals were, in effect, converted into *tert*-butyl radicals by the reaction



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_2\cdot + CH_3-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3 \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}H-CH_3 + CH_3-\underset{\cdot}{\overset{\displaystyle CH_3}{\overset{|}{C}}}-CH_3$$

What results would Brown and Russell have obtained?

Problem 3.19 Keeping in mind the availability of D_2O, suggest a way to make I from *tert*-butyl chloride. (*Hint:* See Sec. 3.16.)

The work of Brown and Russell is just one example of the way in which we can gain insight into a chemical reaction by using isotopically labeled compounds. We shall encounter many other examples in which isotopes, used either as *tracers*, as in this case, or for the detection of *isotope effects* (Sec. 11.15), give us information about reaction mechanisms that we could not get in any other way.

Besides deuterium and tritium, isotopes commonly used in organic chemistry include: ^{14}C, available as $^{14}CH_3OH$ and $Ba^{14}CO_3$; ^{18}O, as $H_2{}^{18}O$; ^{15}N, as $^{15}NH_3$, $^{15}NO_3{}^-$, and $^{15}NO_2{}^-$; ^{36}Cl, as chlorine or chloride; ^{131}I, as iodide.

Problem 3.20 Bromination of methane is slowed down by the addition of HBr (Problem 14, p. 71); this is attributed to the reaction

$$CH_3\cdot + HBr \longrightarrow CH_4 + Br\cdot$$

which, as the reverse of one of the chain-carrying steps, slows down bromination. How might you test whether or not this reaction actually occurs in the bromination mixture?

Problem 3.21 In Sec. 2.12 the reaction

$$\text{Cl}\cdot + \text{Cl}_2 \longrightarrow \text{Cl}_2 + \text{Cl}\cdot$$

was listed as probable but unproductive. Given ordinary chlorine (made up of ^{35}Cl and ^{37}Cl) and ^{36}Cl$_2$, and a mass spectrometer, how would you go about finding out whether or not the reaction actually occurs?

3.30 Combustion

The reaction of alkanes with oxygen to form carbon dioxide, water, and—most important of all—*heat*, is the chief reaction occurring in the internal combustion engine; its tremendous practical importance is obvious.

The mechanism of this reaction is extremely complicated and is not yet fully understood. There seems to be no doubt, however, that it is a free-radical chain reaction. The reaction is extremely exothermic and yet requires a very high temperature, that of a flame, for its initiation. As in the case of chlorination, a great deal of energy is required for the bond-breaking that generates the initial reactive particles; once this energy barrier is surmounted, the subsequent chain-carrying steps proceed readily and with the evolution of energy.

A higher compression ratio has made the modern gasoline engine more efficient than earlier ones, but has at the same time created a new problem. Under certain conditions the smooth explosion of the fuel-air mixture in the cylinder is replaced by **knocking**, which greatly reduces the power of the engine.

The problem of knocking has been successfully met in two general ways: (a) proper selection of the hydrocarbons to be used as fuel, and (b) addition of tetraethyllead.

Experiments with pure compounds have shown that hydrocarbons of differing structures differ widely in knocking tendency. The relative antiknock tendency of a fuel is generally indicated by its **octane number**. An arbitrary scale has been set up, with *n*-heptane, which knocks very badly, being given an octane number of zero, and 2,2,4-trimethylpentane ("iso-octane") being given the octane number of 100. There are available today fuels with better antiknock qualities than "iso-octane."

The gasoline fraction obtained by direct distillation of petroleum (*straight-run gasoline*) is improved by addition of compounds of higher octane number; it is sometimes entirely replaced by these better fuels. Branched-chain alkanes and alkenes, and aromatic hydrocarbons generally have excellent antiknock qualities; these are produced from petroleum hydrocarbons by *catalytic cracking* (Sec. 3.31) and *catalytic reforming* (Sec. 12.4). Highly branched alkanes are synthesized from alkenes and alkanes by *alkylation* (Sec. 6.16).

In 1922 T. C. Midgley, Jr., and T. A. Boyd (of the General Motors Research Laboratory) found that the octane number of a fuel is greatly improved by addition of a small amount of tetraethyllead, $(C_2H_5)_4Pb$. Gasoline so treated is called *ethyl* gasoline or *leaded* gasoline. Nearly 50 years of research has finally shown that tetraethyllead probably works by producing tiny particles of lead oxides, on whose surface certain reaction chains are broken.

In addition to carbon dioxide and water, however, the gasoline engine discharges other substances into the atmosphere, substances that are either smogproducing or downright poisonous: unburned hydrocarbons, carbon monoxide, nitrogen oxides, and, from leaded gasoline, various compounds of lead—in the United States, hundreds of tons of lead a day. Growing public concern about these pollutants has caused a minor revolution in the petroleum and auto industries. *Converters* are being developed to clean up exhaust emissions: by catalytic oxidation of hydrocarbons and carbon monoxide, and by the breaking down of nitrogen oxides into nitrogen and oxygen. But most of these oxidation catalysts contain platinum, which is poisoned by lead; there has been a move to get the lead out of gasoline—not, initially, to cut down on lead pollution, but to permit converters to function. This has, in turn, brought back the problem of knocking, which is being met in two ways: (a) by lowering the compression ratio of the new automobiles being built; and (b) by increasing the octane number of gasoline through changes in hydrocarbon composition—through addition of aromatics and through increased use of isomerization (Sec. 3.13).

3.31 Pyrolysis: cracking

Decomposition of a compound by the action of heat alone is known as **pyrolysis**. This word is taken from the Greek *pyr*, fire, and *lysis*, a loosing, and hence to chemists means "cleavage by heat"; compare *hydro-lysis*, "cleavage by water."

The pyrolysis of alkanes, particularly when petroleum is concerned, is known as **cracking**. In *thermal cracking* alkanes are simply passed through a chamber heated to a high temperature. Large alkanes are converted into smaller alkanes, alkenes, and some hydrogen. This process yields predominantly ethylene (C_2H_4) together with other small molecules. In a modification called *steam cracking*, the hydrocarbon is diluted with steam, heated for a fraction of a second to 700–900°, and rapidly cooled. Steam cracking is of growing importance in the production of hydrocarbons as chemicals, including ethylene, propylene, butadiene, isoprene, and cyclopentadiene. Another source of smaller hydrocarbons is *hydrocracking*, carried out in the presence of hydrogen at high pressure and at much lower temperatures (250–450°).

The low-molecular-weight alkenes obtained from these cracking processes can be separated and purified, and are the most important raw materials for the large-scale synthesis of aliphatic compounds.

Most cracking, however, is directed toward the production of fuels, not chemicals, and for this *catalytic cracking* is the major process. Higher boiling petroleum fractions (typically, gas oil), are brought into contact with a finely divided silica-alumina catalyst at 450–550° and under slight pressure. Catalytic cracking not only increases the yield of gasoline by breaking large molecules into smaller ones, but also improves the quality of the gasoline: this process involves *carbonium ions* (Sec. 5.15), and yields alkanes and alkenes with the highly branched structures desirable in gasoline.

Through the process of *alkylation* (Sec. 6.16) some of the smaller alkanes and alkenes are converted into high-octane synthetic fuels.

Finally, by the process of *catalytic reforming* (Sec. 12.4) enormous quantities of the aliphatic hydrocarbons of petroleum are converted into *aromatic* hydro carbons which are used not only as superior fuels but as the starting materials in the synthesis of most aromatic compounds (Chap. 10).

3.32 Determination of structure

One of the commonest and most important jobs in organic chemistry is to determine the structural formula of a compound just synthesized or isolated from a natural source.

The compound will fall into one of two groups, although at first we probably shall not know *which* group. It will be either (a) a previously reported compound, which we must identify, or (b) a new compound, whose structure we must prove.

If the compound has previously been encountered by some other chemist who determined its structure, then a description of its properties will be found somewhere in the chemical literature, together with the evidence on which its structure was assigned. In that case, we need only to show that our compound is identical with the one previously described.

If, on the other hand, our compound is a new one that has never before been reported, then we must carry out a much more elaborate proof of structure.

Let us see—in a general way now, and in more detail later—just how we would go about this job. We are confronted by a flask filled with gas, or a few milliliters of liquid, or a tiny heap of crystals. We must find the answer to the question: *what is it?*

First, we purify the compound and determine its physical properties: melting point, boiling point, density, refractive index, and solubility in various solvents. In the laboratory today, we would measure various spectra of the compound (Chap. 13), in particular the infrared spectrum and the nmr spectrum; indeed, because of the wealth of information to be gotten in this way, spectroscopic examination might well be the first order of business after purification. From the mass spectrum we would get a very accurate molecular weight.

We would carry out a qualitative elemental analysis to see what elements are present (Sec. 2.25). We might follow this with a quantitative analysis, and from this and the molecular weight we could calculate a molecular formula (Sec. 2.26); we would certainly do this if the compound is suspected of being a new one.

Next, we study systematically the behavior of the compound toward certain reagents. This behavior, taken with the elemental analysis, solubility properties, and spectra, generally permits us to *characterize* the compound, that is, to decide what family the unknown belongs to. We might find, for example, that the compound is an alkane, or that it is an alkene, or an aldehyde, or an ester.

Now the question is: *which* alkane is it? Or which alkene, or which aldehyde, or which ester? To find the answer, we first go to the chemical literature and look up compounds of the particular family to which our unknown belongs.

If we find one described whose physical properties are identical with those of our unknown, then the chances are good that the two compounds are identical. For confirmation, we generally convert the unknown by a chemical reaction into a new compound called a **derivative**, and show that this derivative is identical with the product derived in the same way from the previously reported compound.

If, on the other hand, we do not find a compound described whose physical properties are identical with those of our unknown, then we have a difficult job on our hands: we have a new compound, and must prove its structure. We may carry out a *degradation*: break the molecule apart, identify the fragments, and deduce what the structure must have been. To clinch any proof of structure, we attempt to *synthesize* the unknown by a method that leaves no doubt about its structure.

Problem 3.22 The final step in the proof of structure of an unknown alkane was its synthesis by the coupling of lithium di(*tert*-butyl)copper with *n*-butyl bromide. What was the alkane?

In Chap. 13, after we have become familiar with more features of organic structure, we shall see how spectroscopy fits into the general procedure outlined above.

3.33 Analysis of alkanes

An unknown compound is characterized as an alkane on the basis of negative evidence.

Upon qualitative elemental analysis, an alkane gives negative tests for all elements except carbon and hydrogen. A quantitative combustion, if one is carried out, shows the absence of oxygen; taken with a molecular weight determination, the combustion gives the molecular formula, C_nH_{2n+2}, which is that of an alkane.

An alkane is insoluble not only in water but also in dilute acid and base and in concentrated sulfuric acid. (As we shall see, most kinds of organic compounds dissolve in one or more of these solvents.)

An alkane is unreactive toward most chemical reagents. Its infrared spectrum lacks the absorption bands characteristic of groups of atoms present in other families of organic compounds (like OH, C=O, C=C, etc.).

Once the unknown has been characterized as an alkane, there remains the second half of the problem: finding out *which* alkane.

On the basis of its physical properties—boiling point, melting point, density, refractive index, and, most reliable of all, its infrared and mass spectra—it may be identified as a previously studied alkane of known structure.

If it turns out to be a new alkane, the proof of structure can be a difficult job. Combustion and molecular weight determination give its molecular formula. Clues about the arrangement of atoms are given by its infrared and nmr spectra. (For compounds like alkanes, it may be necessary to lean heavily on x-ray diffraction and mass spectrometry.)

Final proof lies in synthesis of the unknown by a method that can lead only to the particular structure assigned.

(The spectroscopic analysis of alkanes will be discussed in Secs. 13.15–13.16.)

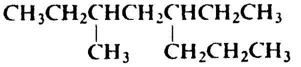
PROBLEMS

1. Give the structural formula of:

(a) 2,2,3,3-tetramethylpentane
(b) 2,3-dimethylbutane
(c) 3,4,4,5-tetramethylheptane
(d) 3,4-dimethyl-4-ethylheptane
(e) 2,4-dimethyl-4-ethylheptane
(f) 2,5-dimethylhexane
(g) 2-methyl-3-ethylpentane
(h) 2,2,4-trimethylpentane

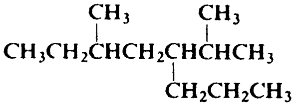
2. Draw out the structural formula and give the IUPAC name of:

(a) $(CH_3)_2CHCH_2CH_2CH_3$
(b) $CH_3CH_2C(CH_3)_2CH_2CH_3$
(c) $(C_2H_5)_2C(CH_3)CH_2CH_3$
(d) $CH_3CH_2CH(CH_3)CH(CH_3)CH(CH_3)_2$
(e)



$CH_3CH_2\underset{CH_3}{CH}CH_2\underset{CH_2CH_2CH_3}{CH}CH_2CH_3$

(f) $(CH_3)_3CCH_2C(CH_3)_3$
(g) $(CH_3)_2CHCH_2CH_2CH(C_2H_5)_2$
(h) $(CH_3)_2CHCH(CH_3)CH_2C(C_2H_5)_2CH_3$
(i) $(CH_3)_2CHC(C_2H_5)_2CH_2CH_2CH_3$
(j)



$CH_3CH_2\overset{CH_3}{CH}CH_2\underset{CH_2CH_2CH_3}{CH}\overset{CH_3}{CH}CH_3$

3. Pick out a compound in Problem 1 or 2 that has: (a) no tertiary hydrogen; (b) one tertiary hydrogen; (c) two tertiary hydrogens; (d) no secondary hydrogen; (e) two secondary hydrogens; (f) half the number of secondary hydrogens as primary hydrogens.

4. Pick out a compound (if any) in Problem 1 or 2 that contains:

(a) one isopropyl group
(b) two isopropyl groups
(c) one isobutyl group
(d) two isobutyl groups
(e) one *sec*-butyl group
(f) two *sec*-butyl groups
(g) one *tert*-butyl group
(h) two *tert*-butyl groups
(i) an isopropyl group and a *sec*-butyl group
(j) a *tert*-butyl group and an isobutyl group
(k) a methyl, an ethyl, a *n*-propyl, and a *sec*-butyl group

5. What alkane or alkanes of molecular weight 86 have: (a) two monobromo derivatives? (b) three? (c) four? (d) five? (e) How many dibromo derivatives does the alkane in (a) have?

6. How many mono-, di-, and trichloro derivatives are possible for cyclopentane? (Structure given in Sec. 9.5.)

7. Without referring to tables, list the following hydrocarbons in order of decreasing boiling points (i.e., highest boiling at top, lowest at bottom):

(a) 3,3-dimethylpentane
(b) *n*-heptane
(c) 2-methylheptane
(d) *n*-pentane
(e) 2-methylhexane

8. Write balanced equations, naming all organic products, for the following reactions:

(a) isobutyl bromide + Mg/ether
(b) *tert*-butyl bromide + Mg/ether
(c) product of (a) + H_2O
(d) product of (b) + H_2O
(e) product of (a) + D_2O
(f) *sec*-butyl chloride + Li, then CuI
(g) product of (f) + ethyl bromide

9. Write equations for the preparation of *n*-butane from:

(a) *n*-butyl bromide
(b) *sec*-butyl bromide
(c) ethyl chloride
(d) 1-butene, $CH_3CH_2CH{=}CH_2$
(e) 2-butene, $CH_3CH{=}CHCH_3$

10. Draw structures of all products expected from monochlorination at room temperature of:

(a) *n*-hexane
(b) isohexane
(c) 2,2,4-trimethylpentane
(d) 2,2-dimethylbutane

11. Predict the proportions of products in the previous problem.

12. (a) Reaction of an aldehyde with a Grignard reagent is an important way of making alcohols. Why must one scrupulously dry the aldehyde before adding it to the Grignard reagent? (b) Why would one not prepare a Grignard reagent from $BrCH_2CH_2OH$?

13. On the basis of bond strengths in Table 1.2, page 21, add the following free radicals to the stability sequence of Sec. 3.24:

(a) *vinyl*, $H_2C{=}CH\cdot$
(b) *allyl*, $H_2C{=}CHCH_2\cdot$
(c) *benzyl*, $C_6H_5CH_2\cdot$

Check your answer on page 211.

14. On the basis of your answer to Problem 13, predict how the following would fit into the sequence (Sec. 3.23) that shows ease of abstraction of hydrogen atoms:

(a) *vinylic* hydrogen, $H_2C{=}CH{-}H$
(b) *allylic* hydrogen, $H_2C{=}CHCH_2{-}H$
(c) *benzylic* hydrogen, $C_6H_5CH_2{-}H$

Check your answer against the facts on page 210.

15. Free-radical chlorination of *either* *n*-propyl or isopropyl bromide gives 1-bromo-2-chloropropane, and of *either* isobutyl or *tert*-butyl bromide gives 1-bromo-2-chloro-2-methylpropane. What appears to be happening? Is there any pattern to this behavior?

16. (a) If a rocket were fueled with kerosene and liquid oxygen, what weight of oxygen would be required for every liter of kerosene? (Assume kerosene to have the average composition of n-$C_{14}H_{30}$.) (b) How much heat would be evolved in the combustion of one liter of kerosene? (Assume 157 kcal/mole for each $-CH_2-$ group and 186 kcal/mole for each $-CH_3$ group.) (c) If it were to become feasible to fuel a rocket with free hydrogen atoms, what weight of fuel would be required to provide the same heat as a liter of kerosene and the necessary oxygen? (Assume H_2 as the sole product.)

17. By what two quantitative methods could you show that a product isolated from the chlorination of propane was a monochloro or a dichloro derivative of propane? Tell exactly what results you would expect from each of the methods.

18. On the basis of certain evidence, including its infrared spectrum, an unknown compound of formula $C_{10}H_{22}$ is suspected of being 2,7-dimethyloctane. How could you confirm or disprove this tentatively assigned structure?

19. (a) A solution containing an unknown amount of methyl alcohol (CH_3OH) dissolved in *n*-octane is added to an excess of methylmagnesium iodide dissolved in the high-boiling solvent, *n*-butyl ether. A gas is evolved, and is collected and its volume measured: 1.04 cc (corrected to STP). What is the gas, and how is it formed? What weight of methyl alcohol was added to the Grignard reagent?

(b) A sample of 4.12 mg of an unknown alcohol, ROH, is added to methylmagnesium iodide as above; there is evolved 1.56 cc of gas (corrected to STP). What is the molecular weight of the alcohol? Suggest a possible structure or structures for the alcohol.

(c) A sample of 1.79 mg of a compound of mol. wt. about 90 gave 1.34 ml of the gas (corrected to STP). How many "active (that is, acidic) hydrogens" are there per molecule? Assuming all these to be in $-OH$ groups, suggest a structure for the alcohol. (This is an example of the *Zerewitinoff active hydrogen determination*.)

20. (a) *tert*-Butyl peroxide is a stable, easy-to-handle liquid that serves as a convenient source of free radicals:

$$(CH_3)_3CO{-}OC(CH_3)_3 \xrightarrow[\text{or light}]{130^\circ} 2(CH_3)_3CO\cdot$$

A mixture of isobutane and CCl_4 is quite stable at 130–140°. If a small amount of *tert*-butyl peroxide is added, a reaction occurs that yields (chiefly) *tert*-butyl chloride and chloroform. A small amount of *tert*-butyl alcohol ($(CH_3)_3COH$, equivalent to the peroxide used) is also isolated. Give all steps in a likely mechanism for this reaction.

(b) When irradiated with ultraviolet light, or in the presence of a small amount of peroxides, *tert*-butyl hypochlorite, $(CH_3)_3C{-}O{-}Cl$, reacts with alkanes to form, in equimolar amounts, alkyl chlorides and *tert*-butyl alcohol. Outline all steps in a likely mechanism for this reaction.

Chapter

4

Stereochemistry I. Stereoisomers

4.1 Stereochemistry and stereoisomerism

The science of organic chemistry, we said, is based on the relationship between molecular structure and properties. That part of the science which deals with structure *in three dimensions* is called **stereochemistry** (Gr.: *stereos*, solid).

One aspect of stereochemistry is *stereoisomerism*. Isomers, we recall, are different compounds that have the same molecular formula. The particular kind of isomers that are different from each other *only* in the way the atoms are oriented in space (but are like one another with respect to which atoms are joined to which other atoms) are called **stereoisomers.**

Pairs of stereoisomers exist that differ so little in structure—and hence in properties that of all the physical measurements we can make, only one, involving a special instrument and an unusual kind of light, can distinguish between them. Yet, despite this close similarity, the existence of such stereoisomers provides us with one of our most sensitive probes into mechanisms of chemical reactions; very often, one of these isomers is selected for study, not because it is different from ordinary compounds in its three-dimensional chemistry, but because it can be made to reveal what ordinary compounds hide. And, again despite their close similarity, one isomer of such a pair may serve as a nourishing food, or as an antibiotic, or as a powerful heart stimulant, and the other isomer may be useless.

In this chapter, we shall learn how to predict the existence of the kinds of stereoisomers called *enantiomers* and *diastereomers*, how to represent and designate their structures, and, in a general way, how their properties will compare. Then, in following chapters, we shall begin to use what we learn in this one. In Secs. 5.5–5.6, we shall learn about the kind of stereoisomers called *geometric isomers*. In Chapter 7, the emphasis will shift from what these stereoisomers *are*, to how they are formed, what they do, and what they can tell us.

We have already (Secs. 3.3 and 3.5) begun our study of the branch of stereochemistry called *conformational analysis*; we shall return to it, especially in Chap. 9, and make use of it throughout the rest of the book.

4.2 Isomer number and tetrahedral carbon

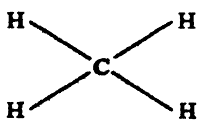
Let us begin our study of stereochemistry with methane and some of its simple substitution products. Any compound, however complicated, that contains carbon bonded to four other atoms can be considered to be a derivative of methane; and whatever we learn about the shape of the methane molecule can be applied to the shapes of vastly more complicated molecules.

The evidence of electron diffraction, X-ray diffraction, and spectroscopy shows that when carbon is bonded to four other atoms its bonds are directed toward the corners of a tetrahedron. But as early as 1874, years before the direct determination of molecular structure was possible, the tetrahedral carbon atom was proposed by J. H. van't Hoff, while he was still a student at the University of Utrecht. His proposal was based upon the evidence of **isomer number**.

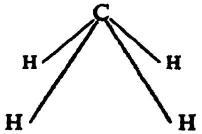
For any atom Y, *only one substance of formula* CH_3Y *has ever been found.* Chlorination of methane yields only one compound of formula CH_3Cl; brominations yields only one compound of formula CH_3Br. Similarly, only one CH_3F is known, and only one CH_3I. Indeed, the same holds true if Y represents, not just an atom, but a group of atoms (unless the group is so complicated that in itself it brings about isomerism); there is only one CH_3OH, only one CH_3COOH, only one CH_3SO_3H.

What does this suggest about the arrangement of atoms in methane? It suggests that every hydrogen atom in methane is equivalent to every other hydrogen atom, so that replacement of any one of them gives rise to the same product. If the hydrogen atoms of methane were not equivalent, then replacement of one would yield a different compound than replacement of another, and isomeric substitution products would be obtained.

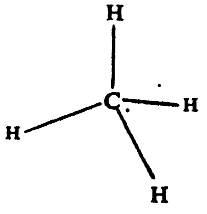
In what ways can the atoms of methane be arranged so that the four hydrogen atoms are equivalent? There are three such arrangements: (a) a *planar* arrangement (I) in which carbon is at the center of a rectangle (or square) and a hydrogen atom is at each corner; (b) a *pyramidal* arrangement (II) in which carbon is at the apex of a pyramid and a hydrogen atom is at each corner of a square base; (c) a *tetrahedral* arrangement (III) in which carbon is at the center of a tetrahedron and a hydrogen atom is at each corner.



I



II



III

How do we know that each of these arrangements could give rise to only one substance of formula CH_3Y? As always for problems like this, the answer lies in the use of molecular models. (Gumdrops and toothpicks can be used to make structures like I and II, for which the bond angles of ordinary molecular models are not suited.) For example, we make two identical models of I. In one model we replace, say, the upper right-hand H with a different atom Y, represented by a differently colored ball or gumdrop; in the other model we similarly replace, say, the lower right-hand H. We next see whether or not the two resulting models are *superimposable*; that is, we see whether or not, by any manipulations except bending or breaking bonds, we can make the models coincide in all their parts. If the two models are superimposable, they simply represent two molecules of the same compound; if the models are not superimposable, they represent molecules of different compounds which, since they have the same molecular formula, are by definition *isomers* (p. 37). Whichever hydrogen we replace in I (or in II or III), we get the same structure. From any arrangement other than these three, we would get more than one structure.

As far as compounds of the formula CH_3Y are concerned, the evidence of isomer number limits the structure of methane to one of these three possibilities.

Problem 4.1 How many isomers of formula CH_3Y would be possible if methane were a pyramid with a *rectangular* base? What are they? (*Hint:* If you have trouble with this question now, try it again after you have studied Sec. 4.7.)

For any atom Y *and for any atom* Z, *only one substance of formula* CH_2YZ *has ever been found.* Halogenation of methane, for example, yields only one compound of formula CH_2Cl_2, only one compound of formula CH_2Br_2, and only one compound of formula CH_2ClBr.

Of the three possible structures of methane, only the tetrahedral one is consistent with this evidence.

Problem 4.2 How many isomers of formula CH_2YZ would be expected from each of the following structures for methane? (a) Structure I with carbon at the center of a rectangle; (b) structure I with carbon at the center of a square; (c) structure II; (d) structure III.

Thus, only the tetrahedral structure for methane agrees with the evidence of isomer number. It is true that this is negative evidence; one might argue that isomers exist which have never been isolated or detected simply because the experimental techniques are not good enough. But, as we said before, any compound that contains carbon bonded to four other atoms can be considered to be a derivative of methane; in the preparation of hundreds of thousands of compounds of this sort, the number of isomers obtained has always been consistent with the concept of the tetrahedral carbon atom.

There is additional, positive evidence for the tetrahedral carbon atom: the finding of just the kind of isomers—*enantiomers*—that are predicted for compounds of formula CWXYZ. It was the existence of enantiomers that convinced van't Hoff that the carbon atom is tetrahedral. But to understand what enantiomers are, we must first learn about the property called *optical activity*.

4.3 Optical activity. Plane-polarized light

Light possesses certain properties that are best understood by considering it to be a wave phenomenon in which the vibrations occur at right angles to the direction in which the light travels. There are an infinite number of planes passing through the line of propagation, and ordinary light is vibrating in all these planes. If we consider that we are looking directly into the beam of a flashlight, Fig. 4.1

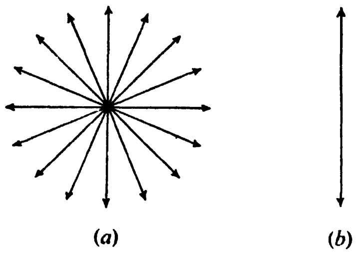


Figure 4.1. Schematic representation of (*a*) ordinary light and (*b*) plane-polarized light. Light traveling perpendicular to page; vibrations in plane of page.

shows schematically the sort of vibrations that are taking place, all perpendicular to a line between our eye and the paper (flashlight). **Plane-polarized light** *is light whose vibrations take place in only one of these possible planes.* Ordinary light is turned into plane-polarized light by passing it through a lens made of the material known as Polaroid or more traditionally through pieces of *calcite* (a particular crystalline form of $CaCO_3$) so arranged as to constitute what is called a *Nicol prism.*

An **optically active substance** *is one that rotates the plane of polarized light.* When polarized light, vibrating in a certain plane, is passed through an optically active substance, it emerges vibrating in a different plane.

4.4 The polarimeter

How can this rotation of the plane of polarized light—this optical activity—be detected? It is both detected and measured by an instrument called the **polarimeter**, which is represented schematically in Fig. 4.2. It consists of a light source, two lenses (Polaroid or Nicol), and between the lenses a tube to hold the substance that is being examined for optical activity. These are arranged so that the light

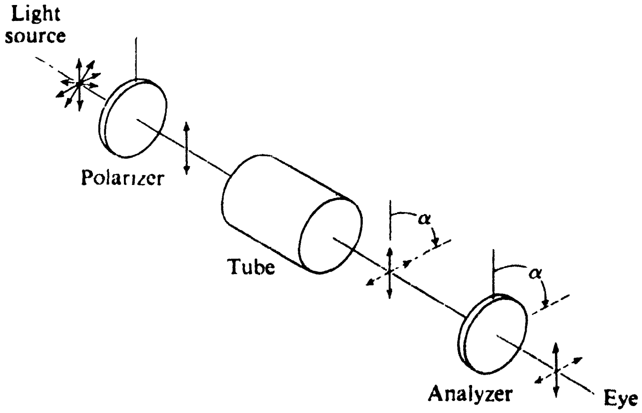


Figure 4.2. Schematic representation of a polarimeter. Solid lines: before rotation. Broken lines: after rotation. α is angle of rotation.

passes through one of the lenses (*polarizer*), then the tube, then the second lens (*analyzer*), and finally reaches our eye. When the tube is empty, we find that the maximum amount of light reaches our eye when the two lenses are so arranged that they pass light vibrating in the same plane. If we rotate the lens that is nearer our eye, say, we find that the light dims, and reaches a minimum when the lens is at right angles to its previous position.

Let us adjust the lenses so that a maximum amount of light is allowed to pass. (In practice, it is easier to detect a minimum than a maximum; the principle remains the same.) Now let us place the sample to be tested in the tube. If the substance does not affect the plane of polarization, light transmission is still at a maximum and the substance is said to be **optically inactive**. If, on the other hand, the substance rotates the plane of polarization, then the lens nearer our eye must be rotated to conform with this new plane if light transmission is again to be a maximum, and the substance is said to be **optically active**. If the rotation of the plane, and hence our rotation of the lens, is to the right (clockwise), the substance is **dextrorotatory** (Latin: *dexter*, right); if the rotation is to the left (counterclockwise), the substance is **levorotatory** (Latin: *laevus*, left).

We can determine not only that the substance has rotated the plane, and in which direction, but also *by how much*. The amount of rotation is simply the number of degrees that we must rotate the lens to conform with the light. The symbols **+** and **−** are used to indicate rotations to the right and to the left, respectively.

The lactic acid (p. 121) that is extracted from muscle tissue rotates light to the right, and hence is known as *dextrorotatory* lactic acid, or (+)-lactic acid. The 2-methyl-1-butanol that is obtained from fusel oil (a by-product of the fermentation of starch to ethyl alcohol) rotates light to the left, and is known as *levorotatory* 2-methyl-1-butanol, or (−)-2-methyl-1-butanol.

4.5 Specific rotation

Since optical rotation of the kind we are interested in is caused by individual molecules of the active compound, *the amount of rotation depends upon how many molecules the light encounters in passing through the tube.*

The light will encounter twice as many molecules in a tube 20 cm long as in a tube 10 cm long, and the rotation will be twice as large. If the active compound is in solution, the number of molecules encountered by the light will depend upon the concentration. For a given tube length, light will encounter twice as many molecules in a solution of 2 g per 100 cc of solvent as in a solution containing 1 g per 100 cc of solvent, and the rotation will be twice as large. When allowances are made for the length of tube and the concentration, it is found that the amount of rotation, as well as its direction, is a characteristic of each individual optically active compound.

Specific rotation is the number of degrees of rotation observed if a 1-decimeter tube is used, and the compound being examined is present to the extent of 1g/cc. This is usually calculated from observations with tubes of other lengths and at different concentrations by means of the equation

$$[\alpha] = \frac{\alpha}{l \times d}$$

$$\text{specific rotation} = \frac{\text{observed rotation (degrees)}}{\text{length (dm)} \times \text{g/cc}}$$

where *d* represents density for a pure liquid or concentration for a solution.

The specific rotation is as much a property of a compound as its melting point, boiling point, density, or refractive index. Thus the specific rotation of the 2-methyl-1-butanol obtained from fusel oil is

$$[\alpha]_D^{20} = -5.756°$$

Here 20 is the temperature and D is the wavelength of the light used in the measurement (*D* line of sodium, 5893 A).

Problem 4.3 The concentration of cholesterol dissolved in chloroform is 6.15 g per 100 ml of solution. (a) A portion of this solution in a 5-cm polarimeter tube causes an observed rotation of −1.2°. Calculate the specific rotation of cholesterol. (b) Predict the observed rotation if the same solution were placed in a 10-cm tube (c) Predict the observed rotation if 10 ml of the solution were diluted to 20 ml and placed in a 5-cm tube.

Problem 4.4 A sample of a pure liquid in a 10-cm tube is placed in a polarimeter, and a reading of +45° is made. How could you establish that [α] is really +45° and not −315°? That it is +45° and not +405° or, for that matter, +765°?

4.6 Enantiomerism: the discovery

The optical activity we have just described was discovered in 1815 at the Collège de France by the physicist Jean-Baptiste Biot.

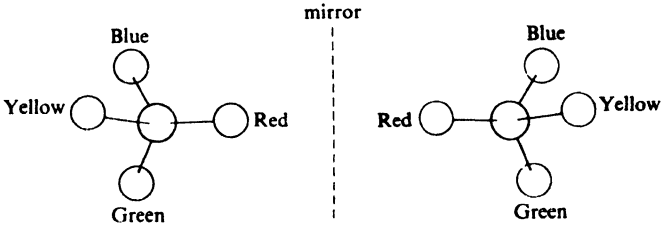
In 1848 at the École normale in Paris the chemist Louis Pasteur made a set of observations which led him a few years later to make a proposal that is the foundation of stereochemistry. Pasteur, then a young man, had come to the École normale from the Royal College of Besançon (where he had received his *baccalaurent ès sciences* with the rating of *médiocre* in chemistry), and had just won his *docteur ès sciences.* To gain some experience in crystallography, he was repeating another chemist's earlier work on salts of tartaric acid when he saw something that no one had noticed before: optically inactive sodium ammonium tartrate existed as a mixture of two different kinds of crystals, which were *mirror images* of each other. Using a hand lens and a pair of tweezers, he carefully and laboriously separated the mixture into two tiny piles—one of right-handed crystals and the other of left-handed crystals—much as one might separate right-handed and left-handed gloves lying jumbled together on a shop counter. Now, although the original mixture was optically inactive, each set of crystals dissolved in water was found to be *optically active*! Furthermore, the specific rotations of the two solutions were exactly *equal, but of opposite sign*: that is to say, one solution rotated plane-polarized light to the right, and the other solution an equal number of degrees to the left. In all other properties the two substances were identical.

Since the difference in optical rotation was observed *in solution*, Pasteur concluded that it was characteristic, not of the crystals, but of the *molecules*. He proposed that, like the two sets of crystals themselves, the molecules making up the crystals were *mirror images of each other*. He was proposing the existence of isomers whose structures differ only in being mirror images of each other, and whose properties differ only in the direction of rotation of polarized light.

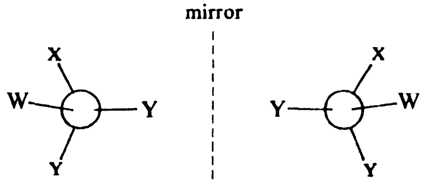
There remained only for van't Hoff to point out that a *tetrahedral* carbon atom would account not only for the absence of isomers of formula CH_3Y and CH_2YZ, but also for the existence of mirror-image isomers—*enantiomers*—like Pasteur's tartaric acids.

4.7 Enantiomerism and tetrahedral carbon

Let us convince ourselves that such mirror-image isomers should indeed exist. Starting with the actual, tetrahedral arrangement for methane, let us make a model of a compound CWXYZ, using a ball of a different color for each different atom or group represented as W, X, Y, and Z. Let us then imagine that we are holding this model before a mirror, and construct a second model of what its mirror image would look like. We now have two models which look something like this:



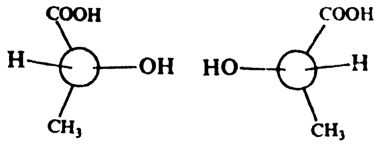
which are understood to stand for this:



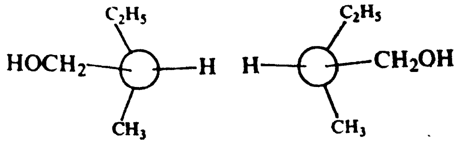
Not superimposable: isomers

Are these two models superimposable? *No.* We may twist and turn them as much as we please (so long as no bonds are broken), but although two groups of each may coincide, the other two do not. The models are not superimposable, and therefore must represent two isomers of formula CWXYZ.

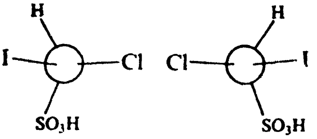
As predicted, mirror-image isomers do indeed exist, and thousands of instances besides the tartaric acids are known. There are, for example, two isomeric *lactic acids* and two *2-methyl-1-butanols*, two *chloroiodomethanesulfonic acids* and two *sec-butyl chlorides*.



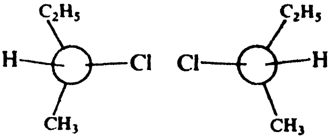
Lactic acid



2-Methyl-1-butanol



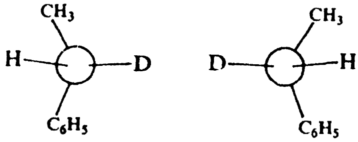
Chloroiodomethanesulfonic acid



sec-Butyl chloride

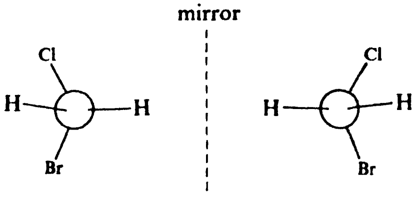
As we can see, the structures of each pair are mirror images; as we can easily verify by use of models, the structures of each pair are not superimposable and therefore represent isomers. (In fact, we have *already* verified this, since the models we made for CWXYZ can, of course, stand for any of these.)*

At this point we do not need to know the chemistry of these compounds, or even what structure a particular collection of letters (—COOH, say, or —CH_2OH) stands for; we can tell when atoms or groups are the *same* or *different* from each other, and whether or not a model can be superimposed on its mirror image. Even two isotopes of the same element, like protium (ordinary hydrogen, H) and deuterium (heavy hydrogen, D) are different enough to permit detectable isomerism:



α-Deuterioethylbenzene

We must remember that *everything* (except, of course, a vampire) has a mirror image, including all molecules. Most molecules, however, are superimposable on their mirror images, as, for example, bromochloromethane, and do not show this mirror-image isomerism.



Bromochloromethane
Superimposable: no isomerism

Mirror-image isomers are called *enantiomers*. Since they differ from one another only in the way the atoms are oriented in space, enantiomers belong to the general class called *stereoisomers*. Later on we shall encounter stereoisomers that are *not* mirror images of each other; these are called *diastereomers*. *Any two stereoisomers are thus classified either as enantiomers or as diastereomers, depending upon whether or not they are mirror images of each other.*

The non-superimposability of mirror images that brings about the existence of enantiomers also, as we shall see, gives them their optical activity, and hence enantiomers are often referred to as (one kind of) *optical isomers*. We shall make no use of the term *optical isomer*, since it is hard to define- indeed, is often used undefined- and of doubtful usefulness.

4.8 Enantiomerism and optical activity

Most compounds do not rotate the plane of polarized light. How is it that *some* do? It is not the particular chemical family that they belong to, since optically active compounds are found in all families. To see what special structural feature gives rise to optical activity, let us look more closely at what happens when polarized light is passed through a sample of a single pure compound.

When a beam of polarized light passes through an individual molecule, in nearly every instance its plane is rotated a tiny amount by interaction with the charged particles of the molecule; the direction and extent of rotation varies with the orientation of the particular molecule in the beam. For most compounds, because of the random distribution of the large number of molecules that make up even the smallest sample of a single pure compound, for every molecule that the light encounters, there is another (identical) molecule oriented *as the mirror image of the first*, which exactly cancels its effect. The net result is no rotation, that is, optical inactivity. Thus optical inactivity is not a property of individual molecules, but rather of the *random distribution of molecules that can serve as mirror images of each other.*

Optical inactivity requires, then, that one molecule of a compound act as the mirror image of another. But in the special case of CWXYZ, we have found (Sec. 4.7) a molecule whose mirror image is not just another, identical molecule, but rather a molecule of a different, isomeric compound. In a pure sample of a single enantiomer, no molecule can serve as the mirror image of another; there is no exact canceling-out of rotations, and the net result is optical activity. Thus, the same non-superimposability of mirror images that gives rise to enantiomerism also is responsible for optical activity.

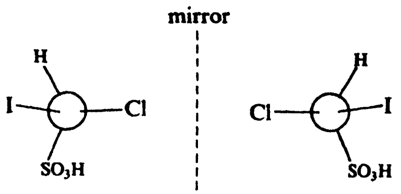
4.9 Prediction of enantiomerism. Chirality

Molecules that are not superimposable on their mirror images are **chiral.**

Chirality is the necessary and sufficient condition for the existence of enantiomers. That is to say: *a compound whose molecules are chiral can exist as enantiomers; a compound whose molecules are achiral* (without chirality) *cannot exist as enantiomers.*

When we say that a molecule and its mirror image are superimposable, we mean that if—in our mind's eye—we were to bring the image from behind the mirror where it seems to be, it could be made to coincide in all its parts with the molecule. To decide whether or not a molecule is chiral, therefore, we make a model of it and a model of its mirror image, and see if we can superimpose them. This is the safest way, since properly handled it must give us the right answer. It is the method that we should use until we have become quite familiar with the ideas involved; even then, it is the method we should use when we encounter a new type of compound.

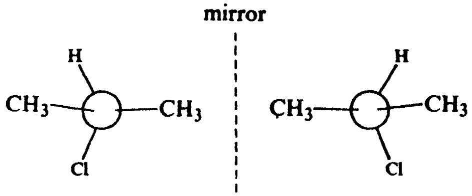
After we have become familiar with the models themselves, we can draw pictures of the models, and *mentally* try to superimpose them. Some, we find, are not superimposable, like these:



Chloroiodomethanesulfonic acid
Not superimposable: enantiomers

These molecules are chiral, and we know that chloroiodomethanesulfonic acid can exist as enantiomers, which have the structures we have just made or drawn.

Others, we find, are superimposable, like these:



Isopropyl chloride
Superimposable: no enantiomers

These molecules are achiral, and so we know that isopropyl chloride cannot exist as enantiomers.

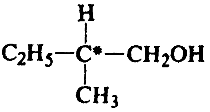
> "I call any geometrical figure, or any group of points, *chiral*, and say it has *chirality*, if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself."—Lord Kelvin, 1893.

In 1964, Cahn, Ingold, and Prelog (see p. 130) proposed that chemists use the terms "chiral" and "chirality" as defined by Kelvin. Based on the Greek word for "hand" (*cheir*), chirality means "handedness," in reference to that pair of non-superimposable mirror images we constantly have before us: our two hands. There has been wide-spread acceptance of Kelvin's terms, and they have largely displaced the earlier "dissymmetric" and "dissymmetry" (and the still earlier—and less accurate—"asymmetric" and "asymmetry"), although one must expect to encounter the older terms in the older chemical literature.

Whatever one calls it, it is non-superimposability-on-mirror-image that is the necessary and sufficient condition for enantiomerism; it is also a necessary—but *not* sufficient—condition for optical activity (see Sec. 4.13).

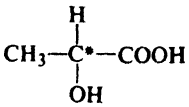
4.10 The chiral center

So far, all the chiral molecules we have talked about happen to be of the kind CWXYZ; that is, in each molecule there is a carbon (C*) that holds four different groups.



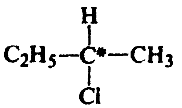
$$C_2H_5-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C^*}}-CH_2OH$$

2-Methyl-1-butanol



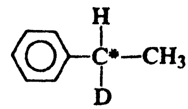
$$CH_3-\overset{\displaystyle H}{\underset{\displaystyle OH}{C^*}}-COOH$$

Lactic acid



$$C_2H_5-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C^*}}-CH_3$$

sec-Butyl chloride



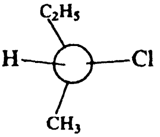
α-Deuterioethylbenzene

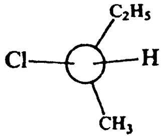
A carbon atom to which four different groups are attached is a **chiral center.** (Sometimes it is called *chiral carbon.* when it is necessary to distinguish it from *chiral nitrogen, chiral phosphorus,* etc.)

Many—*but not all*—molecules that contain a chiral center are chiral. Many—*but not all*—chiral molecules contain a chiral center. There are molecules that contain chiral centers and yet are achiral (Sec. 4.18). There are chiral molecules that contain no chiral centers (see, for example, Problem 6, p. 315).

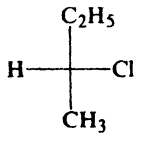
The presence or absence of a chiral center is thus no criterion of chirality. However, most of the chiral molecules that we shall take up do contain chiral centers, and it will be useful for us to look for such centers; if we find a chiral center, then we should consider the *possibility* that the molecule is chiral, and hence can exist in enantiomeric forms. We shall later (Sec. 4.18) learn to recognize the kind of molecule that may be achiral in spite of the presence of chiral centers; such molecules contain more than one chiral center.

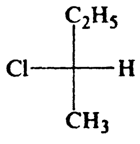
After becoming familiar with the use of models and of pictures of models, the student can make use of even simpler representations of molecules containing chiral centers, which can be drawn much faster. This is a more dangerous method, however, and must be used properly to give the right answers. We simply draw a cross and attach to the four ends the four groups that are attached to the chiral center. The chiral center is understood to be located where the lines cross. Chemists have agreed that such a diagram stands for a particular structure: *the horizontal lines represent bonds coming toward us out of the plane of the paper, whereas the vertical lines represent bonds going away from us behind the plane of the paper.* That is to say:





can be represented by





In testing the superimposability of two of these flat, two-dimensional representations of three-dimensional objects, we must follow a certain procedure and obey certain rules. First, we use these representations only for molecules that contain a chiral center. Second, we draw one of them, and then draw the other as its mirror image. (Drawing these formulas *at random* can lead to some interesting but quite *wrong* conclusions about isomer numbers.) Third, in our mind's eye we may slide these formulas or rotate them end for end, *but we may not remove them from the plane of the paper.* Used with caution, this method of representation is convenient; it is not foolproof, however, and in doubtful cases models or pictures of models should be used.

Problem 4.5 Using cross formulas, decide which of the following compounds are chiral. Check your answers by use of stick-and-ball formulas, and finally by use of models.

(a) 1-chloropentane	(e) 2-chloro-2-methylpentane
(b) 2-chloropentane	(f) 3-chloro-2-methylpentane
(c) 3-chloropentane	(g) 4-chloro-2-methylpentane
(d) 1-chloro-2-methylpentane	(h) 1-chloro-2-bromobutane

Problem 4.6 (a) Neglecting stereoisomers for the moment, draw all isomers of formula C_3H_6DCl. (b) Decide, as in Problem 4.5, which of these are chiral.

4.11 Enantiomers

Isomers that are mirror images of each other are called **enantiomers.** The two different lactic acids whose models we made in Sec. 4.7 are enantiomers (Gr.: *enantio-*, opposite). So are the two 2-methyl-1-butanols, the two *sec*-butyl chlorides, etc. How do the properties of enantiomers compare?

Enantiomers have identical physical properties, except for the direction of rotation of the plane of polarized light. The two 2-methyl-1-butanols, for example,

	(+)-2-Methyl-1-butanol	(−)-2-Methyl-1-butanol (Fermentation Product)
Specific rotation	+5.756°	−5.756°
Boiling point	128.9°	128.9°
Density	0.8193	0.8193
Refractive index	1.4107	1.4107

have identical melting points, boiling points, densities, refractive indices, and any other physical constant one might measure, except for this: one rotates plane-polarized light to the right, the other to the left. This fact is not surprising, since the interactions of both kinds of molecule with their fellows should be the same. Only the *direction* of rotation is different; the *amount* of rotation is the same, the specific rotation of one being +5.756°, the other −5.756°. It is reasonable that these molecules, being so similar, can rotate light by the same amount. The molecules are mirror images, and so are their properties: the mirror image of a clockwise rotation is a counterclockwise rotation—and of exactly the same *magnitude.*

Enantiomers have identical chemical properties except toward optically active reagents. The two lactic acids are not only acids, but acids of exactly the same strength; that is, dissolved in water at the same concentration, both ionize to exactly the same degree. The two 2-methyl-1-butanols not only form the same products—*alkenes* on treatment with hot sulfuric acid, *alkyl bromides* on treatment with HBr, *esters* on treatment with acetic acid—but also form them at exactly the same rate. This is quite reasonable, since the atoms undergoing attack in each case are influenced in their reactivity by exactly the same combination of substituents. The reagent approaching either kind of molecule encounters the same environment, except, of course, that one environment is the mirror image of the other.

In the special case of a reagent that is itself optically active, on the other hand, the influences exerted on the reagent are *not* identical in the attack on the two enantiomers, and reaction rates will be different—so different, in some cases, that reaction with one isomer does not take place at all. In biological systems, for example, such stereochemical specificity is the rule rather than the exception, since the all-important catalysts, *enzymes*, and most of the compounds they work on, are optically active. The sugar (+)-glucose plays a unique role in animal metabolism (Sec. 34.3) and is the basis of a multimillion-dollar fermentation industry (Sec. 15.5); yet (−)-glucose is neither metabolized by animals nor fermented by yeasts. When the mold *Penicillium glaucum* feeds on a mixture of enantiomeric tartaric acids, it consumes only the (+)-enantiomer and leaves (−)-tartaric acid behind. The hormonal activity of (−)-adrenaline is many times that of its enantiomer; only one stereoisomer of chloromycetin is an antibiotic. (+)-Ephedrine not only has no activity as a drug, but actually interferes with the action of its enantiomer. Among amino acids, only one asparagine and one leucine are sweet, and only one glutamic acid enhances the flavor of food. It is (−)-carvone that gives oil of spearmint its characteristic odor; yet the enantiomeric (+)-carvone is the essence of caraway.

Consider, as a crude analogy, a right and left hand of equal strength (the enantiomers) hammering a nail (an optically inactive reagent) and inserting a right-handed screw (an optically active reagent). Hammering requires exactly corresponding sets of muscles in the two hands, and can be done at identical rates. Inserting the screw uses different sets of muscles: the right thumb pushes, for example, whereas the left thumb pulls.

Or, let us consider reactivity in the most precise way we know: by the transition-state approach (Sec. 2.22).

Take first the reactions of two enantiomers with an optically inactive reagent. The reactants in both cases are of exactly the same energy: one enantiomer plus the reagent, and the other enantiomer plus the same reagent. The two transition states for the reactions are mirror images (they are enantiomeric), and hence are of exactly the same energy, too. Therefore, the energy differences between reactants and transition states—the E_{act}'s—are identical, and so are the rates of reaction.

Now take the reactions of two enantiomers with an optically *active* reagent. Again the reactants are of the same energy. The two transition states, however, are *not* mirror images of each other (they are diastereomeric), and hence are of *different* energies; the E_{act}'s are different, and so are the rates of reaction.

4.12 The racemic modification

A mixture of equal parts of enantiomers is called a **racemic modification**. *A racemic modification is optically inactive:* when enantiomers are mixed together, the rotation caused by a molecule of one isomer is exactly canceled by an equal and opposite rotation caused by a molecule of its enantiomer.

The prefix **±** is used to specify the racemic nature of the particular sample, as, for example, (±)-lactic acid or (±)-2-methyl-1-butanol.

It is useful to compare a racemic modification with a compound whose molecules are superimposable on their mirror images, that is, with an achiral compound. They are both optically inactive, and for exactly the same reason. Because of the random distribution of the large number of molecules, for every molecule that the light encounters there is a second molecule, a mirror image of the first, aligned just right to cancel the effect of the first one. In a racemic modification this second molecule happens to be an isomer of the first; for an achiral compound it is not an isomer, but another, identical molecule (Sec. 4.8).

(For an optically active substance uncontaminated by its enantiomer, we have seen, such cancellation of rotation cannot occur since no other molecule can serve as the mirror image of another, no matter how random the distribution.)

Problem 4.7 To confirm the statements of the three preceding paragraphs, make models of: (a) a pair of enantiomers, e.g., CHClBrI; (b) a pair of identical achiral molecules, e.g., CH_2ClBr; (c) a pair of identical chiral molecules, e.g., CHClBrI. (d) Which pairs are mirror images?

The identity of most physical properties of enantiomers has one consequence of great practical significance. They cannot be separated by ordinary methods: not by fractional distillation, because their boiling points are identical; not by fractional crystallization, because their solubilities in a given solvent are identical (unless the solvent is optically active); not by chromatography, because they are held equally strongly on a given adsorbent (unless it is optically active). The separation of a racemic modification into enantiomers—the *resolution* of a racemic modification—is therefore a special kind of job, and requires a special kind of approach (Sec. 7.9).

The first resolution was, of course, the one Pasteur carried out with his hand lens and tweezers (Sec. 4.6). But this method can almost never be used, since racemic modifications seldom form mixtures of crystals recognizable as mirror images. Indeed, even sodium ammonium tartrate does not, unless it crystallizes at a temperature below 28°. Thus partial credit for Pasteur's discovery has been given to the cool Parisian climate—and, of course, to the availability of tartaric acid from the winemakers of France.

The method of resolution nearly always used—one also discovered by Pasteur—involves the use of optically active reagents, and is described in Sec. 7.9.

Although popularly known chiefly for his great work in bacteriology and medicine, Pasteur was by training a chemist, and his work in chemistry alone would have earned him a position as an outstanding scientist.

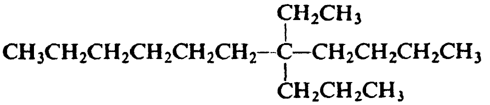
4.13 Optical activity: a closer look

We have seen (Sec. 4.8) that, like enantiomerism, optical activity results from—and *only* from—chirality: the non-superimposability of certain molecules on their mirror images. Whenever we observe (molecular) optical activity, we know we are dealing with chiral molecules.

Is the reverse true? Whenever we deal with chiral molecules—with compounds that exist as enantiomers—must we always observe optical activity? *No.* We have just seen that a 50:50 mixture of enantiomers is optically inactive. Clearly, if we are to *observe* optical activity, the material we are dealing with must contain an *excess* of one enantiomer: enough of an excess that the net optical rotation can be detected by the particular polarimeter at hand.

Furthermore, this excess of one enantiomer must persist long enough for the optical activity to be measured. If the enantiomers are rapidly interconverted, then before we could measure the optical activity due to one enantiomer, it would be converted into an equilibrium mixture, which—since enantiomers are of exactly the same stability—must be a 50:50 mixture and optically inactive.

Even if all these conditions are met, the magnitude—and hence the detectability—of the optical rotation depends on the structure of the particular molecule concerned. In compound I, for example, the four groups attached to the chiral center differ only in chain length.



$$CH_3CH_2CH_2CH_2CH_2CH_2-\underset{\displaystyle CH_2CH_2CH_3}{\overset{\displaystyle CH_2CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_2CH_2CH_3$$

I

Ethyl-*n*-propyl-*n*-butyl-*n*-hexylmethane

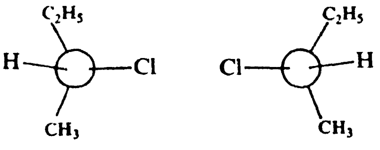
It has been calculated that this compound should have the tiny specific rotation of 0.00001° —far below the limits of detection by any existing polarimeter. In 1965, enantiomerically pure samples of both enantiomers of I were prepared (see Problem 19, p. 1026), and each was found to be optically inactive.

At our present level of study, the matter of speed of interconversion will give us no particular trouble. Nearly all the chiral molecules we encounter in this book lie at either of two extremes, which we shall easily recognize: (a) molecules—like those described in this chapter—which owe their chirality to chiral centers; here interconversion of enantiomers (*configurational* enantiomers) is so slow—because bonds have to be broken—that we need not concern ourselves at all about interconversion; (b) molecules whose enantiomeric forms (*conformational* enantiomers) are interconvertible simply by rotations about single bonds; here—for the compounds we shall encounter—interconversion is so fast that ordinarily we need not concern ourselves at all about the existence of the enantiomers.

4.14 Configuration

The arrangement of atoms that characterizes a particular stereoisomer is called its **configuration**.

Using the test of superimposability, we conclude, for example, that there are two stereoisomeric *sec*-butyl chlorides; their *configurations* are I and II. Let us



I II

sec-Butyl chloride

say that, by methods we shall take up later (Sec. 7.9), we have obtained in the laboratory samples of two compounds of formula $C_2H_5CHClCH_3$. We find that one rotates the plane of polarized light to the right, and the other to the left; we put them into two bottles, one labeled "(+)-*sec*-butyl chloride" and the other "(−)-*sec*-butyl chloride."

We have made two models to represent the two configurations of this chloride. We have isolated two isomeric compounds of the proper formula. Now the question arises, which configuration does each isomer have? Does the (+)-isomer, say, have configuration I or configuration II? How do we know which structural formula, I or II, to draw on the label of each bottle? That is to say, how do we *assign configuration*?

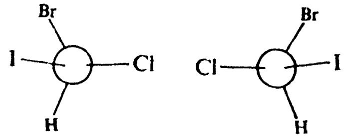
Until 1949 the question of configuration could not be answered in an absolute sense for any optically active compound. But in that year J. M. Bijvoet—most fittingly Director of the van't Hoff Laboratory at the University of Utrecht (Sec. 4.2)—reported that, using a special kind of x-ray analysis (the method of anomalous scattering), he had determined the actual arrangement in space of the atoms of an optically active compound. The compound was a salt of (+)-tartaric acid, the same acid that—almost exactly 100 years before—had led Pasteur to his discovery of optical isomerism. Over the years prior to 1949, the relationships between the configuration of (+)-tartaric acid and the configurations of hundreds of optically active compounds had been worked out (by methods that we shall take up later, Sec. 7.5); when the configuration of (+)-tartaric acid became known, these other configurations, too, immediately became known. (In the case of the *sec*-butyl chlorides, for example, the (−)-isomer is known to have configuration I, and the (+)-isomer configuration II.)

4.15 Specification of configuration: R and S

Now, a further problem arises. How can we specify a particular configuration in some simpler, more convenient way than by always having to draw its picture? The most generally useful way yet suggested is the use of the prefixes R and S. According to a procedure proposed by R. S. Cahn (The Chemical Society, London), Sir Christopher Ingold (University College, London), and V. Prelog (Eidgenössiche Technische Hochschule, Zurich), two steps are involved.

Step 1. Following a set of *sequence rules* (Sec. 4.16), we assign a sequence of priority to the four atoms or groups of atoms attached to the chiral center.

In the case of CHClBrI, for example, the four atoms attached to the chiral center are all different and priority depends simply on atomic number, the atom of higher number having higher priority. Thus I, Br, Cl, H.

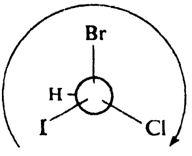


I II

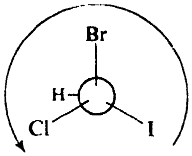
Bromochloroiodomethane

Step 2. We visualize the molecule oriented so that the group of *lowest* priority is directed *away* from us, and observe the arrangement of the remaining groups. If, in proceeding from the group of highest priority to the group of second priority and thence to the third, our eye travels in a clockwise direction, the configuration is specified **R** (Latin: *rectus*, right); if counterclockwise, the configuration is specified **S** (Latin: *sinister*, left).

Thus, configurations I and II are viewed like this:



R



S

and are specified R and S, respectively.

A complete name for an optically active compound reveals—if they are known—both configuration and direction of rotation, as, for example, (S)-(+)-*sec*-butyl chloride. A racemic modification can be specified by the prefix RS, as, for example, (RS)-*sec*-butyl chloride.

(Specification of compounds containing more than one chiral center is discussed in Sec. 4.19.)

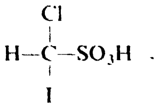
We must not, of course, confuse the direction of optical rotation of a compound—a physical property of a real substance, like melting point or boiling point—with the direction in which our eye happens to travel when we imagine a molecule held in an arbitrary manner. So far as we are concerned, unless we happen to know what has been established experimentally for a specific compound, we have no idea whether (+) or (−) rotation is associated with the (R)- or the (S)-configuration.

4.16 Sequence rules

For ease of reference and for convenience in reviewing, we shall set down here those sequence rules we shall have need of. The student should study Rules 1 and 2 now, and Rule 3 later when the need for it arises.

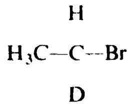
Sequence Rule 1. If the four atoms attached to the chiral center are all different, priority depends on atomic number, with the atom of higher atomic number getting higher priority. If two atoms are isotopes of the same element, the atom of higher mass number has the higher priority.

For example, in chloroiodomethanesulfonic acid the sequence is I, Cl, S, H; in *α*-deuterioethyl bromide it is Br, C, D, H.



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{H{-}C{-}SO_3H} \\ | \\ \mathrm{I} \end{array}$$

Chloroiodomethanesulfonic acid



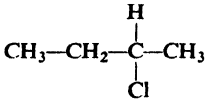
$$\begin{array}{c} \mathrm{H} \\ \mathrm{H_3C{-}C{-}Br} \\ \mathrm{D} \end{array}$$

α-Deuterioethyl bromide

Problem 4.8 Make models and then draw both stick-and-ball pictures and cross formulas for the enantiomers of: (a) chloroiodomethanesulfonic acid and (b) *α*-deuterioethyl bromide. Label each as R or S.

Sequence Rule 2. If the relative priority of two groups cannot be decided by Rule 1, it shall be determined by a similar comparison of the next atoms in the groups (and so on, if necessary, working outward from the chiral center). That is to say, if two atoms attached to the chiral center are the same, we compare the atoms attached to each of these first atoms.

For example, take *sec*-butyl chloride, in which two of the atoms attached to the chiral center are themselves carbon. In CH_3 the second atoms are H, H, H;

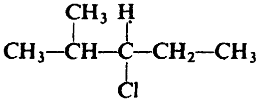


$$CH_3{-}CH_2{-}\overset{H}{\underset{Cl}{C}}{-}CH_3$$

sec-Butyl chloride

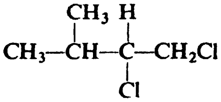
in C_2H_5 they are C, H, H. Since carbon has a higher atomic number than hydrogen, C_2H_5 has the higher priority. A complete sequence of priority for *sec*-butyl chloride is therefore Cl, C_2H_5, CH_3, H.

In 3-chloro-2-methylpentane the C, C, H of isopropyl takes priority over the C, H, H of ethyl, and the complete sequence of priority is Cl, isopropyl, ethyl, H.



$$CH_3{-}\overset{CH_3}{CH}{-}\overset{H}{\underset{Cl}{C}}{-}CH_2{-}CH_3$$

3-Chloro-2-methylpentane



$$CH_3{-}\overset{CH_3}{CH}{-}\overset{H}{\underset{Cl}{C}}{-}CH_2Cl$$

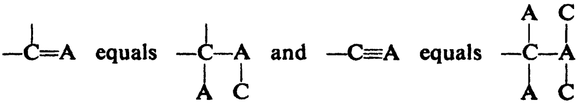
1,2-Dichloro-3-methylbutane

In 1,2-dichloro-3-methylbutane the Cl, H, H of CH_2Cl takes priority over the C, C, H of isopropyl. Chlorine has a higher atomic number than carbon, and the fact that there are *two* C's and only *one* Cl does not matter. (One higher number is worth more than two—or three—of a lower number.)

Problem 4.9 Into what sequence of priority must these alkyl groups always fall: CH_3, 1°, 2°, 3°?

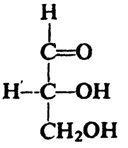
Problem 4.10 Specify as R or S each of the enantiomers you drew: (a) in Problem 4.5 (p. 126); (b) in Problem 4.6 (p. 126).

Sequence Rule 3. (*The student should defer study of this rule until he needs it.*) Where there is a double or triple bond, both atoms are considered to be duplicated or triplicated. Thus,



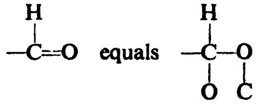
$$-\overset{|}{C}{=}A \quad \text{equals} \quad -\overset{|}{\underset{A}{C}}{-}\underset{C}{A} \quad \text{and} \quad -C{\equiv}A \quad \text{equals} \quad -\overset{A}{\underset{A}{C}}{-}\overset{C}{\underset{C}{A}}$$

For example, in glyceraldehyde the OH group has the highest priority of all,



$$\begin{array}{c} H \\ | \\ C{=}O \\ | \\ H{-}C{-}OH \\ | \\ CH_2OH \end{array}$$

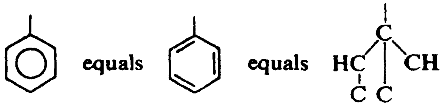
Glyceraldehyde



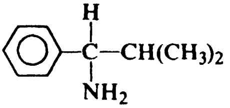
$$-\overset{H}{C}{=}O \quad \text{equals} \quad -\overset{H}{\underset{O}{C}}{-}\underset{C}{O}$$

and the O, O, H of —CHO takes priority over the O, H, H of $-CH_2OH$. The complete sequence is then —OH, —CHO, $-CH_2OH$, —H.

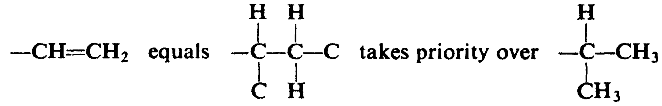
The phenyl group, C_6H_5— is handled as though it had one of the Kekulé structures:



In 1-amino-2-methyl-1-phenylpropane, for example, the C, C, C, of phenyl takes priority over the C, C, H of isopropyl, but not over N, which has a higher atomic number. The entire sequence is then NH_2, C_6H_5, C_3H_7, H.



The vinyl group, $CH_2{=}CH$—, takes priority over isopropyl.



$$-CH{=}CH_2 \quad \text{equals} \quad -\overset{\displaystyle H}{\underset{\displaystyle C}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-C \quad \text{takes priority over} \quad -\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-CH_3$$

Following the "senior" branch. —CH_2—C, we arrive at C in vinyl as compared with H in the —CH_2—H of isopropyl.

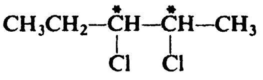
Problem 4.11 Draw and specify as R or S the enantiomers (if any) of:

(a) 3-chloro-1-pentene
(b) 3-chloro-4-methyl-1-pentene
(c) $HOOCCH_2CHOHCOOH$, malic acid
(d) $C_6H_5CH(CH_3)NH_2$
(e) methylethyl-*n*-propylisopropylmethane
(f) $C_6H_5CHOHCOOH$, mandelic acid
(g) $CH_3CH(NH_2)COOH$, alanine

4.17 Diastereomers

Next, we must learn what stereoisomers are possible for compounds whose molecules contain, not just one, but *more than one* chiral center. (In Chapter 34, we shall be dealing regularly with molecules that contain *five* chiral centers.)

Let us start with 2,3-dichloropentane. This compound contains two chiral centers, C-2 and C-3. (What four groups are attached to each of these carbon atoms?) How many stereoisomers are possible?

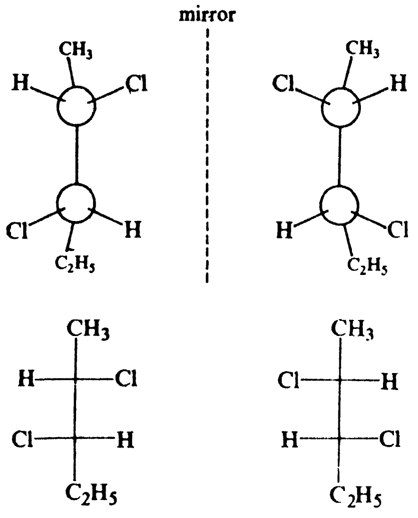


$$CH_3CH_2-\underset{\displaystyle Cl}{\overset{*}{C}}H-\underset{\displaystyle Cl}{\overset{*}{C}}H-CH_3$$

2,3-Dichloropentane

Using models, let us first make structure I and its mirror image II, and see if these are superimposable. We find that I and II are not superimposable, and hence must be enantiomers. (As before, we may represent the structures by pictures, and mentally try to superimpose these. Or, we may use the simple "cross" representations, being careful, as before (Sec. 4.10), not to remove the drawings from the plane of the paper or blackboard.)

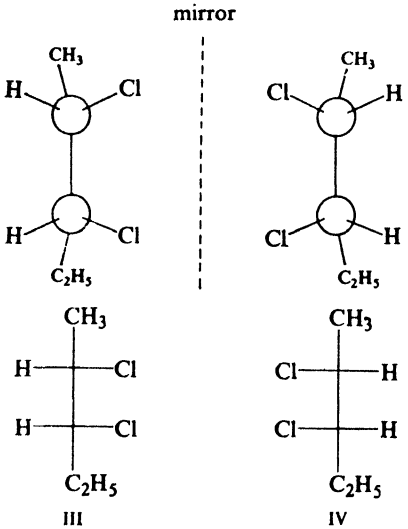
Next, we try to interconvert I and II by rotations about carbon–carbon bonds. We find that they are not interconvertible in this way, and hence each of them is capable of retaining its identity and, if separated from its mirror image, of showing optical activity.



I II

Not superimposable
Enantiomers

Are there any other stereoisomers of 2,3-dichloropentane? We can make structure III, which we find to be non-superimposable on either I or II: it is not, of



III IV

Not superimposable
Enantiomers

course, the mirror image of either. What is the relationship between III and I? Between III and II? They are stereoisomers but not enantiomers. *Stereoisomers that are not mirror images of each other are called* **diastereomers**. Compound III is a diastereomer of I, and similarly of II.

Now, is III chiral? Using models, we make its mirror image, structure IV, and find that this is not superimposable on (or interconvertible with) III. Structures III and IV represent a second pair of enantiomers. Like III, compound IV is a diastereomer of I and of II.

How do the properties of diastereomers compare?

Diastereomers have similar chemical properties, since they are members of the same family. Their chemical properties are ***not identical,*** however. In the reaction of two diastereomers with a given reagent, neither the two sets of reactants nor the two transition states are mirror images, and hence—except by sheer coincidence—will not be of equal energies. E_{act}'s will be different and so will the rates of reaction.

Diastereomers have different physical properties: different melting points, boiling points, solubilities in a given solvent, densities, refractive indexes, and so on. Diastereomers differ in specific rotation; they may have the same or opposite signs of rotation, or some may be inactive.

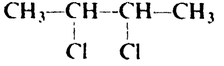
As a result of their differences in boiling point and in solubility, they can, in principle at least, be separated from each other by fractional distillation or fractional crystallization; as a result of differences in molecular shape and polarity, they differ in adsorption, and can be separated by chromatography.

Given a mixture of all four stereoisomeric 2,3-dichloropentanes, we could separate it, by distillation, for example, into two fractions but no further. One fraction would be the racemic modification of I plus II; the other fraction would be the racemic modification of III plus IV. Further separation would require *resolution* of the racemic modifications by use of optically active reagents (Sec. 7.9).

Thus the presence of two chiral centers can lead to the existence of as many as four stereoisomers. For compounds containing three chiral centers, there could be as many as eight stereoisomers; for compounds containing four chiral centers, there could be as many as sixteen stereoisomers, and so on. The maximum number of stereoisomers that can exist is equal to 2^n, where n is the number of chiral centers. (In any case where *meso* compounds exist, as discussed in the following section, there will be fewer than this maximum number.)

4.18 *Meso* structures

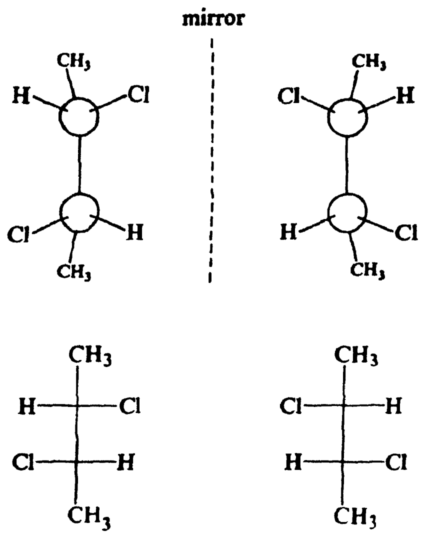
Now let us look at 2,3-dichlorobutane, which also has two chiral centers. Does this compound, too, exist in four stereoisomeric forms?



$$\mathrm{CH_3-\underset{\displaystyle Cl}{\underset{|}{\overset{*}{C}H}}-\underset{\displaystyle Cl}{\underset{|}{\overset{*}{C}H}}-CH_3}$$

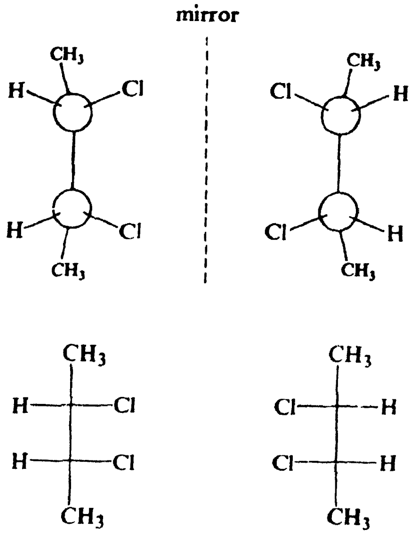
2,3-Dichlorobutane

Using models as before, we arrive first at the two structures V and VI. These are mirror images that are not superimposable or interconvertible; they are therefore enantiomers, and each should be capable of optical activity.



V VI

Not superimposable
Enantiomers



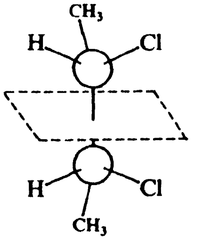
VII VIII

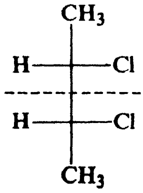
Superimposable
A *meso* compound

Next, we make VII, which we find to be a diastereomer of V and of VI. We now have three stereoisomers; is there a fourth? *No.* If we make VIII, the mirror image of VII, we find the two to be superimposable; turned end-for-end, VII coincides in every respect with VIII. In spite of its chiral centers, VII is not chiral. It cannot exist in two enantiomeric forms, and it cannot be optically active. It is called a *meso* compound.

A* meso compound *is one whose molecules are superimposable on their mirror images even though they contain chiral centers. A *meso* compound is optically inactive for the same reason as any other compound whose molecules are achiral: the rotation caused by any one molecule is cancelled by an equal and opposite rotation caused by another molecule that is the mirror image of the first (Sec. 4.8).

We can often recognize a *meso* structure on sight by the fact that (in at least one of its conformations) one half of the molecule is the mirror image of the other half. This can be seen for *meso*-2,3-dichlorobutane by imagining the molecule to be cut by a plane lying where the dotted line is drawn. The molecule has *a plane of symmetry*, and cannot be chiral. (*Caution:* If we do not see a plane of symmetry, however, this does not necessarily mean that the molecule is chiral.)





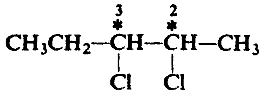
Problem 4.12 Draw stereochemical formulas for all the possible stereoisomers of the following compounds. Label pairs of enantiomers, and *meso* compounds. Tell which isomers, if separated from all other stereoisomers, will be optically active. Pick out several examples of diastereomers.

(a) 1,2-dibromopropane
(b) 3,4-dibromo-3,4-dimethylhexane
(c) 2,4-dibromopentane
(d) 2,3,4-tribromohexane
(e) 1,2,3,4-tetrabromobutane
(f) 2-bromo-3-chlorobutane
(g) 1-chloro-2-methylbutane
(h) 1,3-dichloro-2-methylbutane

4.19 Specification of configuration: more than one chiral center

Now, how do we specify the configuration of compounds which, like these, contain more than one chiral center? They present no special problem; we simply specify the configuration about *each* of the chiral centers, and by use of numbers tell which specification refers to which carbon.

Consider, for example, the 2,3-dichloropentanes (Sec. 4.17). We take each of the chiral centers, C-2 and C-3, in turn—ignoring for the moment the existence



$$CH_3CH_2-\underset{Cl}{\overset{\overset{3}{*}}{C}}H-\underset{Cl}{\overset{\overset{2}{*}}{C}}H-CH_3$$

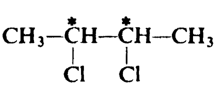
2,3-Dichloropentane

of the other—and follow the steps of Sec. 4.15 and use the Sequence Rules of

Sec. 4.16. In order of priority, the four groups attached to C-2 are Cl, CH_3CH_2CHCl-, CH_3, H. On C-3 they are Cl, CH_3CHCl-, CH_3CH_2-, H. (Why is CH_3CHCl- "senior" to CH_3CH_2-?)

Taking in our hands—or in our mind's eye—a model of the particular stereoisomer we are interested in, we focus our attention first on C-2 (ignoring C-3), and then on C-3 (ignoring C-2). Stereoisomer I (p. 134), for example, we specify (2S,3S)-2,3-dichloropentane. Similarly, II is (2R,3R), III is (2S,3R), and IV is (2R,3S). These specifications help us to analyze the relationships among the stereoisomers. As enantiomers, I and II have opposite—that is, mirror-image—configurations about both chiral centers: 2S,3S and 2R,3R. As diastereomers, I and III have opposite configurations about one chiral center, and the same configuration about the other: 2S,3S and 2S,3R.

We would handle 2,3-dichlorobutane (Sec. 4.18) in exactly the same way. Here it happens that the two chiral centers occupy equivalent positions along the chain, and so it is not necessary to use numbers in the specifications. Enantiomers V and VI (p. 136) are specified (S,S)- and (R,R)-2,3-dichlorobutane, respectively. The *meso* isomer, VII, can, of course, be specified either as (R,S)- or (S,R)-2,3-dichlorobutane—the absence of numbers emphasizing the equivalence of the two specifications. The mirror-image relationship between the two ends of this molecule is consistent with the *opposite* designations of R and S for the two chiral centers. (Not all (R,S)-isomers, of course, are *meso* structures—only those whose two halves are chemically equivalent.)



$$CH_3-\underset{\displaystyle Cl}{\overset{*}{C}}H-\underset{\displaystyle Cl}{\overset{*}{C}}H-CH_3$$

2,3-Dichlorobutane

Problem 4.13 Give the R/S specification for each stereoisomer you drew in Problem 4.12 (p. 137).

4.20 Conformational isomers

In Sec. 3.5, we saw that there are several different staggered conformations of *n*-butane, each of which lies at the bottom of an energy valley—at an *energy minimum*—separated from the others by energy hills (see Fig. 3.4, p. 79). *Different conformations corresponding to energy minima are called* **conformational isomers,** *or* **conformers.** Since conformational isomers differ from each other only in the way their atoms are oriented in space, they, too, are stereoisomers. Like stereoisomers of any kind, a pair of conformers can either be mirror images of each other or not.

n-Butane exists as three conformational isomers, one *anti* and two *gauche* (Sec. 3.5). The *gauche* conformers, II and III, are mirror images of each other, and hence are (conformational) enantiomers. Conformers I and II (or I and III) are *not* mirror images of each other, and hence are (conformational) diastereomers.

Although the barrier to rotation in *n*-butane is a little higher than in ethane, it is still low enough that—at ordinary temperatures, at least—interconversion of conformers is easy and rapid. Equilibrium exists, and favors a higher population of the more stable *anti* conformer; the populations of the two *gauche* conformers—

mirror images, and hence of exactly equal stability—are, of course, equal. Put differently, any given molecule spends the greater part of its time as the *anti* conformer, and divides the smaller part equally between the two *gauche* conformers. As a result of the rapid interconversion, these isomers cannot be separated.

Problem 4.14 Return to Problem 3.4 (p. 79) and, for each compound: (a) tell how many conformers there are, and label pairs of (conformational) enantiomers; (b) give the order of relative abundance of the various conformers.

Easy interconversion is characteristic of nearly every set of conformational isomers, and is the quality in which such isomers differ most from the kind of stereoisomers we have encountered so far in this chapter. This difference in interconvertibility is due to a difference in height of the energy barrier separating stereoisomers, which is, in turn, due to a difference in origin of the barrier. By definition, interconversion of conformational isomers involves rotation about single bonds; the rotational barrier is—in most cases—a very low one and interconversion is easy and fast. The other kind of stereoisomers, *configurational isomers*, or *inversional isomers*, differ from one another in configuration about a chiral center. Interconversion here involves the breaking of a covalent bond, for which there is a very high barrier: 50 kcal/mole or more (Sec. 1.14). Interconversion is difficult, and—unless one deliberately provides conditions to bring it about—is negligibly slow.

Interconvertibility of stereoisomers is of great practical significance because it limits their *isolability*. Hard-to-interconvert stereoisomers can be separated (with special methods, of course, for resolution of enantiomers) and studied individually; among other things, their optical activity can be measured. Easy-to-interconvert isomers cannot be separated, and single isolated isomers cannot be studied; optical activity cannot be observed, since any chiral molecules are present only as non-resolvable racemic modifications.

Our general approach to stereoisomers involves, then, two stages; first, we test the *superimposability* of possible isomeric structures, and then we test their *interconvertibility*. Both tests are best carried out with models. We make models of the two molecules and, without allowing any rotations about single bonds, we try to superimpose them: if they cannot be superimposed, they represent isomers. Next, we allow the models all possible rotations about single bonds, and repeatedly try to superimpose them: if they still cannot be superimposed, they are non-interconvertible, and represent *configurational isomers*; but if they can be superimposed after rotation, they are interconvertible and represent *conformational isomers*.

In dealing with those aspects of stereochemistry that depend on isolation of stereoisomers—isomer number or optical activity, for example, or study of the reactions of a single stereoisomer—we can ignore the existence of easy-to-interconvert isomers, which means *most* conformational isomers. For convenience the following "ground rule" will hold for discussions and problems in this book: unless specifically indicated otherwise, *the terms "stereoisomers," "enantiomers," and "diastereomers" will refer only to configurational isomers, including geometric isomers* (Sec. 5.6), and will exclude conformational isomers. The latter will be referred to as "conformational isomers," "conformers," "conformational enantiomers," and "conformational diastereomers."

There is no sharp boundary between easy-to-interconvert and hard-to-interconvert stereoisomers. Although we can be sure that interconversion of configurational isomers will be hard, we cannot be sure that interconversion of conformational isomers will be easy. Depending upon the size and nature of substituents, the barrier to rotation about single bonds can be of any height, from the low one in ethane to one comparable to that for breaking a covalent bond. Some conformational isomers exist that are readily isolated, kept, and studied; indeed, study of such isomers (*atropisomers*) makes up a large and extremely important part of stereochemistry, one which, unfortunately, we shall not be able to take up in this beginning book. Other conformational isomers exist that can be isolated, not at ordinary temperatures, but at lower temperatures, where the average collision energy is lower. The conformational isomers that we shall encounter in this book, however, have low rotational barriers, and we may assume—until we learn otherwise—that when we classify stereoisomers as configurational or conformational, we at the same time classify them as hard-to-interconvert or easy-to-interconvert.

Problem 4.15 At low temperatures, where collision energies are small, two isomeric forms of the badly crowded $CHBr_2CHBr_2$ have been isolated by crystallization (a) Give a formula or formulas (Newman projections) corresponding to each of the separable forms. (b) Which, if either, of the materials, as actually isolated at low temperatures, would be optically active? Explain.

PROBLEMS

1. What is meant by each of the following?

(a) optical activity
(b) dextrorotatory
(c) levorotatory
(d) specific rotation
(e) chirality
(f) chiral molecule
(g) chiral center
(h) superimposable
(i) enantiomers
(j) diastereomers
(k) *meso* compound
(l) racemic modification
(m) configuration
(n) conformations
(o) R
(p) S
(q) +
(r) −
(s) configurational isomers
(t) conformational isomers

2. (a) What is the necessary and sufficient condition for enantiomerism? (b) What is a necessary but not a sufficient condition for optical activity? (c) What conditions must be met for the observation of optical activity? (d) How can you tell from its formula whether or not a compound can exist as enantiomers? (e) What restrictions, if any, must be applied to the use of planar formulas in (d)? To the use of models in (d)? (f) Exactly how do you go about deciding whether a molecule should be specified as R or as S?

3. Compare the dextrorotatory and levorotatory forms of *sec*-butyl alcohol, $CH_3CH_2CHOHCH_3$, with respect to:

(a) boiling point
(b) melting point
(c) specific gravity
(d) specific rotation
(e) refractive index
(f) solubility in 100 g of water
(g) rate of reaction with HBr
(h) infrared spectrum
(i) nmr spectrum
(j) adsorption on alumina
(k) retention time in gas chromatography
(l) specification as R or S

4. Which of the following objects are chiral?

(a) nail, screw, pair of scissors, knife, spool of thread;
(b) glove, shoe, sock, pullover sweater, coat sweater, scarf tied around your neck;
(c) child's block, rubber ball, Pyramid of Cheops, helix (p. 1157), double helix (p. 1179);

(d) basketball, football, tennis racket, golf club, baseball bat, shotgun barrel, rifle barrel;
(e) your hand, your foot, your ear, your nose, yourself.

5. Assuming both your hands to be of equal strength and skill, which of the following operations could you perform with equal speed and efficiency?

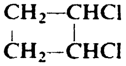
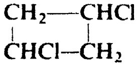
(a) driving a screw, sawing a board, drilling a hole;
(b) opening a door, opening a milk bottle, opening a coffee jar, turning on the hot water;
(c) signing your name, sharpening a pencil, throwing a ball, shaking hands with another right hand, turning to page 142.

6. Draw and specify as R or S the enantiomers (if any) of:

(a) 3-bromohexane
(b) 3-chloro-3-methylpentane
(c) 1,2-dibromo-2-methylbutane
(d) 1,3-dichloropentane
(e) 3-chloro-2,2,5-trimethylhexane
(f) 1-deuterio-1-chlorobutane, $CH_3CH_2CH_2CHDCl$

7. (a) What is the lowest molecular weight alkane that is chiral? Draw stereochemical formulas of the enantiomers and specify each as R or S. (b) Is there another alkane of the same molecular weight that is also chiral? If there is, give its structure and name, and specify the enantiomers as R or S.

8. Draw stereochemical formulas for all the possible stereoisomers of the following compounds. Label pairs of enantiomers, and *meso* compounds. Tell which isomers, if separated from all other stereoisomers, will be optically active. Give one isomer of each set its R/S specification.

(a) $CH_3CHBrCHOHCH_3$
(b) $CH_3CHBrCHBrCH_2Br$
(c) $C_6H_5CH(CH_3)CH(CH_3)C_6H_5$
(d) $CH_3CH_2CH(CH_3)CH_2CH_2CH(CH_3)CH_2CH_3$
(e) $CH_3CH(C_6H_5)CHOHCH_3$
(f) $CH_3CHOHCHOHCHOHCH_2OH$
(g) $HOCH_2(CHOH)_3CH_2OH$
(h)  (*Make models.*)
(i) 

(j) methylethyl-*n*-propyl-*n*-butylammonium chloride, $(RR'R''R'''N)^+Cl^-$ (See Sec. 1.12.)
(k) methylethyl-*n*-propyl-*sec*-butylammonium chloride

9. (a) In a study of chlorination of propane, four products (A, B, C, and D) of formula $C_3H_6Cl_2$ were isolated. What are their structures?

(b) Each was chlorinated further, and the number of trichloro products ($C_3H_5Cl_3$) obtained from each was determined by gas chromatography. A gave one trichloro product; B gave two: and C and D each gave three. What is the structure of A? Of B? Of C and D?

(c) By another synthetic method, compound C was obtained in optically active form. Now what is the structure of C? Of D?

(d) When optically active C was chlorinated, one of the trichloropropanes (E) obtained was optically active, and the other two were optically inactive. What is the structure of E? Of the other two?

10. Draw configurational isomers (if any) of: (a) CH_2BrCH_2Cl; (b) $CH_3CHBrCH_2Cl$. (c) For each substance of (a) and (b), draw all conformers. Label pairs of conformational enantiomers.

11. The more stable conformer of *n*-propyl chloride, $CH_3CH_2—CH_2Cl$, is the *gauche*. What does this indicate about the interaction between —Cl and —CH_3? How do you account for this interaction? (*Hint:* See Sec. 1.19.)

12. (a) What must be the dipole moment of the *anti* conformation of 1,2-dichloroethane, $CH_2Cl—CH_2Cl$? (b) At 32° in the gas phase, the measured dipole moment of

1,2-dichloroethane is 1.12 D. What does this single fact tell you about the conformational make-up of the compound? (c) The dipole moment of a mixture of X and Y is given by the expression

$$\mu^2 = N_X\mu_X{}^2 + N_Y\mu_Y{}^2$$

where N is the mole fraction of each kind of molecule. From bond moments, it has been estimated that the *gauche* conformation of 1,2-dichloroethane should have a dipole moment of about 3.2 D. Calculate the conformational composition of 1,2-dichloroethane at 32° in the gas phase.

Chapter

5

Alkenes I. Structure and Preparation

Elimination

5.1 Unsaturated hydrocarbons

In our discussion of the alkanes we mentioned briefly another family of hydrocarbons, the **alkenes**, which contain less hydrogen, carbon for carbon, than the alkanes, and which can be converted into alkanes by addition of hydrogen. The alkenes were further described as being obtained from alkanes by loss of hydrogen in the cracking process.

Since alkenes evidently contain less than the maximum quantity of hydrogen, they are referred to as **unsaturated hydrocarbons**. This unsaturation can be satisfied by reagents other than hydrogen and gives rise to the characteristic chemical properties of alkenes.

5.2 Structure of ethylene. The carbon–carbon double bond

The simplest member of the alkene family is **ethylene**, C_2H_4. In view of the ready conversion of ethylene into ethane, we can reasonably expect certain structural similarities between the two compounds.

To start, then, we connect the carbon atoms by a covalent bond, and then attach two hydrogen atoms to each carbon atom. At this stage we find that each carbon atom possesses only six electrons in its valence shell, instead of the required eight, and that the entire molecule needs an additional pair of electrons if it is to be neutral. We can solve both these problems by assuming that the carbon atoms can share two pairs of electrons. To describe this sharing of two pairs of electrons, we say that the carbon atoms are joined by a *double bond. The* **carbon–carbon double bond** *is the distinguishing feature of the alkene structure.*

$$\mathrm{H}:\overset{\mathrm{H}}{\ddot{\mathrm{C}}}::\overset{\mathrm{H}}{\ddot{\mathrm{C}}}:\mathrm{H}$$

Ethylene

Quantum mechanics gives a more detailed picture of ethylene and the carbon–carbon double bond. To form bonds with three other atoms, carbon makes use of three equivalent hybrid orbitals: sp^2 orbitals, formed by the mixing of *one s* and *two p* orbitals. As we have seen (Sec. 1.10), sp^2 orbitals lie in one plane, that of the carbon nucleus, and are directed toward the corners of an equilateral triangle; the angle between any pair of orbitals is thus 120°. This **trigonal** arrangement (Fig. 5.1) permits the hybrid orbitals to be as far apart as possible. Just as mutual repulsion among orbitals gives four tetrahedral bonds, so it gives three trigonal bonds.

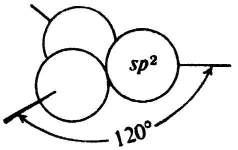


Figure 5.1. Atomic orbitals: hybrid sp^2 orbitals. Axes directed toward corners of equilateral triangle.

If we arrange the two carbons and four hydrogens of ethylene to permit maximum overlap of orbitals, we obtain the structure shown in Fig. 5.2. Each carbon atom lies at the center of a triangle, at whose corners are located the two hydrogen atoms and the other carbon atom. Every bond angle is 120°. Although distributed differently about the carbon nucleus, these bonds individually are very similar to the bonds in ethane, being cylindrically symmetrical about a line joining the nuclei, and are given the same designation: *σ bond* (*sigma bond*).

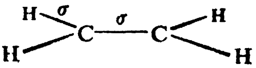


Figure 5.2. Ethylene molecule: only σ bonds shown.

The molecule is not yet complete, however. In forming the sp^2 orbitals, each carbon atom has used only two of its three *p* orbitals. The remaining *p* orbital consists of two equal lobes, one lying above and the other lying below the plane of the three sp^2 orbitals (Fig. 5.3); it is occupied by a single electron. If the *p* orbital of one carbon atom overlaps the *p* orbital of the other carbon atom, the electrons pair up and an additional bond is formed.

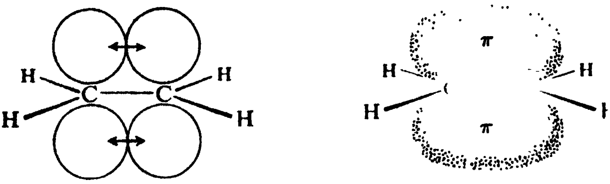


Figure 5.3. Ethylene molecule: carbon–carbon double bond. Overlap of *p* orbitals gives π bond; π cloud above and below plane.

Because it is formed by the overlap of *p* orbitals, and to distinguish it from the differently shaped σ bonds, this bond is called a π *bond* (*pi bond*). It consists of two parts, one electron cloud that lies above the plane of the atoms, and another electron cloud that lies below. Because of less overlap, the π bond is weaker than the carbon–carbon σ bond. As we can see from Fig. 5.3, this overlap can occur only when all six atoms lie in the same plane. Ethylene, then, is a *flat molecule*.

The carbon-carbon "double bond" is thus made up of a strong σ bond and a weak π bond. The total bond energy of 163 kcal is greater than that of the carbon-carbon single bond of ethane (88 kcal). Since the carbon atoms are held more tightly together, the C—C distance in ethylene is less than the C—C distance in ethane; that is to say, the carbon–carbon double bond is shorter than the carbon–carbon single bond.

The σ bond in ethylene has been estimated to have a strength of about 95 kcal: stronger than the one in ethane because it is formed by overlap of sp^2 orbitals (Sec. 5.4). On this basis, we would estimate the strength of the π bond to be 68 kcal.

This quantum mechanical structure of ethylene is verified by direct evidence. Electron diffraction and spectroscopic studies show ethylene (Fig. 5.4) to be a flat molecule, with bond angles very close to 120°. The C—C distance is 1.34 A as compared with the C—C distance of 1.53 A in ethane.

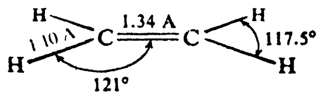
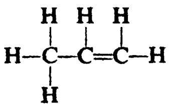


Figure 5.4. Ethylene molecule: shape and size.

In addition to these direct measurements, we shall soon see that two important aspects of alkene chemistry are consistent with the quantum mechanical picture of the double bond, and are most readily understood in terms of that picture. These are (a) the concept of *hindered rotation* and the accompanying phenomenon of *geometric isomerism* (Sec. 5.6), and (b) the kind of reactivity characteristic of the carbon–carbon double bond (Sec. 6.2).

5.3 Propylene

The next member of the alkene family is **propylene**, C_3H_6. In view of its great similarity to ethylene, it seems reasonable to assume that this compound also contains a carbon–carbon double bond. Starting with two carbons joined by a double bond, and attaching the other atoms according to our rule of one bond per hydrogen and four bonds per carbon, we arrive at the structure



$$\begin{array}{ccccccccc} & & \mathrm{H} & & \mathrm{H} & & \mathrm{H} & & \\ & & | & & | & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & = & \mathrm{C} & - & \mathrm{H} \\ & & | & & & & & & \\ & & \mathrm{H} & & & & & & \end{array}$$

Propylene

5.4 Hybridization and orbital size

The carbon–carbon double bond in alkenes is shorter than the carbon–carbon single bond in alkanes because four electrons bind more tightly than two. But, in addition, certain other bonds in alkenes are significantly shorter than their counterparts in alkanes: for example, the C—H distance is 1.103 A in ethylene compared with 1.112 A in ethane. To account for this and other differences in bond length, we must consider differences in hybridization of carbon.

The carbon–hydrogen bonds of ethylene are single bonds just as in, say, ethane, but they are formed by overlap of sp^2 orbitals of carbon, instead of sp^3 orbitals as in ethane. Now, compared with an sp^3 orbital, an sp^2 orbital has less *p* character and more *s* character. A *p* orbital extends some distance from the nucleus; an *s* orbital, on the other hand, lies close about the nucleus. As the *s* character of a hybrid orbital increases, the effective size of the orbital decreases and, with it, the length of the bond to a given second atom. Thus an sp^2–s carbon–hydrogen bond should be shorter than an sp^3–s carbon–hydrogen bond.

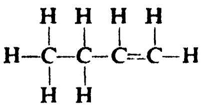
Benzene, in most ways a quite different kind of molecule from ethylene (Sec. 10.1), also contains sp^2–s carbon–hydrogen bonds; the C—H bond distance is 1.084 A, almost exactly the same as in ethylene. Acetylene (Sec. 8.2) contains *sp*-hybridized carbon which, in view of the even greater *s* character of the orbitals, should form even shorter bonds than in ethylene; this expectation is correct, the *sp*–*s* bond being only 1.079 A.

A consideration of hybridization and orbital size would lead one to expect an sp^2–sp^3 bond to be shorter than an sp^3–sp^3 bond. In agreement, the carbon–carbon single bond distance in propylene is 1.501 A, as compared with the carbon–carbon distance of 1.534 A in ethane. The sp–sp^3 carbon–carbon single bond in methylacetylene (Sec. 8.19) is even shorter, 1.459 A. These differences in carbon–carbon single bond lengths are greater than the corresponding differences in carbon–hydrogen bond lengths; however, another factor (Sec. 8.18) besides the particular hybridization of carbon may be at work here.

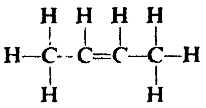
Consideration of hybridization and orbital size helps us to understand other properties of molecules besides bond length: the relative acidities of certain hydrocarbons (Sec. 8.10), for example, and the relative basicities of certain amines (Sec. 31.11). We might reasonably expect shorter bonds to be stronger bonds, and in agreement Table 1.2 (p. 21) shows that the C—H bond dissociation energy in ethylene (104 kcal) is larger than that in ethane (98 kcal), and the C—C (single) bond dissociation energy in propylene (92 kcal) is greater than that in ethane (88 kcal). Indeed, as will be discussed in Sec. 8.19, by affecting the stability of molecules, changes in hybridization may be of more fundamental importance than has been generally recognized.

5.5 The butylenes

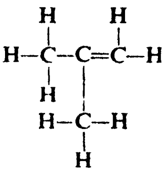
Going on to the **butylenes**, C_4H_8, we find that there are a number of possible arrangements. First of all, we may have a straight-chain skeleton as in *n*-butane, or a branched-chain structure as in isobutane. Next, even when we restrict ourselves to the straight-chain skeleton, we find that there are two possible arrangements that differ in position of the double bond in the chain. So far, then, we have a total of three structures; as indicated, these are given the names *1-butene*, *2-butene*, and *isobutylene*.



1-Butene



2-Butene



Isobutylene

How do the facts agree with the prediction of three isomeric butylenes? Experiment has shown that not three but *four* alkenes of the formula C_4H_8 exist; they have the physical properties shown in Table 5.1.

Table 5.1 PHYSICAL PROPERTIES OF THE BUTYLENES

Name	b.p., °C	m.p., °C	Density (−20°)	Refractive Index (−12.7°)
Isobutylene	−7	−141	0.640	1.3727
1-Butene	−6	< −195	.641	1.3711
trans-2-Butene	+1	−106	.649	1.3778
cis-2-Butene	+4	−139	.667	1.3868

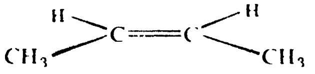
On hydrogenation, the isomer of b.p. −7° yields isobutane; this butylene evidently contains a branched chain, and has therefore the structure we have designated isobutylene.

On hydrogenation, the other three isomers all yield the same compound, *n*-butane; they evidently have a straight-chain skeleton. In ways that we shall study later (Sec. 6.29), it is possible to break an alkene molecule apart at the double bond, and from the fragments obtained deduce the position of the double bond in the molecule. When this procedure is carried out, the isomer of b.p. −6° yields products indicating clearly that the double bond is at the end of the chain; this butylene has therefore the structure we have designated 1-butene. When the same procedure is carried out on the two remaining isomers, both yield the same mixture of products; these products show that the double bond is in the middle of the chain.

Judging from the products of hydrogenation and the products of cleavage, we would conclude that the butylenes of b.p. +1° and +4° *both* have the structure we have designated 2-butene. Yet the differences in boiling point, melting point, and other physical properties show clearly that they are not the same compound, that is, that they are isomers. In what way can their structures differ?

To understand the kind of isomerism that gives rise to two 2-butenes, we must examine more closely the structure of alkenes and the nature of the carbon–carbon double bond. Ethylene is a flat molecule. We have seen that this flatness is a result of the geometric arrangement of the bonding orbitals, and in particular the overlap that gives rise to the π orbital. For the same reasons, a portion of any alkene must also be flat, the two doubly-bonded carbons and the four atoms attached to them lying in the same plane.

If we examine the structure of 2-butene more closely, and particularly if we use molecular models, we find that there are two quite different ways, I and II, in which the atoms can be arranged (aside from the infinite number of possibilities arising from rotation about the single bonds). In one of the structures the methyl groups lie on the same side of the molecule (I), and in the other structure they lie on opposite sides of the molecule (II).



I

II

Now the question arises: can we expect to isolate two isomeric 2-butenes corresponding to these two different structures, or are they too readily interconverted—like, say, the conformations of *n*-butane (Sec. 3.5)?

Conversion of I into II involves rotation about the carbon–carbon double bond. The possibility of isolating isomers depends upon the energy required for this rotation. We have seen that the formation of the π bond involves overlap of the *p* orbitals that lie above and below the plane of the σ orbitals. To pass from one of these 2-butenes to the other, the molecule must be twisted so that the *p* orbitals no longer overlap; that is, the π bond must be broken (see Fig. 5.5).

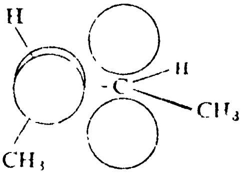


Figure 5.5. Hindered rotation about carbon–carbon double bond. Rotation would prevent overlap of *p* orbitals and would break π bond.

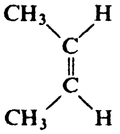
Breaking the π bond requires about 70 kcal of energy, at room temperature an insignificant proportion of collisions possess this necessary energy, and hence the rate of this interconversion is extremely small. Because of this 70-kcal energy barrier, then, *there is* **hindered rotation** *about the carbon–carbon double bond.* As a result of this hindered rotation, two isomeric 2-butenes can be isolated. These are, of course, the butylenes of b.p. +1° and b.p. +4°.

5.6 Geometric isomerism

Since the isomeric 2-butenes differ from one another *only* in the way the atoms are oriented in space (but are like one another with respect to which atoms are attached to which other atoms), they belong to the general class we have called *stereoisomers* (Sec. 4.1). They are not, however, mirror images of each other, and hence are not enantiomers. As we have already said, *stereoisomers that are not mirror images of each other are called* **diastereomers.**

The particular kind of diastereomers that owe their existence to hindered rotation about double bonds are called **geometric isomers.** The isomeric 2-butenes, then, are diastereomers, and more specifically, geometric isomers.

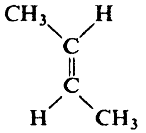
We recall that the arrangement of atoms that characterizes a particular stereoisomer is called its *configuration*. The configurations of the isomeric 2-butenes are the structures I and II. These configurations are differentiated in their names by the prefixes **cis-** (Latin: on this side) and **trans-** (Latin: across), which indicate that the methyl groups are on the same side or on opposite sides of the molecule. In a way that we are not prepared to take up at this time, the isomer of b.p. +4° has been assigned the *cis* configuration and the isomer of b.p. +1° the *trans* configuration.



I

cis-2-Butene

b.p. +4°



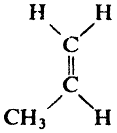
II

trans-2-Butene

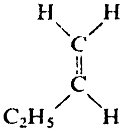
b.p. +1°

Geometric isomers

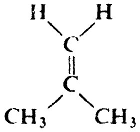
There is hindered rotation about *any* carbon–carbon double bond, but it gives rise to geometric isomerism only if there is a certain relationship among the groups attached to the doubly-bonded carbons. We can look for this isomerism by drawing the possible structures (or better yet, by constructing them from molecular models), and then seeing if these are indeed isomeric, or actually identical. On this basis we find that propylene, 1-butene, and isobutylene should not show isomerism; this conclusion agrees with the facts. Many higher alkenes may, of course, show geometric isomerism



Propylene



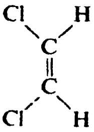
1-Butene



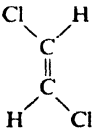
Isobutylene

No geometric isomerism

If we consider compounds other than hydrocarbons, we find that 1,1-dichloro- and 1,1-dibromoethene should not show isomerism, whereas the 1,2-dichloro- and 1,2-dibromoethenes should. In every case these predictions have been found correct. Isomers of the following physical properties have been isolated.



cis-

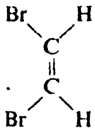


trans-

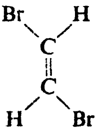
1,2-Dichloroethene

b.p. 60° m.p. −80°

b.p. 48° m.p. −50°



cis-



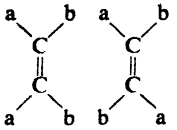
trans-

1,2-Dibromoethene

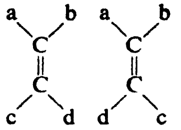
b.p. 110° m.p. −53°

b.p. 108° m.p. −6°

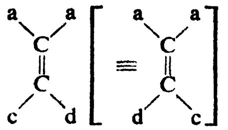
As we soon conclude from our examination of these structures, geometric isomerism cannot exist if either carbon carries two identical groups. Some possible combinations are shown below.



Isomerism



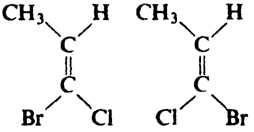
Isomerism



No isomerism

The phenomenon of geometric isomerism is a general one and can be encountered in any class of compounds that contain carbon–carbon double bonds (or even double bonds of other kinds).

The prefixes *cis* and *trans* work very well for disubstituted ethylenes and some trisubstituted ethylenes. But how are we to specify configurations like these?

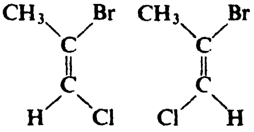


Z *E*

1-Bromo-1-chloropropene

$CH_3 > H$

$Br > Cl$

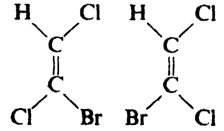


Z *E*

2-Bromo-1-chloropropene

$Br > CH_3$

$Cl > H$



Z *E*

1-Bromo-1,2-dichloroethene

$Cl > H$

$Br > Cl$

Which groups are our reference points? Looking at each doubly-bonded carbon in turn, we arrange its two atoms or groups in their Cahn-Ingold-Prelog sequence. We then take the group of higher priority on the one carbon and the group of higher priority on the other carbon, and tell whether they are on the same side of the molecule or on opposite sides. So that it will be clear that we are using this method of specification, we use the letter *Z* to mean *on the same side*, and the letter *E* to mean *on opposite sides*. (From the German: *zusammen*, together, and *entgegen*, opposite.)

In so far as chemical and physical properties are concerned, geometric isomers show the same relationship to each other as do the other diastereomers we have encountered (Sec. 4.17). They contain the same functional groups and hence show similar chemical properties. Their chemical properties are *not identical*, however, since their structures are neither identical nor mirror images; they react with the same reagents, but at different rates.

As the examples above illustrate, geometric isomers have different physical properties: different melting points, boiling points, refractive indices, solubilities, densities, and so on. On the basis of these different physical properties, they can be distinguished from each other and, once the configuration of each has been determined, identified. On the basis of these differences in physical properties they can, in principle at least, be separated. (See Sec. 4.17.)

When we take up the physical properties of the alkenes (Sec. 5.9), we shall discuss one of the ways in which we can tell whether a particular substance is the *cis*- or *trans*-isomer, that is, one of the ways in which we *assign configuration*.

A pair of geometric isomers are, then, diastereomers. Where do they fit into the other classification scheme, the one based on how the stereoisomers are interconverted

(Sec. 4.20)? We shall discuss this question in more detail later (Sec. 7.1), but for the moment we can say this. In the important quality of *isolability*, geometric isomers resemble configurational isomers, and for a very good reason: in both cases interconversion requires bond breaking—a π bond in the case of geometric isomers.

5.7 Higher alkenes

As we can see, the butylenes contain one carbon and two hydrogens more than propylene, which in turn contains one carbon and two hydrogens more than ethylene. The alkenes, therefore, form another homologous series, the increment being the same as for the alkanes: CH_2. The general formula for this family is C_nH_{2n}.

As we ascend the series of alkenes, the number of isomeric structures for each member increases even more rapidly than in the case of the alkane series; in addition to variations in the carbon skeletons, there are variations in the position of the double bond for a given skeleton, and the possibility of geometric isomerism.

Problem 5.1 Neglecting enantiomerism, draw structures of: (a) the six isomeric pentylenes (C_5H_{10}); (b) the four chloropropylenes (C_3H_5Cl); (c) the eleven chlorobutylenes (C_4H_7Cl). Specify as *Z* or *E* each geometric isomer.

5.8 Names of alkenes

Common names are seldom used except for three simple alkenes: *ethylene*, *propylene*, and *isobutylene*. The various alkenes of a given carbon number are, however, sometimes referred to collectively as the *pentylenes* (*amylenes*), *hexylenes*, *heptylenes*, and so on. (One sometimes encounters the naming of alkenes as derivatives of ethylene: as, for example, *tetramethylethylene* for $(CH_3)_2C{=}C(CH_3)_2$.) Most alkenes are named by the IUPAC system.

The rules of the IUPAC system are:

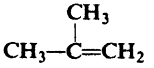
1. Select as the parent structure the longest continuous chain *that contains the carbon–carbon double bond*; then consider the compound to have been derived from this structure by replacement of hydrogen by various alkyl groups. The parent structure is known as *ethene*, *propene*, *butene*, *pentene*, and so on, depending upon the number of carbon atoms; each name is derived by changing the ending *-ane* of the corresponding alkane name to **-ene**:

$H_2C{=}CH_2$
Ethene

$CH_3{-}CH{=}CH_2$
Propene

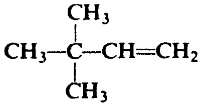
$CH_3CH_2CH{=}CH_2$
1-Butene

$CH_3CH{=}CHCH_3$
2-Butene
(*cis-* or *trans-*)



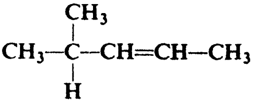
$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$

2-Methylpropene



$CH_3{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH{=}CH_2$

3,3-Dimethyl-1-butene



$CH_3{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}CH{=}CH{-}CH_3$

4-Methyl-2-pentene
(*cis- or trans-*)

2. Indicate by a number the position of the double bond in the parent chain. Although the double bond involves two carbon atoms, designate its position by the number of the *first* doubly-bonded carbon encountered when numbering from the end of the chain nearest the double bond; thus *1-butene* and *2-butene*.

3. Indicate by numbers the positions of the alkyl groups attached to the parent chain.

Problem 5.2 Give the structural formula of: (a) 2,3-dimethyl-2-butene; (b) 3-bromo-2-methylpropene; (c) *cis*-2-methyl-3-heptene; (d) (*E*)-2-chloro-2-butene.

Problem 5.3 Referring to your answer to Problem 5.1 (p. 151), give IUPAC names for: (a) the isomeric pentylenes; (b) the isomeric chloropropenes.

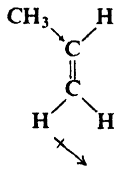
5.9 Physical properties

As a class, the alkenes possess physical properties that are essentially the same as those of the alkanes. They are insoluble in water, but quite soluble in nonpolar solvents like benzene, ether, chloroform, or ligroin. They are less dense than water. As we can see from Table 5.2, the boiling point rises with increasing carbon number; as with the alkanes, the boiling point rise is 20–30° for each added carbon, except for the very small homologs. As before, branching lowers the boiling point. A comparison of Table 5.2 with Table 3.3 (p. 86) shows that the boiling point of an alkene is very nearly the same as that of the alkane with the corresponding carbon skeleton.

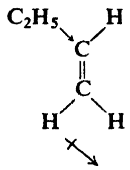
Table 5.2 ALKENES

Name	Formula	M.p., °C	B.P., °C	Density (at 20°C)
Ethylene	$CH_2{=}CH_2$	−169	−102	
Propylene	$CH_2{=}CHCH_3$	−185	− 48	
1-Butene	$CH_2{=}CHCH_2CH_3$		−6.5	
1-Pentene	$CH_2{=}CH(CH_2)_2CH_3$		30	0.643
1-Hexene	$CH_2{=}CH(CH_2)_3CH_3$	−138	63.5	.675
1-Heptene	$CH_2{=}CH(CH_2)_4CH_3$	−119	93	.698
1-Octene	$CH_2{=}CH(CH_2)_5CH_3$	−104	122.5	.716
1-Nonene	$CH_2{=}CH(CH_2)_6CH_3$		146	.731
1-Decene	$CH_2{=}CH(CH_2)_7CH_3$	− 87	171	.743
cis-2-Butene	*cis*-$CH_3CH{=}CHCH_3$	−139	4	
trans-2-Butene	*trans*-$CH_3CH{=}CHCH_3$	−106	1	
Isobutylene	$CH_2{=}C(CH_3)_2$	−141	−7	
cis-2-Pentene	*cis*-$CH_3CH{=}CHCH_2CH_3$	−151	37	.655
trans-2-Pentene	*trans*-$CH_3CH{=}CHCH_2CH_3$		36	.647
3-Methyl-1-butene	$CH_2{=}CHCH(CH_3)_2$	−135	25	.648
2-Methyl-2-butene	$CH_3CH{=}C(CH_3)_2$	−123	39	.660
2,3-Dimethyl-2-butene	$(CH_3)_2C{=}C(CH_3)_2$	− 74	73	.705

Like alkanes, alkenes are at most only weakly polar. Since the loosely held π electrons of the double bond are easily pulled or pushed, dipole moments are larger than for alkanes. They are still small, however: compare the dipole moments shown for propylene and 1-butene, for example, with the moment of 1.83 D for methyl chloride. The bond joining the alkyl group to the doubly-bonded carbon has a small polarity, which is believed to be in the direction shown, that is, with the alkyl group releasing electrons to the doubly-bonded carbon. Since this polarity is not canceled by a corresponding polarity in the opposite direction, it gives a net dipole moment to the molecule.

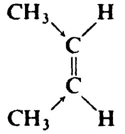


$\mu = 0.35$ D



$\mu = 0.37$ D

cis-2-Butene, with two methyl groups on one side of the molecule and two hydrogens on the other, should have a small dipole moment. In *trans*-2-butene, on the other hand, with one methyl and one hydrogen on each side of the molecule, the bond moments should cancel out. Although the dipole moments have not been measured directly, a small difference in polarity is reflected in the higher boiling point of the *cis*-isomer.

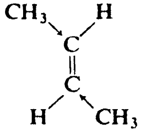


cis-2-Butene

expect small +⟶

b.p. +4°

m.p −139°



trans-2-Butene

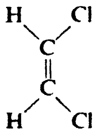
expect $\mu = 0$

b.p. +1°

m.p. −106°

This same relationship exists for many pairs of geometric isomers. Because of its higher polarity the *cis*-isomer is generally the higher boiling of a pair; because of its lower symmetry it fits into a crystalline lattice more poorly, and thus generally has the lower melting point.

The differences in polarity, and hence the differences in melting point and boiling point, are greater for alkenes that contain elements whose electronegativities differ widely from that of carbon. For example:

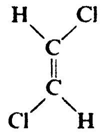


cis

$\mu = 1.85$ D

b.p. 60°

m.p. −80°

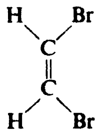


trans

$\mu = 0$

b.p. 48°

m.p. −50°

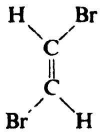


cis

$\mu = 1.35$ D

b.p. 110°

m.p. −53°

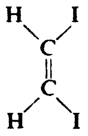


trans

$\mu = 0$

b.p. 108°

m.p. −6°

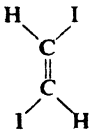


cis

$\mu = 0.75$ D

b.p. 188°

m.p. −14°



trans

$\mu = 0$

b.p. 192°

m.p. +72°

The relationship between configuration and boiling point or melting point is only a rule of thumb, to which there are many exceptions (for example, the boiling points of the diiodoethenes). Measurement of dipole moment, on the other hand, frequently enables us positively to designate a particular isomer as *cis* or *trans*.

Problem 5.4 (a) Indicate the direction of the net dipole moment for each of the dihaloethenes. (b) Would *cis*-2,3-dichloro-2-butene have a larger or smaller dipole moment than *cis*-1,2-dichloroethene? (c) Indicate the direction of the net dipole moment of *cis*-1,2-dibromo-1,2-dichloroethene. Will it be larger or smaller than the dipole moment of *cis*-1,2-dichloroethene? Why?

5.10 Industrial source

Alkenes are obtained in industrial quantities chiefly by the cracking of petroleum (Sec. 3.31). The smaller alkenes can be obtained in pure form by fractional distillation and are thus available for conversion into a large number of important aliphatic compounds. Higher alkenes, which cannot be separated from the complicated cracking mixture, remain as valuable components of gasoline.

1-Alkenes of even carbon number, consumed in large quantities in the manufacture of detergents, are available through controlled ionic polymerization of ethylene by the Ziegler-Natta method (Sec. 32.6).

5.11 Preparation

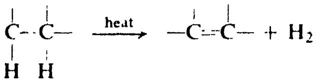
Alkenes containing up to five carbon atoms can be obtained in pure form from the petroleum industry. Pure samples of more complicated alkenes must be prepared by methods like those outlined below.

The introduction of a carbon-carbon double bond into a molecule containing only single bonds must necessarily involve the **elimination** of atoms or groups from two adjacent carbons:

$$-\underset{\underset{Y}{|}}{\overset{|}{C}}-\underset{\underset{Z}{|}}{\overset{|}{C}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}-$$

Elimination

In the cracking process already discussed, for example, the atoms eliminated are both hydrogen atoms:

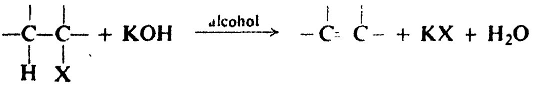


$$-\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{H}{|}}{\overset{|}{C}}- \xrightarrow{\text{heat}} -\overset{|}{C}=\overset{|}{C}- + H_2$$

The elimination reactions described below not only can be used to make simple alkenes, but also—and this is much more important—provide the best general ways to introduce carbon-carbon double bonds into molecules of all kinds.

PREPARATION OF ALKENES

1. **Dehydrohalogenation of alkyl halides.** Discussed in Sec. 5.12 5.14.



$$-\underset{\underset{H}{|}}{\overset{|}{C}}-\underset{\underset{X}{|}}{\overset{|}{C}}- + KOH \xrightarrow{\text{alcohol}} -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$$

Ease of dehydrohalogenation of alkyl halides

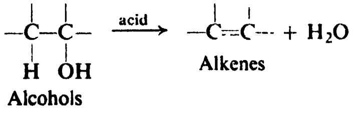
3° > 2° > 1°

Examples:

$$\underset{n\text{-Butyl chloride}}{CH_3CH_2CH_2CH_2Cl} \xrightarrow{\text{KOH (alc)}} \underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2}$$

$$\underset{sec\text{-Butyl chloride}}{CH_3CH_2CHClCH_3} \xrightarrow{\text{KOH (alc)}} \underset{\substack{\text{2-Butene}\\ 80\%}}{CH_3CH{=}CHCH_3} + \underset{\substack{\text{1-Butene}\\ 20\%}}{CH_3CH_2CH{=}CH_2}$$

2. **Dehydration of alcohols.** Discussed in Sec. 5.19–5.23.

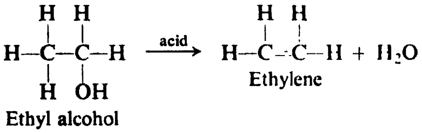


$$\underset{\text{Alcohols}}{-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-} \xrightarrow{\text{acid}} \underset{\text{Alkenes}}{-\overset{|}{C}{=}\overset{|}{C}-} + H_2O$$

Ease of dehydration of alcohols

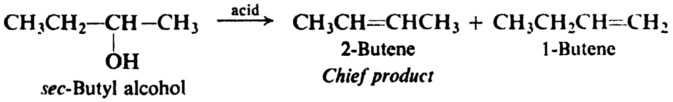
$3^\circ > 2^\circ > 1^\circ$

Examples:



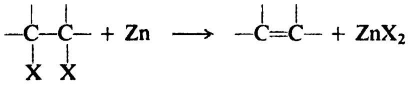
$$\underset{\text{Ethyl alcohol}}{H-\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}-\underset{OH}{\overset{H}{\overset{|}{\underset{|}{C}}}}-H} \xrightarrow{\text{acid}} \underset{\text{Ethylene}}{H-\overset{H}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}-H} + H_2O$$

$$\underset{n\text{-Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow{\text{acid}} \underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2} + \underset{\substack{\text{2-Butene}\\ \textit{Chief product}}}{CH_3CH{=}CHCH_3}$$



$$\underset{sec\text{-Butyl alcohol}}{CH_3CH_2-\underset{OH}{\underset{|}{CH}}-CH_3} \xrightarrow{\text{acid}} \underset{\substack{\text{2-Butene}\\ \textit{Chief product}}}{CH_3CH{=}CHCH_3} + \underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2}$$

3. **Dehalogenation of vicinal dihalides.** Discussed in Sec. 5.11.

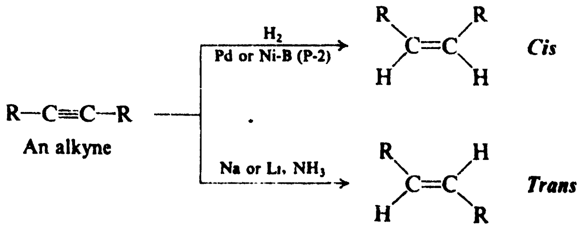


$$-\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- + Zn \longrightarrow -\overset{|}{C}{=}\overset{|}{C}- + ZnX_2$$

Example:

$$\underset{\text{2,3-Dibromobutane}}{CH_3CHBrCHBrCH_3} \xrightarrow{Zn} \underset{\text{2-Butene}}{CH_3CH{=}CHCH_3}$$

4. **Reduction of alkynes.** Discussed in Sec. 8.9.



The most important of these methods of preparation—since they are the most generally applicable—are the **dehydrohalogenation of alkyl halides** and the **dehydration of alcohols.** Both methods suffer from the disadvantage that, where the structure permits, hydrogen can be eliminated from the carbon on either side of the carbon bearing the —X or —OH; this frequently produces isomers. Since the isomerism usually involves only the position of the double bond, it is not important in the cases where we plan to convert the alkene into an alkane.

As we shall see later, alkyl halides are generally prepared from the corresponding alcohols, and hence both these methods ultimately involve preparation from alcohols; however, dehydrohalogenation generally leads to fewer complications and is often the preferred method despite the extra step in the sequence.

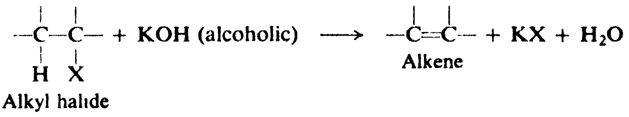
Dehalogenation of vicinal (Latin: *vicinalis*, neighboring) dihalides is severely limited by the fact that these dihalides are themselves generally prepared from the alkenes. However, it is sometimes useful to convert an alkene to a dihalide while we perform some operation on another part of the molecule, and then to regenerate the alkene by treatment with zinc; this procedure is referred to as *protecting the double bond.*

When a pure *cis*- or *trans*-alkene is wanted, uncontaminated with its stereoisomer, it can often be prepared by reduction of an alkyne with the proper reagent (Sec. 8.9).

5.12 Dehydrohalogenation of alkyl halides

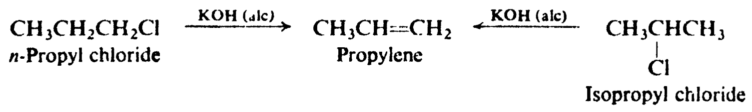
Alkyl halides are converted into alkenes by **dehydrohalogenation**: *elimination of the elements of hydrogen halide.* Dehydrohalogenation involves removal of the halogen atom together with a hydrogen atom from a carbon adjacent to the one bearing the halogen. It is not surprising that the reagent required for the elimination of what amounts to a molecule of acid is a strong base.

Dehydrohalogenation: elimination of HX



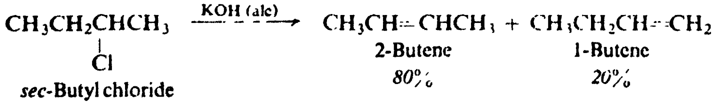
$$\underset{\text{Alkyl halide}}{-\underset{H}{\underset{|}{\overset{|}{C}}}-\underset{X}{\underset{|}{\overset{|}{C}}}-} + \text{KOH (alcoholic)} \longrightarrow \underset{\text{Alkene}}{-\overset{|}{C}{=}\overset{|}{C}-} + KX + H_2O$$

The alkene is prepared by simply heating together the alkyl halide and a solution of potassium hydroxide in alcohol. For example:



$$\underset{n\text{-Propyl chloride}}{CH_3CH_2CH_2Cl} \xrightarrow{\text{KOH (alc)}} \underset{\text{Propylene}}{CH_3CH{=}CH_2} \xleftarrow{\text{KOH (alc)}} \underset{\text{Isopropyl chloride}}{CH_3\underset{Cl}{\underset{|}{C}}HCH_3}$$

$$\underset{n\text{-Butyl chloride}}{CH_3CH_2CH_2CH_2Cl} \xrightarrow{\text{KOH (alc)}} \underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2}$$



$$\underset{sec\text{-Butyl chloride}}{CH_3CH_2\underset{Cl}{\underset{|}{C}}HCH_3} \xrightarrow{\text{KOH (alc)}} \underset{80\%}{\underset{\text{2-Butene}}{CH_3CH{=}CHCH_3}} + \underset{20\%}{\underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2}}$$

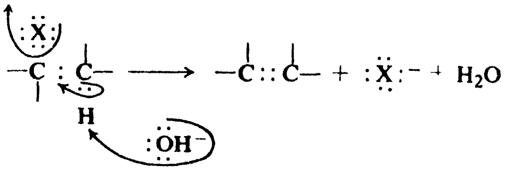
As we can see, in some cases this reaction yields a single alkene, and in other cases yields a mixture. *n*-Butyl chloride, for example, can eliminate hydrogen only from C-2 and hence yields only 1-butene. *sec*-Butyl chloride, on the other hand, can eliminate hydrogen from either C-1 or C-3 and hence yields both 1-butene and 2-butene. Where the two alkenes can be formed, 2-butene is the chief product; this fact fits into a general pattern for dehydrohalogenation which is discussed in Sec. 5.14.

Problem 5.5 Give structures of all alkenes expected from dehydrohalogenation of: (a) 1-chloropentane, (b) 2-chloropentane, (c) 3-chloropentane, (d) 2-chloro-2-methylbutane, (e) 3-chloro-2-methylbutane, (f) 2-chloro-2,3-dimethylbutane, (g) 1-chloro-2,2-dimethylpropane.

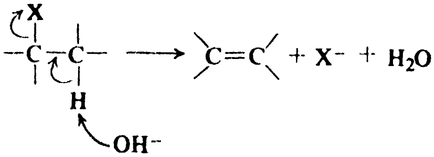
Problem 5.6 What alkyl halide (*if any*) would yield each of the following pure alkenes upon dehydrohalogenation? (a) isobutylene, (b) 1-pentene, (c) 2-pentene, (d) 2-methyl-1-butene, (e) 2-methyl-2-butene, (f) 3-methyl-1-butene.

5.13 Mechanism of dehydrohalogenation

The function of hydroxide ion is to pull a hydrogen ion away from carbon; simultaneously a halide ion separates and the double bond forms. We should notice that, in contrast to free radical reactions, the breaking of the C—H and C—X bonds occurs in an unsymmetrical fashion: hydrogen relinquishes *both* electrons to carbon, and halogen retains *both* electrons. The electrons left behind by hydrogen are now available for formation of the second bond (the π bond) between the carbon atoms.



represented as



where arrows show the direction of electron shift

What supplies the energy for the breaking of the carbon–hydrogen and carbon–halogen bonds?

(a) First, there is formation of the bond between the hydrogen ion and the very strong base, hydroxide ion.

(b) Next, there is formation of the π bond which, although weak, does supply about 70 kcal/mole of energy.

(c) Finally—and this is extremely important—there is the energy of solvation of the halide ions. Alcohol, like water, is a polar solvent. A liberated halide ion is surrounded by a cluster of these polar molecules; each solvent molecule is oriented so that the positive end of its dipole is near the negative ion (Fig. 5.6).

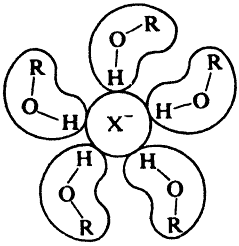


Figure 5.6. Ion-dipole interaction: solvated halide ion.

Although each of these *ion-dipole bonds* (Sec. 1.21) is weak, in the aggregate they supply a great deal of energy. (We should recall that the ion-dipole bonds in hydrated sodium and chloride ions provide the energy for the breaking down of the sodium chloride crystalline lattice, a process which in the absence of water requires a temperature of 801°.) *Just as a hydrogen ion is pulled out of the molecule by a hydroxide ion, so a halide ion is pulled out by solvent molecules.*

The free-radical reactions of the alkanes, which we studied in Chap. 3, are chiefly gas phase reactions. It is significant that ionic reactions (like the one just discussed) occur chiefly in solution.

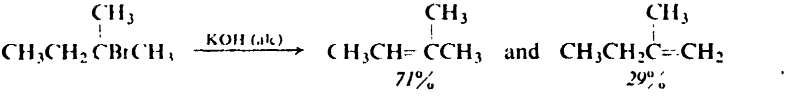
(We shall return to dehydrohalogenation after we have learned a little more chemistry (Sec. 14.20), and have a look at the *evidence* for this mechanism.)

5.14 Orientation and reactivity in dehydrohalogenation

In cases where a mixture of isomeric alkenes can be formed, which isomer, if any, will predominate? Study of many dehydrohalogenation reactions has shown that one isomer generally does predominate, and that it is possible to predict which isomer this will be—that is, to predict the *orientation* of elimination—on the basis of molecular structure.

$$CH_3CH_2CHBrCH_3 \xrightarrow{\text{KOH (alc)}} \underset{81\%}{CH_3CH{=}CHCH_3} \text{ and } \underset{19\%}{CH_3CH_2CH{=}CH_2}$$

$$CH_3CH_2CH_2CHBrCH_3 \xrightarrow{\text{KOH (alc)}} \underset{71\%}{CH_3CH_2CH{=}CHCH_3} \text{ and } \underset{29\%}{CH_3CH_2CH_2CH{=}CH_2}$$



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}BrCH_3 \xrightarrow{\text{KOH (alc)}} \underset{71\%}{CH_3CH{=}\overset{\overset{CH_3}{|}}{C}CH_3} \text{ and } \underset{29\%}{CH_3CH_2\overset{\overset{CH_3}{|}}{C}{=}CH_2}$$

Once more, orientation is determined by the relative rates of competing reactions. For *sec*-butyl bromide, attack by base at any one of three hydrogens (those on C-1) can lead to the formation of 1-butene; attack at either of two hydrogens (on C-3) can lead to the formation of 2-butene. We see that 2-butene is the preferred product—that is, is formed faster—*despite* a probability factor of 3:2 working against its formation. The other examples fit the same pattern: the preferred product is the alkene that has the greater number of alkyl groups attached to the doubly-bonded carbon atoms.

Ease of formation of alkenes

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2,\ RCH{=}CHR > RCH{=}CH_2$$

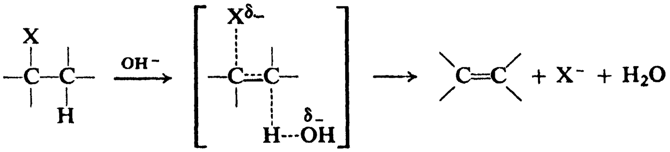
In Sec. 6.4 we shall find evidence that the stability of alkenes follows exactly the same sequence.

Stability of alkenes

$$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2,\ RCH{=}CHR > RCH{=}CH_2 > CH_2{=}CH_2$$

In dehydrohalogenation, the more stable the alkene the more easily it is formed.

Examination of the transition state involved shows that it is reasonable that the more stable alkene should be formed faster:



Transition state:
partly formed double bond

The double bond is partly formed, and the transition state has thus acquired alkene character. Factors that stabilize an alkene also stabilize an *incipient* alkene in the transition state.

Alkene stability not only determines *orientation* of dehydrohalogenation, but also is an important factor in determining the *reactivity* of an alkyl halide toward elimination, as shown at the top of the next page.

Reactant	⟶	*Product*	*Relative rates*	*Relative rates per* H
CH_3CH_2Br	⟶	$CH_2{=}CH_2$	1.0	1.0
$CH_3CH_2CH_2Br$	⟶	$CH_3CH{=}CH_2$	3.3	5.0
$CH_3CHBrCH_3$	⟶	$CH_3CH{=}CH_2$	9.4	4.7
$(CH_3)_3CBr$	⟶	$(CH_3)_2C{=}CH_2$	120	40

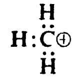
As one proceeds along a series of alkyl halides from 1° to 2° to 3°, the structure by definition becomes more branched at the carbon carrying the halogen. This increased branching has two results: it provides a greater number of hydrogens for attack by base, and hence a more favorable probability factor toward elimination; and it leads to a more highly branched, more stable alkene, and hence a more stable transition state and lower E_{act}. As a result of this combination of factors, **in dehydrohalogenation the order of reactivity of RX is 3° > 2° > 1°.**

Problem 5.7 Predict the major product of each dehydrohalogenation in Problem 5.5, page 157.

5.15 Carbonium ions

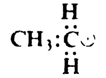
To account for the observed facts, we saw earlier, a certain mechanism was advanced for the halogenation of alkanes; the heart of this mechanism is the fleeting existence of free radicals, highly reactive neutral particles bearing an odd electron.

Before we can discuss the preparation of alkenes by dehydration of alcohols, we must first learn something about another kind of reactive particle: the **carbonium ion,** *a group of atoms that contains a carbon atom bearing only six electrons.* Carbonium ions are classified as primary, secondary, or tertiary after the carbon bearing the positive charge. They are named by use of the word *cation.* For example:



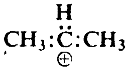
$$\begin{array}{c} \mathrm{H} \\ \mathrm{H}:\overset{..}{\underset{..}{\mathrm{C}}}\oplus \\ \mathrm{H} \end{array}$$

Methyl cation



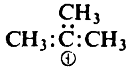
$$\begin{array}{c} \mathrm{H} \\ \mathrm{CH_3}:\overset{..}{\underset{..}{\mathrm{C}}}\oplus \\ \mathrm{H} \end{array}$$

Ethyl cation
(*primary*, 1°)



$$\begin{array}{c} \mathrm{H} \\ \mathrm{CH_3}:\overset{..}{\mathrm{C}}:\mathrm{CH_3} \\ \oplus \end{array}$$

Isopropyl cation
(*secondary*, 2°)



$$\begin{array}{c} \mathrm{CH_3} \\ \mathrm{CH_3}:\overset{..}{\mathrm{C}}:\mathrm{CH_3} \\ \oplus \end{array}$$

tert-Butyl cation
(*tertiary*, 3°)

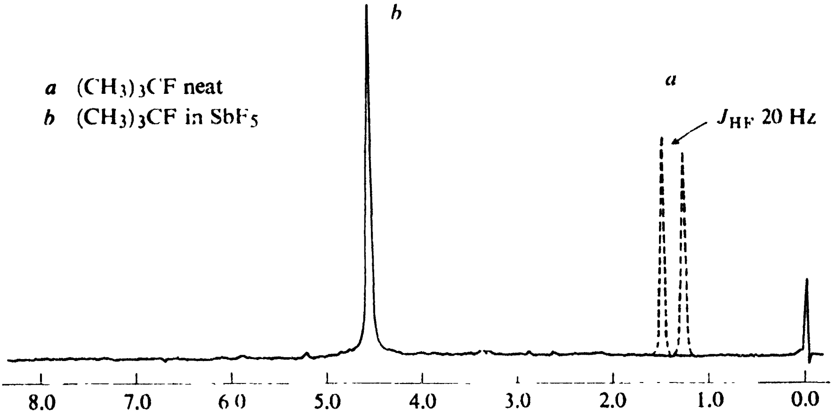
Like the free radical, the carbonium ion is an exceedingly reactive particle, and for the same reason: the tendency to complete the octet of carbon. Unlike the free radical, the carbonium ion carries a positive charge.

One kind of unusually stable carbonium ion (Sec. 12.19) was recognized as early as 1902 by the salt-like character of certain organic compounds. But direct observation of simple alkyl cations should be exceedingly difficult, by virtue of the very reactivity—and hence short life—that we attribute to them. Nevertheless, during the 1920's and 1930's, alkyl cations were proposed as intermediates in many organic reactions, and their existence was generally accepted, due largely to the work of three chemists: Hans Meerwein of Germany, "the father of modern carbonium ion chemistry;" Sir Christopher Ingold of England; and Frank Whitmore of the United States. The evidence consisted of a wide variety of observations made in studying the chemistry of alkenes, alcohols, alkyl halides, and many other kinds of organic compounds: observations that revealed a basically similar pattern of behavior most logically attributed to intermediate carbonium ions. A sizable part of this book will be devoted to seeing what that pattern is.

In 1963, George Olah (now at Case Western Reserve University) reported the *direct observation* of simple alkyl cations. Dissolved in the extremely powerful Lewis acid SbF_5, alkyl fluorides (and, later, other halides) were found to undergo ionization to form the cation, which could be studied at leisure. There was a

$$RF + SbF_5 \longrightarrow R^+ \, SbF_6^-$$

dramatic change in the nmr spectrum (Chap. 13), from the spectrum of the alkyl fluoride to the spectrum of a molecule that contained no fluorine but instead sp^2-hybridized carbon with a very low electron density. Figure 5.7 shows what was observed for the *tert*-butyl fluoride system: a simple spectrum but, by its very simplicity, enormously significant. Although potentially very reactive, the *tert*-butyl cation can do little in this environment except try to regain the fluoride ion—and the SbF_5 is an even stronger Lewis acid than the cation.



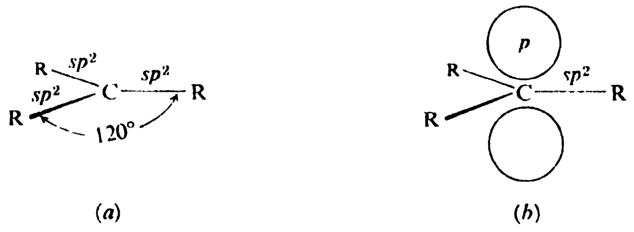
Courtesy of *The Journal of American Chemical Society*

Figure 5.7. Proton nmr spectrum of (*a*) *tert*-butyl fluoride and (*b*) *tert*-butyl cation. In (*a*), proton signal split into two peaks by coupling with nearby fluorine. In (*b*), single peak, shifted far downfield; strong deshielding due to low electron density on positive carbon.

By methods like this, Olah has opened the door to the study not just of the existence of organic cations of many kinds, but of intimate details of their structure.

5.16 Structure of carbonium ions

In a carbonium ion, the electron-deficient carbon is bonded to three other atoms, and for this bonding uses sp^2 orbitals; the bonds are trigonal, directed to the corners of an equilateral triangle. This part of a carbonium ion is therefore



(*a*) (*b*)

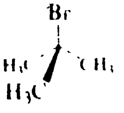
Figure 5.8. A carbonium ion. (*a*) Only σ bonds shown. (*b*) Empty *p* orbital above and below plane of σ bonds.

flat, the electron-deficient carbon and the three atoms attached to it lying in the same plane (Fig. 5.8*a*).

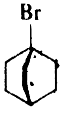
But our description of the molecule is not yet quite complete. Carbon has left a *p* orbital, with its two lobes lying above and below the plane of the σ bonds (Fig. 5.8*b*); in a carbonium ion, the *p* orbital is *empty*. Although formally empty, this *p* orbital, we shall find, is intimately involved in the chemistry of carbonium ions: in their stability, and the stability of various transition states leading to their formation.

There can be little doubt that carbonium ions actually are flat. The quantum mechanical picture of a carbonium ion is exactly the same as that of boron trifluoride (Sec. 1.10), a molecule whose flatness is firmly established. Nmr and infrared spectra of the stabilized carbonium ions studied by Olah are consistent with sp^2 hybridization and flatness: in particular, infrared and Raman spectra of the *tert*-butyl cation are strikingly similar to those of trimethylboron, known to be flat.

Evidence of another kind indicates that carbonium ions not only normally *are* flat, but have a strong *need to be* flat. Consider the three tertiary alkyl bromides: *tert*-butyl bromide: and I and II, which are *bicyclic* (two-ringed) compounds with

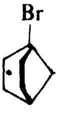


tert-Butyl bromide



I

1-Bromobicyclo-[2.2.2]octane

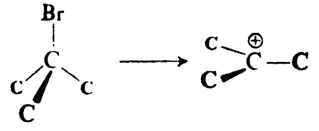


II

1-Bromobicyclo-[2.2.1]heptane

bromine at the bridgehead. The impact of a high-energy electron can remove bromine from an alkyl bromide and generate a carbonium ion; the energy of the electron required to do the job can be measured. On electron impact, I requires 5 kcal mole more energy to form the carbonium ion than does *tert*-butyl bromide, and II requires 20 kcal mole more energy.

How are we to interpret these facts? On conversion into a carbonium ion, three carbons must move into the plane of the electron-deficient carbon: easy for



Alkyl bromide *Tetrahedral*

Carbonium ion *Trigonal*

the open-chain *tert*-butyl group; but difficult for I, where the three carbons are tied back by the ring system; and still more difficult for II, where they are tied back more tightly by the smaller ring.

Imagine—or, better, *make*—a model of I or II. You could squash the top of the molecule flat, but only by distorting the angles of the other bonds away from their normal tetrahedral angle, and thus introducing *angle strain* (Sec. 9.7).

Now, why is there this need to be flat? Partly, to permit formation of the strongest possible σ bonds through sp^2 hybridization. But there is a second advantage of flatness, one which is related to the major factor determining carbonium ion stability, *accommodation of charge.*

5.17 Stability of carbonium ions. Accommodation of charge

The characteristic feature of a carbonium ion is, by definition, the electron-deficient carbon and the attendant positive charge. The relative stability of a carbonium ion is determined chiefly by how well it *accommodates* that charge.

According to the laws of electrostatics, **the stability of a charged system is increased by dispersal of the charge.** Any factor, therefore, that tends to spread out the positive charge of the electron-deficient carbon and distribute it over the rest of the ion must stabilize a carbonium ion.

Consider a substituent, G, attached to an electron-deficient carbon in place of a hydrogen atom. Compared with hydrogen, G may either release electrons or withdraw electrons (Sec. 1.23).

Carbonium Ion Stability

$G\rightarrow\overset{|}{\underset{|}{C}}\oplus$ $G\leftarrow\overset{|}{\underset{|}{C}}\oplus$

G releases electrons: *disperses charge, stabilizes cation*

G withdraws electrons: *intensifies charge, destabilizes cation*

An electron-releasing substituent tends to reduce the positive charge at the electron-deficient carbon; in doing this, the substituent itself becomes somewhat positive. This dispersal of the charge stabilizes the carbonium ion.

An electron-withdrawing substituent tends to intensify the positive charge on the electron-deficient carbon, and hence makes the carbonium ion less stable.

We consider (Sec. 1.23) electronic effects to be of two kinds: *inductive effects*, related to the electronegativity of substituents; and *resonance effects.* In the case of carbonium ions, we shall see (Sec. 8.21), a resonance effect involves overlap of the "empty" p orbital of the electron-deficient carbon with orbitals on other, nearby atoms; the result is, of course, that the p orbital is no longer empty, and the electron-deficient carbon no longer so positive. Maximum overlap depends on coplanarity in this part of the molecule, and it is here that we find the second advantage of flatness in a carbonium ion.

So far, we have discussed only factors operating *within* a carbonium ion to make it more or less stable than another carbonium ion. But what is *outside* the carbonium ion proper—its environment—can be even more important in determining how fast a carbonium ion is formed, how long it lasts, and what happens to it. There are *anions*, one of which may stay close by to form an ion pair. There is the *solvent*: a cluster of solvent molecules, each with the positive end of its dipole turned toward the cation; possibly one solvent molecule—or two—playing a special role through overlap of one or both lobes of the p orbital. There may be a *neighboring group effect* (Chap. 28), in which a substituent on a neighboring carbon approaches closely enough to share its electrons and form a covalent bond: an internal factor, actually, but in its operation much like an external factor.

In all this we see the characteristic of carbonium ions that underlies their whole pattern of behavior: a *need for electrons to complete the octet of carbon.*

5.18 Relative stabilities of alkyl cations

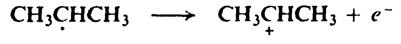
The amount of energy required to remove an electron from a molecule or atom is called the *ionization potential.* (It is really the ionization *energy.*) The ionization potential of a free radical is, by definition, the ΔH for the conversion of the radical into a carbonium ion:

$$R\cdot \longrightarrow R^+ + e^- \qquad \Delta H = \text{ionization potential}$$

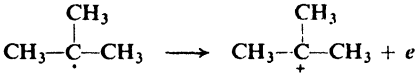
In ways that we cannot go into, the ionization potentials of many free radicals have been measured. For example:

$$CH_3\cdot \longrightarrow CH_3^+ + e^- \qquad \Delta H = 229 \text{ kcal/mole}$$

$$CH_3CH_2\cdot \longrightarrow CH_3CH_2^+ + e^- \qquad \Delta H = 202$$



$$CH_3\underset{\cdot}{C}HCH_3 \longrightarrow CH_3\underset{+}{C}HCH_3 + e^- \qquad \Delta H = 182$$



$$CH_3-\underset{\cdot}{\overset{CH_3}{\overset{|}{C}}}-CH_3 \longrightarrow CH_3-\underset{+}{\overset{CH_3}{\overset{|}{C}}}-CH_3 + e \qquad \Delta H = 171$$

As we can see, the values decrease in the order: $CH_3\cdot > 1° > 2° > 3°$.

Bond dissociation energies have already shown (Sec. 3.24) that the amount of energy required to form free radicals from alkanes decreases in the same order: $CH_3\cdot > 1° > 2° > 3°$. If we combine these two sets of data—ionization potentials and bond dissociation energies—we see (Fig. 5.9) that, relative to the various alkanes concerned, the order of stability of carbonium ions is:

Stability of carbonium ions $3° > 2° > 1° > CH_3^+$

Differences in stability between carbonium ions are much larger than between free radicals. The *tert*-butyl free radical, for example, is 13 kcal more stable than the methyl free radical; the *tert*-butyl cation is 71 kcal more stable than the methyl cation.

What we really want as standards for stability of carbonium ions are, of course, the kinds of compounds they are generated from: alcohols at this particular point or, later, alkyl halides (Chap. 14). However, the relative stabilities of most ordinary neutral molecules closely parallel the relative stabilities of the alkanes, so that the relative order of stabilities that we have arrived at is certainly valid whatever the source of the carbonium ions. To take an extreme example, the difference in stability between methyl and *tert*-butyl cations relative to the alkanes, as we have just calculated it, is 71 kcal. Relative to other standards, the difference in stability is: alcohols, 57 kcal; chlorides, 74 kcal; bromides, 78 kcal; and iodides, 76 kcal.

Now, by definition, the distinction among primary, secondary, and tertiary cations is the number of alkyl groups attached to the electron-deficient carbon. The facts are, then, *that the greater the number of alkyl groups, the more stable the carbonium ion.*

Methyl cation Primary cation Secondary cation Tertiary cation

Electron release: *Disperses charge, stabilizes ion*

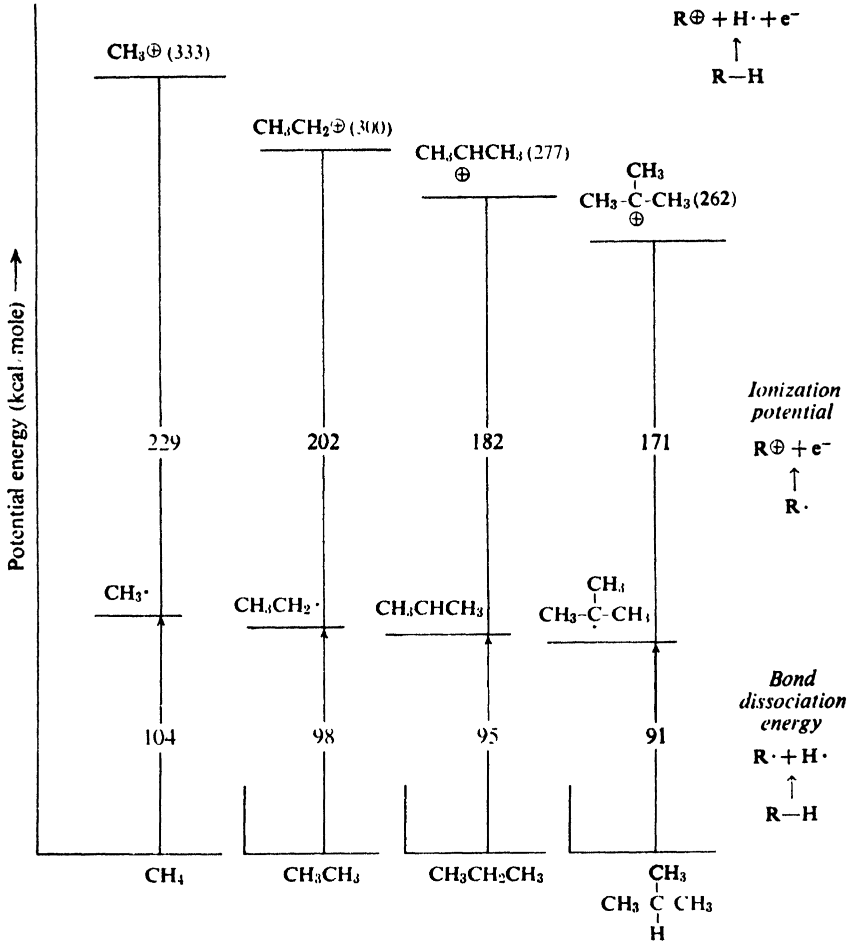


Figure 5.9. Relative stabilities of alkyl cations. (Plots aligned with each other for easy comparison.)

If our generalization about dispersal of charge applies in this case, alkyl groups must *release electrons* here: possibly through an inductive effect, possibly through resonance (*hyperconjugation*, Sec. 8.21).

The electronic effects of alkyl groups are the most poorly understood of all such effects. Dipole moments indicate that they are electron-releasing when attached to a π electron system, but weakly electron-withdrawing in saturated hydrocarbons. Ingold (p. 160) has suggested that alkyl groups can do pretty much what is demanded of them by other groups in the molecule. This much seems clear: (a) in general, carbonium ions and incipient carbonium ions are stabilized by electron release; (b) alkyl groups stabilize carbonium ions; (c) alkyl groups affect a wide variety of reactions in a manner consistent with their being electron-releasing.

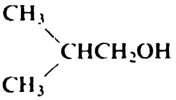
5.19 Dehydration of alcohols

Alcohols are compounds of the general formula, ROH, where R is any alkyl group: the hydroxyl group, —OH, is characteristic of alcohols, just as the carbon–carbon double bond is characteristic of alkenes. An alcohol is named simply by naming the alkyl group that holds the hydroxyl group and following this by the word *alcohol*. It is classified as *primary* (1°), *secondary* (2°), or *tertiary* (3°), depending upon the nature of the carbon atom holding the hydroxyl group (Sec. 3.11). For example:

CH_3CH_2OH

Ethyl alcohol

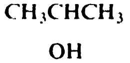
A primary alcohol



$(CH_3)_2CHCH_2OH$

Isobutyl alcohol

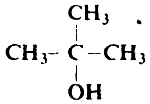
A primary alcohol



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

Isopropyl alcohol

A secondary alcohol

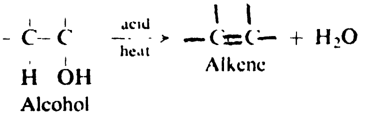


$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

tert-Butyl alcohol

A tertiary alcohol

An alcohol is converted into an alkene by **dehydration**: *elimination of a molecule of water*. Dehydration requires the presence of an acid and the application of heat. It is generally carried out in either of two ways: (a) heating the alcohol with sulfuric or phosphoric acid to temperatures as high as 200°, or (b) passing the alcohol vapor over alumina, Al_2O_3, at 350–400°, alumina here serving as a Lewis acid (Sec. 1.22).



$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow[heat]{acid} -\overset{|}{C}=\overset{|}{C}- + H_2O$$

Alcohol

Alkene

Dehydration: elimination of H_2O

The various classes of alcohols differ widely in ease of dehydration, the order of reactivity being

Ease of dehydration of alcohols 3° > 2° > 1°

The following examples show how these differences in reactivity affect the experimental conditions of the dehydration. (Certain tertiary alcohols are so prone to dehydration that they can be distilled only if precautions are taken to protect the system from the acid fumes in the ordinary laboratory.)

$$CH_3CH_2OH \xrightarrow[170°]{95\%\ H_2SO_4} CH_2{=}CH_2$$

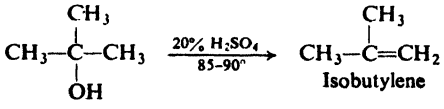
Ethyl alcohol — Ethylene

$$CH_3CH_2CH_2CH_2OH \xrightarrow[140°]{75\%\ H_2SO_4} CH_3CH{=}CHCH_3$$

n-Butyl alcohol — 2-Butene, *Chief product*

$$CH_3CH_2CHOHCH_3 \xrightarrow[100°]{60\%\ H_2SO_4} CH_3CH{=}CHCH_3$$

sec-Butyl alcohol — 2-Butene, *Chief product*



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[85\text{-}90°]{20\%\ H_2SO_4} CH_3-\overset{CH_3}{C}{=}CH_2$$

tert-Butyl alcohol — Isobutylene

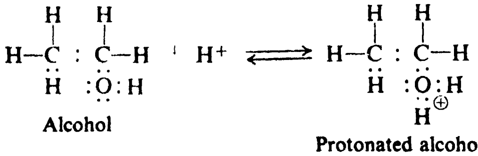
Where isomeric alkenes can be formed, we again find the tendency for one isomer to predominate. Thus, *sec*-butyl alcohol, which might yield both 2-butene and 1-butene, actually yields almost exclusively the 2-isomer (see Sec. 5.23).

The formation of 2-butene from *n*-butyl alcohol illustrates a characteristic of dehydration that is not shared by dehydrohalogenation: the double bond can be formed at a position remote from the carbon originally holding the —OH group. This characteristic is accounted for later (Sec. 5.22). It is chiefly because of the greater certainty as to where the double bond will appear that dehydrohalogenation is often preferred over dehydration as a method of making alkenes.

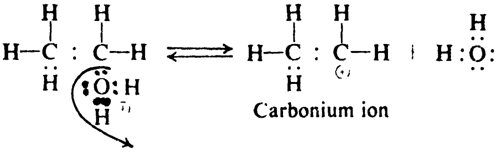
5.20 Mechanism of dehydration of alcohols

The generally accepted mechanism for the dehydration of alcohols is summarized in the following equations; for the sake of simplicity, ethyl alcohol is used as the example. The alcohol unites (step 1) with a hydrogen ion to form the protonated alcohol, which dissociates (step 2) into water and a carbonium ion; the carbonium ion then loses (step 3) a hydrogen ion to form the alkene.

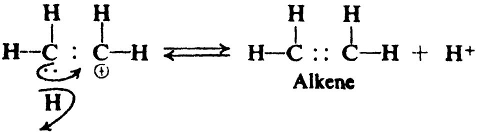
(1)



(2)

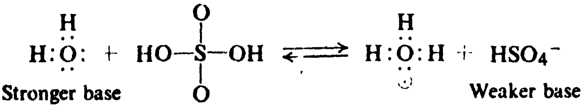


(3)

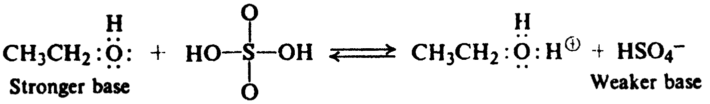


The double bond is thus formed in two stages, —OH being lost (as H_2O) in step (2) and —H being lost in step (3). This is in contrast to dehydrohalogenation (Sec. 5.13), where the halogen and hydrogen are lost simultaneously.

The first step is simply an acid-base equilibrium in the Lowry-Bronsted sense (Sec. 1.22). When sulfuric acid, for example, is dissolved in water, the following reaction occurs:



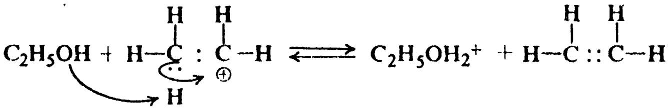
The hydrogen ion is transferred from the very weak base, HSO_4^-, to the stronger base, H_2O, to form the oxonium ion, H_3O^+; the basic properties of each are due of course, to the unshared electrons that are available for sharing with the hydrogen ion. An alcohol also contains an oxygen atom with unshared electrons and hence displays basicity comparable to that of water. The first step of the mechanism is more properly represented as



$$CH_3CH_2:\overset{H}{\ddot{\underset{..}{O}}}: + HO-\overset{O}{\underset{O}{S}}-OH \rightleftharpoons CH_3CH_2:\overset{H}{\ddot{\underset{..}{O}}}:H^{\oplus} + HSO_4^-$$

where the hydrogen ion is transferred from the bisulfate ion to the stronger base, ethyl alcohol, to yield the substituted oxonium ion, $C_2H_5OH_2^+$, the protonated alcohol.

In a similar way, step (3) does not actually involve the expulsion of a naked hydrogen ion, but rather a transfer of the hydrogen ion to a base, the strongest one around, C_2H_5OH.

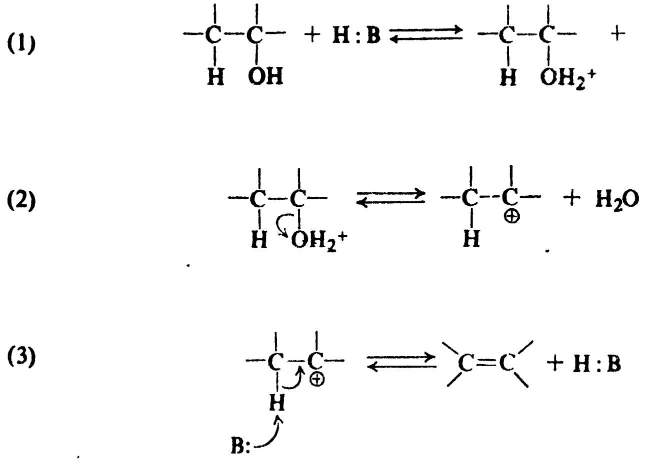


$$C_2H_5OH + H-\overset{H}{\underset{H}{C}}:\overset{H}{\underset{\oplus}{C}}-H \rightleftharpoons C_2H_5OH_2^+ + H-\overset{H}{C}::\overset{H}{C}-H$$

For convenience we shall frequently show the addition or expulsion of a hydrogen ion, H^+, but it should be understood that in all cases this actually involves the transfer of a proton from one base to another.

In summary, the mechanism for dehydration is the following:

Dehydration



$$(1)\quad -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}- + H:B \rightleftharpoons -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH_2^+}{C}}- + B$$

$$(2)\quad -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH_2^+}{C}}- \rightleftharpoons -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{\oplus}{C}}- + H_2O$$

$$(3)\quad -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{\oplus}{C}}- \;\; B: \rightleftharpoons \;>C=C< + H:B$$

All three reactions are shown as equilibria, since each step is readily reversible; as we shall soon see, the exact reverse of this reaction sequence is involved in the formation of alcohols from alkenes (Sec. 6.10). Equilibrium (1) lies very far to the right; sulfuric acid, for example, is known to be nearly completely ionized in alcohol solution. Since there is a very low concentration of carbonium ions present at any time, equilibrium (2) undoubtedly lies very far to the left. Occasionally one of these few carbonium ions undergoes reaction (3) to form the alkene. Under the conditions of dehydration the alkene, being quite volatile, is generally driven from the reaction mixture, and thus equilibrium (3) is shifted to the right. As a consequence the entire reaction system is forced toward completion.

The carbonium ion is formed by dissociation of the protonated alcohol; this involves separation of a charged particle, R^+, from a neutral particle, H_2O. It is obvious that this process requires much less energy than would formation of a carbonium ion from the alcohol itself, since the latter process involves separation of a positive particle from a negative particle. Viewed in another way, the carbonium ion (a Lewis acid) releases the weak base, water, much more readily than it

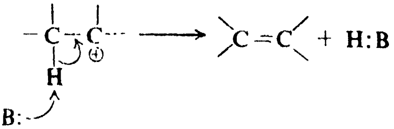
$$ROH_2^{\oplus} \longrightarrow R^{\oplus} + \underset{\substack{\text{Weak base:}\\ \textit{good leaving group}}}{H_2O} \qquad \textbf{Easy}$$

$$ROH \longrightarrow R^{\oplus} + \underset{\substack{\text{Strong base:}\\ \textit{poor leaving group}}}{OH^-} \qquad \textbf{Difficult}$$

releases the extremely strong base, hydroxide ion; that is to say, water is a much better *leaving group* than hydroxide ion. Indeed, the evidence indicates that separation of a hydroxide ion from an alcohol almost never occurs; reactions involving cleavage of the C—O bond of an alcohol seem in nearly every case to require an acidic catalyst, the function of which, as in the present case, is to form the protonated alcohol.

Finally, we must realize that even dissociation of the protonated alcohol is made possible only by solvation of the carbonium ion (compare Sec. 5.13). Energy for the breaking of the carbon-oxygen bond is supplied by the formation of many ion-dipole bonds between the carbonium ion and the polar solvent.

As we shall see, a carbonium ion can undergo a number of different reactions; just which one occurs depends upon experimental conditions. All reactions of a carbonium ion have a common end: *they provide a pair of electrons to complete the octet of the positively charged carbon.* In the present case a hydrogen ion is eliminated from the carbon adjacent to the positive, electron-deficient carbon; the pair of electrons formerly shared by this hydrogen are available for formation of a π bond.



We can see how the mechanism accounts for the fact that dehydration is catalyzed by acids. Now let us see how the mechanism also accounts for the fact that the ease with which alcohols undergo dehydration follows the sequence 3° > 2° > 1°.

Problem 5.8 According to the **principle of microscopic reversibility**, a reaction and its reverse follow exactly the same path but in opposite directions. On this basis write a detailed mechanism for the *hydration of alkenes*, a reaction that is the exact reverse of the dehydration of alcohols. (Check your answer in Sec. 6.10.)

5.21 Ease of formation of carbonium ions

The ease with which alcohols undergo dehydration follows the sequence 3° > 2° > 1°. There is evidence that a controlling factor in dehydration is the formation of the carbonium ion, and that one alcohol is dehydrated more easily than another chiefly because it forms a carbonium ion more easily.

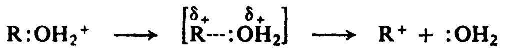
Carbonium ions can be formed from compounds other than alcohols, and in reactions other than elimination. In all these cases the evidence indicates that the ease of formation of carbonium ions follows the same sequence:

Ease of formation of carbonium ions $3° > 2° > 1° > CH_3^+$

In listing carbonium ions in order of their ease of formation, we find that we have at the same time listed them in order of their stability. **The more stable the carbonium ion, the more easily it is formed.**

Is it reasonable that the more stable carbonium ion should be formed more easily? To answer this question, we must look at a reaction in which a carbonium ion is formed, and consider the nature of the transition state.

In the dehydration of an alcohol, the carbonium ion is formed by loss of water from the protonated alcohol, ROH_2^+, that is, by breaking of the carbon–oxygen bond. In the reactant the positive charge is mostly on oxygen, and in the product it is on carbon. In the transition state the C—O bond must be partly broken, oxygen having partly pulled the electron pair away from carbon. The positive charge originally on oxygen is now divided between carbon and oxygen. Carbon has partly gained the positive charge it is to carry in the final carbonium ion.



$$\mathrm{R{:}OH_2^+} \longrightarrow \left[\overset{\delta_+}{\mathrm{R}}\text{---}{:}\overset{\delta_+}{\mathrm{O}}\mathrm{H_2}\right] \longrightarrow \mathrm{R^+} + {:}\mathrm{OH_2}$$

Reactant	Transition state	Products
Oxygen *has full* *positive charge*	*Carbon and oxygen* *have partial* *positive charges*	*Carbon* *has full* *positive charge*

Electron-releasing groups tend to disperse the partial positive charge (δ_+) developing on carbon, and in this way stabilize the transition state. Stabilization of the transition state lowers E_{act} and permits a faster reaction (see Fig. 5.10).

Thus the same factor, electron release, that stabilizes the carbonium ion also stabilizes the *incipient* carbonium ion in the transition state. The more stable carbonium ion is formed faster.

We shall return again and again to the relationship between electronic effects and dispersal of charge, and between dispersal of charge and stability. We shall find that these relationships will help us to understand carbonium ion reactions of many kinds, and, in fact, all reactions in which a charge—positive or negative—develops or disappears. These will include reactions as seemingly different from dehydra-

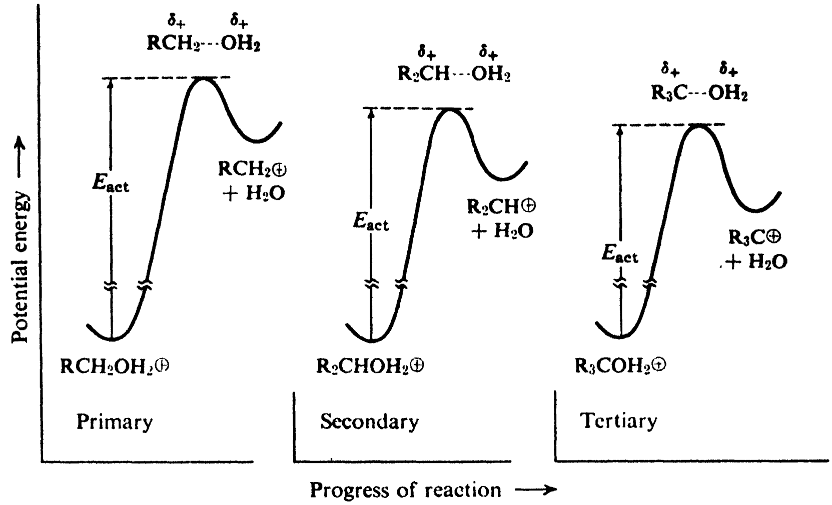


Figure 5.10. Molecular structure and rate of reaction. Stability of transition state parallels stability of carbonium ion: more stable carbonium ion formed faster. (Plots aligned with each other for easy comparison.)

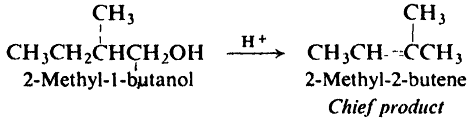
tion of alcohols as: addition to alkenes, aromatic and aliphatic substitution, rearrangements, acidity and basicity.

5.22 Rearrangement of carbonium ions

Very often, dehydration gives alkenes that do not fit the mechanism as we have so far seen it. The double bond appears in unexpected places; sometimes the carbon skeleton is even changed. For example:

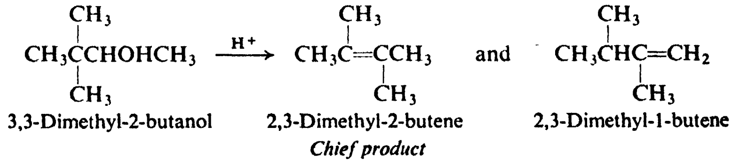
$$CH_3CH_2CH_2CH_2OH \xrightarrow{H^+} CH_3CH{=}CHCH_3$$

n-Butyl alcohol → 2-Butene *Chief product*



$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH \xrightarrow{H^+} CH_3CH{=}\overset{CH_3}{\overset{|}{C}}CH_3$$

2-Methyl-1-butanol → 2-Methyl-2-butene *Chief product*



$$CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CHOHCH_3 \xrightarrow{H^+} CH_3\overset{CH_3}{\overset{|}{C}}{=}\underset{CH_3}{\underset{|}{C}}CH_3 \quad \text{and} \quad CH_3\overset{CH_3}{\overset{|}{C}}H\underset{CH_3}{\underset{|}{C}}{=}CH_2$$

3,3-Dimethyl-2-butanol → 2,3-Dimethyl-2-butene *Chief product* and 2,3-Dimethyl-1-butene

Take the formation of 2-butene from *n*-butyl alcohol. Loss of water from the protonated alcohol gives the *n*-butyl carbonium ion. Loss of the proton from the carbon adjacent to the positive carbon could give 1-butene but *not* the 2-butene that is the major product.

$$\mathrm{CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2} \longrightarrow \mathrm{H_2O + CH_3CH_2CH_2CH_2^{\oplus}} \longrightarrow \mathrm{CH_3CH_2CH{=}CH_2}$$

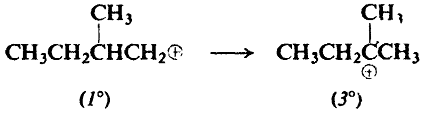
The other examples are similar. In each case we conclude that if, indeed, the alkene is formed from a carbonium ion, *it is not the same carbonium ion that is initially formed from the alcohol.*

A similar situation exists for many reactions besides dehydration. The idea of intermediate carbonium ions accounts for the facts *only* if we add this to the theory: ***a carbonium ion can rearrange to form a more stable carbonium ion.***

n-Butyl alcohol, for example, yields the *n*-butyl cation; this rearranges to the *sec*-butyl cation, which loses a hydrogen ion to give (predominantly) 2-butene:

$$\begin{aligned}
&\mathrm{CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2} \longrightarrow \mathrm{CH_3CH_2CH_2CH_2^{\oplus} + H_2O}\\
&\underset{(1^\circ)}{\mathrm{CH_3CH_2CH_2CH_2^{\oplus}}} \longrightarrow \underset{(2^\circ)}{\mathrm{CH_3CH_2\underset{\oplus}{C}HCH_3}} \qquad \textit{Rearrangement}\\
&\mathrm{CH_3CH_2\underset{\oplus}{C}HCH_3} \longrightarrow \underset{\substack{\text{2-Butene}\\ \textit{Chief product}}}{\mathrm{CH_3CH{=}CHCH_3 + H^+}}
\end{aligned}$$

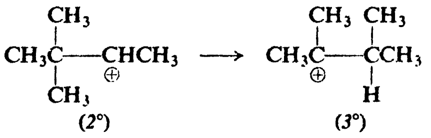
In a similar way, the 2-methyl-1-butyl cation rearranges to the 2-methyl-2-butyl cation,



$$\underset{(1^\circ)}{\mathrm{CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2^{\oplus}}} \longrightarrow \underset{(3^\circ)}{\mathrm{CH_3CH_2\underset{\oplus}{\overset{CH_3}{\overset{|}{C}}}CH_3}}$$

Rearrangement

and the 3,3-dimethyl-2-butyl cation rearranges to the 2,3-dimethyl-2-butyl cation.

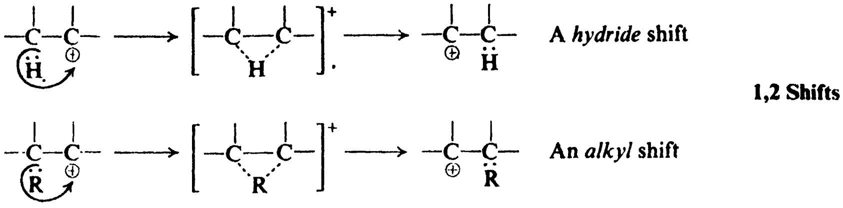


$$\underset{(2^\circ)}{\mathrm{CH_3\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-\!\!-}\underset{\oplus}{C}HCH_3}} \longrightarrow \underset{(3^\circ)}{\mathrm{CH_3\underset{\oplus}{\overset{CH_3}{\overset{|}{C}}}{-\!\!-}\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_3}}$$

Rearrangement

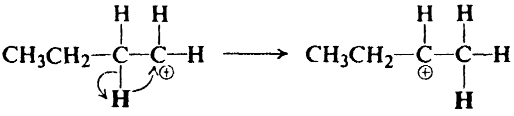
We notice that in each case rearrangement occurs in the way that yields the more stable carbonium ion: primary to a secondary, primary to a tertiary, or secondary to a tertiary.

Just how does this rearrangement occur? Frank Whitmore (of The Pennsylvania State University) pictured rearrangement as taking place in this way: a hydrogen atom or alkyl group migrates *with a pair of electrons* from an adjacent carbon to the carbon bearing the positive charge. The carbon that loses the migrating group acquires the positive charge. A migration of hydrogen with a pair of electrons is known as a **hydride shift**; a similar migration of an alkyl group is known as an **alkyl shift**. These are just two examples of the most common kind of rearrangement, the **1,2-shifts**: *rearrangements in which the migrating group moves from one atom to the very next atom.*



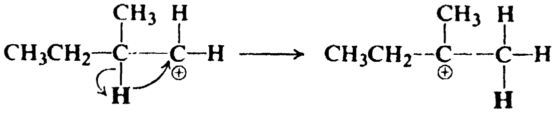
We can account for rearrangements in dehydration in the following way. A carbonium ion is formed by the loss of water from the protonated alcohol. **If a 1,2-shift of hydrogen or alkyl can form a more stable carbonium ion, then such a rearrangement takes place.** The new carbonium ion now loses a proton to yield an alkene.

In the case of the *n*-butyl cation, a shift of hydrogen yields the more stable *sec*-butyl cation; migration of an ethyl group would simply form a different *n*-butyl cation. In the case of the 2-methyl-1-butyl cation, a hydride shift yields a tertiary cation, and hence is preferred over a methyl shift, which would only yield a secondary cation. In the case of the 3,3-dimethyl-2-butyl cation, on the other hand, a methyl shift can yield a tertiary cation and is the rearrangement that takes place.



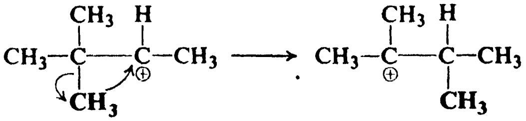
$CH_3CH_2-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{\oplus}{C}}-H \longrightarrow CH_3CH_2-\overset{H}{\underset{\oplus}{C}}-\overset{H}{\underset{H}{C}}-H$

n-Butyl (*1°*) → *sec*-Butyl (*2°*)



$CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-\overset{H}{\underset{\oplus}{C}}-H \longrightarrow CH_3CH_2-\overset{CH_3}{\underset{\oplus}{C}}-\overset{H}{\underset{H}{C}}-H$

2-Methyl-1-butyl (*1°*) → 2-Methyl-2-butyl (*3°*)



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{H}{\underset{\oplus}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{\oplus}{C}}-\overset{H}{\underset{CH_3}{C}}-CH_3$

3,3-Dimethyl-2-butyl (*2°*) → 2,3-Dimethyl-2-butyl (*3°*)

Historically, it was the occurrence of rearrangements that was chiefly responsible for the development of the carbonium ion theory. Reactions of seemingly quite different kinds involved rearrangements that followed the same general pattern; the search for a common basis led to the concept of the carbonium ion. Today, the occurrence (or non-occurrence) of rearrangements of the kind we have seen here is the best—and sometimes the *only*—evidence for (or against) the intermediate formation of carbonium ions.

In our short acquaintance with the carbonium ion, we have encountered two of its reactions. **A carbonium ion may:**

(a) eliminate a hydrogen ion to form an alkene;
(b) rearrange to a more stable carbonium ion.

This list will grow rapidly.

In rearrangement, as in every other reaction of a carbonium ion, the electron-deficient carbon atom gains a pair of electrons, this time at the expense of a neighboring carbon atom, one that can better accommodate the positive charge.

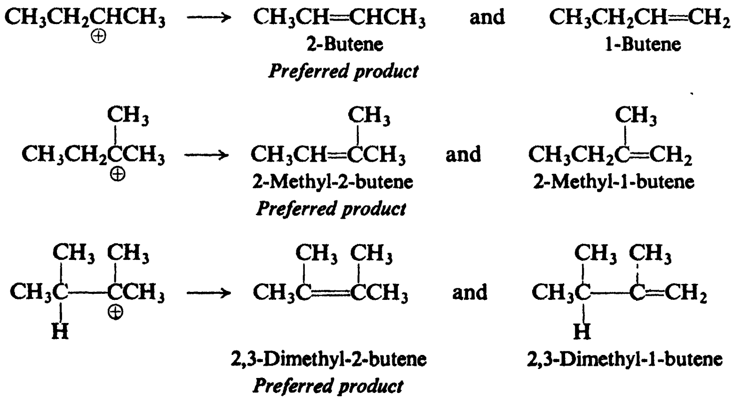
5.23 Orientation and reactivity in dehydration

At this point, we know this much about dehydration of alcohols.

(a) It involves the formation of a carbonium ion. How fast dehydration takes place depends chiefly upon how fast this carbonium ion is formed, which, in turn, depends upon how stable the carbonium ion is. The stability of the carbonium ion depends upon the dispersal of the positive charge, which is determined by electron-release or electron-withdrawal by the attached groups.

(b) If this initially formed carbonium ion can rearrange via a 1,2-shift to form a more stable carbonium ion, it will do so.

This brings us to the last step of dehydration. (c) The carbonium ion—either the original one or the one formed by rearrangement—loses a proton to form an alkene. Now, if isomeric alkenes can be formed in this step, which, if any, will predominate? The examples we have already encountered give us the answer:



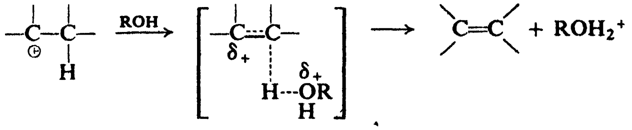
$$CH_3CH_2\underset{\oplus}{C}HCH_3 \longrightarrow \underset{\substack{\text{2-Butene}\\ \textit{Preferred product}}}{CH_3CH{=}CHCH_3} \quad \text{and} \quad \underset{\text{1-Butene}}{CH_3CH_2CH{=}CH_2}$$

$$CH_3CH_2\overset{CH_3}{\underset{\oplus}{C}}CH_3 \longrightarrow \underset{\substack{\text{2-Methyl-2-butene}\\ \textit{Preferred product}}}{CH_3CH{=}\overset{CH_3}{C}CH_3} \quad \text{and} \quad \underset{\text{2-Methyl-1-butene}}{CH_3CH_2\overset{CH_3}{C}{=}CH_2}$$

$$CH_3\overset{CH_3}{\underset{H}{C}}{-}\overset{CH_3}{\underset{\oplus}{C}}CH_3 \longrightarrow \underset{\substack{\text{2,3-Dimethyl-2-butene}\\ \textit{Preferred product}}}{CH_3\overset{CH_3}{C}{=}\overset{CH_3}{C}CH_3} \quad \text{and} \quad \underset{\text{2,3-Dimethyl-1-butene}}{CH_3\overset{CH_3}{\underset{H}{C}}{-}\overset{CH_3}{C}{=}CH_2}$$

Here, as in dehydrohalogenation, the preferred alkene is the more highly substituted one, that is, the *more stable* one (Sec. 6.4). **In dehydration, the more stable alkene is the preferred product.**

Once more, examination of the transition state involved shows that it is reasonable that the more stable alkene should be formed faster:



Transition state: *partly formed double bond*

As the proton is pulled away by the base (the solvent), the electrons it leaves behind become shared by the two carbons, and the carbon–carbon bond acquires double-bond character. Factors that stabilize an alkene also stabilize an *incipient* alkene in the transition state.

Problem 5.9 Predict the *major* product of dehydration of each of the following: (a) $(CH_3)_2C(OH)CH_2CH_3$, (b) $(CH_3)_2CHCHOHCH_3$, (c) $(CH_3)_2C(OH)CH(CH_3)_2$.

PROBLEMS

1. Give the structural formula of:

(a) 3,6-dimethyl-1-octene
(b) 3-chloropropene
(c) 2,4,4-trimethyl-2-pentene
(d) *trans*-3,4-dimethyl-3-hexene
(e) (*Z*)-3-chloro-4-methyl-3-hexene
(f) (*E*)-1-deuterio-2-chloropropene
(g) (R)-3-bromo-1-butene
(h) (S)-*trans*-4-methyl-2-hexene

2. Draw out the structural formula and give the IUPAC name of:

(a) isobutylene
(b) *cis*-$CH_3CH_2CH{=}CHCH_2CH_3$
(c) $(CH_3)_3CCH{=}CH_2$
(d) *trans*-$(CH_3)_2CHCH{=}CHCH(CH_3)_2$
(e) $(CH_3)_2CHCH_2CH{=}C(CH_3)_2$
(f) $(CH_3CH_2)_2C{=}CH_2$

3. Indicate which of the following compounds show geometric (*cis-trans*) isomerism, draw the isomeric structures, and specify each as *Z* or *E*.

(a) 1-butene
(b) 2-butene
(c) 1,1-dichloroethene
(d) 1,2-dichloroethene
(e) 2-methyl-2-butene
(f) 1-pentene
(g) 2-pentene
(h) 1-chloropropene
(i) 1-chloro-2-methyl-2-butene
(j) 3-methyl-4-ethyl-3-hexene
(k) 2,4-hexadiene ($CH_3CH{=}CHCH{=}CHCH_3$)

4. There are 13 isomeric hexylenes (C_6H_{12}) disregarding geometric isomerism. (a) Draw the structure and give the IUPAC name for each. (b) Indicate which ones show geometric isomerism, draw the isomeric structures, and specify each as *Z* or *E*. (c) One of the hexylenes is chiral. Which one is it? Draw structures of the enantiomers, and specify each as R or S.

5. In which of the following will *cis*-3-hexene differ from *trans*-3-hexene?

(a) b.p.
(b) m.p.
(c) adsorption on alumina
(d) infrared spectrum
(e) dipole moment
(f) refractive index
(g) rate of hydrogenation
(h) product of hydrogenation
(i) solubility in ethyl alcohol
(j) density
(k) retention time in gas chromatography

(l) Which *one* of the above would absolutely prove the configuration of each isomer?

6. Write balanced equations for preparation of propylene from:

(a) $CH_3CH_2CH_2OH$ (*n*-propyl alcohol)
(b) $CH_3CHOHCH_3$ (isopropyl alcohol)
(c) isopropyl chloride
(d) the alkyne, $CH_3C{\equiv}CH$
(e) propylene bromide (1,2-dibromopropane)

7. Give structures of the products expected from dehydrohalogenation of:

(a) 1-bromohexane
(b) 2-bromohexane
(c) 1-bromo-2-methylpentane
(d) 2-bromo-2-methylpentane
(e) 3-bromo-2-methylpentane
(f) 4-bromo-2-methylpentane
(g) 1-bromo-4-methylpentane
(h) 3-bromo-2,3-dimethylpentane

8. In those cases in Problem 7 where more than one product can be formed, predict the *major* product.

9. Which alcohol of each pair would you expect to be more easily dehydrated?

(a) $CH_3CH_2CH_2CH_2CH_2OH$ or $CH_3CH_2CH_2CHOHCH_3$
(b) $(CH_3)_2C(OH)CH_2CH_3$ or $(CH_3)_2CHCHOHCH_3$
(c) $(CH_3)_2CHC(OH)(CH_3)_2$ or $(CH_3)_2CHCH(CH_3)CH_2OH$

10. (a) Show all steps in the synthesis of propylene from propane by ordinary laboratory methods (*not* cracking). (b) If the steps in (a) were carried out starting with *n*-butane, would a single product or a mixture be expected?

11. When dissolved in SbF_5, *n*-propyl fluoride and isopropyl fluoride give solutions with identical nmr spectra, indicating that identical species are present. How do you account for this?

12. (a) When neopentyl alcohol, $(CH_3)_3CCH_2OH$, is heated with acid, it is slowly converted into an 85:15 mixture of two alkenes of formula C_5H_{10}. What are these alkenes, and how are they formed? Which one would you think is the major product, and why?

(b) Would you expect neopentyl bromide, $(CH_3)_3CCH_2Br$, to undergo the kind of dehydrohalogenation described in Sec. 5.13? Actually, when heated in aqueous alcohol, neopentyl bromide slowly reacts to yield, among other products, the same alkenes as those in (a). Suggest a mechanism for this particular kind of dehydrohalogenation. Why does this reaction, unlike that in (a), *not* require acid catalysis?

13. When 3,3-dimethyl-1-butene is treated with hydrogen chloride there is obtained a mixture of 3-chloro-2,2-dimethylbutane and 2-chloro-2,3-dimethylbutane. What does the formation of the second product suggest to you? Propose a likely mechanism for this reaction, which is an example of *electrophilic addition*. Check your answer in Secs. 6.10 and 6.12.