MORRISON AND BOYD

ORGANIC CHEMISTRY

Sixth Edition

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Organic Chemistry

Robert Thornton Morrison
Robert Neilson Boyd
New York University

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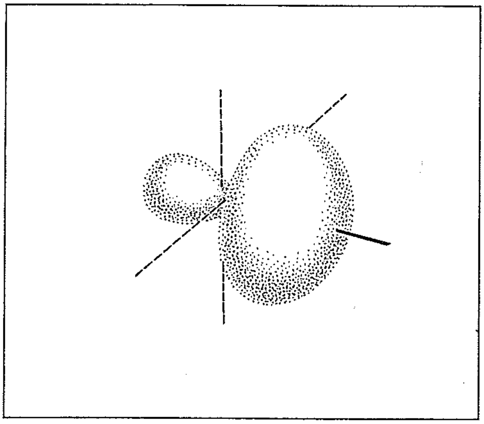


Structure and Properties

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 are 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 millennia and non-renewable. They—particularly petroleum—are being consumed at an alarming rate to meet our constantly increasing demands for power. Today, less than ten percent of the petroleum used goes into making chemicals; most of it is simply burned to supply energy. There *are*, fortunately, alternative sources of power—solar, geothermal, wind, waves, tides, nuclear energy—but where are we to find an alternative reservoir of organic raw material? Eventually, of course, we shall have to go to the place where the fossil fuels originally came from—the *biomass*—but this time directly, without the intervening millennia. The biomass is renewable and, used properly, can last as long on this planet as we can. In the meantime, it has been suggested, petroleum is too valuable to burn.

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 1200, chlorophyll on page 1059, and oxytocin on page 1217.)

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 more than ten million compounds of carbon are known today and that this number is growing by half a million a 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. Biology, on the molecular level, *is* organic chemistry.

It is not farfetched to say that we are living in the Age of Carbon. Every day the newspapers bring to our attention compounds of carbon: cholesterol and polyunsaturated fats, growth hormones and steroids, insecticides and pheromones, carcinogens and chemotherapeutic agents, DNA and genes. Wars are fought over petroleum. Twin catastrophes threaten us, both arising from the accumulation in the atmosphere of compounds of carbon: depletion of the ozone layer, due chiefly to the chlorofluorocarbons; and the greenhouse effect, due to methane, chlorofluorocarbons, and, most of all, carbon dioxide. It is perhaps symbolic that for 1990 the journal *Science* selected as the molecule of the year *diamond*, one of the allotropic forms of carbon. And for 1991 the choice was another, newly discovered allotrope of carbon, C_{60} *buckminsterfullerene*—which has generated excitement in the chemical world not seen, it has been said, "since the days of Kekulé".

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 Wöhler, 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 plastic balls, and the electrons that join them by lines or dots or plastic 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.

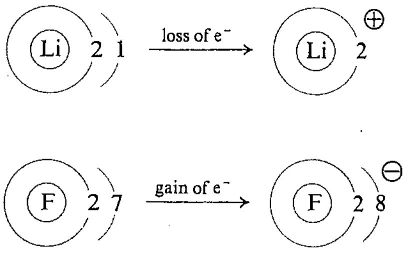
1.3 The chemical bond before 1926

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 of 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.

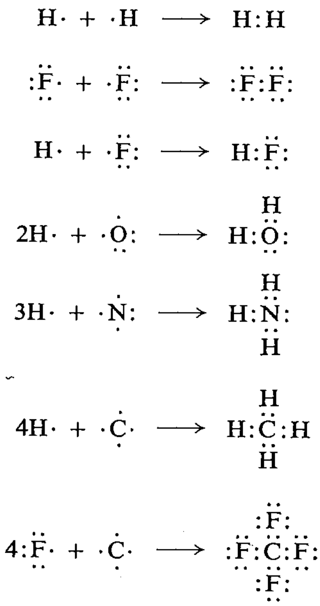


$\text{Li} \longrightarrow \text{Li}^+ + e^-$

$\text{F} + e^- \longrightarrow \text{F}^-$

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.

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.



$$\mathrm{H}\cdot + \cdot\mathrm{H} \longrightarrow \mathrm{H}:\mathrm{H}$$

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

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

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

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

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

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

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.

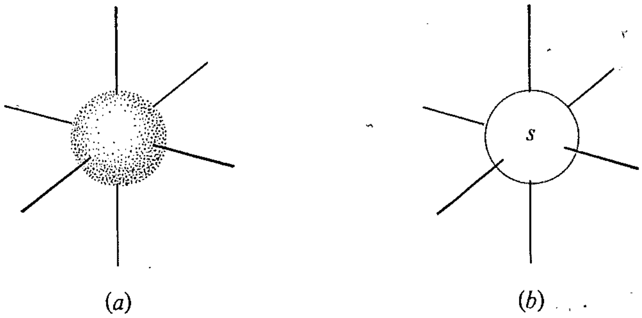
1.5 Atomic orbitals

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



(*a*) (*b*)

Figure 1.1 Atomic orbitals: *s* orbital. The nucleus is at the center.

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.

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 2*p* orbital is dumbbell-shaped. It consists of two lobes with the atomic nucleus lying between them. The axis of each 2*p* 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.

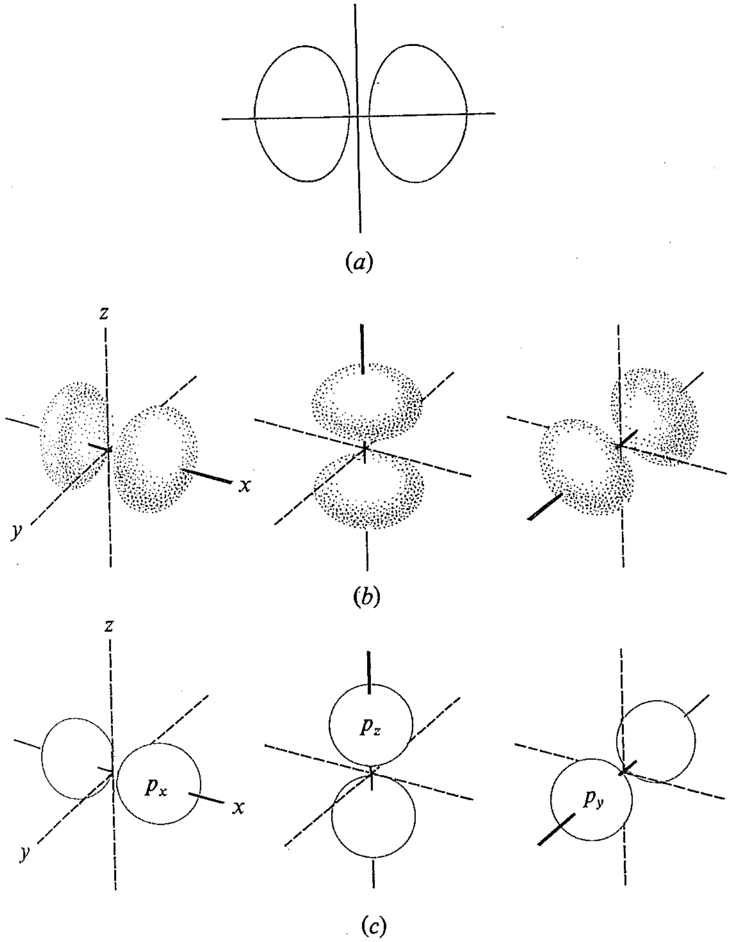


Figure 1.2 Atomic orbitals: *p* orbitals. Axes mutually perpendicular. (*a*) Cross-section showing the two lobes of a single orbital. (*b*) Approximate shape as pairs of distorted ellipsoids. (*c*) Representation as pairs of not-quite-touching spheres.

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 Å; 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/mol less energy than the hydrogen atoms from which it was made. We say that the hydrogen–hydrogen bond has a length of 0.74 Å and a strength of 104 kcal.

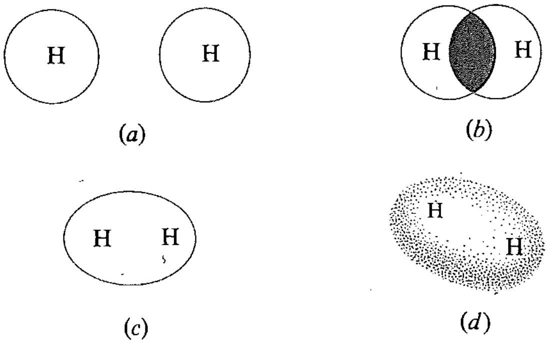
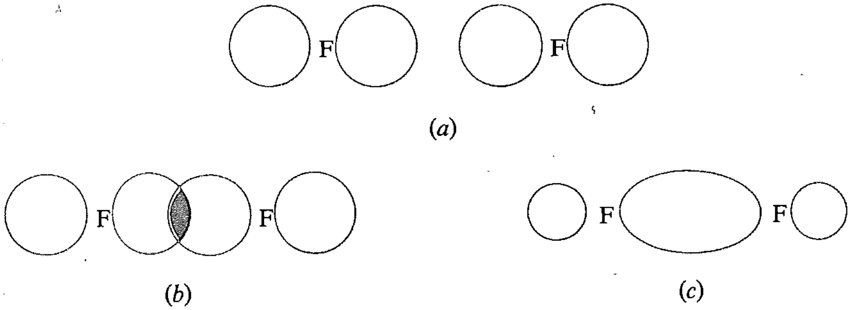


Figure 1.3 Bond formation: H_2 molecule. (*a*) Separate *s* orbitals. (*b*) Overlap of *s* orbitals. (*c*) and (*d*) The σ bond orbital.

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 Å and a strength of about 38 kcal.



(*a*)

(*b*)

(*c*)

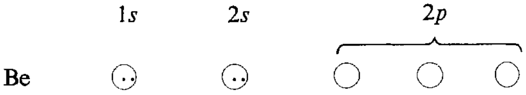
Figure 1.4 Bond formation: F_2 molecule. (*a*) Separate *p* orbitals. (*b*) Overlap of *p* orbitals. (*c*) The σ bond orbital.

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.*

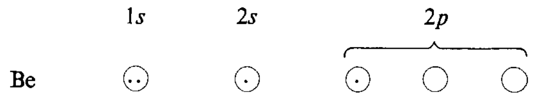
1.9 Hybrid orbitals: *sp*

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.



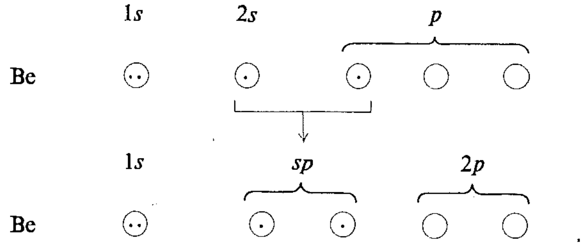
To arrive at this divalent beryllium atom, let us do a little electronic bookkeeping. First, we "promote" one of the 2*s* electrons to an empty *p* orbital:



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* orbital and one *p* orbital 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



sp Hybridization

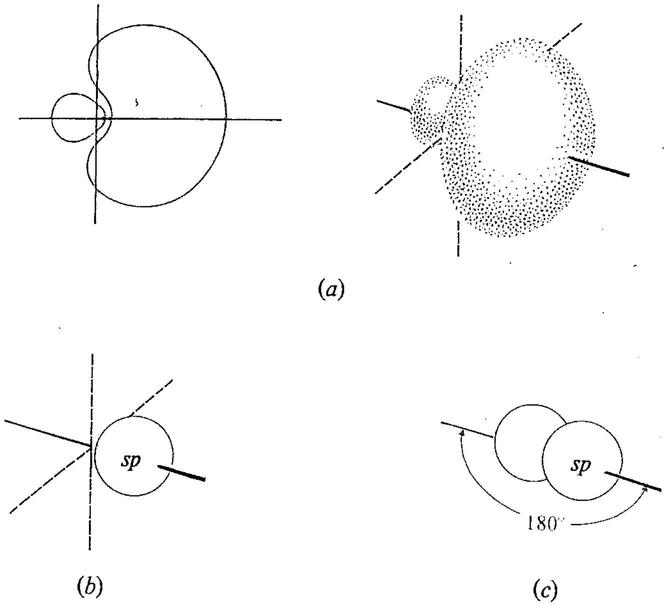


Figure 1.5 Atomic orbitals: hybrid *sp* orbitals. (*a*) Cross-section and approximate shape of a single orbital. Strongly directed along one axis. (*b*) Representation as a sphere, with the small back lobe omitted. (*c*) Two orbitals, with axes lying along a straight line.

stronger the bond it can form. Three highly significant results emerge from the calculations: (a) the "best" hybrid orbital is much more strongly directed than either the *s* or *p* orbital; (b) the two best orbitals are exactly equivalent to each other; and (c) these orbitals point in exactly opposite directions—*the arrangement that permits them to get as far away from each other as possible* (remember the Pauli exclusion principle). The angle between the orbitals is thus 180°.

These particular hybrid orbitals are called *sp* orbitals, since they are considered to arise from the mixing of *one s* orbital and *one p* orbital. They have the shape shown in Fig. 1.5*a*; for convenience we shall neglect the small back lobe and represent the front lobe as a sphere.

Using this *sp-hybridized* beryllium, let us construct beryllium chloride. An extremely important concept emerges here: **bond angle**. For maximum overlap between the *sp* orbitals of beryllium and the *p* orbitals of the chlorines, the two chlorine nuclei must lie along the axes of the *sp* orbitals; that is, they must be located on exactly opposite sides of the beryllium atom (Fig. 1.6). The angle between the beryllium–chlorine bonds must therefore be 180°.

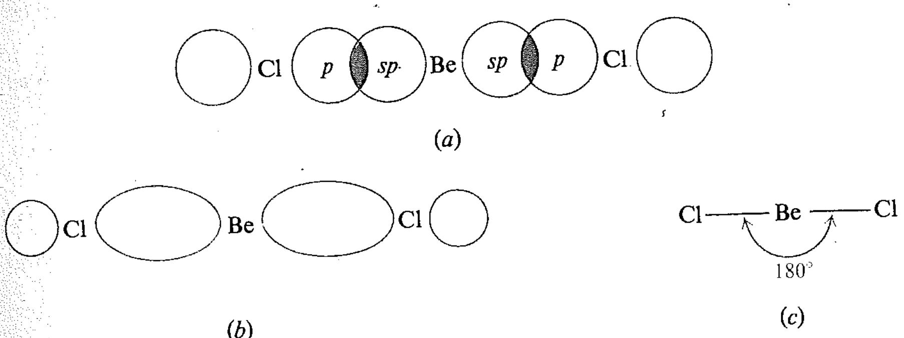
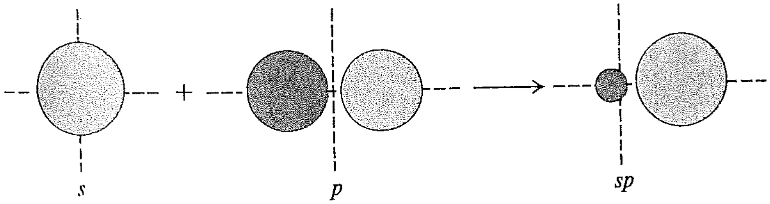


Figure 1.6 Bond formation: $BeCl_2$ molecule. (*a*) Overlap of *sp* and *p* orbitals. (*b*) The σ bond orbitals. (*c*) Shape of the molecule.

Experiment has shown that, as calculated, beryllium chloride is a *linear molecule*, all three atoms lying along a single straight line.

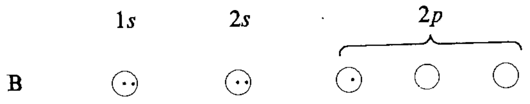
There is nothing magical about the increase in directional character that accompanies hybridization. The two lobes of the *p* orbital are of opposite *phase* (Sec. 28.2); combination with an *s* orbital amounts to *addition* on one side of the nucleus, but *subtraction* on the other.



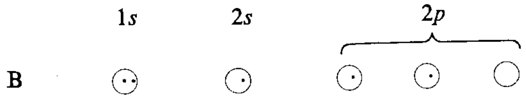
If you are curious about phase and its effect on bonding, read Secs. 28.1–28.4, which you can understand at this point.

1.10 Hybrid orbitals: sp^2

Next, let us look at boron trifluoride, BF_3. Boron (Table 1.1) has only one unpaired electron, which occupies a 2*p* orbital. For three bonds we need three

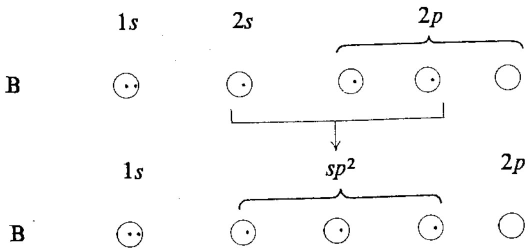


unpaired electrons, and so we promote one of the 2*s* electrons to a 2*p* orbital:



One electron promoted: three unpaired electrons

If, now, we are to "make" the most stable molecule possible, we must "make" the strongest bonds possible; for these we must provide the most strongly directed atomic orbitals that we can. Again, hybridization provides such orbitals: three hybrid orbitals, exactly equivalent to each other. Each one has the shape shown in



sp^2 Hybridization

Fig. 1.7; as before, we shall neglect the small back lobe and represent the front lobe as a sphere.

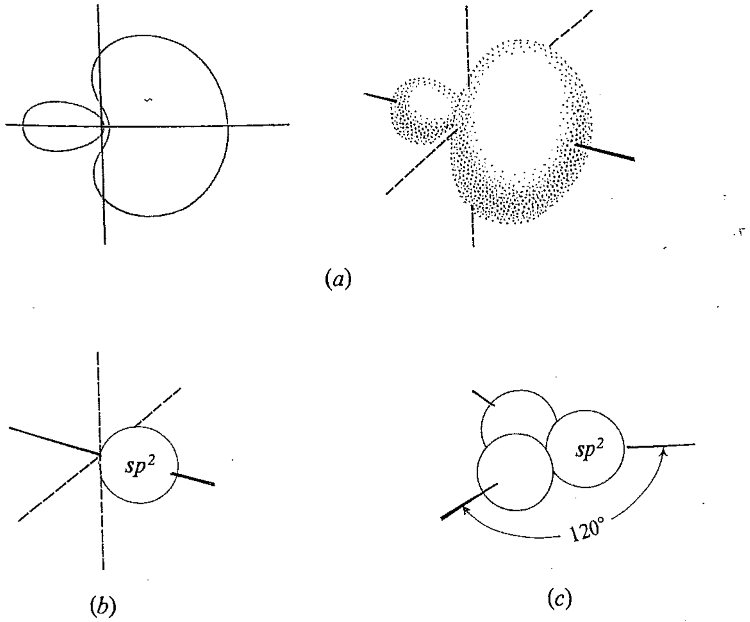


Figure 1.7 Atomic orbitals: hybrid sp^2 orbitals. (*a*) Cross-section and approximate shape of a single orbital. It is strongly directed along one axis. (*b*) Representation as a sphere, with the small back lobe omitted. (*c*) Three orbitals, with the axes directed toward the corners of an equilateral triangle.

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°.

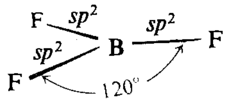


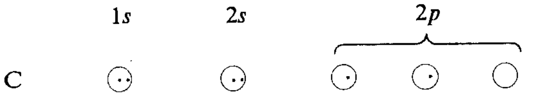
Figure 1.8 BF_3 molecule.

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

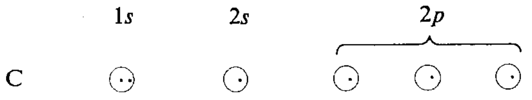
1.11 Hybrid orbitals: sp^3

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.

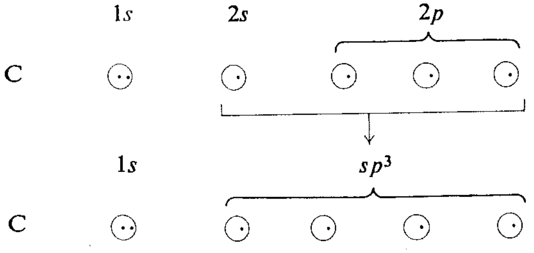


To provide four unpaired electrons, we promote one of the 2*s* electrons to the empty *p* orbital:



One electron promoted: four unpaired electrons

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 neglect the small back lobe and represent the front lobe as a sphere.

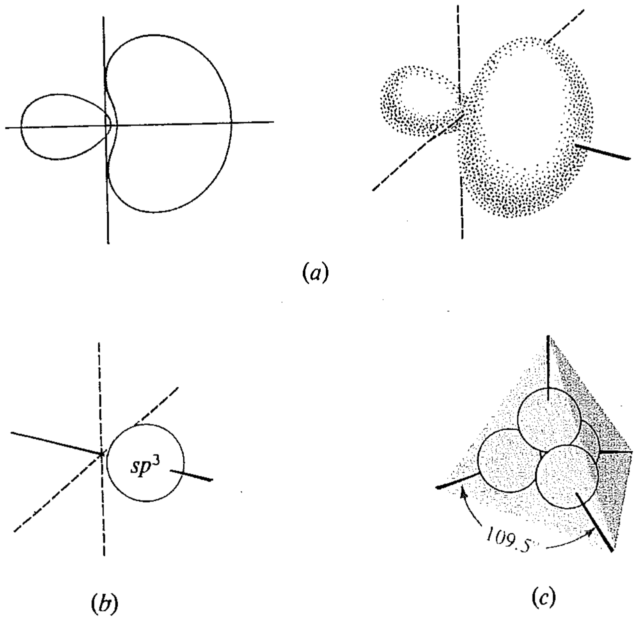


Figure 1.9 Atomic orbitals: hybrid sp^3 orbitals. (*a*) Cross-section and approximate shape of a single orbital. It is strongly directed along one axis. (*b*) Representation as a sphere, with the small back lobe omitted. (*c*) Four orbitals, with the axes directed toward the corners of a tetrahedron.

Now, how are sp^3 orbitals arranged in space? The answer is no surprise to us: in the way that lets them get as far away from each other as possible. They are directed to the corners of a regular tetrahedron. The angle between any two 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 four 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).

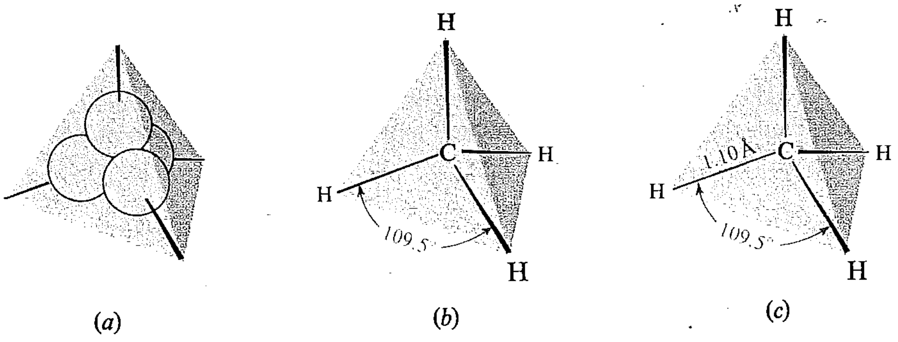


Figure 1.10 Bond formation: CH_4 molecule. (*a*) Tetrahedral sp^3 orbitals. (*b*) Predicted shape: H nuclei located for maximum overlap. (*c*) Shape and size.

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 Å; the angle between any pair of bonds is the tetrahedral angle 109.5°. It takes 104 kcal/mol 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 conveniently related to the arrangement of atomic orbitals—including hybrid orbitals—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.

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

Since compounds of carbon are held together chiefly by covalent bonds, organic chemistry, too, is much concerned with molecular size and shape. To help us in our study, we should make frequent use of molecular models. Figure 1.11 shows methane as represented by three different kinds of models: stick-and-ball, framework, and space-filling. These last are made to scale, and reflect accurately not only bond angles but also relative lengths of bonds and sizes of atoms.

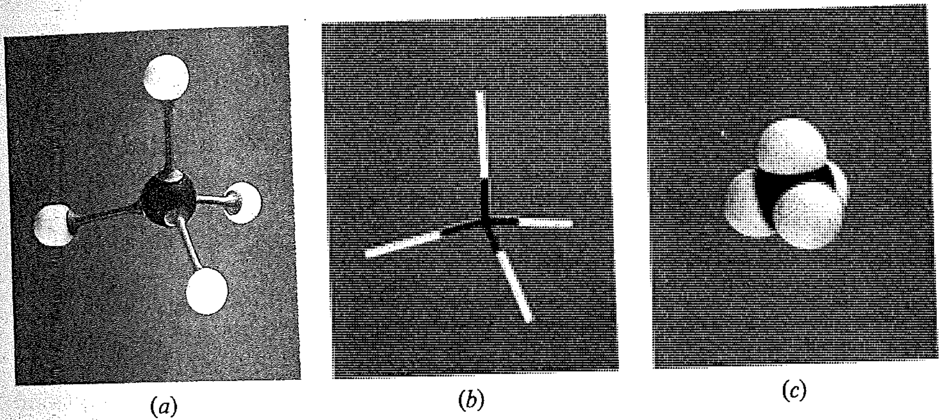
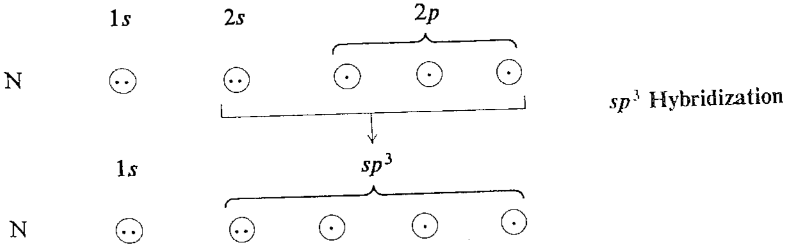


Figure 1.11 Models of methane molecule. (*a*) Stick-and-ball (Allyn & Bacon). (*b*) Framework (Prentice Hall). (*c*) Space-filling (Corey–Pauling–Koltun, CPK); 1.25 cm equals 1.00 Å.

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. 1.12). The fourth sp^3 orbital of nitrogen contains a pair of electrons.

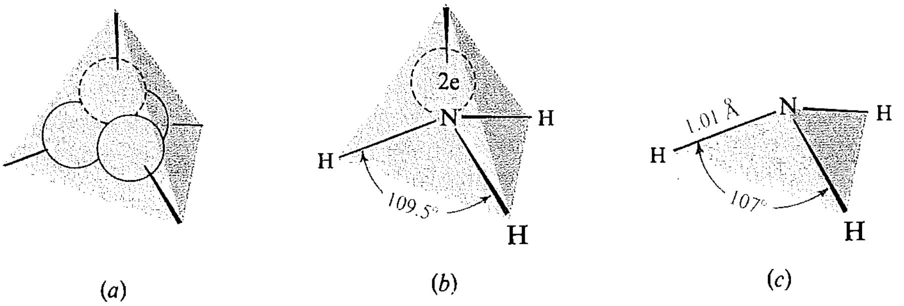


Figure 1.12 Bond formation: NH_3 molecule. (*a*) Tetrahedral sp^3 orbitals. (*b*) Predicted shape, showing the unshared pair: H nuclei located for maximum overlap. (*c*) Shape and size.

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 angles slightly. The nitrogen–hydrogen bond length is 1.01 Å; it takes 103 kcal/mol 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. 1.13). There is an energy barrier of only 6 kcal/mol 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.

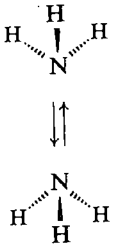
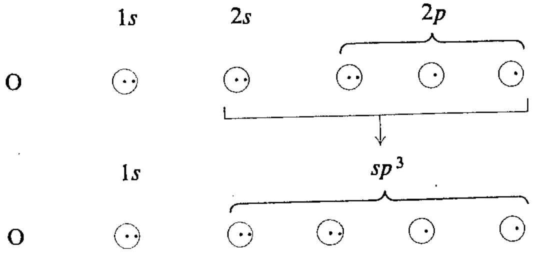


Figure 1.13 Inversion of ammonia.

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. 1.14).



sp^3 Hybridization

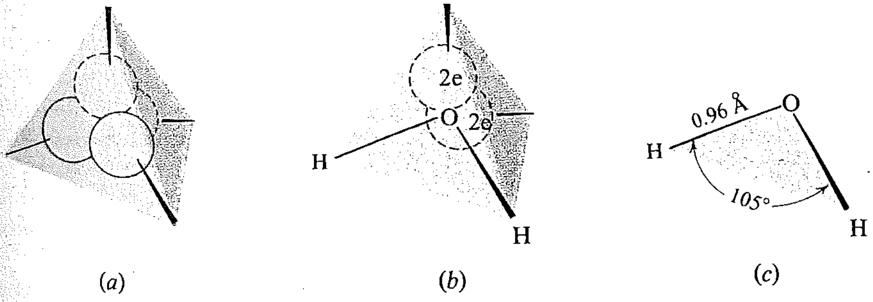


Figure 1.14 Bond formation: H_2O molecule. (*a*) Tetrahedral *sp*^{3} orbitals. (*b*) Predicted shape, showing the unshared pairs: H nuclei located for maximum overlap. (*c*) Shape and size.

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 Å; it takes 118 kcal/mol to break one of the bonds of water.

If we examine Fig. 1.15 we can see the fundamental similarity in shape of the methane, ammonia, and water molecules: a similarity that, by the approach we have used, stems from a similarity in bonding.

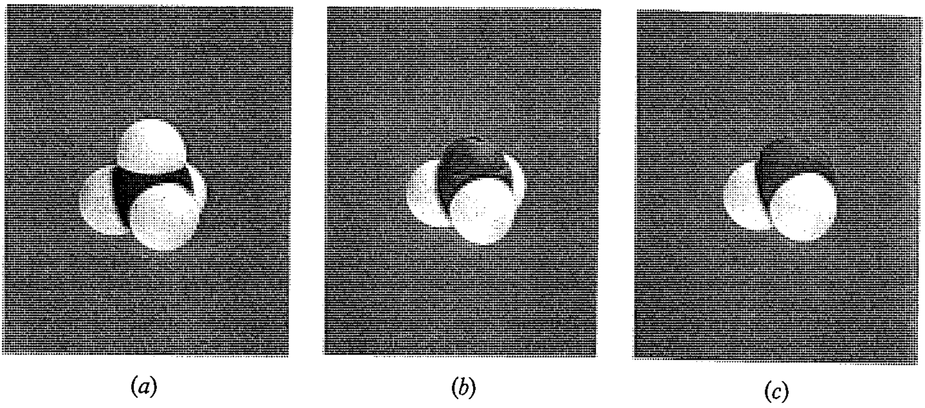

(*a*) (*b*) (*c*)

Figure 1.15 Models of (*a*) methane, (*b*) ammonia, (*c*) 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/mol) to very strong bonds like H—F (136 kcal/mol). Although the accepted values may change as experimental methods improve, certain trends are clear.

Table 1.2 HOMOLYTIC BOND DISSOCIATION ENERGIES, KCAL/MOL

$A{:}B \longrightarrow A\cdot + \cdot B$ ΔH = Homolytic 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	92	t-C_4H_9—CH_3	80	t-C_4H_9—Cl	79	t-C_4H_9—Br	63
$H_2C{=}CH$—H	108	$H_2C{=}CH$—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	110	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

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:

$$\begin{array}{llll}
CH_4 & \longrightarrow & CH_3 + H\cdot & D(CH_3\text{—}H) = 104\ \text{kcal/mol} \\
CH_3 & \longrightarrow & CH_2 + H\cdot & D(CH_2\text{—}H) = 106 \\
CH_2 & \longrightarrow & CH + H\cdot & D(CH\text{—}H) = 106 \\
CH & \longrightarrow & C + H\cdot & D(C\text{—}H) = \ 81
\end{array}$$

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

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

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

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.

$$A{:}B \longrightarrow A\cdot + B\cdot \qquad \text{Homolysis: } \textit{one electron to each fragment}$$

$$A{:}B \longrightarrow A + {:}B \qquad \text{Heterolysis: } \textit{both electrons to one fragment}$$

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

The bond dissociation energies given in Table 1.2 are for homolysis, and are therefore *homolytic* bond dissociation energies. But bond dissociation energies have also been measured for heterolysis; some of these *heterolytic* bond dissociation energies are given in Table 1.3.

Table 1.3 HETEROLYTIC BOND DISSOCIATION ENERGIES, KCAL/MOL

$A{:}B \longrightarrow A^+ + {:}B^-$ $\qquad \Delta H$ = Heterolytic bond dissociation energy or $D(A^+\text{—}B^-)$

H—H	401	CH_3—H	313
H—F	370	CH_3—F	256
H—Cl	334	CH_3—Cl	227
H—Br	324	CH_3—Br	219
H—I	315	CH_3—I	212
H—OH	390	CH_3—OH	274

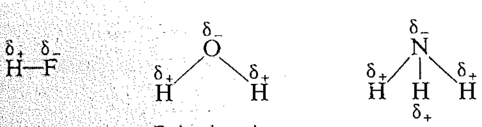
CH_3—Cl	227	CH_3—Br	219	CH_3—I	212	CH_3—OH	274
C_2H_5—Cl	191	C_2H_5—Br	184	C_2H_5—I	176	C_2H_5—OH	242
n-C_3H_7—Cl	185	n-C_3H_7—Br	178	n-C_3H_7—I	171	n-C_3H_7—OH	235
i-C_3H_7—Cl	170	i-C_3H_7—Br	164	i-C_3H_7—I	156	i-C_3H_7—OH	222
t-C_4H_9—Cl	157	t-C_4H_9—Br	149	t-C_4H_9—I	140	t-C_4H_9—OH	208
H_2C=CH—Cl	207	H_2C=CH—Br	200	H_2C=CH—I	194		
H_2C=$CHCH_2$—Cl	173	H_2C=$CHCH_2$—Br	165	H_2C=$CHCH_2$—I	159	H_2C=$CHCH_2$—OH	223
C_6H_5—Cl	219	C_6H_5—Br	210	C_6H_5—I	202	C_6H_5—OH	275
$C_6H_5CH_2$—Cl	166	$C_6H_5CH_2$—Br	157	$C_6H_5CH_2$—I	149	$C_6H_5CH_2$—OH	215

If we examine these values, we see that they are considerably bigger than those in Table 1.2. 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/mol 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. 7.5), 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. (We say "delta plus" and "delta minus".) 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:

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

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 1.4. We shall be interested in the values of dipole moments as indications of the relative polarities of different molecules.

Table 1.4 DIPOLE MOMENTS, D

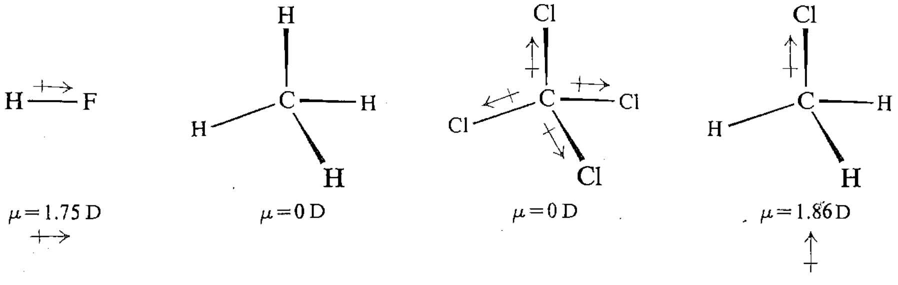
H_2	0	HF	1.75	CH_4	0
O_2	0	H_2O	1.84	CH_3Cl	1.86
N_2	0	NH_3	1.46	CCl_4	0
Cl_2	0	NF_3	0.24	CO_2	0
Br_2	0	BF_3	0		

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. 1.16). In methyl chloride, CH_3Cl, the polarity 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.



Hydrogen fluoride

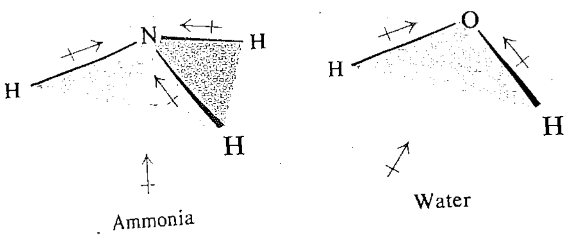
Methane

Carbon tetrachloride

Methyl chloride

Figure 1.16 Dipole moments of some molecules. Polarity of bonds and of molecules.

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.

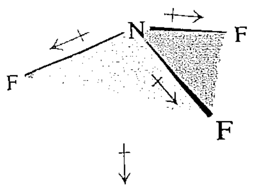


Ammonia

Water

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.

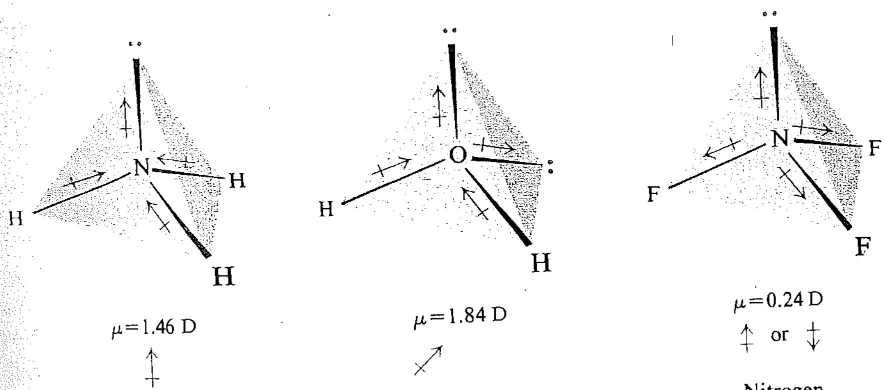


Nitrogen trifluoride

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. 1.17); these opposing moments are evidently of about the same size,



$\mu = 1.46$ D
Ammonia

$\mu = 1.84$ D
Water

$\mu = 0.24$ D
or
Nitrogen trifluoride

Figure 1.17 Dipole moments of some molecules. Contribution from unshared pairs. In NF_3, the moment due to the unshared pair opposes the vector sum of the 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 moment 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. Organic compounds are *real* substances—not just collections of letters written on a piece of paper—and we must learn how to handle them.

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. 1.18 and 1.19). 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 °C.

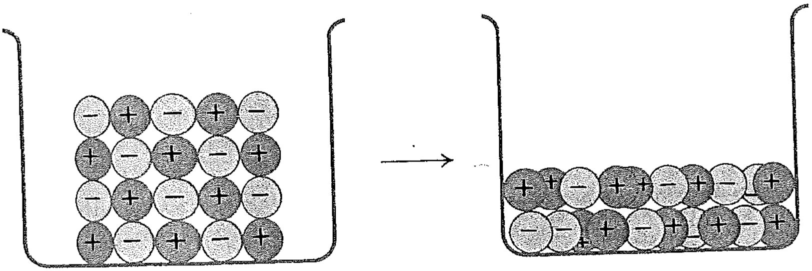


Figure 1.18 Melting of an ionic crystal. The units are ions.

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 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 °C.

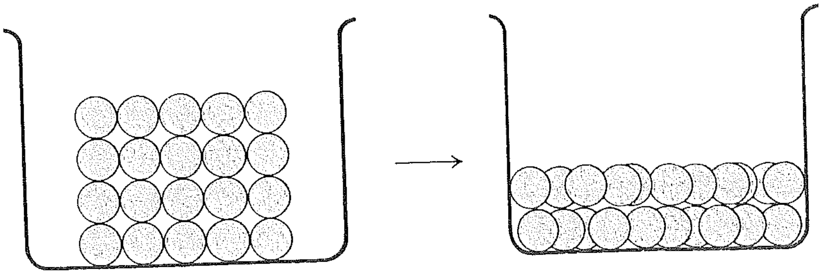
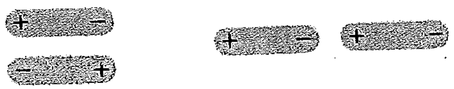


Figure 1.19 Melting of a non-ionic crystal. The units are molecules.

1.19 Intermolecular forces

What kinds 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.*

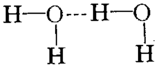
Dipole–dipole interaction is the attraction of the positive end of one polar molecule for the negative end of another polar molecule. In hydrogen chloride, for example, the relatively positive hydrogen of one molecule is attracted to the relatively negative chlorine of another:



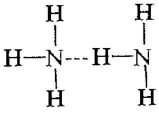
As a result of dipole–dipole interaction, polar molecules are generally held to each other more strongly than are non-polar molecules of comparable molecular weight; this difference in strength of intermolecular forces is reflected in the physical properties of the compounds concerned.

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/mol, and is thus much weaker than the covalent bond—about 50–100 kcal/mol—that holds it to the first electronegative atom. It is much stronger, however, than other dipole–dipole attractions. Hydrogen bonding is generally indicated in formulas by a broken line:

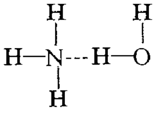
$H{-}F\cdots H{-}F$



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



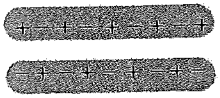
$H{-}\overset{H}{\underset{H}{N}}\cdots H{-}\overset{H}{\underset{H}{N}}$



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

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.

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 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.

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.

In Chapter 7, we shall discuss in detail all of these intermolecular forces—these kinds of *secondary bonding*.

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. 1.20 and 1.21). 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.

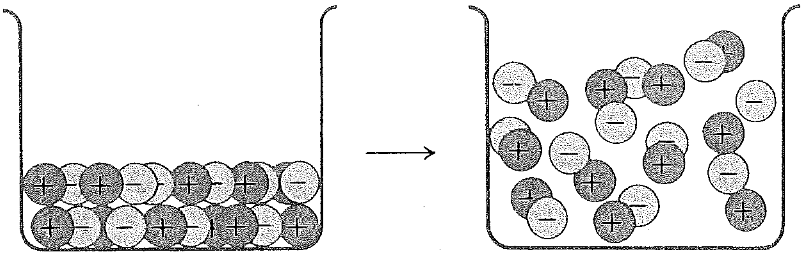


Figure 1.20 Boiling of an ionic liquid. The units are ions and ion pairs.

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 °C. 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 °C, and even polar hydrogen chloride boils at only −85 °C.

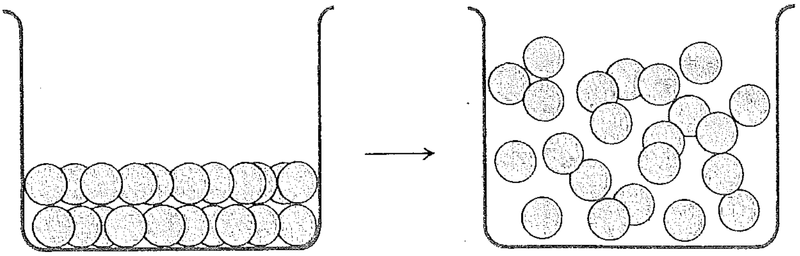
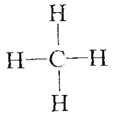


Figure 1.21 Boiling of a non-ionic liquid. The units are molecules.

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.

There are organic compounds, too, that contain hydrogen bonded to oxygen or nitrogen, and here, too, hydrogen bonding occurs. Let us take, for example, methane and replace one of its hydrogens with a hydroxyl group, —OH. The resulting compound, CH_3OH, is *methanol*, the smallest member of the *alcohol* family. Structurally, it resembles not only methane, but also water:

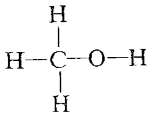


$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H{-}C{-}H} \\ | \\ \mathrm{H} \end{array}$$

Methane

$H—O—H$

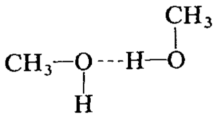
Water



$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{O{-}H} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

Methanol

Like water, it is an associated liquid with a boiling point "abnormally" high for a compound of its size and polarity.



$$\begin{array}{ccc} & & \mathrm{CH_3} \\ & & | \\ \mathrm{CH_3{-}O} & \cdots & \mathrm{H{-}O} \\ | & & \\ \mathrm{H} & & \end{array}$$

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 °C; 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_3OCH_3; (b) CH_3F; (c) CH_3Cl; (d) CH_3NH_2; (e) $(CH_3)_2NH$; (f) $(CH_3)_3N$.

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.

Now, what are these bonds that are formed between solute and solvent? Let us consider first the case of **ionic solutes**.

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 kinds 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. 1.22).

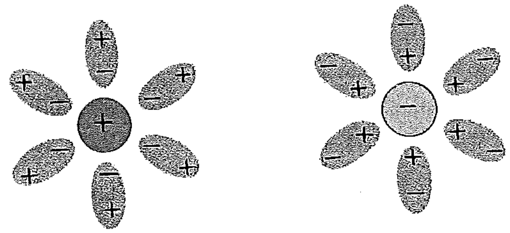


Figure 1.22 Ion–dipole interactions: a solvated cation and anion.

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

Now let us turn to the dissolution of **non-ionic solutes.**

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—van der Waals interactions—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.

An understanding of the nature of solutions is fundamental to an understanding of organic chemistry. Most organic reactions are carried out in solution and, it is becoming increasingly clear, the solvent does much more than simply bring different molecules together so that they can react with each other. The solvent is *involved* in the reactions that take place in it: just how much it is involved, and in what ways, is only now being realized. In Chapter 7, when we know a little more about organic reactions and how they take place, we shall return to this subject—which we have barely touched upon here—and examine in detail the role played by the solvent.

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 the new acid H_3O^+ and the 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^-.

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

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

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^+

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

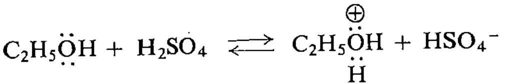
$$\underset{\text{Stronger acid}}{NH_4^+} + \underset{\text{Stronger base}}{OH^-} \rightleftarrows \underset{\text{Weaker acid}}{H_2O} + \underset{\text{Weaker base}}{NH_3}$$

(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.

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

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

Like water, many organic compounds that contain oxygen can act as bases and accept protons; ethyl alcohol and diethyl 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*.



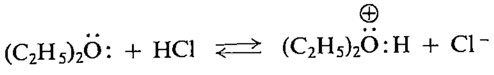
$$C_2H_5\ddot{O}H + H_2SO_4 \rightleftarrows C_2H_5\overset{\oplus}{\ddot{O}}H + HSO_4^-$$
$$\qquad\qquad\qquad\qquad\qquad\qquad H$$

Ethyl alcohol

I

An oxonium ion

Protonated ethyl alcohol



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

Diethyl ether

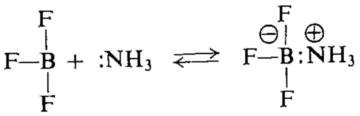
II

An oxonium ion

Protonated diethyl ether

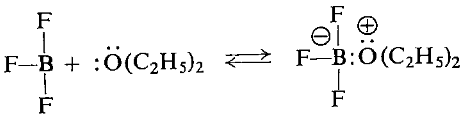
According to the **Lewis** definition, *a base is a substance that can furnish an electron pair to form a covalent bond*, and *an acid is a substance that can take up an electron pair to form a covalent bond.* Thus **an acid is an electron-pair acceptor** and **a base is an electron-pair donor**. This 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 such bases as ammonia or diethyl ether.



$$F{-}\underset{F}{\overset{F}{B}} + :NH_3 \rightleftarrows F{-}\underset{F}{\overset{F}{\overset{\ominus}{B}}}:\overset{\oplus}{N}H_3$$

Acid Base



$$F{-}\underset{F}{\overset{F}{B}} + :\ddot{O}(C_2H_5)_2 \rightleftarrows F{-}\underset{F}{\overset{F}{\overset{\ominus}{B}}}:\overset{\oplus}{\ddot{O}}(C_2H_5)_2$$

Acid Base

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 $SnCl_6{}^{2-}$) 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 *Lewis 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

$$\begin{array}{r} H{-}CH_3 < H{-}NH_2 < H{-}OH < H{-}F \\ H{-}SH < H{-}Cl \end{array}$$

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

Acidity

$$\begin{array}{c} H{-}F < H{-}Cl < H{-}Br < H{-}I \\ H{-}OH < H{-}SH < H{-}SeH \end{array}$$

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^{2-}. (d) What relationship is there between charge and basicity?

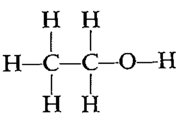
1.23 Isomerism

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 °C. Analysis (by the methods described later, Sec. 2.28) 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 *dimethyl ether* is a gas with a boiling point of −24 °C. 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 dimethyl ether shows that it contains carbon, hydrogen, and oxygen in the same proportion 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.

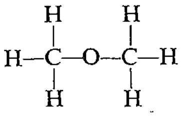
Here we have two substances, ethyl alcohol and dimethyl ether, which have the same molecular formula, C_2H_6O, and yet quite clearly are different compounds. How can we account for the existence of these two compounds? The answer is: *they differ in molecular structure*. Ethyl alcohol has the structure represented by I, and dimethyl 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.



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

I

Ethyl alcohol



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

II

Dimethyl ether

Different compounds that have the same molecular formula are called **isomers** (Greek: *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 dimethyl *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^{2-}
(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) dimethyl ether
(g) the fluoroborate ion, BF_4^-
(h) $(CH_3)_3N$

4. In many complex ions, e.g., $Co(NH_3)_6^{3+}$, 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
(b) ICl
(c) I_2
(d) CH_2Cl_2
(e) $CHCl_3$
(f) CH_3OH
(g) dimethyl ether
(h) $(CH_3)_3N$
(i) CF_2Cl_2

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.

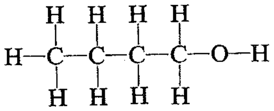
You should work all the problems that you can; you should get help with the ones you cannot work yourself. The first problems in each set are easy, but provide the drill in drawing formulas, naming compounds, and using reactions that even the best student needs. The later problems in each set are the 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. You will find more complete answers to all the problems, together with suggestions about how to approach each type of problem, in the Study Guide.

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

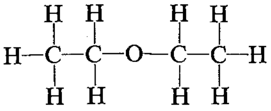
7. What do the differences in properties between lithium acetylacetonate (m.p. very high, insoluble in chloroform) and beryllium acetylacetonate (m.p. 108 °C, b.p. 270 °C, soluble in chloroform) suggest about their structures?

8. *n*-Butyl alcohol (b.p. 118 °C) has a much higher boiling point than its isomer diethyl ether (b.p. 35 °C), 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



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

Diethyl 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) $HCl(aq) + NaHCO_3(aq) \rightleftharpoons H_2CO_3 + NaCl$
(b) $NaOH(aq) + NaHCO_3(aq) \rightleftharpoons Na_2CO_3 + H_2O$
(c) $NH_3(aq) + HNO_3(aq) \rightleftharpoons NH_4NO_3(aq)$
(d) $NaCN(aq) \leftrightharpoons HCN(aq) + NaOH(aq)$
(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 (un-ionized) 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. How might you account for the following orders of acidity? Be as specific as you can.

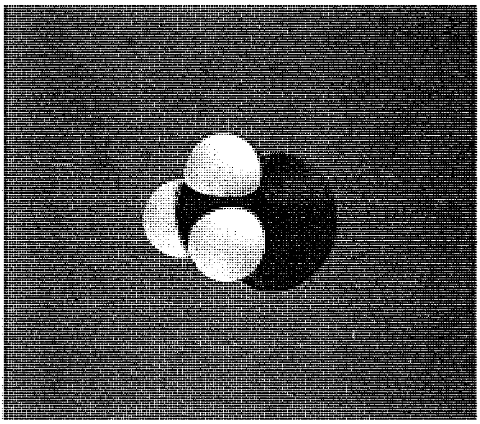
$$HClO_4 > HClO_2 > HClO \quad \text{and} \quad H_2SO_4 > H_2SO_3$$

13. For each of the following molecular formulas, draw structures like those in Sec. 1.23 (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
(b) C_3H_8
(c) C_4H_{10}
(d) C_3H_7Cl
(e) C_3H_8O
(f) C_2H_4O

14. 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?

5



Alkyl Halides

Nucleophilic Aliphatic Substitution

5.1 Homolytic and heterolytic chemistry

Chemistry owes its existence as a science, of course, to the chemical change: the conversion of one substance into another. Old molecules are changed into new ones, which means that old bonds must be broken, and new bonds must be formed—covalent bonds, mostly, in the case of organic chemistry.

Now, the breaking of a covalent bond, we have seen (Sec. 1.14), can take place in two fundamentally different ways, depending upon what happens to the two electrons making up the bonding pair: in homolysis, one electron goes to each fragment; in heterolysis, both electrons go to the same fragment. The nouns "homolysis" and "heterolysis" are used only in their literal sense (p. 22) to mean bond-*breaking*. But the adjectives "homolytic" and "heterolytic"—for want of better words—are used in a broader sense, to include the bond-making process as well, and so define two broad classes of organic reactions.

Thus, **homolytic reactions** are those in which the electrons of the bonding pair are taken away—or provided—*singly*. Whether bonds are being broken,

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

or formed,

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

or simultaneously broken and formed,

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

each of the atoms being separated takes one of the bonding electrons, and each of the atoms being joined together provides one of the bonding electrons.

Heterolytic reactions are those in which the bonding electrons are taken away—or provided—*in pairs*. Whether bonds are being broken,

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

or formed,

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

or simultaneously broken and formed,

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

one of the atoms being separated takes both bonding electrons, and one of the atoms being joined together provides both electrons.

Homolytic chemistry is thus the chemistry of the odd electron; heterolytic chemistry is the chemistry of the electron pair. Where homolytic chemistry deals with the neutral particles called free radicals, heterolytic chemistry deals with positive and negative charges, with cations and anions. Homolytic reactions are typically carried out in the gas phase, or in solvents whose principal function is to provide an inert medium in which the reacting molecules can move about. Heterolytic reactions are typically carried out in solution; and the solvents, as we shall see, exert powerful effects—just how powerful is only now being realized.

So far, the reaction we have been chiefly concerned with—free-radical substitution, as exemplified by the halogenation of alkanes—is a part of homolytic chemistry. Now let us begin our study of heterolytic chemistry. The larger part of organic chemistry is heterolytic, and it is the kind that will take up most of our time in the remainder of this book. The reaction we shall start with is, like halogenation, substitution, but of a quite different kind: heterolytic, and of the specific type called *nucleophilic aliphatic substitution*.

5.2 Relative rates of competing reactions

In our study of nucleophilic substitution, we shall enormously broaden our understanding of the principle underlying all of organic chemistry: that chemical behavior depends upon molecular structure. Before we go further, let us remind ourselves of how, in general, we approach the matter of chemical behavior.

In a reaction vessel there is a collection of molecules, banging blindly about, colliding with one another. In principle, a number of options are open to them: a number of reactions that they can conceivably undergo. Which of these reactions actually takes place—or, at least, predominates—is the one that *goes fastest*. Chemical behavior thus comes down to a matter of *relative rates of competing reactions*.

As we have seen from our study of halogenation of alkanes, relative rates of reaction thus determine

(a) *what* happens: a halogen atom, for example, attaches itself to a hydrogen of methane and abstracts the hydrogen; the alternative, attachment to carbon with expulsion of a hydrogen atom, is vastly slower and, in effect, does not take place (Sec. 2.21).

(b) *where* it happens: a halogen atom abstracts hydrogen from ethane in preference to methane; it abstracts a tertiary hydrogen in preference to a primary hydrogen (Sec. 3.23).

(c) even *whether* it happens: a chlorine atom abstracts hydrogen from an alkane; an iodine atom does not, because it recombines with another iodine atom faster (Sec. 2.20).

A chemical reaction is, then, the result of a *competition*; it is a race that is won by the fastest runner. And, we have learned, the most important factor determining how fast a reaction goes is the energy of activation. What our collection of molecules tend to do, by and large, is *what is easiest for them.* They follow the course that makes the smallest demand for energy; that is, they undergo the reaction with the smallest E_{act}.

And, finally, to help us understand E_{act}—to interpret and, sometimes, even to predict—we have our all-important intellectual tool, the transition state. The more stable the transition state relative to the reactant, then the smaller the E_{act} and the faster the reaction. It is the concept of the transition state that is our mental link between molecular structure and chemical behavior.

What we have said above is based on the premise that the products we *obtain* from a chemical reaction, and their relative proportions, reflect the relative rates at which they are initially *formed*; that is to say, once formed, a particular product sits and waits unchanged for the completion of reaction. For most of the reactions we study this premise is correct; under the conditions employed, most organic reactions are essentially irreversible, that is, they are one-way reactions.

But this is *not always* the case. Some reactions are reversible, and equilibrium exists among the various products; what we then obtain reflects, not which product is initially formed faster, but which product is eventually favored by the equilibrium. We shall see examples of this kind of behavior. Irreversibility, therefore, is not something that can be simply assumed for an organic reaction. It must be established by experiment; and only when it has been established are we justified in interpreting product composition on the basis of relative rates.

In our study of nucleophilic substitution, we shall have much to do with competition between reaction pathways: in this chapter, competition between different mechanisms for substitution itself; in later chapters, competition between nucleophilic substitution and a reaction of a quite different type, elimination. We shall be concerned with the relative rates at which these competing reactions take place, and the kinds of transition states they pass through. Most important, we shall learn about the factors that determine the stability of these transition states, factors that we shall work with throughout the rest of our study of organic chemistry.

5.3 Structure. The functional group

In this introduction to nucleophilic substitution, we shall deal chiefly with a family of compounds already familiar to us, the *alkyl halides.* Alkyl halides have the general formula RX, in which R is an alkyl or substituted alkyl group.

$$R{-}X$$

An alkyl halide

The characteristic feature of the alkyl halide structure is the halogen atom, —X, and the characteristic reactions of an alkyl halide are those that take place at the halogen atom. *The atom or group of atoms that defines the structure of a particular family of organic compounds and, at the same time, determines their properties is called the* **functional group.**

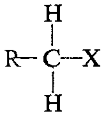
In alkyl halides the functional group is the halogen atom. We must not forget that an alkyl halide has an alkyl group attached to this functional group; under the proper conditions, the alkyl portion of these molecules undergoes the reactions typical of alkanes. However, the reactions that are *characteristic* of the family ar the ones that occur at the halogen atom.

A large part of organic chemistry is therefore the chemistry of the variou functional groups. We shall learn to associate a particular set of properties with particular group wherever we may find it. When we encounter a complicate molecule, which contains a number of different functional groups, we may expec the properties of this molecule to be roughly a composite of the properties of th various functional groups. A compound that contains both —X and —OH, fo example, is both an alkyl halide and an alcohol; depending upon experimenta conditions, it may undergo reactions characteristic of either kind of compounc The properties of one group may be modified, of course, by the presence of anothe group, and it is important for us to understand these modifications; but our poin of departure is the chemistry of individual functional groups.

In this chapter, we shall take up alkyl halides in a systematic way. We sha outline their chemistry, and then concentrate on their most important reaction nucleophilic substitution.

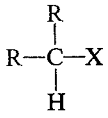
5.4 Classification and nomenclature

We classify a carbon atom as *primary, secondary,* or *tertiary,* according to th number of other carbon atoms attached to it (Sec. 3.11). An alkyl halide is classifie according to the kind of carbon that bears the halogen:



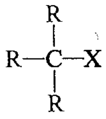
$$\mathrm{R-\overset{H}{\underset{H}{C}}-X}$$

Primary
(1°)



$$\mathrm{R-\overset{R}{\underset{H}{C}}-X}$$

Secondary
(2°)



$$\mathrm{R-\overset{R}{\underset{R}{C}}-X}$$

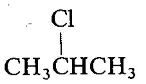
Tertiary
(3°)

As members of the same family, containing the same functional group, alk halides of different classes tend to undergo the same kinds of reactions. They diff in rates of reaction, however, and these differences in rates may lead to othe deeper differences.

As we have seen (Secs. 3.8 and 3.10), alkyl halides can be given two kinds names: **common names** (for the simpler halides); and **IUPAC names**, in which th compound is simply named as an alkane with a halogen attached as a side chai For example:

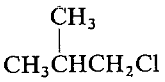
$CH_3CH_2CH_2CH_2Br$

n-Butyl bromide
1-Bromobutane
(1°)



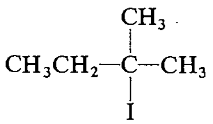
$$\mathrm{CH_3\overset{Cl}{C}HCH_3}$$

Isopropyl chloride
2-Chloropropane
(2°)



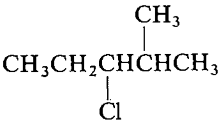
$$\mathrm{CH_3\overset{CH_3}{C}HCH_2Cl}$$

Isobutyl chloride
1-Chloro-2-methylpropane
(1°)



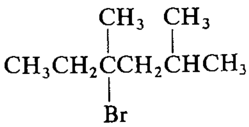
$$\mathrm{CH_3CH_2-\overset{CH_3}{\underset{I}{C}}-CH_3}$$

tert-Pentyl iodide
2-Iodo-2-methylbutane
(3°)



$$\mathrm{CH_3CH_2\underset{Cl}{C}H\overset{CH_3}{C}HCH_3}$$

3-Chloro-2-methylpentane
(2°)



$$\mathrm{CH_3CH_2\overset{CH_3}{\underset{Br}{C}}CH_2\overset{CH_3}{C}HCH_3}$$

4-Bromo-2,4-dimethylhexane
(3°)

We should notice that similar names do not always mean the same classification; for example, isopropyl chloride is a secondary chloride, whereas isobutyl chloride is a primary chloride.

Problem 5.1 Label as primary, secondary, or tertiary each of the isomeric chloropentanes whose structures you drew in Problem 3.5, p. 87.

5.5 Physical properties

Because of their greater molecular weights, haloalkanes have considerably higher boiling points (Table 5.1) than alkanes with the same number of carbons.

Table 5.1 ALKYL HALIDES

	Chloride		Bromide		Iodide	
Name	B.p., °C	Relative density at 20 °C	B.p., °C	Relative density at 20 °C	B.p., °C	Relative density at 20 °C
Methyl	−24		5		43	2.279
Ethyl	12.5		38	1.440	72	1.933
n-Propyl	47	0.890	71	1.335	102	1.747
n-Butyl	78.5	0.884	102	1.276	130	1.617
n-Pentyl	108	0.883	130	1.223	157	1.517
n-Hexyl	134	0.882	156	1.173	180	1.441
n-Heptyl	160	0.880	180		204	1.401
n-Octyl	185	0.879	202		225.5	
Isopropyl	36.5	0.859	60	1.310	89.5	1.705
Isobutyl	69	0.875	91	1.261	120	1.605
sec-Butyl	68	0.871	91	1.258	119	1.595
tert-Butyl	51	0.840	73	1.222	100*dec.*	
Cyclohexyl	142.5	1.000	165			
Vinyl (Haloethene)	−14		16		56	
Allyl (3-Halopropene)	45	0.938	71	1.398	103	
Crotyl (1-Halo-2-butene)	84				132	
Methylvinylcarbinyl (3-Halo-1-butene)	64					
Propargyl (3-Halopropyne)	65		90	1.520	115	
Benzyl	179	1.102	201		93^{10}	
α-Phenylethyl	92^{15}		85^{10}			
β-Phenylethyl	92^{20}		92^{11}		127^{19}	
Diphenylmethyl	173^{19}		184^{20}			
Triphenylmethyl	310		230^{15}			
Dihalomethane	40	1.336	99	2.49	180*dec.*	3.325
Trihalomethane	61	1.489	151	2.89	*subl.*	4.008
Tetrahalomethane	77	1.595	189.5	3.42	*subl.*	4.32
1,1-Dihaloethane	57	1.174	110	2.056	179	2.84
1,2-Dihaloethane	84	1.257	132	2.180	*dec.*	2.13
Trihaloethylene	87		164	2.708		
Tetrahaloethylene	121				*subl.*	
Benzal halide	205		140^{20}			
Benzotrihalide	221	1.38				

For a given alkyl group, the boiling point increases with increasing atomic weight of the halogen, so that a fluoride is the lowest boiling, an iodide the highest boiling.

For a given halogen, the boiling point rises with increasing carbon number; as with alkanes, the boiling point rise is 20–30 degrees for each added carbon, except for the very small homologs. As before, branching—involving either alkyl groups or the halogen itself—lowers the boiling point.

In spite of their modest polarity, alkyl halides are insoluble in water, probably because of their inability to form hydrogen bonds. They are soluble in the typical organic solvents of low polarity, like benzene, ether, chloroform, or ligroin.

Iodo, bromo, and polychloro compounds are more dense than water.

Alkanes and alkyl halides, then, have the physical properties we might expect of compounds of low polarity, whose molecules are held together by van der Waals forces or weak dipole–dipole attraction. They have relatively low melting points and boiling points, and are soluble in non-polar solvents and insoluble in water.

There is a further result of their low polarity: while alkanes and alkyl halides are themselves good solvents for other compounds of low polarity—each other, for example—they cannot solvate simple ions appreciably, and hence cannot dissolve inorganic salts.

5.6 Preparation

In the laboratory alkyl halides are most often prepared by the methods outlined below.

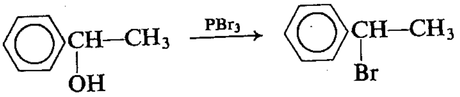
PREPARATION OF ALKYL HALIDES

1. From alcohols. Discussed in Secs. 5.6 and 6.13.

$$\text{R—OH} \xrightarrow{\text{HX or PX}_3} \text{R—X}$$

Examples:

$$\underset{n\text{-Propyl alcohol}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}} \xrightarrow[\text{NaBr, H}_2\text{SO}_4\text{, heat}]{\text{conc. HBr or}} \underset{n\text{-Propyl bromide}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}}$$



1-Phenylethanol
α-Phenylethyl alcohol

1-Bromo-1-phenylethane
α-Phenylethyl bromide

$$\underset{\text{Ethyl alcohol}}{\text{CH}_3\text{CH}_2\text{OH}} \xrightarrow{\text{P + I}_2} \underset{\text{Ethyl iodide}}{\text{CH}_3\text{CH}_2\text{I}}$$

2. Halogenation of certain hydrocarbons. Discussed in Secs. 3.19, 11.3, 16.13–16.14.

$$\text{R—H} \xrightarrow{\text{X}_2} \text{R—X + HX}$$

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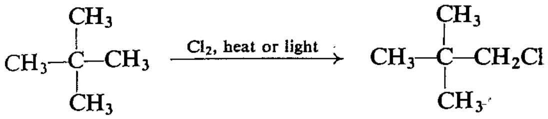
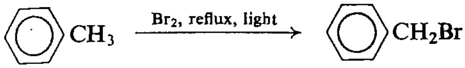
Examples:



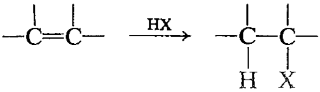
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow{Cl_2,\text{ heat or light}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Cl$$

Neopentane Neopentyl chloride



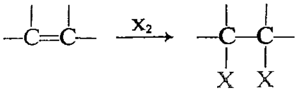
Toluene Benzyl bromide

3. Addition of hydrogen halides to alkenes. Discussed in Secs. 9.5–9.6.



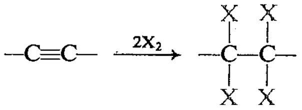
$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow{HX} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{X}{C}}-$$

4. Addition of halogens to alkenes and alkynes



$$-\overset{|}{C}=\overset{|}{C}- \xrightarrow{X_2} -\overset{|}{\underset{X}{C}}-\overset{|}{\underset{X}{C}}-$$

Discussed in Secs. 9.12–9.13 and 10.2–10.3.



$$-C\equiv C- \xrightarrow{2X_2} -\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-$$

Discussed in Sec. 12.7.

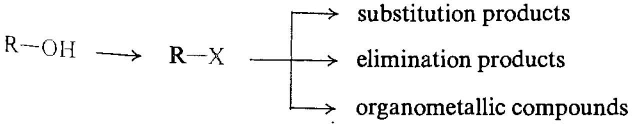
5. Halide exchange. Discussed in Sec. 5.6.

$$R-X + I^- \xrightarrow{\text{acetone}} R-I + X^-$$

Alkyl halides are nearly always prepared from alcohols. Alcohols, in turn, are readily available in a wide variety of shapes and sizes. Simpler alcohols are produced commercially (Sec. 6.6); the more complicated ones are readily synthesized (Secs. 18.14–18.16). Although certain alcohols tend to undergo rearrangement (Sec. 6.13) during replacement of —OH by —X, this tendency can be minimized by use of phosphorus halides.

$$\underset{\text{An alcohol}}{R-OH} \xrightarrow{HX\text{ or }PX_3} \underset{\text{An alkyl halide}}{R-X}$$

In the laboratory, alcohols are the most common starting point for the synthesis of aliphatic compounds, and one of the commonest first steps in such a synthesis is the conversion of the alcohol into an alkyl halide. Once the alkyl halide is made,



the synthesis can follow any one of dozens of pathways, depending upon the reaction that the alkyl halide is allowed to undergo—and, as we shall see in the following section, there are dozens of possibilities.

Alkyl halides are *almost never* prepared by direct halogenation of alkanes. *From the standpoint of synthesis in the laboratory, an alkane is a dead-end.* Halogenation generally gives a mixture of isomers; even if, occasionally, one isomer greatly predominates—as in the bromination of isobutane, say—it is probably not the one we want. How much more practical simply to pick an alcohol that has the —OH in the proper position, and then to replace that —OH by halide!

An alkyl iodide is often prepared from the corresponding bromide or chloride by treatment with a solution of sodium iodide in acetone; the less soluble sodium bromide or sodium chloride precipitates from solution and can be removed by filtration.

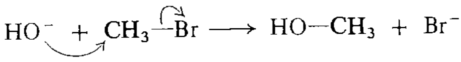
5.7 Reactions. Nucleophilic aliphatic substitution

When methyl bromide is treated with sodium hydroxide in a solvent that dissolves both reagents, there is obtained methanol and sodium bromide. This is a *substitution* reaction: the —OH group is substituted for —Br in the original compound. An alkyl halide has been converted into an alcohol.

$$\underset{\text{Methyl bromide}}{CH_3{:}Br} + {:}OH^- \longrightarrow \underset{\text{Methanol}}{CH_3{:}OH} + {:}Br^-$$

It is clearly heterolytic: the departing halide ion takes with it the electron pair it has been sharing with carbon; hydroxide ion brings with it the electron pair needed to bind it to carbon. Carbon loses one pair of electrons and gains another pair. This is just one example of the class of reactions called *nucleophilic aliphatic substitution*.

With formulas where a bond is represented by a line instead of a pair of dots, we can use curved arrows to show the movement of electrons.



$$HO^- + CH_3{-}Br \longrightarrow HO{-}CH_3 + Br^-$$

Nucleophilic substitution is characteristic of alkyl halides. To see why this is so, we must look at the functional group of this family: halogen.

A halide ion is an extremely weak base. This is shown by its readiness to release a proton to other bases, that is, by the high acidity of the hydrogen halides. In an alkyl halide, halogen is attached to carbon; and, just as halide readily releases a proton, so it readily releases carbon—again, to other bases. These bases possess an unshared pair of electrons and are seeking a relatively positive site, that is, are seeking a nucleus with which to share their electron pair.

Basic, electron-rich reagents that tend to attack the nucleus of carbon are called **nucleophilic reagents** (from the Greek, *nucleus-loving*) or simply **nucleophiles**. When this attack results in substitution, the reaction is called **nucleophilic substitution**.

$$\underset{\text{Substrate}}{R{:}W} + \underset{\text{Nucleophile}}{{:}Z} \longrightarrow R{:}Z + \underset{\substack{\text{Leaving}\\\text{group}}}{{:}W^-}$$

The carbon compound that undergoes a particular kind of reaction—here, the compound on which substitution takes place—is called the **substrate**. In the case of nucleophilic substitution, the substrate is characterized by the presence of a leaving group: the group that becomes displaced from carbon and, taking the electron pair with it, departs from the molecule.

It should be understood that the nucleophile $:Z$ can be negatively charged or neutral; the product $R{:}Z$ will then be neutral or positively charged. The substrate $R{:}W$ can be neutral or positively charged; the leaving group will then be negatively charged or neutral.

In the example we started with, methyl bromide is the substrate, bromide is the leaving group, and hydroxide ion is the nucleophile.

Because the weakly basic halide ion is a good leaving group, then, alkyl halides are good substrates for nucleophilic substitution. They react with a large number of nucleophilic reagents, both inorganic and organic, to yield a wide variety of important products. As we shall see, these reagents include not only negative ions like hydroxide and cyanide, but also neutral bases like ammonia and water; their characteristic feature is an unshared pair of electrons.

As a synthetic tool, nucleophilic substitution is one of the three or four most useful classes of organic reactions. Nucleophilic substitution is the work-horse of organic synthesis; in its various forms, it is the reaction we shall turn to first when faced with the basic job of replacing one functional group by another. The synthesis of aliphatic compounds, we said, most often starts with alcohols. But the —OH group, we shall find, is a very poor leaving group; it is only conversion of alcohols into alkyl halides—or other compounds with good leaving groups—that opens the door to nucleophilic substitution.

A large number of nucleophilic substitutions are listed below to give an idea of the versatility of alkyl halides; many will be left to later chapters for detailed discussion.

REACTIONS OF ALKYL HALIDES

1. Nucleophilic substitution

$R{:}X + {:}Z$	$\longrightarrow$	$R{:}Z + {:}X^-$	
$R{:}X + {:}OH^-$	$\longrightarrow$	$R{:}OH + {:}X^-$	Alcohol
$+ H_2O$	$\longrightarrow$	$R{:}OH$	Alcohol
$+ {:}OR'^-$	$\longrightarrow$	$R{:}OR'$	Ether (Williamson synthesis, Sec. 6.20)
$+ {:}C{\equiv}CR'$	$\longrightarrow$	$R{:}C{\equiv}CR'$	Alkyne (Sec. 12.12)
$+ \overset{\delta-}{R'}-\overset{\delta+}{M}$	$\longrightarrow$	$R{:}R'$	Alkane (coupling, Sec. 3.17)
$+ {:}I^-$	$\longrightarrow$	$R{:}I$	Alkyl iodide
$+ {:}CN^-$	$\longrightarrow$	$R{:}CN$	Nitrile (Sec. 19.8)

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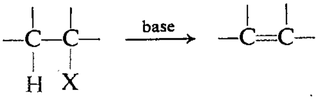
$\mathrm{R{:}X\ +\ R'COO{:}^-}$	$\longrightarrow$	$\mathrm{R'COO{:}R}$	Ester
$\mathrm{+\ {:}NH_3}$	$\longrightarrow$	$\mathrm{R{:}NH_2}$	Primary amine (Sec. 22.10)
$\mathrm{+\ {:}NH_2R'}$	$\longrightarrow$	$\mathrm{R{:}NHR'}$	Secondary amine (Sec. 22.13)
$\mathrm{+\ {:}NHR'R''}$	$\longrightarrow$	$\mathrm{R{:}NR'R''}$	Tertiary amine (Sec. 22.13)
$\mathrm{+\ {:}P(C_6H_5)_3}$	$\longrightarrow$	$\mathrm{R{:}P(C_6H_5)_3{}^+X^-}$	Phosphonium salt (Sec. 21.10)
$\mathrm{+\ {:}SH^-}$	$\longrightarrow$	$\mathrm{R{:}SH}$	Thiol (mercaptan)
$\mathrm{+\ {:}SR'^-}$	$\longrightarrow$	$\mathrm{R{:}SR'}$	Thioether (sulfide)
$\mathrm{R{:}X\ +\ Ar{-}H\ +\ AlCl_3}$	$\longrightarrow$	$\mathrm{Ar{-}R}$	Alkylbenzene (Friedel-Crafts reaction, Sec. 16.7)
$\mathrm{+\ [CH(COOC_2H_5)_2]^-}$	$\longrightarrow$	$\mathrm{R{:}CH(COOC_2H_5)_2}$	(Malonic ester synthesis, Sec. 25.2)
$\mathrm{+\ [CH_3COCHCOOC_2H_5]^-}$	$\longrightarrow$	$\mathrm{CH_3CO\underset{\ddot{R}}{C}HCOOC_2H_5}$	(Acetoacetic ester synthesis, Sec. 25.3)

2. **Dehydrohalogenation: elimination.** Discussed in Secs. 8.13 and 8.25.



$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- \xrightarrow{\text{base}} -\overset{|}{C}=\overset{|}{C}-$$

3. **Preparation of Grignard reagent.** Discussed in Secs. 3.16 and 18.14.

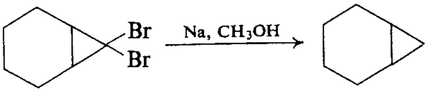
$$\mathrm{RX + Mg \xrightarrow{dry\ ether} RMgX}$$

4. **Reduction.** Discussed in Sec. 3.15.

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

Examples:

$$\mathrm{(CH_3)_3CCl \xrightarrow{Mg} (CH_3)_3CMgCl \xrightarrow{D_2O} (CH_3)_3CD}$$



7,7-Dibromonorcarane Norcarane

With nucleophilic substitution we shall encounter many things new to us: a new reaction, of course—several new reactions, actually—and a new kind of reactive particle, the *carbocation.* To find out what is going on in these reactions, we shall use a new tool, *kinetics,* and use an old tool, *stereochemistry,* in a new way. We shall be introduced to new factors affecting reactivity—*dispersal of charge, polar factors, steric hindrance*—factors that we shall work with throughout the rest of our study.

With alcohols and ethers in Chapter 6, we shall encounter *acid catalysis,* and discover the simplest possible way to convert a very poor leaving group into a very good one.

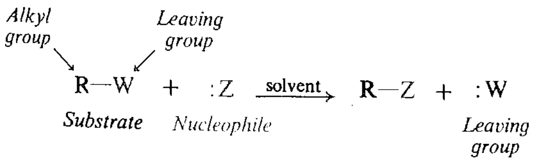
In Chapter 7, still working with nucleophilic substitution, we shall see how reactivity—and, with it, the course of reaction—is affected by the *solvent.* Then, in Chapter 29, we shall use nucleophilic substitution as the starting point for our study of *symphoria*—the bringing together of reactants into the proper spatial relationship—and see how, to an extent never before possible, we can control what happens in an organic reaction: rate, orientation, and even the stereochemical outcome.

Alkyl halides undergo not only substitution but also **elimination,** a reaction that we shall take up in Chapter 8. Both elimination and substitution are brought about by basic reagents, and hence there will always be *competition* between the two reactions. We shall be interested to see how this competition is affected by such factors as the structure of the halide and the particular nucleophilic reagent used.

Alkyl halides are the substances most commonly **converted into organometallic compounds**: compounds that contain carbon attached to a metal—magnesium (as in the Grignard reagent), lithium, copper, and a host of others. We have already met some of these compounds, and shall have a great deal to do with them as we go along. As we shall see (Sec. 12.13), conversion of alkyl halides into organometallic compounds changes the nature of the central carbon atom in a fundamental way, and gives us a class of reagents with unique properties.

5.8 Nucleophilic aliphatic substitution. Nucleophiles and leaving groups

The components required for nucleophilic substitution are: *substrate, nucleophile,* and *solvent.* The substrate consists of two parts, *alkyl group* and *leaving group.* We shall be concerned with the alkyl group throughout much of the chapter; we



$$\text{R—W} + :\text{Z} \xrightarrow{\text{solvent}} \text{R—Z} + :\text{W}$$

shall study the roles played by the solvent in Chapter 7. At this point let us examine the other components of these systems, nucleophiles and leaving groups.

We have already seen enough to realize that basicity plays an important part in our understanding of nucleophiles and leaving groups. Nucleophiles are characterized by being bases, and leaving groups are characterized by being *weak* bases. We may find a rough correlation between *degree* of basicity, on the one hand, and nucleophilic power or leaving ability, on the other: the stronger of two bases is often the more powerful nucleophile, and the weaker of two bases is often the better leaving group. But this holds true only for closely related sets of nucleophiles or sets of leaving groups: ones that, among other things, involve the same central element—oxygen, say, or nitrogen. There are many exceptions to such a correlation, and clearly basicity is only *one* of the factors involved.

We should have clear in our minds the distinction between basicity and nucleophilic power or leaving ability. All have to do with the tendency—or, in the case of leaving ability, *lack* of tendency—to share an electron pair to form a covalent bond. But there are two fundamental differences:

(a) Basicity is a matter of *equilibrium*; nucleophilic power and leaving ability are matters of *rate*. Of two bases, one is said to be the stronger because at equilibrium it holds a greater proportion of the acid. Of two nucleophiles, one is said to be the more powerful because it attacks carbon *faster*; of two leaving groups, one is said to be the better because it leaves carbon *faster*.

(b) Basicity (in the Lowry–Brønsted sense) involves interaction with a proton; nucleophilic power and leaving ability involve interactions with carbon.

It is not surprising, then, that there is no exact parallel between basicity and these two other properties. The surprise, perhaps, is that the parallel is as good as it is.

Let us have a look at some of the **nucleophiles** we shall be working with. Many of the products formed are new to us, but at this point we need see only how the structure of a particular product is the natural result of the structure of a particular nucleophile. For now, we shall use alkyl halides as our examples of substrates.

Some nucleophiles are anions, like *hydroxide* ion;

$$R{-}X + \underset{\substack{\text{Hydroxide}\\ \text{ion}}}{:OH^-} \longrightarrow \underset{\text{An alcohol}}{R{-}OH} + :X^-$$

cyanide (the strongly basic anion of the very weak acid, HCN);

$$R{-}X + \underset{\substack{\text{Cyanide}\\ \text{ion}}}{:CN^-} \longrightarrow \underset{\text{A nitrile}}{R{-}CN} + :X^-$$

or even another *halide* ion which, while only weakly basic, does after all possess unshared electrons.

$$R{-}X + \underset{\substack{\text{Iodide}\\ \text{ion}}}{:I^-} \longrightarrow \underset{\substack{\text{Alkyl}\\ \text{iodide}}}{R{-}I} + :X^-$$

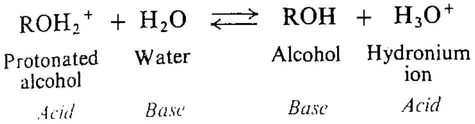
But neutral molecules, too, can possess unshared electrons, be basic, and hence act as nucleophiles. *Water*, for example, attacks an alkyl halide to yield, ultimately, an alcohol. But the oxygen of water already has two hydrogens, and when it attaches

$$R{-}X + :OH_2 \longrightarrow \underset{\substack{\text{Protonated}\\ \text{alcohol}}}{R{-}OH_2^+} + :X^-$$

itself to carbon there is formed initially, not the alcohol itself, but its conjugate acid, the protonated alcohol. This easily changes itself into the alcohol by loss of the proton.

$$\underset{\substack{\text{Protonated}\\ \text{alcohol}}}{R{-}OH_2^+} \rightleftarrows \underset{\text{Alcohol}}{R{-}OH} + H^+$$

An important point arises here. For convenience we shall often show the loss or gain of a hydrogen ion, H^+. But it should be understood that we are *not* actually dealing with a naked proton, but rather with the *transfer* of a proton from one base



$$\underset{\substack{\text{Protonated}\\\text{alcohol}\\ \textit{Acid}}}{ROH_2^+} + \underset{\substack{\text{Water}\\ \textit{Base}}}{H_2O} \rightleftarrows \underset{\substack{\text{Alcohol}\\ \textit{Base}}}{ROH} + \underset{\substack{\text{Hydronium}\\\text{ion}\\ \textit{Acid}}}{H_3O^+}$$

to another. In the present case, for example, protonated alcohol is converted into alcohol by transfer of the proton to water—about as basic as the alcohol itself, and much more abundant.

Problem 5.2 What product would you expect to obtain from the reaction of *n*-propyl bromide with methanol, CH_3OH? Write equations for all steps involved.

Next, let us look briefly at some of the **leaving groups** we shall encounter. So far we have used alkyl halides as our chief examples, and we shall continue to do this in following sections. But we should realize that these reactions take place in exactly the same ways with a variety of other substrates: compounds which, like alkyl halides, contain good leaving groups.

Of these other substrates, *alkyl esters of sulfonic acids*, $ArSO_2OR$, are most commonly used in place of alkyl halides. Like alkyl halides, the sulfonates are made from alcohols, as we shall find in Chapter 6. (Also in Chapter 6 we shall see how *alcohols* themselves, by means of a special trick, can be instantaneously converted into substrates.)

Now let us begin our study of the mechanism of nucleophilic aliphatic substitution. For generations this reaction has fascinated chemists, including many of the "greats" whose names are—or will become—familiar to us: J. A. LeBel, G. N. Lewis, T. M. Lowry; and that giant of organic chemistry, Emil Fischer, who, we shall find, opened up the two vast fields of carbohydrates and proteins.

In its various forms, nucleophilic aliphatic substitution has been the most widely studied—and most strongly disputed—area of organic chemistry. The fascination—and the argument—has lain in two related questions. The bond to the leaving group is being broken and the bond to the nucleophile is being formed. (a) What is the *timing* of these two processes? (b) Where does the energy required to break the bond to the leaving group come from?

We shall begin our study of the mechanism where the modern history of the reaction begins: with the *kinetics* of nucleophilic aliphatic substitution. But, first, what *is* kinetics?

5.9 Rate of reaction: effect of concentration. Kinetics

We have seen (Sec. 2.18) that the rate of a chemical reaction can be expressed as a product of three factors:

$$\text{rate} = \begin{matrix}\text{collision}\\\text{frequency}\end{matrix} \times \begin{matrix}\text{energy}\\\text{factor}\end{matrix} \times \begin{matrix}\text{probability}\\\text{factor}\end{matrix}$$

So far, we have used this relationship in comparing rates of *different* reactions: to help us understand orientation and relative reactivity, and why a particular reaction takes place at all. So that comparisons of this sort may be as fair as possible, we keep the conditions that we can control—temperature, concentration—the same. If this is done, then closely related reactions proceed at different rates chiefly because they have different energy factors, that is to say, different E_{act} values; and to account for different E_{act} values we must estimate relative stabilities of transition states.

It is also useful to study an *individual* reaction to see how its rate is affected by deliberate changes in experimental conditions. We can determine E_{act}, for example, if we measure the rate at different temperatures (Sec. 2.18). But perhaps the most valuable information about a reaction is obtained by studying the effect of *changes in concentration* on its rate.

How does a change in concentration of reactants affect the rate of a reaction at a constant temperature? An increase in concentration cannot alter the fraction of collisions that have sufficient energy, or the fraction of collisions that have the proper orientation; it can serve only to increase the total number of collisions. If more molecules are crowded into the same space, they will collide more often and the reaction will go faster. Collision frequency, and hence rate, depends in a very exact way upon concentration.

The field of chemistry that deals with rates of reaction, and in particular with dependence of rates on concentration, is called **kinetics**. Let us see what kinetics can tell us about nucleophilic aliphatic substitution.

5.10 Kinetics of nucleophilic aliphatic substitution. Second-order and first-order reactions

Let us take a specific example, the reaction of methyl bromide with sodium hydroxide to yield methanol:

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

This reaction would probably be carried out in aqueous ethanol, in which both reactants are soluble.

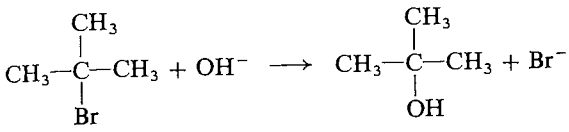
If the reaction results from collision between a hydroxide ion and a methyl bromide molecule, we would expect the rate to depend upon the concentration of both these reactants. If either OH^- concentration, $[OH^-]$, or CH_3Br concentration, $[CH_3Br]$, is doubled, the collision frequency should be doubled and the reaction rate doubled. If either concentration is cut in half, the collision frequency, and consequently the rate, should be halved.

This is found to be so. We say that the rate of reaction depends upon both $[OH^-]$ and $[CH_3Br]$, and we indicate this by the expression

$$\text{rate} = k[CH_3Br][OH^-]$$

If concentrations are expressed in, say, moles per liter, then k is the number which, multiplied by these concentrations, tells us how many moles of methanol are formed in each liter during each second. At a given temperature and for a given solvent, k always has the same value and is characteristic of this particular reaction; k is called the **rate constant**. For example, for the reaction between methyl bromide and hydroxide ion in a mixture of 80% ethanol and 20% water at 55 °C, the value of k is 0.0214 liters per mole per second.

What we have just seen is, of course, not surprising; we all know that an increase in concentration causes an increase in rate. But now let us look at the corresponding reaction between *tert*-butyl bromide and hydroxide ion:



$$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_3 + OH^- \longrightarrow CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 + Br^-$$

As before, if we double [RBr] the rate doubles; if we cut [RBr] in half the rate is halved. But if we double $[OH^-]$, or if we cut $[OH^-]$ in half, there is no change in the rate. *The rate of reaction is independent of* $[OH^-]$.

The rate of reaction of *tert*-butyl bromide depends only upon [RBr]. This is indicated by the expression

$$\text{rate} = k[RBr]$$

For the reaction of *tert*-butyl bromide in 80% alcohol at 55 °C, the rate constant is 0.010 per second. This means that, of every mole of *tert*-butyl bromide present, 0.010 mole reacts each second, whatever the $[OH^-]$.

The methyl bromide reaction is said to follow **second-order kinetics**, since its rate is dependent upon the concentrations of *two* substances. The *tert*-butyl bromide reaction is said to follow **first-order kinetics**; its rate depends upon the concentration of only *one* substance.

5.11 Nucleophilic aliphatic substitution: duality of mechanism

By the 1930s, kinetics studies of nucleophilic substitution had been carried out with a variety of substrates, and the following had been found. Like methyl, primary substrates react by second-order kinetics. Like *tert*-butyl, other tertiary substrates react by first-order kinetics. Secondary substrates show borderline behavior: sometimes second-order, sometimes first-order; often a mixture of the two.

Besides the kinetic order, the rate studies had revealed something else about the substitution: the relative reactivities of the various substrates. Typically, at a given concentration of a nucleophile like OH^-, reactivity was found to vary something like this:

$$CH_3X > 1° > 2° < 3°$$

That is, as one proceeds along the series CH_3, 1°, 2°, 3°, reactivity at first decreases, then passes through a minimum (usually at 2°), and finally rises (see Fig. 5.1). Significantly, the minimum occurs at just the point in the series where the kinetics changes from second-order to first-order.

In 1935, E. D. Hughes and Sir Christopher Ingold (University College, London) took these two sets of facts—kinetic order and relative reactivity—and on them built a broad theory of nucleophilic aliphatic substitution. The keystone of their theory was this: that *nucleophilic aliphatic substitution can proceed by two different mechanisms*. These mechanisms, for reasons that will become clear, they

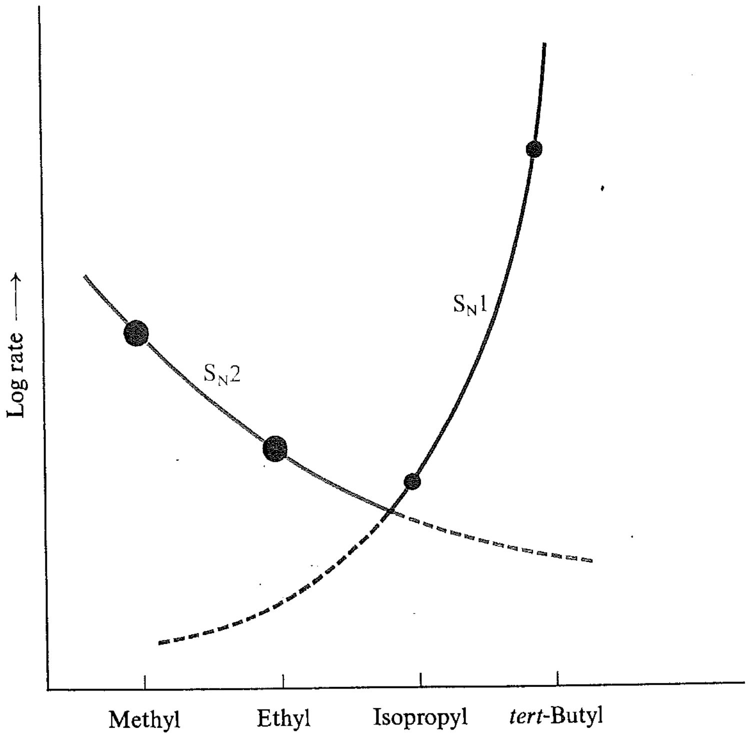


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Figure 5.1 Nucleophilic aliphatic substitution: typical effect on rate caused by variations in structure of substrate, RX. The minimum in rate is attributed to the crossing of two opposing curves, that is, to a change in mechanism from S_N2 to S_N1.

named S_N2 and S_N1. Different substrates react by different kinetic orders because they are reacting by different mechanisms: some, like methyl, by S_N2; others, like *tert*-butyl, by S_N1.

Reactivity passes through a minimum with secondary substrates because the mechanism changes at this point, from S_N2 to S_N1. The occurrence of a minimum or maximum in a property—reactivity, acidity, antibacterial activity—as one proceeds along a logical series, suggests the working of opposing factors. Here, Hughes and Ingold proposed, the factors are the opposing reactivity sequences for the two different mechanisms. As one passes along the series, reactivity by the S_N2

S_N2
vs.
S_N1

$$\mathrm{RX} = \overset{\xleftarrow{\text{S}_\text{N}2\text{ increases}}}{\underset{\xrightarrow[\text{S}_\text{N}1\text{ increases}]{}}{\mathrm{CH_3X}\quad 1^\circ\quad 2^\circ\quad 3^\circ}}$$

mechanism decreases from CH_3 to 1°, and at 2° is so low that the S_N1 reaction begins to contribute significantly; reactivity, now by S_N1, rises sharply to 3° (Fig. 5.1).

In the following sections, we shall see what these two mechanisms are, the facts on which they are based, and how they account for these facts. We shall see, for example, how they account for the difference in kinetic order and, in particular, for the puzzling fact that the rate of the *tert*-butyl bromide reaction is independent of $[OH^-]$. We shall see what factors are believed to be responsible for the opposing reactivity sequences for the two mechanisms. Finally, we shall see how this mechanistic pattern drawn in 1935 has stood the test of time.

5.12 The S_N2 reaction: mechanism and kinetics

The reaction between methyl bromide and hydroxide ion to yield methanol follows second-order kinetics; that is, the rate depends upon the concentrations of both reactants:

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$

$$\text{rate} = k[CH_3Br][OH^-]$$

The simplest way to account for the kinetics is to assume that reaction requires a collision between a hydroxide ion and a methyl bromide molecule. On the basis of evidence we shall shortly discuss, it is known that in its attack the hydroxide ion stays as far away as possible from the bromine; that is to say, it attacks the molecule from the rear.

The reaction is believed to take place as shown in Fig. 5.2. When hydroxide ion collides with a methyl bromide molecule at the face most remote from the bromine, and when such a collision has sufficient energy, a C—OH bond forms and the C—Br bond breaks, liberating the bromide ion.

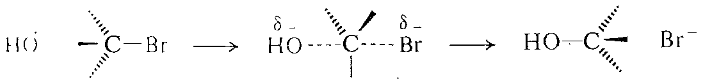


Figure 5.2 The S_N2 reaction: complete inversion of configuration. The nucleophilic reagent attacks the back side.

The transition state can be pictured as a structure in which carbon is partially bonded to both —OH and —Br; the C—OH bond is not completely formed, the C—Br bond is not yet completely broken. Hydroxide has a diminished negative charge, since it has begun to share its electrons with carbon. Bromine has developed a partial negative charge, since it has partly removed a pair of electrons from carbon.

The —OH and —Br are located as far apart as possible; the three hydrogens and the carbon lie in a single plane, all bond angles being 120°. The C—H bonds are thus arranged like the spokes of a wheel, with the C—OH and the C—Br bonds lying along the axle.

We can see how the geometry of this transition state arises. Carbon holds the three hydrogens through overlap of three sp^2 orbitals: trigonal, and hence flat and 120° apart. The partial bonds to the leaving group and the nucleophile are formed through overlap of the remaining p orbitals: 180° apart, and perpendicular to the plane of the sp^2 orbitals.

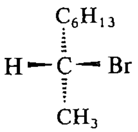
This is the mechanism that is called **S_N2**: *substitution nucleophilic bimolecular.* The term *bi*molecular is used here since the rate-determining step involves collision of two particles.

What evidence is there that alkyl halides can react in this manner? First of all, as we have just seen, the mechanism is consistent with the kinetics of a reaction like the one between methyl bromide and hydroxide ion. In general, **an S_N2 reaction follows second-order kinetics.** Let us look at some of the other evidence.

5.13 The S_N2 reaction: stereochemistry. Inversion of configuration

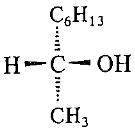
Both 2-bromooctane and 2-octanol are chiral; that is, they have molecules that are not superimposable on their mirror images. Consequently, these compounds can exist as enantiomers, and can show optical activity. Optically active 2-octanol has been obtained by resolution of the racemic modification (Sec. 4.27), and from it optically active 2-bromooctane has been made.

The following configurations have been assigned (Sec. 4.24):



$$\begin{array}{c} C_6H_{13} \\ H-C-Br \\ CH_3 \end{array}$$

(−)-2-Bromooctane
[α] = −39.6°

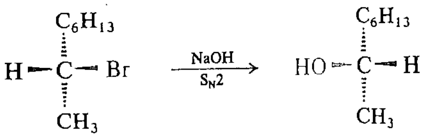


$$\begin{array}{c} C_6H_{13} \\ H-C-OH \\ CH_3 \end{array}$$

(−)-2-Octanol
[α] = −10.3°

We notice that the (−)-bromide and the (−)-alcohol have similar configurations; that is, —OH occupies the same relative position in the (−)-alcohol as —Br does in the (−)-bromide. As we know, compounds of similar configuration do not *necessarily* rotate light in the same direction; they just happen to do so in the present case. (As we also know, compounds of similar configuration are not necessarily given the same specification of *R* and *S* (Sec. 4.24); it just happens that both are *R* in this case.)

Now, when (−)-2-bromooctane is allowed to react with sodium hydroxide under conditions where second-order kinetics are followed, there is obtained (+)-2-octanol.



$$\begin{array}{c} C_6H_{13} \\ H-C-Br \\ CH_3 \end{array} \xrightarrow[S_N2]{NaOH} \begin{array}{c} C_6H_{13} \\ HO-C-H \\ CH_3 \end{array}$$

(−)-2-Bromooctane
[α] = −39.6°
optical purity 100%

(+)-2-Octanol
[α] = +10.3°
optical purity 100%

We see that the —OH group has not taken the position previously occupied by —Br; the alcohol obtained has a configuration *opposite* to that of the bromide. *A reaction that yields a product whose configuration is opposite to that of the reactant is said to proceed with* **inversion of configuration.**

(In this particular case, inversion of configuration happens to be accompanied by a change in specification, from *R* to *S*, but this is not always true. We cannot tell whether a reaction proceeds with inversion or retention of configuration simply by looking at the letters used to specify the reactant and product; we must work out and compare the absolute configurations indicated by those letters.)

Now the question arises: does a reaction like this proceed with *complete* inversion? That is to say, is the configuration of *every* molecule inverted? The answer is *yes*. **An S_N2 reaction proceeds with complete stereochemical inversion.**

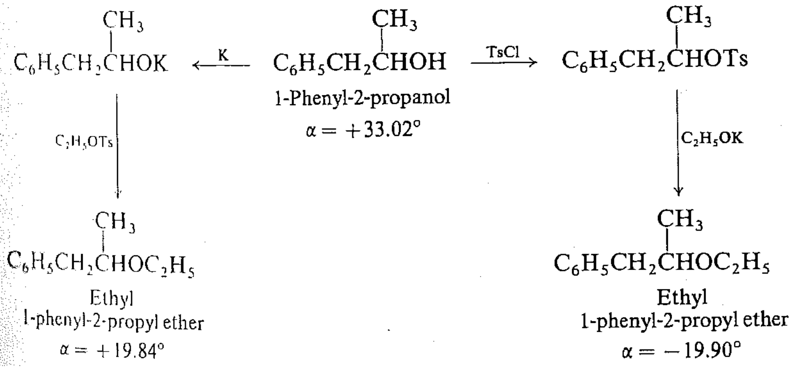
To answer a question like this, we must in general know the optical purity both of the reactant that we start with and of the product that we obtain: in this case, of 2-bromooctane and 2-octanol. To know these we must, in turn, know the maximum rotation of the bromide and of the alcohol; that is, we must know the rotation of an optically pure sample of each.

Suppose, for example, that we know the rotation of optically pure 2-bromooctane to be 39.6° and that of optically pure 2-octanol to be 10.3°. If, then, a sample of optically pure bromide were found to yield optically pure alcohol, we would know that the reaction had proceeded with *complete* inversion. Or—and this is much more practicable—if a sample of a halide of rotation, say, −32.9° (83% optically pure) were found to yield alcohol of rotation +8.55° (83% optically pure), we would draw exactly the same conclusion.

In developing the ideas of S_N1 and S_N2 reactions, Hughes and Ingold studied the reaction of optically active 2-bromooctane and obtained results which led them to conclude that the S_N2 reaction proceeds, within limits of experimental error, with complete inversion.

The particular value that Hughes and Ingold used for the rotation of optically pure 2-bromooctane has been questioned, but the basic idea of complete inversion in S_N2 reactions is established beyond question: by the studies of systems other than alkyl halides and by elegant work involving radioactivity and optical activity (Problem 5.4, below).

Problem 5.3 In 1923 Henry Phillips (Battersea Polytechnic, London) reported the following experiment:

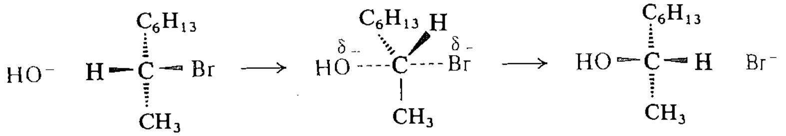


$$\begin{tikzcd} C_6H_5CH_2CH(CH_3)OK \arrow[d, "C_2H_5OTs"] & C_6H_5CH_2CH(CH_3)OH \arrow[l, "K"'] \arrow[r, "TsCl"] & C_6H_5CH_2CH(CH_3)OTs \arrow[d, "C_2H_5OK"] \\ C_6H_5CH_2CH(CH_3)OC_2H_5 & & C_6H_5CH_2CH(CH_3)OC_2H_5 \end{tikzcd}$$

(a) Account for the fact that the ethers obtained by the two routes have *opposite but equal* optical rotations. (*Hint*: See Sec. 4.24.) (b) Does it matter what the optical purity of the starting alcohol is? (c) What is the fundamental significance of this finding?

Problem 5.4 When optically active 2-iodooctane was allowed to stand in acetone solution containing $Na^{131}I$ (radioactive iodide), the alkyl halide was observed to lose optical activity and to exchange its ordinary iodine for radioactive iodine. The rate of each of these reactions depended on both [RI] and [I^-], but loss of optical activity was exactly *twice* as fast as gain of radioactivity. Combining as it does kinetics and stereochemistry, this experiment, reported in 1935 by E. D. Hughes (p. 179), is considered to have established the stereochemistry of the S_N2 reaction: that each molecule undergoing substitution suffers inversion of configuration. Show exactly how this conclusion is justified. (*Hint*: Take one molecule of alkyl halide at a time, and consider what happens when it undergoes substitution.)

It was to account for inversion of configuration that back-side attack was first proposed for substitution of the S_N2 kind. As —OH becomes attached to carbon, three bonds are forced apart until they reach the planar "spoke" arrangement of the transition state; then, as bromide is expelled, they move on to a tetrahedral arrangement *opposite* to the original one. This process has often been likened to the turning-inside-out of an umbrella in a gale.



S_N2: complete inversion

The stereochemistry of the 2-bromooctane reaction indicates back-side attack in accordance with the S_N2 mechanism; studies of other optically active compounds, under conditions where the reactions follow second-order kinetics, show similar results. It is not possible to study the stereochemistry of most halides, since they are not optically active; however, there seems no reason to doubt that they, too, undergo back-side attack.

Inversion of configuration is the general rule for reactions occurring at chiral centers, being much commoner than retention of configuration. Oddly enough, it is the very prevalence of inversion that made its detection difficult. Paul Walden (at the Polytechnicum in Riga, Latvia) discovered the phenomenon of inversion in 1896 when he encountered one of the exceptional reactions in which inversion does *not* take place.

Problem 5.5 Show the absolute configuration and give the *R*/*S* specification and specific rotation of the 2-octanol expected from the S_N2 reaction of 2-bromooctane of $[\alpha] +24.9°$.

But, besides the spatial orientation of attack, there is another feature of the S_N2 reaction, a feature that is even more fundamental since it defines the mechanism: reaction occurs *in a single step*, and hence bond-making and bond-breaking occur simultaneously, in a *concerted* fashion. This feature, too, is supported by the stereochemistry: not by the fact that there is inversion, but by the fact that there is *complete* inversion. Every molecule of substrate suffers the same stereochemical fate—inversion, as it happens. This specificity is completely consistent with the mechanism: the leaving group is still attached to carbon when nucleophilic attack begins, and controls the direction from which that attack occurs. (We shall appreciate the significance of this point better when we see the contrast offered by the S_N1 reaction.)

Actually, we have already encountered a contrasting situation: the free-radical chlorination of optically active 1-chloro-2-methylbutane (Sec. 4.28). First, hydrogen is extracted from the chiral center. Then, in a subsequent step, chlorine becomes attached to that carbon. But, with the hydrogen gone, there is nothing left to direct chlorine to a particular face of the carbon; attack occurs randomly at either face, and the racemic modification is obtained.

The S_N2 mechanism is supported, then, by stereochemical evidence. Indeed, the relationship between mechanism and stereochemistry is so well established that in the absence of other evidence complete inversion is taken to indicate an S_N2 reaction.

We see once more how stereochemistry can give us a kind of information about a reaction that we cannot get by any other means.

5.14 The S_N2 reaction: reactivity. Steric hindrance

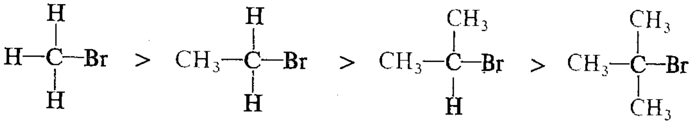
Now let us turn to the matter of *reactivity* in nucleophilic aliphatic substitution, and see how it is affected by changes in the structure of the alkyl group.

According to the dual mechanism theory (Sec. 5.11), the commonly observed order of reactivity, with a minimum at 2°, is simply the composite of two opposing orders of reactivity, one for S_N2 and the other for S_N1. Clearly, a test of this hypothesis would be to carry out substitution under conditions where all members of a series—methyl through 3°—react to a significant extent by, say, second-order kinetics, and measure the second-order rate constants; then, to repeat the process, this time selecting conditions that favor first-order reaction, and measure the first-order rate constants. Let us look at results obtained in this way, first for the S_N2 reaction and then, in a later section, for the S_N1 reaction.

Direct measurement of S_N2 rates for a series of substrates gives results like the following. (DMF is *dimethylformamide*, a solvent that, as we shall find in Sec. 7.6, favors the S_N2 reaction here.)

S_N2 substitution: relative reactivity

$$R{-}Br + Cl^- \xrightarrow{DMF} R{-}Cl + Br^-$$



$$H_3C{-}Br > CH_3CH_2{-}Br > (CH_3)_2CH{-}Br > (CH_3)_3C{-}Br$$

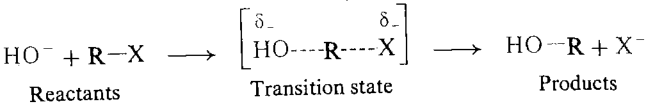
	Methyl	Ethyl	Isopropyl	*tert*-Butyl
Relative rate (S_N2)	37	1.0	0.02	0.0008

As postulated, then, the reactivity of substrates in the S_N2 reaction is:

Reactivity in S_N2 $\qquad$ $CH_3W > 1° > 2° > 3°$

How are we to account for this order of reactivity? As always to answer a question like this, we must take the specific reaction involved—here, the S_N2 reaction—and compare the structure of the reactants with the structure of the transition state. In contrast to free-radical substitution, this time the structure of the transition state is *not* intermediate between the structures of the reactants and products; this time, we cannot simply expect that factors stabilizing the product will also stabilize the transition state.

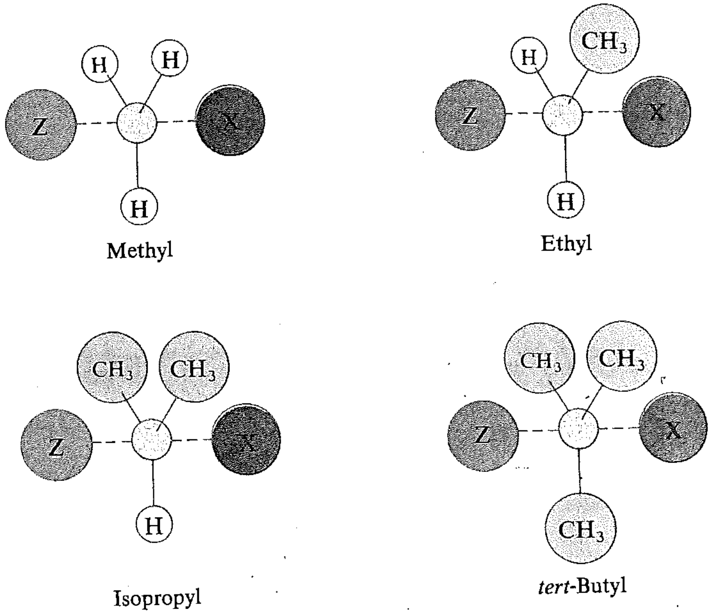
During many reactions, as we shall discover, there is a change in electron distribution such that a negative or positive charge develops in the reacting molecule; and very often reactivity depends upon how easily the molecule accommodates that charge. Accommodation of charge depends, in turn, upon the *polar effects* of substituents, that is, upon how well the substituents tend to withdraw or release electrons. First of all, then, let us examine the S_N2 reaction with regard to changes in electron distribution, again using the reaction of an alkyl halide with hydroxide ion as our example. In the transition state as we have described it (Sec. 5.12), there is a partly formed bond between carbon and hydroxide ion, and a



$$HO^- + R{-}X \longrightarrow \left[\overset{\delta-}{HO}{\cdots}R{\cdots}\overset{\delta-}{X}\right] \longrightarrow HO{-}R + X^-$$

partly broken bond between carbon and halogen; hydroxide ion has brought electrons to carbon, and halide ion has taken electrons away. Unless one of the two processes, bond-making or bond-breaking, has gone much further than the other, carbon is not appreciably more negative or positive than it was at the start of the reaction. If this is so, it would appear that the reactivity sequence for the S_N2 reaction does *not* result from the polar effects of substituent groups.

To understand how structure does influence the rate, let us compare transition state and reactants with regard to *shape*, starting with the methyl bromide reaction. The carbon in reactant and product is tetrahedral, whereas carbon in the transition state is bonded to five atoms. As indicated before, the C—H bonds are arranged like the spokes of a wheel, with the C—OH and C—Br bonds lying along the axle (Fig. 5.3).



Methyl

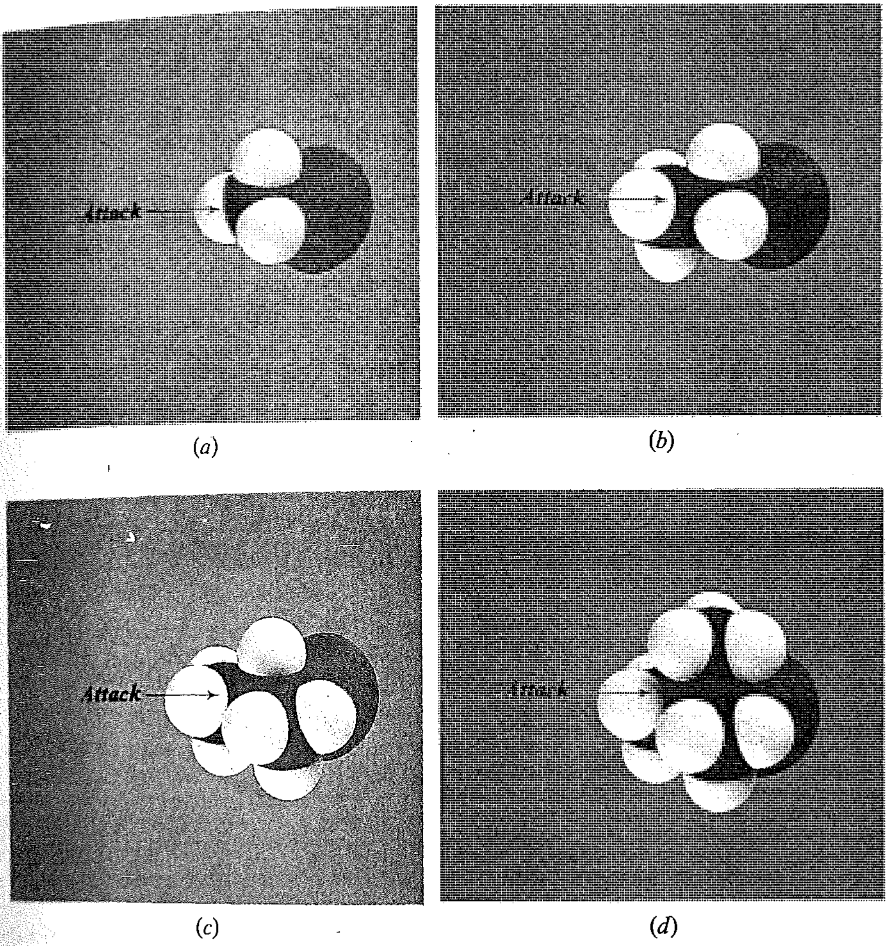
Ethyl

Isopropyl

tert-Butyl

Figure 5.3 Molecular structure and reactivity: the steric factor in the S_N2 reaction. Crowding raises the energy of the transition state and slows down reaction.

What would be the effect of replacing the hydrogens successively by methyl groups? That is, how would the transition state differ as we go from methyl bromide through ethyl bromide and isopropyl bromide to *tert*-butyl bromide? As hydrogen atoms are replaced by the larger methyl groups, there is increased crowding about



(a) (b)

(c) (d)

Figure 5.4 Molecular structure and reactivity: the steric factor in the S_N2 reaction. Models of alkyl bromides: (*a*) methyl, (*b*) ethyl, (*c*) isopropyl, (*d*) *tert*-butyl. As the number of substituents on the carbon bearing —Br increases, crowding at the point of nucleophilic attack increases.

the carbon. As can be seen from scale models (Fig. 5.4), the back side of the molecule, where attack must take place, becomes increasingly inaccessible.

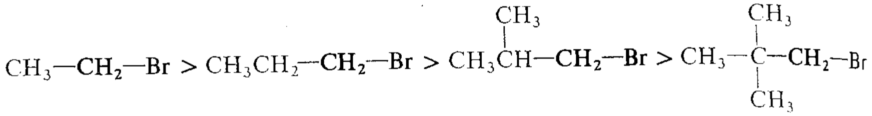
This crowding is particularly severe in the transition state, where the methyls are thrown close to both —OH and —Br (Fig. 5.3). Non-bonded interaction raises the energy of the crowded transition state more than the energy of the roomier reactant; E_{act} is higher and the reaction is slower.

This interpretation is the one that is generally accepted today. *Differences in rate between two S_N2 reactions are due chiefly to* **steric factors,** and not to polar factors; that is to say, differences in rate are related to the *bulk* of the substituents and not to their effect on electron distribution. As the number of substituents attached to the carbon bearing the halogen is increased, the reactivity toward S_N2 substitution decreases, as measurements have shown for the series methyl, 1°, 2°, 3°.

That steric factors are at work here is confirmed by the relative rates of another series of substrates. This time all the substrates are primary, and hence have the

S_N2 substitution: relative reactivity

$$R{-}Br + Cl^- \xrightarrow{DMF} R{-}Cl + Br^-$$



$$CH_3{-}CH_2{-}Br > CH_3CH_2{-}CH_2{-}Br > CH_3\overset{CH_3}{\overset{|}{C}}H{-}CH_2{-}Br > CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2{-}Br$$

	Ethyl	*n*-Propyl	Isobutyl	Neopentyl
Relative rate (S_N2)	1.0	0.69	0.33	0.000 006

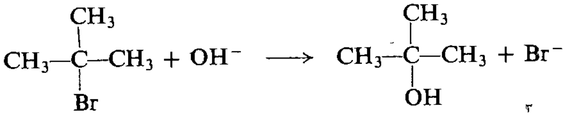
same *number* of substituents—one—attached to the carbon bearing halogen. But now the *size* of the substituent is steadily increased: in ethyl bromide the substituent is methyl; in *n*-propyl bromide, ethyl; in isobutyl bromide, isopropyl; and in neopentyl bromide, *tert*-butyl. And as the size of the (single) substituent increases, so does steric hindrance to attack, and the rate falls off. (See Fig. 5.5, p. 190.)

Thus we see that the S_N2 mechanism is supported by three lines of evidence: kinetics, stereochemistry, and effect of structure on reactivity.

We shall return to the S_N2 reaction later in this chapter, but for now let us turn to another mechanism by which nucleophilic aliphatic substitution can take place.

5.15 The S_N1 reaction: mechanism and kinetics. Rate-determining step

The reaction between *tert*-butyl bromide and hydroxide ion to yield *tert*-butyl alcohol follows first-order kinetics; that is, the rate depends upon the concentration of only one reactant, *tert*-butyl bromide.



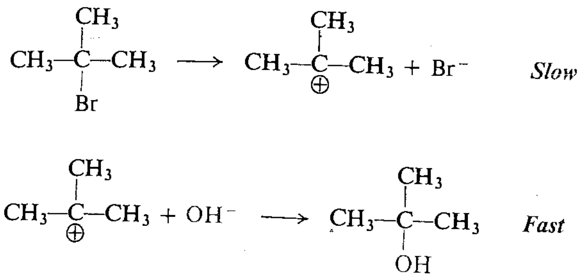
$$CH_3{-}\overset{CH_3}{\underset{Br}{C}}{-}CH_3 + OH^- \longrightarrow CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3 + Br^-$$

$$\text{rate} = k[RBr]$$

How are we to interpret the fact that the rate is independent of $[OH^-]$? If the rate of reaction does not depend upon $[OH^-]$, it can only mean that the reaction *whose rate we are measuring* does not involve OH^-.

These observations are quite consistent with the following mechanism. *tert*-Butyl bromide slowly dissociates (step 1) into a bromide ion and a cation derived from the *tert*-butyl group: a *carbocation*. This carbocation then combines rapidly (step 2) with a hydroxide ion to yield *tert*-butyl alcohol.

The rate of the overall reaction is determined by the slow breaking of the C—Br bond to form the carbocation; once formed, the carbocation reacts rapidly to form the product. It is step (1) whose rate we are actually measuring; this step does not involve OH^-, and its rate does not depend upon $[OH^-]$. *A single step whose rate determines the overall rate of a stepwise reaction is called a* **rate-determining step.**



(1) $$CH_3{-}\overset{CH_3}{\underset{Br}{C}}{-}CH_3 \longrightarrow CH_3{-}\overset{CH_3}{\underset{\oplus}{C}}{-}CH_3 + Br^- \quad \textit{Slow}$$

S_N1

(2) $$CH_3{-}\overset{CH_3}{\underset{\oplus}{C}}{-}CH_3 + OH^- \longrightarrow CH_3{-}\overset{CH_3}{\underset{OH}{C}}{-}CH_3 \quad \textit{Fast}$$

It is not surprising that the rate-determining step here is the one that involves the *breaking* of a bond, an energy-demanding process. We recognize this particular bond-breaking as an example of *heterolysis,* cleavage in which both bonding electrons go to the same fragment: a process that takes even more energy (Sec. 1.14) than the homolysis that we encountered in free-radical substitution. (In Sec. 7.5, we shall find out just where all this energy comes from.)

Nor is it surprising that the combining of the carbocation with hydroxide ion is a very fast step, since it involves only the *formation* of a bond, an energy-releasing process. We recognize this combining as an acid–base reaction in the Lewis sense. We are familiar with hydroxide ion as a strong base; as we shall see, carbocations are powerful Lewis acids.

This is the mechanism that is called $\mathbf{S_N1}$: *substitution nucleophilic unimolecular.* The term *uni*molecular is used here since the rate-determining step involves only *one* molecule (the many necessary solvent molecules being disregarded).

We must not imagine that the laws of chemistry are somehow magically suspended for the second, fast step. It involves a reaction with OH^- and its rate depends on $[OH^-]$. What is special here is that, even if step (2) is slowed down by a low $[OH^-]$, it is still *much* faster than step (1), and any change in its rate does not affect the overall rate.

Let us see what we mean by rate-determining step in a reaction like this,

(1) $$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R + B$$

(2) $$R + C \xrightarrow{k_2} \text{product}$$

where R is a reactive intermediate (carbocation, free radical, carbanion) whose concentration is maintained at some low *steady state* throughout the reaction. The exact kinetics expression for the formation of the product is

(3) $$\text{rate} = \frac{k_1[A]}{1 + \dfrac{k_{-1}[B]}{k_2[C]}}$$

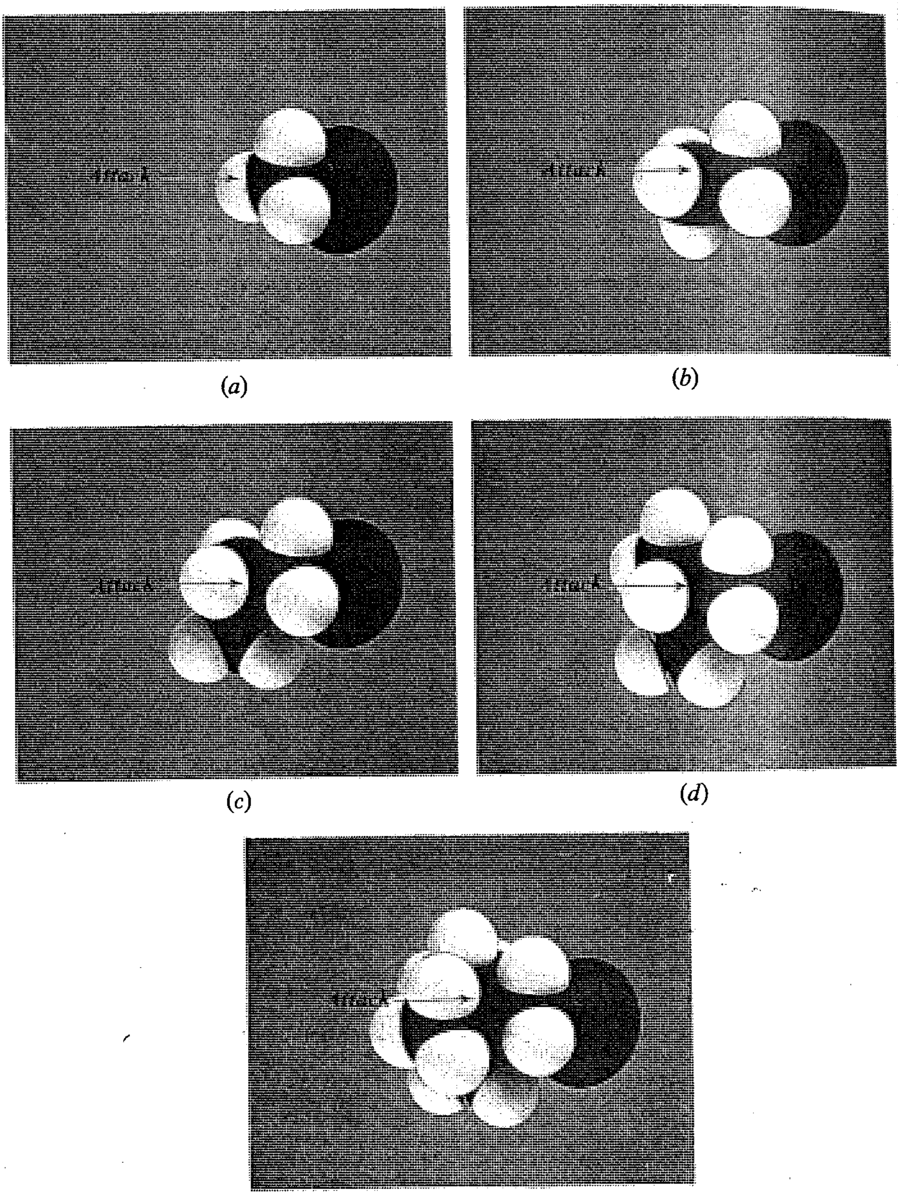
Without going into the derivation of this equation, let us see what it means.

The term $k_1[A]$ is in the numerator and the term $k_2[C]$ is in the denominator of the denominator; the bigger they are, the faster the rate. This is reasonable, since $k_1[A]$ is the rate of step (1) and $k_2[C]$ contributes to the rate of step (2). The term $k_{-1}[B]$ is in the denominator; the bigger it is, the slower the rate. This, too, is understandable, since it contributes to the rate of the reverse of step (1).

Now if $k_2[C]$ happens to be *much larger* than $k_{-1}[B]$, the term $k_{-1}[B]/k_2[C]$ is very small—insignificant relative to 1—and drops out. Under these conditions we get our familiar rate expression for first-order kinetics:

$$\text{rate} = k_1[A]$$

But if $k_2[C]$ is much larger than $k_{-1}[B]$, it must mean that *step (2) is much faster than the reverse of step (1)*. This is the *real* requirement for step (1) to be rate-determining. Does this mean that, contrary to what was said before, step (1)—in the forward direction—need not be slower than step (2)? Step (1) must still be a slow step, for otherwise the reactive intermediate would be formed faster than it could be consumed, and its concentration would build up—contrary to the nature of the reactive intermediate, and a condition different from the one for which the kinetics expression (3) holds.



(*a*) (*b*)

(*c*) (*d*)

(*e*)

Figure 5.5 Molecular structure and reactivity: the steric factor in the S_N2 reaction. Models of alkyl bromides: (*a*) methyl, (*b*) ethyl, (*c*) *n*-propyl, (*d*) isobutyl, (*e*) neopentyl. As the size of the single substituent on the carbon bearing —Br increases, crowding at the point of nucleophilic attack increases.

What evidence is there that alkyl halides can react by the S_N1 mechanism? As we have just seen, the mechanism is consistent with the first-order kinetics of a reaction like the one between *tert*-butyl bromide and hydroxide ion. In general, an S_N1 reaction **follows first-order kinetics**. The rate of the entire reaction is determined by how fast the alkyl halide ionizes, and hence depends only upon the concentration of alkyl halide.

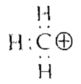
In following sections, we shall look at some of the other evidence. But to understand this evidence, we must know something about the intermediate that lies at the heart of the mechanism—and, indeed, at the heart of much of organic chemistry—the *carbocation*. And so, for a time, we shall find ourselves tracing two intertwining threads through the pattern of organic chemistry: concentrating alternately on the S_N1 reaction and on the fundamental chemistry of carbocations.

5.16 Carbocations

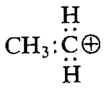
To account for the observed facts, we saw earlier, a certain mechanism was advanced for the halogenation of alkanes; central to this mechanism is the fleeting existence of free radicals, highly reactive neutral particles bearing an odd electron.

To account for a host of observations—of which the first-order kinetics described in the preceding section is just one—another kind of reactive particle has been proposed: the **carbocation**, *a group of atoms that contains a carbon atom bearing only six electrons*.

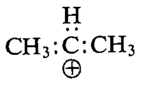
Carbocations are classified as primary, secondary, or tertiary after the carbon bearing the positive charge. They are named by use of the word *cation*. For example:


$\begin{array}{c}\mathrm{H}\\ \mathrm{H{:}\ddot{\underset{\cdot\cdot}{C}}\oplus}\\ \mathrm{H}\end{array}$

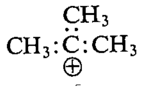
Methyl cation


$\begin{array}{c}\mathrm{H}\\ \mathrm{CH_3{:}\ddot{\underset{\cdot\cdot}{C}}\oplus}\\ \mathrm{H}\end{array}$

Ethyl cation
(*primary*, 1°)


$\begin{array}{c}\mathrm{H}\\ \mathrm{CH_3{:}\ddot{C}{:}CH_3}\\ \oplus\end{array}$

Isopropyl cation
(*secondary*, 2°)


$\begin{array}{c}\mathrm{CH_3}\\ \mathrm{CH_3{:}\ddot{C}{:}CH_3}\\ \oplus\end{array}$

tert-Butyl cation
(*tertiary*, 3°)

We must expect to encounter two other names for what we have called the *carbocation*. *Carbonium ion* is almost the only name used in the older literature; it is still very commonly used, although sometimes with a special meaning. Olah (below) has proposed that *carbenium ion* be used for the species we have described above, with the name *carbonium ion* reserved for such species as CH_5^+ (analogous to *ammonium ion*, etc.); carbenium ions and carbonium ions together would be called *carbocations*.

Like the free radical, the carbocation is an exceedingly reactive particle, and for the same reason: the tendency to complete the octet of carbon. Since it takes a *pair* of electrons to complete the octet here, the carbocation is a Lewis acid, and an extremely powerful one. Unlike the free radical, the carbocation carries a positive charge.

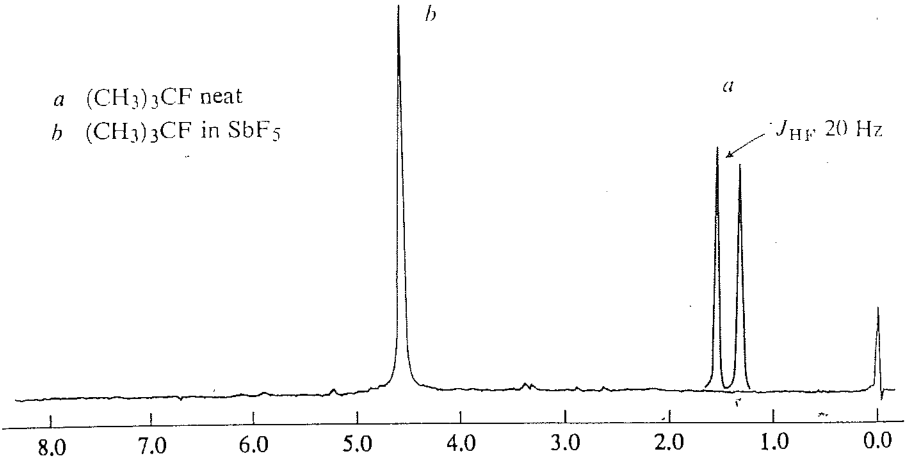
One kind of unusually stable carbocation (Problem 16.10, p. 575) was recognized as early as 1902 by the salt-like character of certain organic compounds. But for simple alkyl cations such direct observation should be exceedingly difficult, because of the very reactivity—and hence short life—that is attributed to them. Nevertheless, during the 1920s and 1930s, 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 alkyl halides, alcohols, alkenes, and many other kinds of organic compounds: observations that revealed a basically similar pattern of behavior most logically attributed to intermediate carbocations. A sizeable part of this book will be devoted to seeing what that pattern is.

In 1963, George Olah (now at University of Southern California) 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 dramatic change in the NMR spectrum (Chap. 17), from the spectrum of the alkyl fluoride to the spectrum of a molecule that contains no fluorine but instead sp^2-hybridized carbon with a very low electron density.

$$RF + SbF_5 \longrightarrow R^+ \, SbF_6^-$$

Figure 5.6 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. This is an acid–base reaction; the SbF_5 (a so-called *superacid*) is an even stronger Lewis acid than the alkyl cation, and keeps the base it has won, the fluoride ion.



Courtesy of *The Journal of American Chemical Society*

Figure 5.6 Proton NMR spectrum of (*a*) *tert*-butyl fluoride and (*b*) *tert*-butyl cation. In (*a*), the proton signal split into two peaks by coupling with nearby fluorine. In (*b*), a single peak, shifted far downfield; there is strong deshielding due to low electron density on the positive carbon.

By methods like this, Olah opened the door to the study not just of the existence of organic cations of many kinds, but of intimate details of their structure.

A highly meaningful sequel to this reaction can be carried out. If, now, the solution containing $R^+SbF_6^-$ is diluted with water, there is obtained the alcohol, ROH. What we have here are, essentially, the two steps proposed for the S_N1 reaction—generation of a carbocation, and its combination with a nucleophile—but observed as discrete processes, separated by as long a time period as we care to wait.

(1) $$RF + SbF_5 \longrightarrow R^+SbF_6^-$$

(2) $$R^+SbF_6^- + H_2O \longrightarrow ROH_2^+ + SbF_6^- \longrightarrow ROH + SbF_5 + HF$$

With only a sextet of electrons on carbon, a carbocation is an unstable, highly reactive particle. It can undergo a wide variety of reactions, as we shall see; just which one occurs depends upon the experimental conditions. But all reactions of a carbocation have a common end: *to provide a pair of electrons to complete the octet of the positively charged carbon.* In the second step of an S_N1 reaction we see perhaps the most direct way of going about this: combining with a nucleophile, a basic, electron-rich molecule.

$$\underset{\text{Carbocation}}{R^+} + \underset{\text{Nucleophile}}{:Z} \longrightarrow R:Z$$

5.17 Structure of carbocations

In a carbocation, the electron-deficient carbon is bonded to three other atoms, and for this bonding uses sp^2 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. This part of a carbocation is therefore *flat*, the electron-deficient carbon and the three atoms attached to it lying in the same plane (Fig. 5.7*a*).

Figure 5.7 A carbocation. (*a*) Only σ bonds shown. (*b*) An empty *p* orbital above and below the plane of the σ bonds.

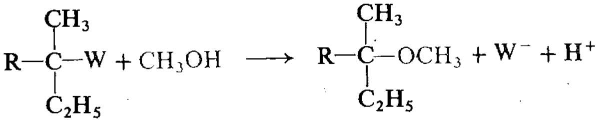
But our description of the molecule is not yet quite complete. Carbon still has a *p* orbital, with its two lobes lying above and below the plane of the σ bonds (Fig. 5.7*b*); in a carbocation, the *p* orbital is *empty*. Although formally empty, this *p* orbital, we shall find, is intimately involved in the chemistry of carbocations: in their stability, and in the stability of various transition states leading to their formation. This comes about through overlap of the *p* orbital with certain nearby orbitals—overlap that is made geometrically possible by the flatness of the carbocation.

There can be little doubt that carbocations actually are flat. The quantum mechanical picture of a carbocation 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 carbocations 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.

5.18 The S_N1 reaction: stereochemistry

We shall continue with the fundamental chemistry of carbocations in Sec. 5.19, but for now let us pick up the thread of our original discussion, nucleophilic substitution, and look at an aspect that is directly related to the shape of carbocations: the stereochemistry of the S_N1 reaction. Here, as in stereochemical studies of the S_N2 reaction (Sec. 5.13), substitution is carried out on an optically active substrate; the product is isolated, and its configuration and optical purity are compared with those of the starting material. As before, relative configurations of reactant and product must have been assigned, and rotations of optically pure samples must be known so that optical purities can be calculated.

Such studies have been made of the reactions between several tertiary substrates and the solvent methanol, CH_3OH: reactions of a type most likely to proceed by S_N1. In each case there is obtained a product of opposite configuration



$$R-\underset{C_2H_5}{\overset{CH_3}{C}}-W + CH_3OH \longrightarrow R-\underset{C_2H_5}{\overset{CH_3}{C}}-OCH_3 + W^- + H^+$$

Optically active

Opposite configuration; lower optical purity

S_N1: racemization plus inversion

from the starting material, and of considerably *lower optical purity*. Optically pure substrate, for example, gives a product that is only about 50% optically pure—and in some cases much less pure than that.

Now, optically pure starting material contains only the one enantiomer, whereas the product clearly must contain both. The product is thus a mixture of the inverted compound and the racemic modification, and we say that the reaction has proceeded with inversion plus *partial racemization*.

Let us get our terms straight. Consider the case where optically pure substrate gives product of opposite configuration and 50% optical purity. Of every 100 molecules of product, 75 are formed with inversion of configuration, and 25 with retention. The 25 of retained configuration cancel the rotation of 25 of the molecules of inverted configuration, leaving an excess of 50 molecules of inverted configuration to provide the observed optical rotation: 50% of the maximum value.

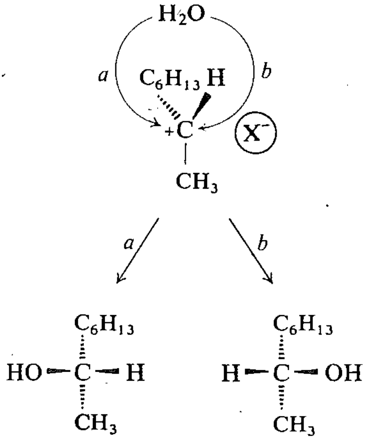
One could say that the reaction proceeds with 75% inversion and 25% retention; equally accurately one could say that reaction proceeds with 50% inversion and 50% racemization. But it is the latter way that we generally use: the percentage of racemization, as we shall see, is a measure of stereochemical randomness, and the percentage of *net* inversion (or, as happens in some kinds of reactions, net retention) is a measure of stereoselectivity (Sec. 10.2).

Problem 5.6 Optically pure (*R*)-α-phenylethyl chloride ($C_6H_5CHClCH_3$) has [α] −109°; optically pure (*R*)-α-phenylethyl alcohol has [α] −42.3°. When chloride of [α] −34° is treated with dilute aqueous NaOH, there is obtained alcohol of [α] +1.7°. Calculate (a) the optical purity of reactant and of product; (b) the percentage of retention and of inversion; (c) the percentage of racemization and of retention or inversion.

How do we account for the stereochemistry observed for the S_N1 reaction? Let us see first why racemization occurs, and then why it is only partial and is accompanied by some net inversion.

In an S_N2 reaction, we saw (Sec. 5.13), the nucleophile attacks the substrate molecule itself, and the *complete* inversion observed is a direct consequence of that fact: the leaving group is still attached to carbon at the time of attack, and directs this attack on every molecule in the same way—to the back side. Now, in an S_N1 reaction the nucleophile attacks, *not* the substrate, but the intermediate, the carbocation; the leaving group has already become detached and, we might have thought, can no longer affect the spatial orientation of attack.

Let us see where this line of reasoning leads us. In the first step the optically active substrate—an alkyl halide, say—dissociates to form halide ion and the carbocation. The nucleophilic reagent, Z:, then attaches itself to the carbocation. But it may attach itself to either face of this flat ion and, depending upon which face, yield one or the other of the two enantiomeric products (see Fig. 5.8). Together, the two enantiomers constitute the racemic modification. Thus, the racemization that accompanies these reactions is consistent with the S_N1 mechanism and the formation of an intermediate carbocation.



Enantiomers

(*a*) Inversion *Predominates*

(*b*) Retention

Figure 5.8 The S_N1 reaction: racemization plus inversion. The nucleophilic reagent attacks both (*a*) the back side and (*b*) the front side of the carbocation. Back-side attack predominates.

(So far, our discussion parallels what was said about the stereochemistry of free-radical chlorination (Sec. 4.28) where, we remember, random attack on the two faces of a free radical gives total racemization.)

Now, if attack on the two faces of the carbocation were purely random, we would expect to obtain equal amounts of the two enantiomers; that is to say, we would expect to obtain only the racemic modification. Yet, although racemization is sometimes very high—90% or more—it is seldom complete, and in general the inverted product exceeds its enantiomer. Reaction proceeds with racemization *plus some net inversion.*

How do we accommodate even this limited net inversion within the framework of the S_N1 mechanism? How do we account for the fact that attack on the carbocation is *not* purely random? Clearly, the excess of inversion is due, in some way, to the leaving group: it must still be exerting a measure of control over the stereochemistry. In the complete absence of the leaving group, the flat carbocation would lose all chirality and could not yield a product with any optical activity. (*Remember*: Synthesis of chiral compounds from achiral reactants always yields the racemic modification.)

How can the leaving group be involved? To find an answer, let us consider the process of heterolysis. As reaction proceeds, the distance between carbon and halogen steadily increases until finally the covalent bond breaks. The two oppositely charged ions are formed—but *not*, immediately, as completely *free* ions. Initially, they must be close together, close enough for electrostatic attraction to be sizable; and so they exist—for a time—as an *ion pair* (Sec. 7.4). As first formed, the ions are in contact with each other. Then, as they diffuse apart, layer after layer of solvent intervenes until finally they are independent of each other, and we speak of "free" ions.

$$\mathrm{R{:}X} \longrightarrow \underset{\substack{\text{Intimate}\\ \text{ion pair}}}{\mathrm{R^+X^-}} \longrightarrow \underset{\substack{\text{Solvent-separated}\\ \text{ion pair}}}{\mathrm{R^+\|X^-}} \longrightarrow \underset{\text{Free ions}}{\mathrm{R^+ + X^-}}$$

Now, nucleophilic attack can, conceivably, take place at any time after the heterolysis, and thus can involve any species from the initially formed ion pair to the free carbocation. Attack on the free carbocation is random, and yields the racemic modification. But attack on the ion pair is not random: the anion clings more or less closely to the front side of the carbocation and thus shields this side from attack; as a result, back-side attack is preferred. To the extent, then, that attack occurs before the ion pair has completely separated, inversion of configuration competes with racemization.

Thus the S_N1 mechanism can accommodate the fact that racemization is not complete. But the important thing—the important contrast to the S_N2 stereochemistry—is that racemization occurs at all. Unlike an S_N2 reaction, which proceeds with complete inversion, **an S_N1 reaction proceeds with racemization.**

That there are two kinds of stereochemistry supports the central idea that there are two different mechanisms. The particular form of the stereochemistry gives powerful support for the particular mechanisms proposed. Complete inversion in the S_N2 reaction supports the idea of concerted bond-breaking and bond-making, *in a single step*; occurrence of racemization in the S_N1 reaction shows that bond-breaking and bond-making occur separately, *in different steps*.

The next aspect of the S_N1 reaction that we shall take up is the matter of *reactivity*. But to understand that, we must first return to the chemistry of carbocations, and examine what will be to us their most important property: their *relative stabilities*.

5.19 Relative stabilities of carbocations

When we wished to compare stabilities of free radicals (Sec. 3.24), we made use of homolytic bond dissociation energies, since these apply to reactions in which free radicals are generated.

Now we wish to compare stabilities of carbocations, and to do this we shall follow exactly the same line of reasoning that we followed for free radicals. This time, however, we must start with the *heterolytic* bond dissociation energies in Table 1.3 (p. 22), since these apply to reactions in which carbocations are generated. In this table we find energies of the bonds that hold bromine to a number of groups.

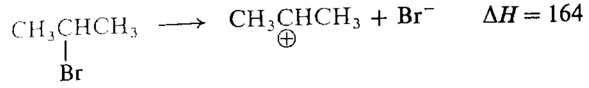
These are the ΔH values of the following reactions:

$$CH_3{-}Br \longrightarrow CH_3^{\oplus} + Br^- \qquad \Delta H = 219\text{ kcal}$$

Methyl bromide Methyl cation

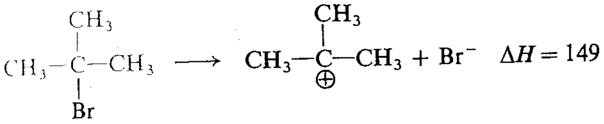
$$CH_3CH_2{-}Br \longrightarrow CH_3CH_2^{\oplus} + Br^- \qquad \Delta H = 184$$

Ethyl bromide Ethyl cation
A 1° cation



$$\underset{\displaystyle Br}{CH_3\underset{|}{C}HCH_3} \longrightarrow CH_3\underset{\oplus}{C}HCH_3 + Br^- \qquad \Delta H = 164$$

Isopropyl bromide Isopropyl cation
A 2° cation



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-CH_3 \longrightarrow CH_3-\overset{\displaystyle CH_3}{\underset{\oplus}{C}}-CH_3 + Br^- \qquad \Delta H = 149$$

tert-Butyl bromide *tert*-Butyl cation
A 3° cation

By definition, this bond dissociation energy is the amount of energy that must be supplied to convert a mole of alkyl bromide into carbocations and bromide ions.

$$R{-}Br \longrightarrow R^+ + Br^- \qquad \Delta H = \text{heterolytic bond dissociation energy}$$

As we can see, the amount of energy needed to form the various classes of carbocations decreases in the order: $CH_3^+ > 1° > 2° > 3°$.

If less energy is needed to form one carbocation than another, it can only mean that, *relative to the alkyl bromide from which it is formed*, the one carbocation contains less energy than the other, that is to say, is *more stable* (see Fig. 5.9).

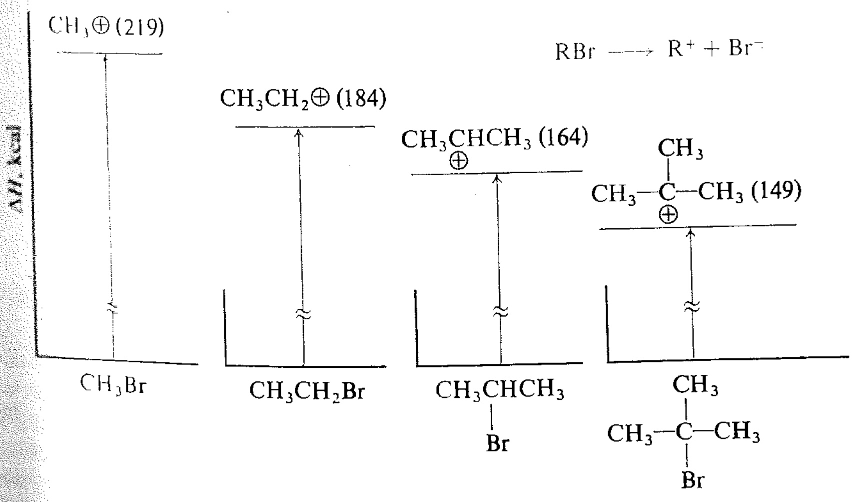


Figure 5.9 Stabilities of carbocations relative to alkyl bromides. (The plots are aligned with each other for easy comparison.)

We are not attempting to compare the absolute energy contents of, say, isopropyl and *tert*-butyl cations; we are simply saying that the difference in energy between isopropyl bromide and isopropyl cations is greater than the difference between *tert*-butyl bromide and *tert*-butyl cations. *When we compare stabilities of carbocations, it must be understood that our standard for each cation is the substrate from which it is formed.* As we shall see, this is precisely the kind of stability that we are interested in.

We used alkyl bromides for our comparison above, but we could just as well have used alkyl fluorides, chlorides, or iodides, or the corresponding alcohols. For all these compounds the bond dissociation energies in Table 1.3 show the same order of stability of carbocations. Even the sizes of the energy differences, in kcal/mol, are very nearly the same, whatever the class of parent compounds. The difference between methyl and *tert*-butyl cations, for example, relative to various substrates is: fluorides, 67 kcal; chlorides, 70 kcal; bromides, 70 kcal; iodides, 72 kcal; and alcohols, 66 kcal.

Relative to the substrate from which each is formed, then, the order of stability of carbocations is:

Stability of carbocations $3° > 2° > 1° > CH_3^+$

We shall find that this same order of stability applies not only when carbocations are formed by heterolysis, but also when they are formed by entirely different processes.

Differences in stability between carbocations are *much* larger than between free radicals. The *tert*-butyl free radical, for example, is only 12 kcal more stable than the methyl free radical; the *tert*-butyl cation is, depending upon the substrate, 66–72 kcal more stable than the methyl cation. As we shall see, these much larger differences in stability give rise to much larger effects on reactivity.

So far in this section, our discussion has been based on bond dissociation energies, which are measured in the gas phase. But nearly all carbocation chemistry takes place in solution, and solvents, as we know, can exert powerful stabilizing effects on ionic solutes. Does the order of stability that we have arrived at hold for carbocations in solution? The answer to this question has been given most directly by measurement, in a variety of solvents, of the ΔH values for the generation of carbocations by Olah's superacid method. The values obtained reveal the same

$$RCl + SbF_5 \longrightarrow R^+SbF_5Cl^- \qquad \Delta H = \text{heat of ionization}$$

order of carbocation stability, relative to the parent substrate, as do the dissociation energies. Even the *differences* in stability, in kcal/mol, are much the same.

So now we have arrived at an order of stability of carbocations which holds for solution as well as for gas phase, and which applies to the generation of carbocations from a wide variety of substrates and, we shall see, in a wide variety of chemical reactions. As we continue our study, we shall add other kinds of carbocations to our series, and examine other kinds of reactions by which they can be generated.

Now, let us see how this order of stability can be accounted for.

5.20 Stabilization of carbocations. Accommodation of charge. Polar effects

The characteristic feature of a carbocation is, by definition, the electron-deficient carbon and the attendant positive charge. The relative stability of a carbocation 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 carbocation.

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. Such *an effect on the availability of electrons at the reaction center is called a* **polar effect.**

Carbocation stability


$$\mathrm{G{\rightarrow}\overset{|}{\underset{|}{C}}\oplus} \qquad \mathrm{G{\leftarrow}\overset{|}{\underset{|}{C}}\oplus}$$

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 carbocation.

An electron-withdrawing substituent tends to intensify the positive charge on the electron-deficient carbon, and hence makes the carbocation less stable.

The order of stability of carbocations, we have just seen, is the following:

Stability of carbocations $3° > 2° > 1° > CH_3^+$

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 carbocation.*


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}\oplus} \qquad \mathrm{R{\rightarrow}\overset{H}{\underset{H}{C}}\oplus} \qquad \mathrm{R{\rightarrow}\overset{R\downarrow}{\underset{H}{C}}\oplus} \qquad \mathrm{R{\rightarrow}\overset{R\downarrow}{\underset{\uparrow R}{C}}\oplus}$$

Methyl cation Primary cation Secondary cation Tertiary cation

Electron release: *Disperses charge, stabilizes ion*

If our generalization about dispersal of charge applies in this case, alkyl groups must *release electrons* here.

Is electron release what we would have expected of alkyl groups? Ingold (p. 179) has suggested that alkyl groups, lacking strong polar tendencies of their own, can do pretty much what is demanded of them by other groups in the molecule. There is increasing evidence that this is so: alkyl groups often tend to stabilize both cations and anions, indicating electron release or electron withdrawal *on demand.* In a carbocation, electron-deficient carbon has an urgent need for electrons—it is like a different element, a very electronegative one—and it *induces* alkyl groups to release electrons to meet that need.

Now, how does a substituent exert its polar 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 electron 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 release or 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 only operate when the substituent is located in certain special ways relative to the charge center. By its very nature, as we shall see (Sec. 11.14), 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.

The nature of the electron release by alkyl groups is not clear. It may be an inductive effect; it may be a resonance effect (*hyperconjugation*, Sec. 11.14), electrons being provided by overlap of σ bonds with the empty *p* orbital of the electron-deficient carbon. It may very well be a combination of the two. When we refer to the inductive effect of alkyl groups in this book, it should be understood that this may well include a contribution from hyperconjugation.

However it arises, the polar effect of alkyl groups is not a powerful one, as such effects go. Yet it leads to very large differences in stability among the various classes of carbocations. And it is these differences that we must keep uppermost in our minds in dealing with the varied chemistry of carbocations.

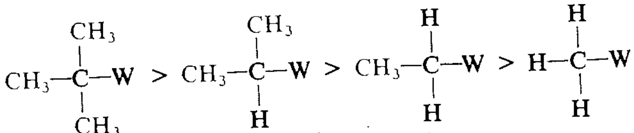
5.21 The S_N1 reaction: reactivity. Ease of formation of carbocations

Once again let us return to nucleophilic substitution, and the matter of how the structure of the alkyl group affects reactivity. We have already seen (Sec. 5.14) that reactivity in S_N2 decreases along the series CH_3W, 1°, 2°, 3°, as postulated by Hughes and Ingold (Sec. 5.11). Now, what are the facts with regard to the other half of their duality theory: does reactivity by S_N1 change in the opposite direction along this same series?

Under conditions that greatly favor S_N1, results like the following have been obtained:

S_N1 substitution: relative reactivity

$$R—W + CF_3COOH \longrightarrow R—OCOCF_3 + H—W$$



$$(CH_3)_3C—W > (CH_3)_2CH—W > CH_3CH_2—W > CH_3—W$$

	tert-Butyl	Isopropyl	Ethyl	Methyl
Relative rate (S_N1)	$> 10^6$	1.0	$< 10^{-4}$	$< 10^{-5}$

Thus, the postulated order of reactivity is confirmed. Also as postulated—see the sharply rising S_N1 curve of Fig. 5.1 (p. 180)—the differences in reactivity are much greater than those found for the S_N2 reaction. By S_N1, tertiary substrates are more than a million times as reactive as secondary, which in turn are at least ten thousand—and probably more than a million—times as reactive as primary.

Even these differences are believed to be underestimations. Reactivities of primary and methyl substrates are *very* much less than the maximum values indicated; it is likely that even the small rates measured for them are in large part not for S_N1, but for S_N2 with the solvent acting as nucleophile (Sec. 7.9).

The reactivity of substrates in the S_N1 reaction, then, follows the sequence:

Reactivity in S_N1 $3° > 2° > 1° > CH_3W$

Now, the rate-determining step in S_N1 is formation of the carbocation; that is to say, one substrate undergoes S_N1 faster than another because it forms a carbocation faster. Our reactivity sequence therefore leads directly to a sequence showing the relative rates of formation of carbocations:

Rate of formation of carbocations $3° > 2° > 1° > CH_3^+$

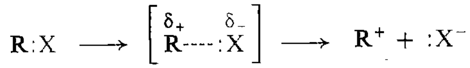
In listing carbocations in order of their rates of formation, we find we have at the same time listed them in order of their stability. **The more stable the carbocation, the faster it is formed.**

This is probably the most useful generalization about structure and reactivity that appears in this book—or, indeed, that exists in organic chemistry. Carbocations are formed from many compounds other than alkyl halides, and in reactions quite different from nucleophilic substitution. *Yet in all these reactions in which carbocations are formed, carbocation stability plays a leading role in governing reactivity and orientation.*

How can we account for the fact that the rate of formation of a carbocation depends upon its stability? As always to answer a question like this, we must take the specific reaction involved—here, the S_N1 reaction—and compare the structure of the reactants with the structure of the transition state.

In an S_N1 reaction of an alkyl halide, the carbocation is formed by heterolysis of the substrate molecule, that is, by breaking of the carbon–halogen bond. In the reactant an electron pair is shared by carbon and halogen; except for a modest polarity, these two atoms are neutral. In the products, halogen has taken away the electron pair, and carbon is left with only a sextet; halide carries a full negative charge, and the carbocation carries a full positive charge centered on carbon.

In the transition state, the C—X bond must be partly broken, halogen having partly pulled the electron pair away from carbon. Halogen has partly gained the negative charge it is to carry in the halide ion. Most important, *carbon has partly gained the positive charge it is to carry in the carbocation.*



$$R{:}X \longrightarrow \left[\overset{\delta_+}{R}\text{----}\overset{\delta_-}{:X}\right] \longrightarrow R^+ + :X^-$$

Reactant — Transition state — Products

Transition state: R *has partial positive charge*

Products: R *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 the E_{act} and permits a faster reaction (see Fig. 5.10).

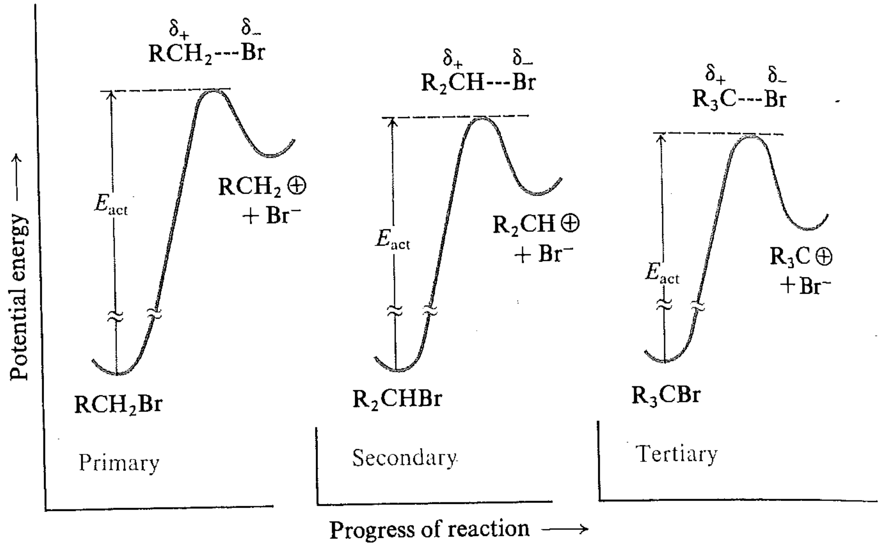


Figure 5.10 Molecular structure and reactivity. The stability of the transition state parallels the stability of the carbocation: the more stable carbocation is formed faster. (The plots are aligned with each other for easy comparison.)

Thus, to the extent that the C—X bond is broken, the alkyl group possesses character of the carbocation it is to become. The same factor, electron release, that stabilizes the carbocation also stabilizes the *incipient* carbocation in the transition state.

In 1979, Edward Arnett (Duke University) and Paul Schleyer (University of Erlangen-Nürnberg) reported "an extraordinary corroboration of the fundamental soundness of the 'carbocation theory of organic chemistry'". For a set of substrates of widely varying structures, they compared the E_{act} values of S_N1 reactions with the heats of ionization in superacid solutions, and found a direct *quantitative* dependence of rate of formation of carbocations on carbocation stability. The more stable the carbocation, they found, the faster it is formed.

As we encounter other reactions in which carbocations are formed, we must, for each of these reactions, examine the structure of the transition state. In most, if not all, of these reactions, we shall find that the transition state differs from the reactants chiefly in being like the product. The *carbocation character* of the transition state will be the factor most affecting E_{act}; hence, the more stable the carbocation, the more stable the transition state leading to its formation, and the faster the carbocation will be formed.

But what we have just learned here will be applied in an even more general way. We shall return again and again to the relationship between polar effects and dispersal of charge, and between dispersal of charge and stability. We shall find that these relationships will help us to understand, not only carbocation reactions of many kinds, but all reactions in which a charge—positive or negative—develops or disappears. These will include reactions as seemingly different from S_N1

substitution as dehydration of alcohols, addition to alkenes, and aromatic substitution—both electrophilic and nucleophilic—and the fundamental properties of acidity and basicity.

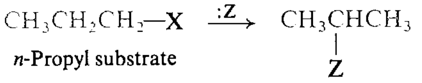
Differences in reactivity by S_N1, then, depend upon differences in stability among the various classes of carbocations. In the next section, we shall see how these same differences in stability lead to rather surprising behavior on the part of carbocations.

Problem 5.7 Neopentyl halides are notoriously slow in nucleophilic substitution, whatever the experimental conditions. How can you account for this?

5.22 Rearrangement of carbocations

We spoke earlier of a pattern of behavior that led to the development of the carbocation theory. The most striking feature of that pattern is the occurrence of *rearrangements.*

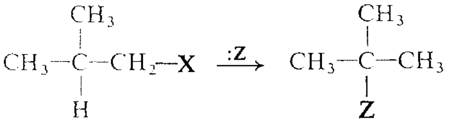
In nucleophilic substitution, for example, it is sometimes observed that the entering group, Z, becomes attached to a different carbon atom than the one that originally held the leaving group, X. For example:



$$CH_3CH_2CH_2{-}X \xrightarrow{:Z} CH_3\underset{\displaystyle Z}{\underset{|}{C}}HCH_3$$

n-Propyl substrate

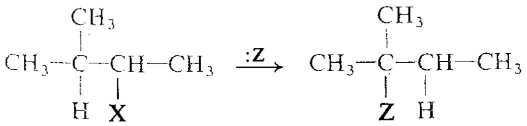
Isopropyl product



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}{-}CH_2{-}X \xrightarrow{:Z} CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle Z}{C}}{-}CH_3$$

Isobutyl substrate

tert-Butyl product



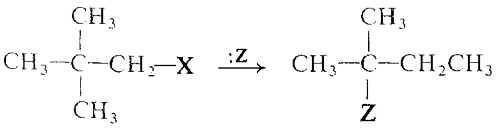
$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}{-}\underset{\displaystyle X}{CH}{-}CH_3 \xrightarrow{:Z} CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle Z}{C}}{-}\underset{\displaystyle H}{CH}{-}CH_3$$

3-Methyl-2-butyl substrate

2-Methyl-2-butyl product
(*tert*-Pentyl product)

In each of these cases we see that, to accommodate Z in the new position, there must be a rearrangement of hydrogen atoms in the substrate. The transformation of a *n*-propyl group into an isopropyl group, for example, requires removal of one H from C–2, and attachment of one H to C–1.

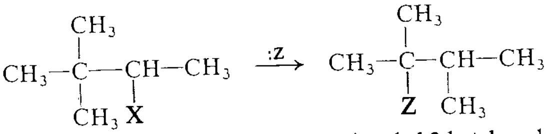
Sometimes, there is even a rearrangement of the carbon skeleton:



$$CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_2{-}X \xrightarrow{:Z} CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle Z}{C}}{-}CH_2CH_3$$

Neopentyl substrate

tert-Pentyl product



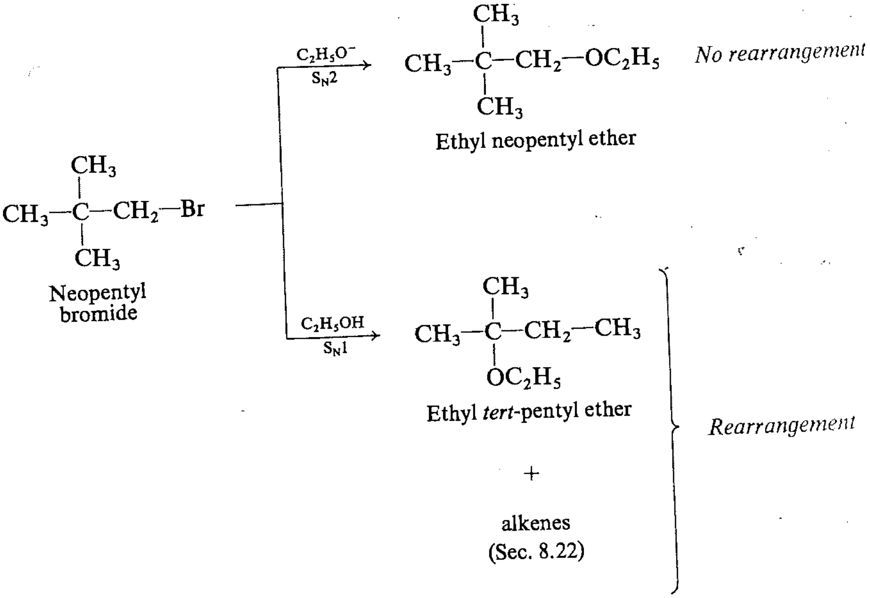
$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{X}{|}}{CH}-CH_3 \xrightarrow{:Z} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Z}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

3,3-Dimethyl-2-butyl substrate 2,3-Dimethyl-2-butyl product

In reactions of quite different types—elimination, addition—rearrangements are also observed, and these rearrangements are of the same pattern as those above. This similarity in behavior suggests a similarity in mechanism. However different the various mechanisms might be, they all have one feature in common: at some stage the same intermediate is formed, and it is this that undergoes the actual rearrangement. This intermediate, as was first clearly proposed in 1922 by Hans Meerwein (p. 191), is the *carbocation.*

Now, of the two mechanisms advanced for nucleophilic substitution, only S_N1 is postulated to involve an intermediate carbocation, and therefore we expect only reactions proceeding by S_N1 to be accompanied by these characteristic rearrangements. By contrast, the single step postulated for S_N2 simply provides no opportunity for such rearrangements.

This expectation is borne out by experiment, as the following example illustrates. Neopentyl substrates are particularly prone to rearrange to *tert*-pentyl products. With the strongly nucleophilic ethoxide ion, $C_2H_5O^-$, neopentyl bromide undergoes a (slow) second-order reaction to yield the unrearranged product, ethyl neopentyl ether. In a solution of the weakly nucleophilic ethanol, C_2H_5OH, it undergoes a (slow) first-order reaction to yield ethyl *tert*-pentyl ether (and other rearrangement products).



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-Br \xrightarrow[S_N2]{C_2H_5O^-} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-OC_2H_5$$

$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-Br \xrightarrow[S_N1]{C_2H_5OH} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OC_2H_5}{|}}{C}}-CH_2-CH_3 + \text{alkenes}$$

Neopentyl bromide

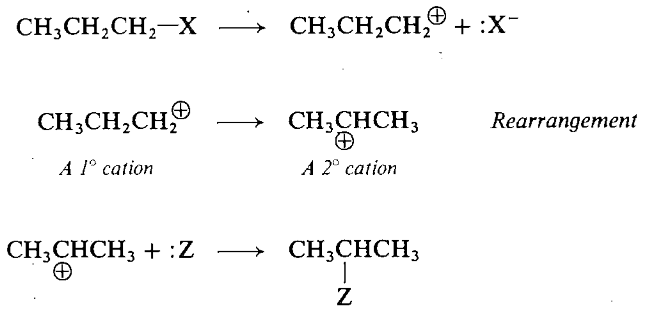
Ethyl neopentyl ether

Ethyl *tert*-pentyl ether

alkenes (Sec. 8.22)

The occurrence or non-occurrence of rearrangement is a striking difference, and it provides one more piece of evidence that there *are* two mechanisms for nucleophilic substitution. In addition, rearrangement gives powerful support to the particular form of the S_N1 mechanism—the intermediacy of carbocations—by linking this mechanism to the mechanisms of those other kinds of reactions where rearrangements are observed. The correlation between rearrangement and intermediate cations is so strong that, in the absence of other information about a particular example of nucleophilic substitution, rearrangement is generally taken as evidence that reaction is by S_N1.

On this basis, then, we can account for the observed products in the following way. A *n*-propyl substrate, for example, yields the *n*-propyl cation; this rearranges to the isopropyl cation, which combines with the nucleophile to give the isopropyl product.

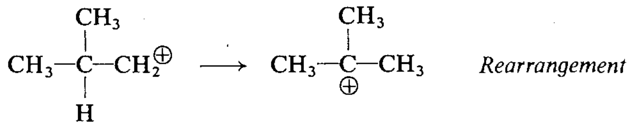


$$CH_3CH_2CH_2{-}X \longrightarrow CH_3CH_2CH_2^{\oplus} + :X^-$$

$$\underset{\text{A 1° cation}}{CH_3CH_2CH_2^{\oplus}} \longrightarrow \underset{\text{A 2° cation}}{CH_3\underset{\oplus}{C}HCH_3} \qquad \textit{Rearrangement}$$

$$CH_3\underset{\oplus}{C}HCH_3 + :Z \longrightarrow CH_3\underset{Z}{\underset{|}{C}}HCH_3$$

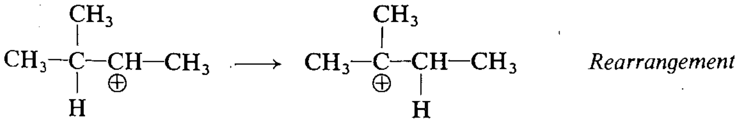
In a similar way, the isobutyl cation rearranges to the *tert*-butyl cation,



$$CH_3{-}\overset{CH_3}{\overset{|}{\underset{\underset{H}{|}}{C}}}{-}CH_2^{\oplus} \longrightarrow CH_3{-}\overset{CH_3}{\overset{|}{\underset{\oplus}{C}}}{-}CH_3 \qquad \textit{Rearrangement}$$

A 1° cation *A 3° cation*

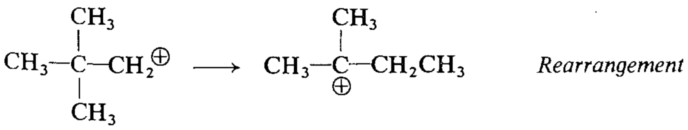
the 3-methyl-2-butyl cation rearranges to the 2-methyl-2-butyl cation,



$$CH_3{-}\overset{CH_3}{\overset{|}{\underset{\underset{H}{|}}{C}}}{-}\underset{\oplus}{C}H{-}CH_3 \longrightarrow CH_3{-}\overset{CH_3}{\overset{|}{\underset{\oplus}{C}}}{-}\underset{\underset{H}{|}}{C}H{-}CH_3 \qquad \textit{Rearrangement}$$

A 2° cation *A 3° cation*

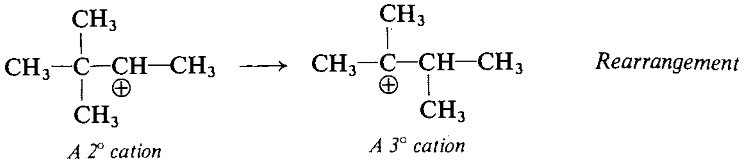
the neopentyl cation rearranges to the *tert*-pentyl cation,



$$CH_3{-}\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}{-}CH_2^{\oplus} \longrightarrow CH_3{-}\overset{CH_3}{\overset{|}{\underset{\oplus}{C}}}{-}CH_2CH_3 \qquad \textit{Rearrangement}$$

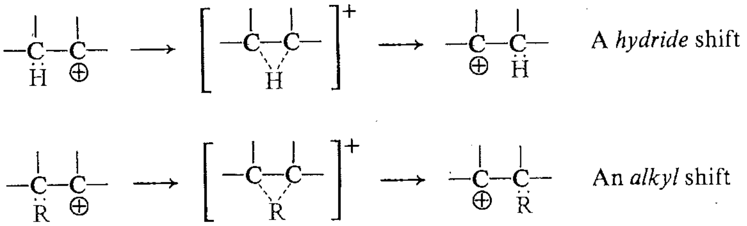
A 1° cation *A 3° cation*

and the 3,3-dimethyl-2-butyl cation rearranges to the 2,3-dimethyl-2-butyl cation.



We see that *in each case rearrangement takes place in such a way that a less stable carbocation is converted into a more stable one*: a primary into a secondary, a primary into a tertiary, or a secondary into a tertiary.

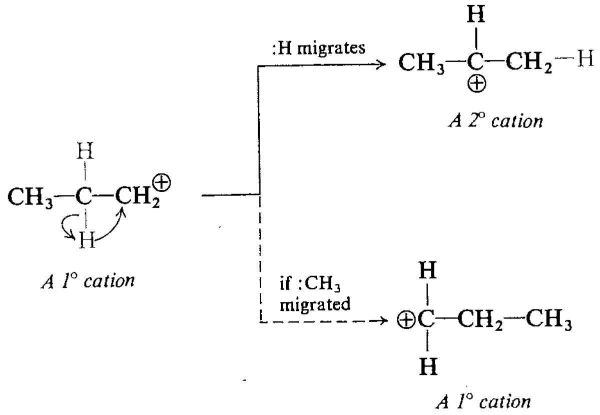
Just how does this rearrangement occur? Frank Whitmore (Pennsylvania State University) pictured rearrangement as taking place in this way: a hydrogen atom or alkyl group migrates *with a pair of electrons* from an adjacent carbon to the carbon bearing the positive charge. The carbon that loses the migrating 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.*



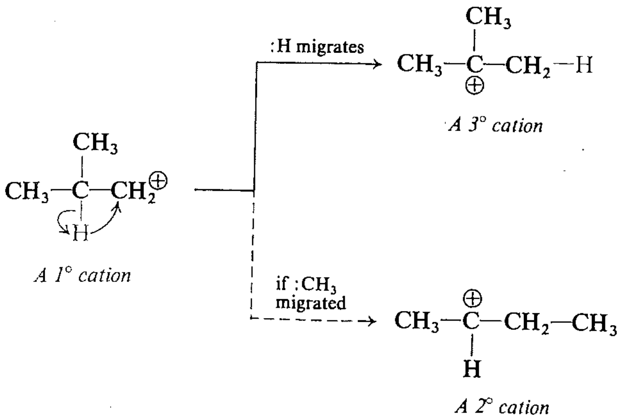
1,2-Shifts

We can account for rearrangements in S_N1 reactions in the following way. A carbocation is formed by loss of the leaving group from the substrate. **If a 1,2-shift of hydrogen or alkyl can form a more stable carbocation, then such a rearrangement takes place.** The new carbocation now combines with the nucleophile to yield the substitution product.

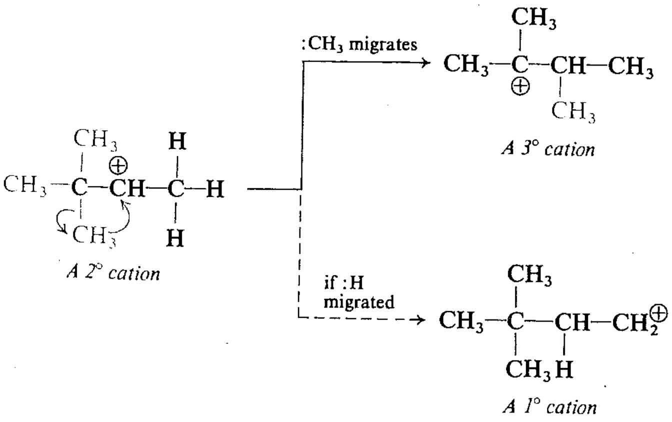
In the case of *n*-propyl cation, for example, a shift of hydrogen yields the more stable isopropyl cation; migration of a methyl group would simply form a different *n*-propyl cation.



In the case of the isobutyl 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.



We can view rearrangement as an intramolecular acid–base reaction in which, as usual, the stronger acid gets the base. The base is the migrating group with its electrons (hydride or alkyl). Competing for it are two Lewis acids: the electron-deficient carbons in the alternative carbocations. In the *n*-propyl–isopropyl rearrangement, for example, C–1 is more electron-deficient and hence the stronger acid, and it ends up holding the base.

Just as the reality of carbocations has been verified, so has the reality of their rearrangement. Prepared under the superacid conditions of Olah, and studied by spectroscopy, carbocations have been *observed* to rearrange; the rates of some rearrangements have even been measured, and the E_{act} values estimated. If water is added, it combines with the rearranged cation, and the —OH appears at the new position in the molecule. Here again we are observing as discrete processes steps proposed for S_N1, this time with rearrangement: first, formation of a carbocation; then, its rearrangement into a new cation; and finally, combination of this new cation with the nucleophile.

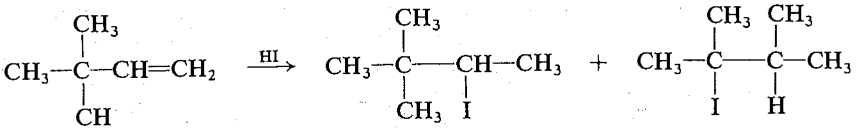
In our short acquaintance with the carbocation, we have encountered two of its reactions. A carbocation may:

(a) combine with a nucleophile;
(b) rearrange to a more stable carbocation.

This list will grow rapidly.

In rearrangement, as in every other reaction of a carbocation, 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.

Problem 5.8 When the alkene 3,3-dimethyl-1-butene is treated with hydrogen iodide, there is obtained a mixture of products:



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH}{C}}-CH{=}CH_2 \xrightarrow{HI} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{I}{CH}-CH_3 + CH_3-\overset{CH_3}{\underset{I}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_3}$$

3,3-Dimethyl-1-butene 3-Iodo-2,2-dimethylbutane 3-Iodo-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*, the reaction most typical of alkenes. Check your answer in Secs. 9.9 and 9.10.

In Chapter 7, we shall look at another aspect of the S_N1 reaction, and examine the factor that makes it all possible: the solvent. For now, let us return to the place where we started, the competition between S_N1 and S_N2.

5.23 S_N2 *vs.* S_N1

We have so far described two mechanisms for nucleophilic substitution: the **S_N2**, characterized by

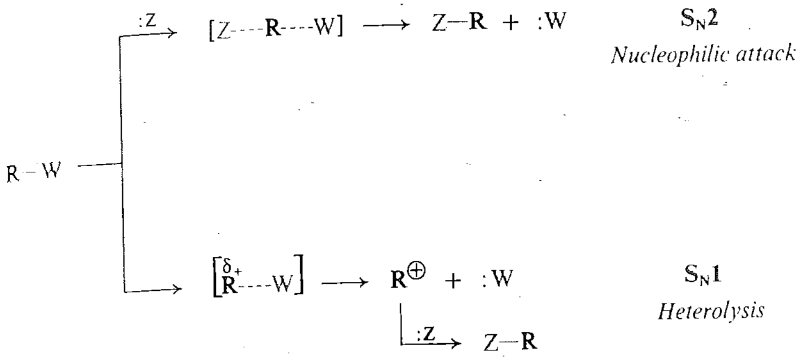
(a) second-order kinetics,
(b) complete stereochemical inversion,
(c) absence of rearrangement, and
(d) the reactivity sequence $CH_3W > 1° > 2° > 3°$;

and the **S_N1**, characterized by

(a) first-order kinetics,
(b) racemization,
(c) rearrangement, and
(d) the reactivity sequence $3° > 2° > 1° > CH_3W$.

Except for a brief discussion in Sec. 5.11, we have discussed these mechanisms as separate topics. Now let us turn to the relationship between the two. For a given substrate under a given set of conditions, which mechanism will be followed? And what, if anything, can we do to throw reaction toward one mechanism or another?

To answer these questions, let us consider just what can happen to a molecule of substrate. It can either suffer back-side attack by the nucleophile, or undergo heterolysis to form a carbocation. Whichever of these two processes goes faster



determines which mechanism predominates. (*Remember*: Heterolysis is the first—and rate-determining—step of the S_N1 mechanism.) Once again, we find, we must turn to the matter of *relative rates of competing reactions.*

Let us examine each of the components of the reaction system, and see what effect it exerts on this competition between nucleophilic attack and heterolysis.

Let us begin with the **substrate**, which consists of two parts, the alkyl group and the leaving group. The *nature of the leaving group* is, of course, vital to the very occurrence of substitution. Whichever process is taking place, nucleophilic attack or heterolysis, the bond to the leaving group is being broken; the easier it is to break this bond—that is, the better the leaving group—the faster the reaction occurs. A better leaving group thus speeds up reaction by both mechanisms; and, as it happens, it speeds up both to about the same degree. As a result, the nature of the leaving group has little effect on which mechanism, S_N2 or S_N1, is predominant.

In contrast, the *nature of the alkyl group, R, of the substrate* exerts a profound effect on which mechanism is to be followed. In R, two structural factors are at work: *steric hindrance*, which largely determines ease of back-side attack; and *ability to accommodate a positive charge*, which largely determines ease of heterolysis. As we proceed along the simple alkyl series CH_3, 1°, 2°, 3°, the group R becomes, by definition, more branched. There is a regular increase in the number of substituents on carbon: bulky, electron-releasing substituents. Steric hindrance increases; back-side attack becomes more difficult and hence slower. At the same time, ability to accommodate a positive charge increases; heterolysis becomes easier and hence faster.

$$\mathrm{RX} = \underset{\xrightarrow[\text{S}_\text{N}1\text{ increases}]{\hspace{6em}}}{\overset{\xleftarrow{\text{S}_\text{N}2\text{ increases}}}{\mathrm{CH_3X}\quad 1^\circ\quad 2^\circ\quad 3^\circ}} \qquad\qquad \begin{matrix} S_N2 \\ vs. \\ S_N1 \end{matrix}$$

The result is the pattern we encountered earlier: for methyl and primary substrates, a predisposition toward S_N2; for tertiary substrates, a predisposition toward S_N1. For secondary substrates there is a tendency toward intermediate behavior: a mixture of the two mechanisms or, as we shall see in Chapter 7, perhaps a mechanism with characteristics of both S_N2 and S_N1.

Despite this predisposition of a particular substrate toward a particular mechanism, we can still control the course of reaction to a considerable degree by our choice of experimental conditions. To see how this can be done, we must examine the other components of the reaction system.

Next, then, let us turn to the **nucleophile**. The key difference between the S_N2 and S_N1 mechanisms is the matter of *when* the nucleophile participates: *in* the rate-determining step of S_N2, but *after* the rate-determining step of S_N1. This difference in timing leads directly to two factors that help determine the mechanism to be followed: the *concentration of the nucleophile*, and the *nature of the nucleophile*.

The rate of S_N2 depends upon the concentration of the nucleophile, [:Z]; reaction, as we have seen (Sec. 5.12), is second-order.

$$\text{rate} = k[\text{RW}][:\text{Z}] \qquad \text{S}_\text{N}2$$

The rate of S_N1 is independent of [:Z]; reaction (Sec. 5.15) is first-order.

$$\text{rate} = k[\text{RW}] \qquad \text{S}_\text{N}1$$

An increase in [:Z] speeds up the second-order reaction but has no effect on the first-order reaction; the fraction of reaction by S_N2 increases. A decrease in [:Z] slows down the second-order reaction but has no effect on the first-order reaction; the fraction of reaction by S_N2 decreases. The net result is that, other things being equal, a *high concentration of nucleophile favors the S_N2 reaction*, and a *low concentration favors the S_N1 reaction.*

Problem 5.9 In 80% ethanol at 55°C, isopropyl bromide reacts with hydroxide ion according to the following kinetic equation, where the rate is expressed as moles per liter per second:

$$\text{rate} = 4.7 \times 10^{-5}[\text{RX}][\text{OH}^-] + 0.24 \times 10^{-5}[\text{RX}]$$

What percentage of the isopropyl bromide reacts by the S_N2 mechanism when $[\text{OH}^-]$ is: (a) 0.001 molar, (b) 0.01 molar, (c) 0.1 molar, (d) 1.0 molar, (e) 5.0 molar?

In the same way, the rate of S_N2 depends upon the nature of the nucleophile: a stronger nucleophile attacks the substrate faster. The rate of S_N1 is independent of the nature of the nucleophile: stronger or weaker, the nucleophile waits until the carbocation is formed. The net result is that, other things being equal, a *strong nucleophile favors the S_N2 reaction*, and a *weak nucleophile favors the S_N1 reaction.*

We have already seen an illustration of this effect in Sec. 5.22. Neopentyl bromide reacts with the strong nucleophile, ethoxide, to give the unrearranged ethyl neopentyl ether: clearly an S_N2 reaction. It reacts with the weak nucleophile, ethanol, to give the rearranged ethyl *tert*-pentyl ether: clearly an S_N1 reaction.

But we have neglected the third component of the system, the one that offers the most scope for control of the reaction: the **solvent**. We shall examine the role of the solvent in detail in Chapter 7.

At the beginnning of this chapter, we said that a chemical reaction is the result of a competition: what actually happens when a particular set of reactants is mixed together under a particular set of conditions is what happens *fastest*. Here, we have been concerned with competition between different pathways for nucleophilic substitution. But in Chapter 8 we shall find still further competition: between nucleophilic substitution and an entirely different type of reaction, *elimination*. In all this, we are concerned with the factors that favor one mechanism or one type of reaction over another, and, where possible, with what we can do to control the outcome.

5.24 Analysis of alkyl halides

Simple alkyl halides respond to the common characterization tests in the same manner as alkanes: they are insoluble in cold concentrated sulfuric acid; they are inert to bromine in carbon tetrachloride, to aqueous permanganate, and to chromic anhydride. They are readily distinguished from alkanes, however, by qualitative analysis (Sec. 2.27), which shows the presence of halogen.

In many cases, the presence of halogen can be detected without a sodium fusion or Schöniger oxidation. An unknown is warmed for a few minutes with alcoholic silver nitrate (the alcohol dissolves both the ionic reagent and the organic compound); halogen is indicated by formation of a precipitate that is insoluble in dilute nitric acid.

As in almost all reactions of organic halides, reactivity toward alcoholic silver nitrate follows the sequence RI > RBr > RCl. For a given halogen atom, reactivity decreases in the order 3° > 2° > 1°, the sequence typical of carbocation formation; as we shall see, allylic halides (Sec. 11.13) and benzylic halides (Sec. 16.18) are highly reactive. Other evidence (stereochemistry, rearrangements) suggests that this reaction is of the S_N1 type. Silver ion is believed to accelerate reaction by *pulling* halide away from the alkyl group.

$$R{:}X + Ag^+ \longrightarrow R^+ + Ag^+X^-$$

(Vinyl and aryl halides do not react, Secs. 11.16 and 26.5.)

As mentioned earlier (Sec. 5.3), substituted alkyl halides also undergo the reactions characteristic of their other functional groups.

(Analysis of alkyl halides by spectroscopy will be discussed in Chapter 17.)

PROBLEMS

1. Give the structural formula of:

(a) 1-bromo-2,2-dimethylpropane
(b) 2-chloro-2,3-dimethylpentane
(c) 1-bromo-3-methylhexane
(d) 2,2-dichloropropane
(e) 1,2-dichloro-3-methylbutane
(f) 3-bromo-2,4-dimethylpentane

2. Draw out the structural formula and give the IUPAC name of:

(a) $(CH_3)_2CHCH_2I$
(b) $(CH_3)_2CHCHClCH_3$
(c) $CH_3CHBrC(CH_3)_2CH_2CH_3$
(d) $(CH_3)_2CClCBr(CH_3)_2$

3. Give the structures and names of the chief organic products expected from the reaction (if any) of *n*-butyl bromide with:

(a) NaOH(aq)
(b) cold conc. H_2SO_4
(c) Zn, H^+
(d) Li, then CuI, ethyl bromide
(e) Mg, ether
(f) product (e) + D_2O
(g) dilute neutral $KMnO_4$
(h) NaI in acetone
(i) Br_2/CCl_4

4. Referring when necessary to the summary on pages 173–174, give structures of the chief organic products expected from the reaction of *n*-butyl bromide with:

(a) NH_3
(b) $C_6H_5NH_2$
(c) NaCN
(d) $NaOC_2H_5$
(e) CH_3COOAg
(f) $NaSCH_3$

5. Referring when necessary to the summary on pages 173–174, give the reagents, inorganic or organic, needed to convert *n*-butyl bromide into:

(a) *n*-butyl iodide
(b) *n*-butyl chloride
(c) *n*-butyl methyl ether ($CH_3CH_2CH_2CH_2OCH_3$)
(d) *n*-butyl alcohol
(e) pentanenitrile ($CH_3CH_2CH_2CH_2CN$)
(f) *n*-butylamine ($CH_3CH_2CH_2CH_2NH_2$)
(g) *n*-butylmagnesium bromide
(h) lithium di-*n*-butylcopper

6. Arrange the compounds of each set in order of reactivity toward S_N2 displacement:

(a) 2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane
(b) 1-bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane
(c) 1-bromobutane, 1-bromo-2,2-dimethylpropane, 1-bromo-2-methylbutane, 1-bromo-3-methylbutane

7. Arrange the compounds of each set in order of reactivity toward S_N1 displacement:

(a) the compounds of Problem 6(a)
(b) the compounds of Problem 6(b)

8. Consider, as an example, the reaction between an alkyl halide and NaOH in a mixture of water and ethanol. In a table, with one column for S_N2 and another for S_N1, compare the two mechanisms with regard to:

(a) stereochemistry
(b) kinetic order
(c) occurrence of rearrangements
(d) relative rates for CH_3X, C_2H_5X, iso-C_3H_7X, *tert*-C_4H_9X
(e) relative rates for RCl, RBr, and RI
(f) effect on rate of a rise in temperature
(g) effect on rate of doubling [RX]
(h) effect on rate of doubling [OH^-]

9. When a dry hydrogen halide, HX, is dissolved in an alcohol, ROH, the resulting solution conducts an electric current. Upon heating, an alkyl halide, RX, is formed. Additional sulfuric acid speeds up the formation of RX. Except for most primary alcohols, rearrangements of the same pattern as in Sec. 5.22 take place. The order of reactivity of alcohols toward HX is $3° > 2° > 1° < CH_3$.

(a) Propose a likely mechanism or mechanisms for this reaction, showing how all the facts are accounted for. (b) The alcohol $ClCH_2CHOHCH_3$, although formally secondary, reacts slowly, and at about the rate of a primary alcohol. How do you account for this?

10. A liquid of boiling point 39–41 °C was insoluble in water, dilute acids or bases, or concentrated H_2SO_4. It did not react with Br_2/CCl_4 or dilute $KMnO_4$. It was subjected to sodium fusion, and the resulting solution was filtered, acidified with nitric acid, and boiled. Addition of $AgNO_3$ gave a precipitate.

(a) On the basis of Table 5.1, what compound or compounds might this have been? (b) Several milliliters of CCl_4 was added to a portion of the acidified solution from the fusion, and the mixture was shaken with chlorine water. A violet color appeared in the CCl_4 layer. Which compound or compounds of (a) are still possible? (c) How would each of the other possibilities have responded in (b)?