# AUCHE 250: ORGANIC CHEMISTRY I



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Brian Rempel

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Detailed Licensing

# Licensing

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# CHAPTER OVERVIEW

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# 1.1: Atomic Structure - The Nucleus

**Key Terms**

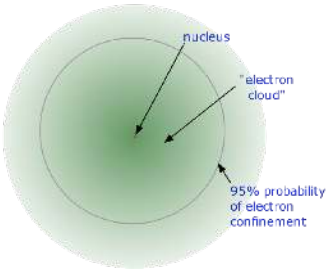
Make certain that you can define, and use in context, the key terms below.

- atomic number
- atomic weight
- electron
- mass number
- neutron
- proton

## The Nuclear Atom

The precise physical nature of atoms finally emerged from a series of elegant experiments carried out between 1895 and 1915. The most notable of these achievements was Ernest Rutherford's famous 1911 alpha-ray scattering experiment, which established that:

- Almost all of the *mass* of an atom is contained within a tiny (and therefore extremely dense) *nucleus* which carries a positive electric charge whose value identifies each element and is known as the *atomic number* of the element.
- Almost all of the *volume* of an atom consists of empty space in which *electrons*, the fundamental carriers of negative electric charge, reside. The extremely small mass of the electron ($1/1840^{th}$ the mass of the hydrogen nucleus) causes it to behave as a quantum particle, which means that its location at any moment cannot be specified; the best we can do is describe its behavior in terms of the probability of its manifesting itself at any point in space. It is common (but somewhat misleading) to describe the volume of space in which the electrons of an atom have a significant probability of being found as the *electron cloud*. The latter has no definite outer boundary, so neither does the atom. The radius of an atom must be defined arbitrarily, such as the boundary in which the electron can be found with 95% probability. Atomic radii are typically 30-300 pm.




The nucleus is itself composed of two kinds of particles. *Protons* are the carriers of positive electric charge in the nucleus; the proton charge is exactly the same as the electron charge, but of opposite sign. This means that in any [electrically neutral] atom, the number of protons in the nucleus (often referred to as the *nuclear charge*) is balanced by the same number of electrons outside the nucleus. The other nuclear particle is the *neutron*. As its name implies, this particle carries no electrical charge. Its mass is almost the same as that of the proton. Most nuclei contain roughly equal numbers of neutrons and protons, so we can say that these two particles together account for almost all the mass of the atom.

> *Because the electrons of an atom are in contact with the outside world, it is possible for one or more electrons to be lost, or some new ones to be added. The resulting electrically-charged atom is called an ion.*

### Atomic Number (Z)

What single parameter uniquely characterizes the atom of a given element? It is not the atom's relative mass, as we will see in the section on isotopes below. It is, rather, the number of protons in the nucleus, which we call the *atomic number* and denote by the symbol *Z*. Each proton carries an electric charge of +1, so the atomic number also specifies the electric charge of the nucleus. In the neutral atom, the *Z protons* within the nucleus are balanced by *Z electrons* outside it.



*Atomic numbers were first worked out in 1913 by Henry Moseley, a young member of Rutherford's research group in Manchester.*

Moseley searched for a measurable property of each element that increases linearly with atomic number. He found this in a class of X-rays emitted by an element when it is bombarded with electrons. The frequencies of these X-rays are unique to each element, and they increase uniformly in successive elements. Moseley found that the square roots of these frequencies give a straight line when plotted against Z; this enabled him to sort the elements in order of increasing atomic number.

You can think of the atomic number as a kind of serial number of an element, commencing at 1 for hydrogen and increasing by one for each successive element. The chemical name of the element and its symbol are uniquely tied to the atomic number; thus the symbol "Sr" stands for strontium, whose atoms all have $Z = 38$.

### Mass Number (A)

The *mass number* equals the sum of the numbers of protons and the number of neutrons in the nucleus. It is sometimes represented by the symbol $A$, so

$$A = Z + N \tag{1.1.1}$$

in which $Z$ is the atomic number and $N$ is the *neutron number*.

## Elements

To date, about 115 different elements have been discovered; by definition, each is chemically unique. To understand why they are unique, you need to understand the structure of the atom (the fundamental, individual particle of an element) and the characteristics of its components. Atoms consist of electrons, protons, and neutrons. Although this is an oversimplification that ignores the other subatomic particles that have been discovered, it is sufficient for discussion of chemical principles. Some properties of these subatomic particles are summarized in Table 1.1.1, which illustrates three important points:

1. Electrons and protons have electrical charges that are identical in magnitude but opposite in sign. Relative charges of −1 and +1 are assigned to the electron and proton, respectively.
2. Neutrons have approximately the same mass as protons but no charge. They are electrically neutral.
3. The mass of a proton or a neutron is about 1836 times greater than the mass of an electron. Protons and neutrons constitute the bulk of the mass of atoms.

The discovery of the electron and the proton was crucial to the development of the modern model of the atom and provides an excellent case study in the application of the scientific method. In fact, the elucidation of the atom's structure is one of the greatest detective stories in the history of science.

Table 1.1.1: Properties of Subatomic Particles*

| Particle | Mass (g) | Atomic Mass (amu) | Electrical Charge (coulombs) | Relative Charge |
|---|---|---|---|---|
| electron | $9.109 \times 10^{-28}$ | 0.0005486 | $-1.602 \times 10^{-19}$ | −1 |
| proton | $1.673 \times 10^{-24}$ | 1.007276 | $+1.602 \times 10^{-19}$ | +1 |
| neutron | $1.675 \times 10^{-24}$ | 1.008665 | 0 | 0 |

In most cases, the symbols for the elements are derived directly from each element's name, such as C for carbon, U for uranium, Ca for calcium, and Po for polonium. Elements have also been named for their properties [such as radium (Ra) for its radioactivity],

for the native country of the scientist(s) who discovered them [polonium (Po) for Poland], for eminent scientists [curium (Cm) for the Curies], for gods and goddesses [selenium (Se) for the Greek goddess of the moon, Selene], and for other poetic or historical reasons. Some of the symbols used for elements that have been known since antiquity are derived from historical names that are no longer in use; only the symbols remain to indicate their origin. Examples are Fe for iron, from the Latin *ferrum*; Na for sodium, from the Latin *natrium*; and W for tungsten, from the German *wolfram*. Examples are in Table 1.1.2.

Table 1.1.2: Element Symbols Based on Names No Longer in Use

| Element | Symbol | Derivation | Meaning |
|---|---|---|---|
| antimony | Sb | stibium | Latin for “mark” |
| copper | Cu | cuprum | from Cyprium, Latin name for the island of Cyprus, the major source of copper ore in the Roman Empire |
| gold | Au | aurum | Latin for “gold” |
| iron | Fe | ferrum | Latin for “iron” |
| lead | Pb | plumbum | Latin for “heavy” |
| mercury | Hg | hydrargyrum | Latin for “liquid silver” |
| potassium | K | kalium | from the Arabic al-qili, “alkali” |
| silver | Ag | argentum | Latin for “silver” |
| sodium | Na | natrium | Latin for “sodium” |
| tin | Sn | stannum | Latin for “tin” |
| tungsten | W | wolfram | German for “wolf stone” because it interfered with the smelting of tin and was thought to devour the tin |

Recall that the nuclei of most atoms contain neutrons as well as protons. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the mass number (A), the sum of the numbers of protons and neutrons.

## Carbon Isotopes

The element carbon (C) has an atomic number of 6, which means that all neutral carbon atoms contain 6 protons and 6 electrons. In a typical sample of carbon-containing material, 98.89% of the carbon atoms also contain 6 neutrons, so each has a mass number of 12. An isotope of any element can be uniquely represented as ${}^{A}_{Z}X$, where X is the atomic symbol of the element. The isotope of carbon that has 6 neutrons is therefore ${}^{12}_{6}C$. The subscript indicating the atomic number is actually redundant because the atomic symbol already uniquely specifies Z. Consequently, ${}^{12}_{6}C$ is more often written as $^{12}$C, which is read as “carbon-12.” Nevertheless, the value of Z is commonly included in the notation for nuclear reactions because these reactions involve changes in Z.

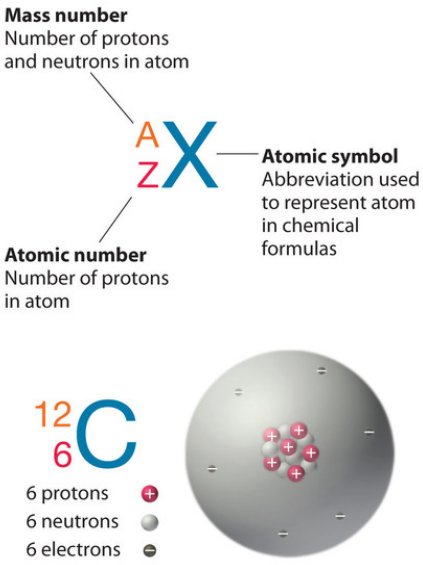



Figure 1.1.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

In addition to $^{12}C$, a typical sample of carbon contains 1.11% $^{13}_{6}C$ ($^{13}$C), with 7 neutrons and 6 protons, and a trace of $^{14}_{6}C$ ($^{14}$C), with 8 neutrons and 6 protons. The nucleus of $^{14}$C is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archaeology. Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. The properties of some common isotopes are in Table 1.1.3.

Table 1.1.3: Properties of Selected Isotopes

| Element | Symbol | Atomic Mass (amu) | Isotope Mass Number | Isotope Masses (amu) | Percent Abundances (%) |
|---|---|---|---|---|---|
| hydrogen | H | 1.0079 | 1 | 1.007825 | 99.9855 |
| | | | 2 | 2.014102 | 0.0115 |
| boron | B | 10.81 | 10 | 10.012937 | 19.91 |
| | | | 11 | 11.009305 | 80.09 |
| carbon | C | 12.011 | 12 | 12 (defined) | 99.89 |
| | | | 13 | 13.003355 | 1.11 |
| oxygen | O | 15.9994 | 16 | 15.994915 | 99.757 |
| | | | 17 | 16.999132 | 0.0378 |
| | | | 18 | 17.999161 | 0.205 |
| iron | Fe | 55.845 | 54 | 53.939611 | 5.82 |
| | | | 56 | 55.934938 | 91.66 |
| | | | 57 | 56.935394 | 2.19 |
| | | | 58 | 57.933276 | 0.33 |
| uranium | U | 238.03 | 234 | 234.040952 | 0.0054 |
| | | | 235 | 235.043930 | 0.7204 |
| | | | 238 | 238.050788 | 99.274 |

Sources of isotope data: G. Audi et al., Nuclear Physics A 729 (2003): 337–676; J. C. Kotz and K. F. Purcell, Chemistry and Chemical Reactivity, 2nd ed., 1991.

### Example 1.1.1

An element with three stable isotopes has 82 protons. The separate isotopes contain 124, 125, and 126 neutrons. Identify the element and write symbols for the isotopes.

**Given**: number of protons and neutrons

**Asked for**: element and atomic symbol

**Strategy**:

A. Refer to the periodic table and use the number of protons to identify the element.
B. Calculate the mass number of each isotope by adding together the numbers of protons and neutrons.
C. Give the symbol of each isotope with the mass number as the superscript and the number of protons as the subscript, both written to the left of the symbol of the element.

**Solution**:

**A** The element with 82 protons (atomic number of 82) is lead: Pb.

**B** For the first isotope, A = 82 protons + 124 neutrons = 206. Similarly, A = 82 + 125 = 207 and A = 82 + 126 = 208 for the second and third isotopes, respectively. The symbols for these isotopes are ${}^{206}_{82}Pb$, ${}^{207}_{82}Pb$, and ${}^{208}_{82}Pb$, which are usually abbreviated as ${}^{206}Pb$, ${}^{207}Pb$, and ${}^{208}Pb$.

### Exercise 1.1.1

Identify the element with 35 protons and write the symbols for its isotopes with 44 and 46 neutrons.

**Answer**

${}^{79}_{35}\text{Br}$ and ${}^{81}_{35}\text{Br}$ or, more commonly, ${}^{79}\text{Br}$ and ${}^{81}\text{Br}$.

## Summary

The atom consists of discrete particles that govern its chemical and physical behavior. Each atom of an element contains the same number of protons, which is the **atomic number** (*Z*). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number** (*A*), which is the sum of the numbers of protons and neutrons. The relative masses of atoms are reported using the **atomic mass unit** (**amu**), which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons.

## Contributors and Attributions


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- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)



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# 1.2: Atomic Structure - Orbitals

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- nodal plane
- node
- orbital
- quantum mechanics
- wave function

For a refresher on quantum numbers view this text

## Atomic Orbitals

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

One way of representing electron probability distributions was illustrated in Figure 6.5.2 for the 1*s* orbital of hydrogen. Because $\Psi^2$ gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of $\Psi^2$ versus distance from the nucleus ($r$) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical, so the probability of finding a 1*s* electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of $r$, the electron probability density is very small but *not* zero.

In contrast, we can calculate the *radial probability* (the probability of finding a 1*s* electron at a distance $r$ from the nucleus) by adding together the probabilities of an electron being at all points on a series of $x$ spherical shells of radius $r_1$, $r_2$, $r_3$,…, $r_{x-1}$, $r_x$. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (part (a) in Figure 1.2.1), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (part (b) in Figure 1.2.1), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 1.2.1. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing $r$ (part (c) in Figure 1.2.1). Because the surface area of the spherical shells increases more rapidly with increasing $r$ than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (part (d) in Figure 1.2.1). Most important, when $r$ is very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (part (d) in Figure 1.2.1).

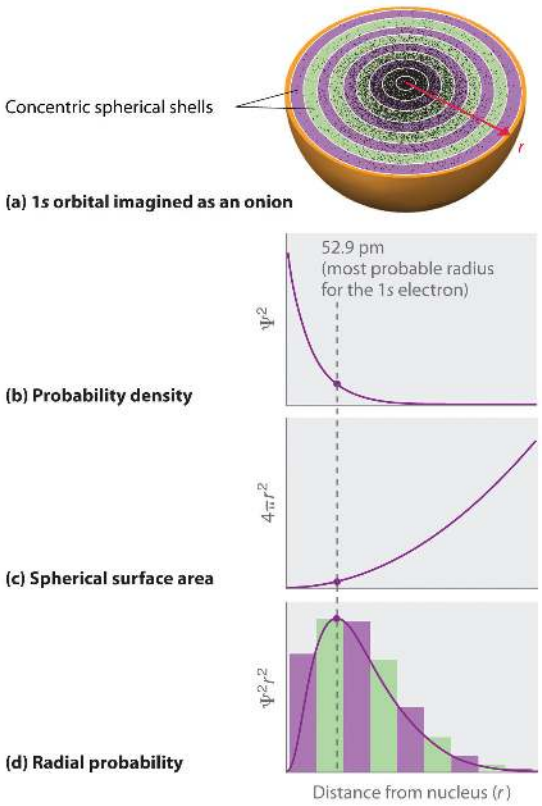



Figure 1.2.1 Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density $\Psi^2$ versus $r$ shows that the electron probability density is greatest at $r = 0$ and falls off smoothly with increasing $r$. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing $r$. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of $r$. Because the surface area of each shell increases more rapidly with increasing $r$ than the electron probability density decreases, a plot of electron probability versus $r$ (the *radial probability*) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at $r = 0.529$ Å (52.9 pm), which is exactly the radius calculated by Bohr for the $n = 1$ orbit. Thus the *most probable radius* obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the quantum mechanical Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 1.2.2 compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing $r$. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure 1.2.2). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.

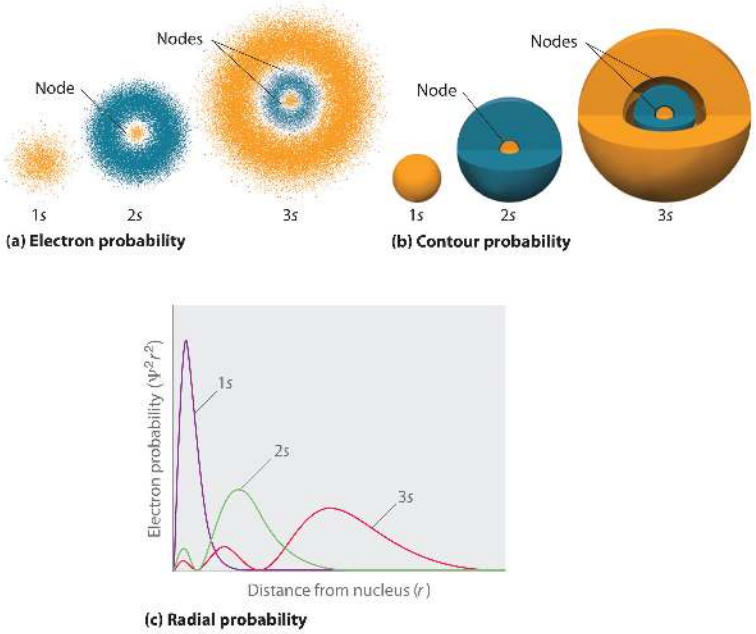



Figure 1.2.2: Probability Densities for the 1*s*, 2*s*, and 3*s* Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1*s*, 2*s*, and 3*s* orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (*r*) in all directions (radial probability), the most probable radius increases as *n* increases, but the 2*s* and 3*s* orbitals have regions of significant electron probability at small values of *r*.

## s Orbitals

Three things happen to *s* orbitals as *n* increases (Figure 1.2.2):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the *s* orbitals also become higher in energy as *n* increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in part (b) in Figure 1.2.2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

## p Orbitals

Only *s* orbitals are spherically symmetrical. As the value of *l* increases, the number of orbitals in a given subshell increases, and the shapes of the orbitals become more complex. Because the 2*p* subshell has $l = 1$, with three values of $m_l$ (−1, 0, and +1), there are three 2*p* orbitals.

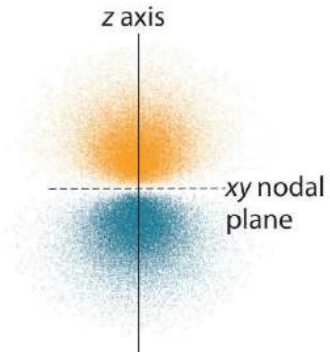



Figure 1.2.2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 1.2.3. Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 1.2.4, the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each *p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

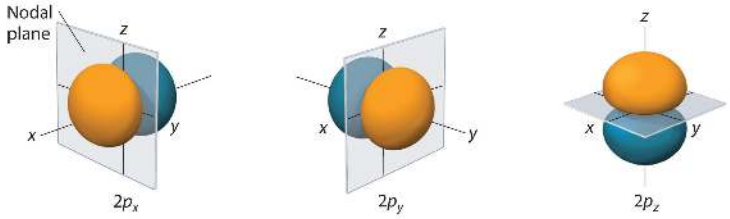



Figure 1.2.4 The Three Equivalent 2*p* Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2*p* orbital. The phase of the wave function is positive (orange) in the region of space where *x*, *y*, or *z* is positive and negative (blue) where *x*, *y*, or *z* is negative.

Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure 1.2.4.

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells. Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals. Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.

## Contributors and Attributions

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# 1.3: Atomic Structure - Electron Configurations

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- ground-state electronic configuration
- Hund's rule
- Pauli exclusion principle
- aufbau principle

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells. Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals. Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.

## Electron Configurations

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and subshells. Commonly, the electron configuration is used to describe the orbitals of an atom in its ground state, but it can also be used to represent an atom that has ionized into a cation or anion by compensating with the loss of or gain of electrons in their subsequent orbitals. Many of the physical and chemical properties of elements can be correlated to their unique electron configurations. The valence electrons, electrons in the outermost shell, are the determining factor for the unique chemistry of the element.

Before assigning the electrons of an atom into orbitals, one must become familiar with the basic concepts of electron configurations. Every element on the periodic table consists of atoms, which are composed of protons, neutrons, and electrons. Electrons exhibit a negative charge and are found around the nucleus of the atom in electron orbitals, defined as the volume of space in which the electron can be found within 95% probability. The four different types of orbitals (s,p,d, and f) have different shapes, and one orbital can hold a maximum of two electrons. The p, d, and f orbitals have different sublevels, thus can hold more electrons.

As stated, the electron configuration of each element is unique to its position on the periodic table. The energy level is determined by the period and the number of electrons is given by the atomic number of the element. Orbitals on different energy levels are similar to each other, but they occupy different areas in space. The 1s orbital and 2s orbital both have the characteristics of an s orbital (radial nodes, spherical volume probabilities, can only hold two electrons, etc.) but, as they are found in different energy levels, they occupy different spaces around the nucleus. Each orbital can be represented by specific blocks on the periodic table. The s-block is the region of the alkali metals including helium (Groups 1 & 2), the d-block are the transition metals (Groups 3 to 12), the p-block are the main group elements from Groups 13 to 18, and the f-block are the lanthanides and actinides series.

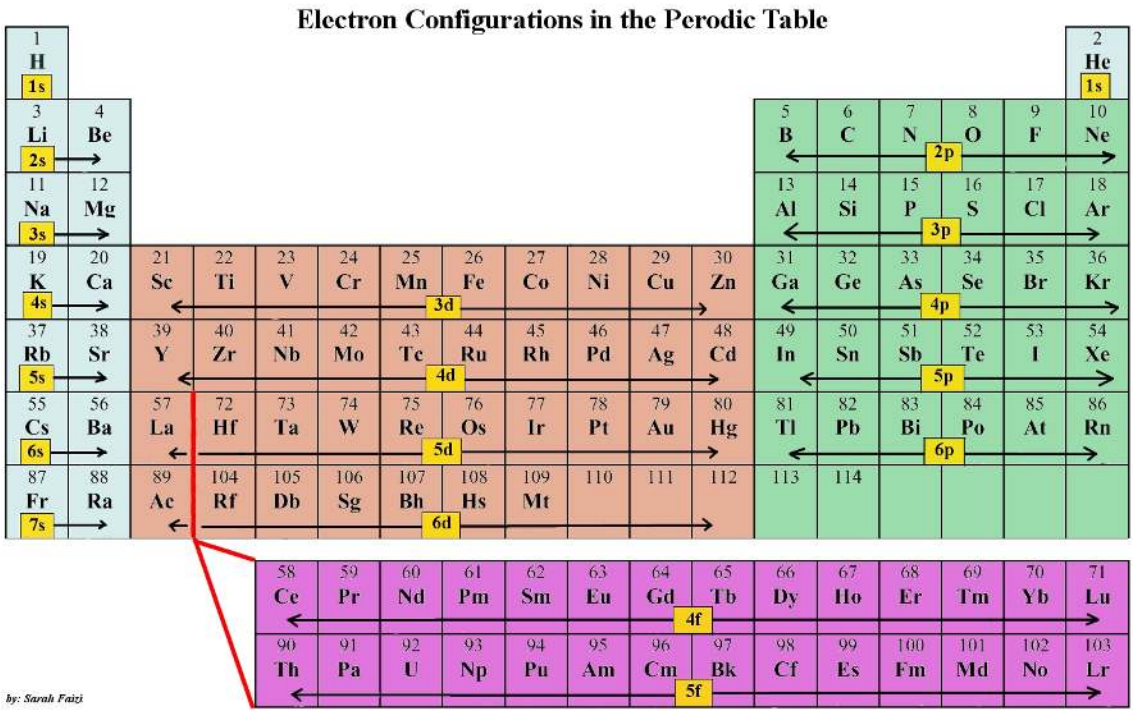



Figure 1.3.1 The Periodic Table

Using the periodic table to determine the electron configurations of atoms is key, but also keep in mind that there are certain rules to follow when assigning electrons to different orbitals. The periodic table is an incredibly helpful tool in writing electron configurations. For more information on how electron configurations and the periodic table are linked, visit the Connecting Electrons to the Periodic Table module.

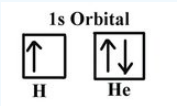
## Rules for Assigning Electron Orbitals

### Pauli Exclusion Principle

The Pauli exclusion principle states that no two electrons can have the same four quantum numbers. The first three (n, l, and $m_l$) may be the same, but the fourth quantum number must be different. A single orbital can hold a maximum of two electrons, which **must** have opposing spins; otherwise they would have the same four quantum numbers, which is forbidden. One electron is spin up ($m_s$ = +1/2) and the other would spin down ($m_s$ = -1/2). This tells us that each subshell has double the electrons per orbital. The s subshell has 1 orbital that can hold up to 2 electrons, the p subshell has 3 orbitals that can hold up to 6 electrons, the d subshell has 5 orbitals that hold up to 10 electrons, and the f subshell has 7 orbitals with 14 electrons.

**Example 1: Hydrogen and Helium**

The first three quantum numbers of an electron are n=1, l=0, $m_l$=0. Only two electrons can correspond to these, which would be either $m_s$ = -1/2 or $m_s$ = +1/2. As we already know from our studies of quantum numbers and electron orbitals, we can conclude that these four quantum numbers refer to the 1s subshell. If only one of the $m_s$ values are given then we would have $1s^1$ (denoting hydrogen) if both are given we would have $1s^2$ (denoting helium). Visually, this is be represented as:



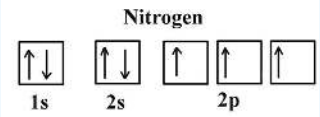

As shown, the 1s subshell can hold only two electrons and, when filled, the electrons have opposite spins.

## Hund's Rule

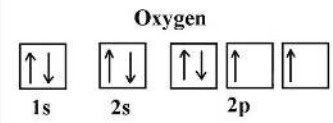
When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital. Atoms at ground states tend to have as many unpaired electrons as possible. When visualizing this processes, think about how electrons are exhibiting the same behavior as the same poles on a magnet would if they came into contact; as the negatively charged electrons fill orbitals they first try to get as far as possible from each other before having to pair up.

### Example 2: Oxygen and Nitrogen

If we look at the correct electron configuration of the Nitrogen (Z = 7) atom, a very important element in the biology of plants: $1s^2\ 2s^2\ 2p^3$




We can clearly see that p orbitals are half-filled as there are three electrons and three p orbitals. This is because Hund's Rule states that the three electrons in the 2p subshell will fill all the empty orbitals first before filling orbitals with electrons in them. If we look at the element after nitrogen in the same period, oxygen (Z = 8) its electron configuration is: $1s^2\ 2s^2\ 2p^4$ (for an atom).




Oxygen has one more electron than nitrogen and as the orbitals are all half filled the electron must pair up.

## Occupation of Orbitals

Electrons fill orbitals in a way to minimize the energy of the atom. Therefore, the electrons in an atom fill the principal energy levels in order of increasing energy (the electrons are getting farther from the nucleus). The relative energy of the orbitals is shown in Figure 1.3.2

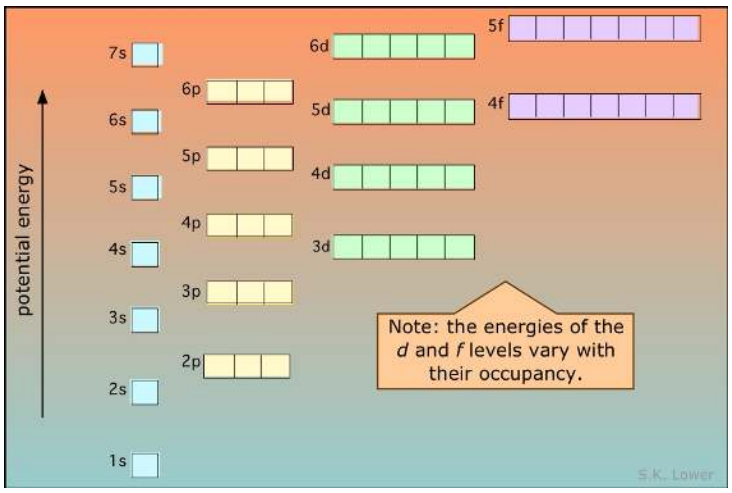



Figure 1.3.2 The relative potential energy of atomic orbitals

The order of levels filled is then:

***1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, and 7p***

The general order in which orbitals are filled is depicted in Figure 1.3.3. Subshells corresponding to each value of *n* are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the 4*s* orbital is

filled prior to the 3*d* orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is [Ar]$4s^1$, and the configuration of calcium is [Ar]$4s^2$. Five 3*d* orbitals are filled by the next 10 elements, the transition metals, followed by three 4*p* orbitals. Notice that the last member of this row is the noble gas krypton ($Z$ = 36), [Ar]$4s^2 3d^{10} 4p^6$ = [Kr], which has filled 4*s*, 3*d*, and 4*p* orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the 5*s*, 4*d*, and 5*p* orbitals are filled sequentially.

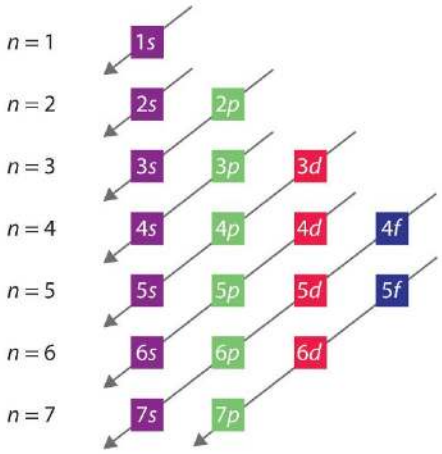



Figure 1.3.3 **:** *Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.*

## The Aufbau Process

Aufbau comes from the German word "aufbauen" meaning "to build." When writing electron configurations, orbitals are built up from atom to atom. When writing the electron configuration for an atom, orbitals are filled in order of increasing atomic number. However, there are some exceptions to this rule.

### ✔ Example 3: 3rd row elements

Following the pattern across a period from B (Z=5) to Ne (Z=10), the number of electrons increases and the subshells are filled. This example focuses on the p subshell, which fills from boron to neon.

- B (Z=5) configuration: $1s^2\ 2s^2\ 2p^1$
- C (Z=6) configuration:$1s^2\ 2s^2\ 2p^2$
- N (Z=7) configuration:$1s^2\ 2s^2\ 2p^3$
- O (Z=8) configuration:$1s^2\ 2s^2\ 2p^4$
- F (Z=9) configuration:$1s^2\ 2s^2\ 2p^5$
- Ne (Z=10) configuration:$1s^2\ 2s^2\ 2p^6$

## The Number of Valence Electrons

The number of valence electrons of an element can be determined by the periodic table group (vertical column) in which the element is categorized. With the exception of groups 3–12 (the transition metals), the units digit of the group number identifies how many valence electrons are associated with a neutral atom of an element listed under that particular column. For example in group 16, the units digit is 6 and elements in this group have 6 valence electrons.

Table 1.3.1 Valence electrons derived from periodic table group

| Periodic table group | Valence electrons |
|---|---|
| Group 1: alkali metals | 1 |
| Group 2: alkaline earth metals | 2 |
| Groups 3-12: transition metals | 2* (The 4s shell is complete and cannot hold any more electrons) |
| Group 13: boron group | 3 |

| Periodic table group | Valence electrons |
|---|---|
| Group 14: carbon group | 4 |
| Group 15: pnictogens | 5 |
| Group 16: chalcogens | 6 |
| Group 17: halogens | 7 |
| Group 18: noble gases | 8** |

** The general method for counting valence electrons is generally not useful for transition metals. Instead the modified **d electron count method** is used.*

*** Except for helium, which has only two valence electrons.*

The electron configuration of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

### Example 1.3.1

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, $Z = 15$. What is its valence electron configuration?

**Given:** atomic number

**Asked for:** orbital diagram and valence electron configuration for phosphorus

**Strategy:**

A. Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.
B. Referring to Figure 1.3.1, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.
C. Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

**Solution:**

**A** Because phosphorus is in the third row of the periodic table, we know that it has a [Ne] closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

**B** The additional five electrons are placed in the next available orbitals, which Figure 1.2.5 tells us are the 3*s* and 3*p* orbitals:

P: [Ne] 3*p* ___ ___ ___
3*s* ___

Because the 3*s* orbital is lower in energy than the 3*p* orbitals, we fill it first:

P: [Ne] 3*p* ___ ___ ___
3*s* ↑↓

Hund's rule tells us that the remaining three electrons will occupy the degenerate 3*p* orbitals separately but with their spins aligned:

P: [Ne] 3*p* ↑ ↑ ↑
3*s* ↑↓

The electron configuration is $[Ne]3s^2 3p^3$.

**C** We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2 3p^3$.

### ? Exercise 1.3.1

Draw an orbital diagram and use it to derive the electron configuration of chlorine, $Z = 17$. What is its valence electron configuration?

**Answer**

$[Ne]3s^2 3p^5$; $3s^2 3p^5$

The sixth row of the periodic table will be different from the preceding two because the 4*f* orbitals, which can hold 14 electrons, are filled between the 6*s* and the 5*d* orbitals. The elements that contain 4*f* orbitals in their valence shell are the lanthanides. When the 6*p* orbitals are finally filled, we have reached the next (and last known) noble gas, radon ($Z = 86$), $[Xe]6s^2 4f^{14} 5d^{10} 6p^6 = [Rn]$. In the last row, the 5*f* orbitals are filled between the 7*s* and the 6*d* orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

### ✓ Example 1.3.2

Write the electron configuration of mercury ($Z = 80$), showing all the inner orbitals.

**Given:** atomic number

**Asked for:** complete electron configuration

**Strategy:**

Using the orbital diagram in Figure 1.3.1 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

**Solution:**

By placing the electrons in orbitals following the order shown in Figure 1.3.1 and using the periodic table as a guide, we obtain

| | | |
|---|---|---|
| $1s^2$ | row 1 | 2 electrons |
| $2s^2 2p^6$ | row 2 | 8 electrons |
| $3s^2 3p^6$ | row 3 | 8 electrons |
| $4s^2 3d^{10} 4p^6$ | row 4 | 18 electrons |
| $5s^2 4d^{10} 5p^6$ | row 5 | 18 electrons |
| | row 1–5 | 54 electrons |

After filling the first five rows, we still have 80 − 54 = 26 more electrons to accommodate. According to Figure 1.3.1, we need to fill the 6*s* (2 electrons), 4*f* (14 electrons), and 5*d* (10 electrons) orbitals. The result is mercury's electron configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} = Hg = [Xe]6s^2 4f^{14} 5d^{10}$$

with a filled 5*d* subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

## Summary

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**.

## Contributors and Attributions

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# 1.4: Development of Chemical Bonding Theory

## Key Terms

Make certain that you can define, and use in context, the key terms below.

- bond strength
- covalent bond
- ionic bond
- Lewis structure
- lone-pair electron
- non-bonding electron

## Study Notes

To draw Lewis structures successfully, you need to know the number of valence electrons present in each of the atoms involved. Memorize the number of valence electrons possessed by each of the elements commonly encountered in organic chemistry: C, H, O, N, S, P and the halogens.

When drawing any organic structure, you must remember that a neutral carbon atom will almost always have four bonds. Similarly, hydrogen always has one bond; neutral oxygen atoms have two bonds; and neutral nitrogen atoms have three bonds. By committing these simple rules to memory, you can avoid making unnecessary mistakes later in the course.

The “wedge-and-broken-line” type of representation, which helps to convey the three-dimensional nature of organic compounds, will be used throughout the course.

## Bonding Overview

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond and the general properties found in typical substances in which the bond type occurs will be discussed.

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involve a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involve one nonmetallic element with another
3. Metallic bonds are found in solid metals (copper, iron, aluminum) with each metal atom bonded to several neighboring metal atoms and the bonding electrons are free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

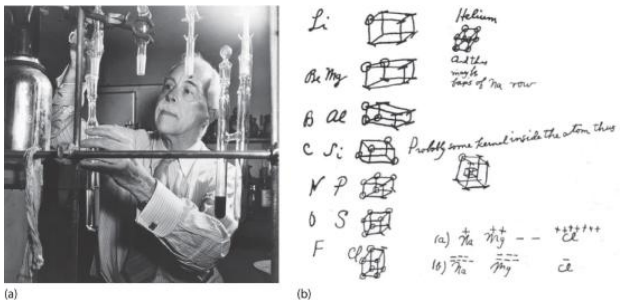



Figure 1.4.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis’s original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

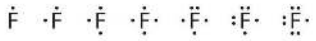
## Lewis Symbols

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called Lewis electron dot symbols, often shortened to *Lewis dot symbols*—that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

**Lewis Dot symbols:**

- provide a convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. Fluorine, for example, with the electron configuration $[He]2s^22p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



| Group | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|
| Electron Configuration | $[He]2s^1$ | $[He]2s^2$ | $[He]2s^22p^1$ | $[He]2s^22p^2$ | $[He]2s^22p^3$ | $[He]2s^22p^4$ | $[He]2s^22p^5$ | $[He]2s^22p^6$ |
| Lewis Dot Symbol | Li · | ·Be· | · B · | · C · | · N · | : O · | : F · | :Ne: |

Figure 1.4.2: Lewis Dot Symbols for the Elements in Period 2

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 1.4.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds. Lewis symbols are a tool to help draw structures. We will see why bonding in molecular compounds follow Lewis' theory in the next section.

Elements in the same period have the same number of valence electrons and similar Lewis symbols. For example, the electron configuration for atomic sulfur is $[Ne]3s^23p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be similar oxygen and look like:



## The Octet Rule

Lewis's major contribution to bonding theory was to recognize that atoms tend to lose, gain, or share electrons to reach a total of eight valence electrons, called an *octet*. This so-called octet rule explains the stoichiometry of most compounds in the *s* and *p* blocks of the periodic table. We now know from quantum mechanics that the number eight corresponds to one *ns* and three *np* valence orbitals, which together can accommodate a total of eight electrons. Remarkably, though, Lewis's insight was made nearly a decade before Rutherford proposed the nuclear model of the atom. Common exceptions to the octet rule are helium, whose $1s^2$ electron configuration gives it a full $n = 1$ shell, and hydrogen, which tends to gain or share its one electron to achieve the electron configuration of helium.

Lewis's idea of an octet explains why noble gases rarely form compounds. They have the stable $s^2p^6$ configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration. This explains why atom combine together to form compounds. By forming bond the makes

the atoms more stable and lower in energy. Making bonds releases energy and represents a driving force for the formation of compounds.

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

## Lewis Structures

Lewis structures represent how Lewis symbols gain, lose, or share electrons to obtain an octet by forming compounds.

## Lewis Structures of Ionic Compounds

Whenever there is a metal present in the structure of an organic compound, there is a high likelihood that at least one ionic bond is present. Ionic bonds are represented differently in Lewis structures than covalent bonds. Great care should be taken whenever drawing the Lewis structure of an organic compounds which contains and ionic bond. Ionic bonds typically are formed when a metal and a nonmetal are part of a compound. Some atoms achieve an octet by fully gaining or losing electrons to form ions. Ionic bonds form through the eletrostatic attraction of the created ions. The formula for table salt is NaCl. It is the result of $Na^+$ ions and $Cl^-$ ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why? Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium ($1s^2 2s^2 2p^6 3s^1$) has one valence electron, so giving it up would result in the same electron configuration as neon ($1s^2 2s^2 2p^6$). Chlorine ($1s^2 2s^2 2p^6 3s^2 3p^7$)has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon ($1s^2 2s^2 2p^6 3s^2 3p^8$) when it gains an electron.

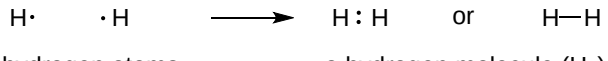
The Lewis structure of an ionic compound show the movement of electrons. For NaCl, sodium is in group 1 and has one valence electron and chlorine is in group 17 and has seven valence electrons. Sodium loses its sole valence electron thereby becomes positively charged. Chlorine gains this electron, gaining a full octet, and a negative charge. After the gain/loss of an electron the new Lewis structures of $Na^+$ and $Cl^-$ are written next to each other representing the ionic bond in NaCl.

## Examples of Lewis Structures of Ionic Compounds

| Metal | | Nonmetal | | Ionic Compound |
|---|---|---|---|---|
| Na· | + | :Cl· | → | $Na^+[:\ddot{Cl}:]^-$ |
| sodium atom | | chlorine atom | | sodium chloride (sodium ion and chloride ion) |
| ·Mg· | + | :O· | → | $Mg^{2+}[:\ddot{O}:]^{2-}$ |
| magnesium atom | | oxygen atom | | magnesium oxide (magnesium ion and oxide ion) |
| ·Ca· | + | 2 :F· | → | $Ca^{2+}[:\ddot{F}:]^-_2$ |
| calcium atom | | fluorine atoms | | calcium fluoride (calcium ion and two fluoride ions) |

## Covalent Bonds and the Lewis Structures of Molecular Compounds

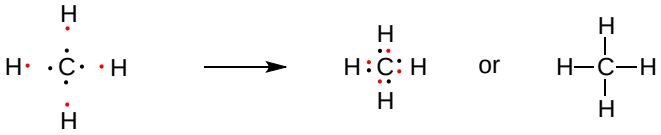
While alkali metals (such as sodium and potassium), alkaline earth metals (such as magnesium and calcium), and halogens (such as fluorine and chlorine) often form ions in order to achieve a full octet, the principle elements of organic chemistry - carbon, hydrogen, nitrogen, and oxygen - instead tend to fill their octet by *sharing* electrons with other atoms, forming covalent bonds. Consider the simplest case of hydrogen gas. An isolated hydrogen atom has only one electron, located in the 1*s* orbital. If two hydrogen atoms come close enough so that their respective 1*s* orbitals overlap, the two electrons can be shared between the two nuclei, and a covalently bonded $H_2$ molecule is formed. In the Lewis structure of $H_2$, each pair of electrons that is shared between two atoms is drawn as a single line, designating a single covalent bond.



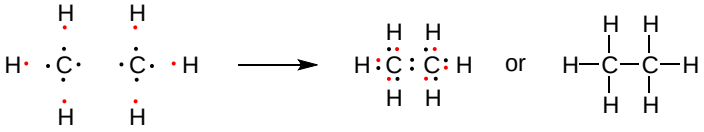

two hydrogen atoms — a hydrogen molecule ($H_2$)

Hydrogen represents a special case, because a hydrogen atom cannot fulfill the octet rule; it needs only two electrons to have a full shell. This is often called the ‘doublet rule’ for hydrogen.

One of the simplest organic molecules is methane with the molecular formula $CH_4$. Methane is the ‘natural gas’ burned in home furnaces and hot water heaters, as well as in electrical power generating plants. To illustrate the covalent bonding in methane using a Lewis structure, we first must recognize that, although a carbon atom has a total of six electrons it's Lewis symbol has four unpaired electrons. Following Lewis' theory the carbon atom wants to form four covalent bonds to fill its octet. In a methane molecule, the central carbon atom shares its four valence electrons with four hydrogen atoms, thus forming four bonds and fulfilling the octet rule (for the carbon) and the ‘doublet rule’ (for each of the hydrogens).




The next relatively simple organic molecule to consider is ethane, which has the molecular formula $C_2H_6$. If we draw each atom's Lewis symbol separately, we can see that the octet/doublet rule can be fulfilled for all of them by forming one carbon-carbon bond and six carbon-hydrogen bonds.




The same approach can be used for molecules in which there is no carbon atom. In a water molecule, the Lewis symbol of the oxygen atom has two unpaired electrons. These are paired with the single electron in the Lewis symbols of the hydrogens' two O-H covalent bonds. The remaining four non-bonding electrons on oxygen called ‘lone pairs’.



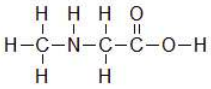

Since the lone pair electrons are often NOT shown in chemical structures, it is important to see mentally add the lone pairs. In the beginning, it can be helpful to physically add the lone pair electrons.



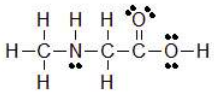

| methylamine | ethanol | chloromethane |
|---|---|---|

## Exercise

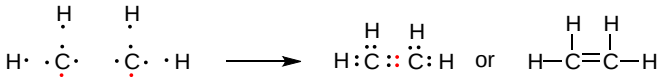
For the following structure, please fill in all of the missing lone pair electrons.



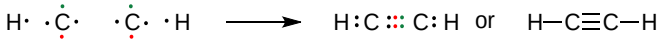
## Answer



When two or more electrons are shared between atoms a multiple covalent bond is formed. The molecular formula for ethene (also known as ethylene, a compound found in fruits, such as apples, that signals them to ripen) is $C_2H_4$. Arranging Lewis symbols of the atoms, you can see that the octet/doublet rule can be fulfilled for all atoms only if the two carbons share *two* pairs of electrons between them. Ethene contains a carbon/carbon double bond.




Following this pattern, the triple bond in ethyne molecular formula $C_2H_2$, (also known as acetylene, the fuel used in welding torches), is formed when the two carbon atoms share *three* pairs of electrons between them.




**? Exercise 1.4.1**

Draw the Lewis structure for ammonia, $NH_3$.

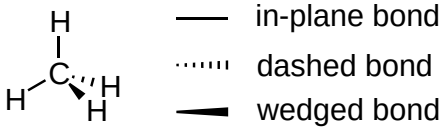
**Answer**



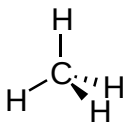
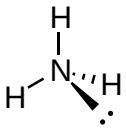
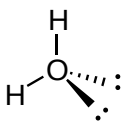
ammonia

## Molecular Shape

A stick and wedge drawing of methane shows the tetrahedral angles...(The wedge is coming out of the paper and the dashed line is going behind the paper. The solid lines are in the plane of the paper.)




The following examples make use of this notation, and also illustrate the importance of including non-bonding valence shell electron pairs when viewing such configurations.

| | | | | | |
|---|---|---|---|---|---|
|  | |  | | |  |
| **Methane** | **Ammonia** | **Water** | | | |

Bonding configurations are readily predicted by valence-shell electron-pair repulsion theory, commonly referred to as **VSEPR** in most introductory chemistry texts. This simple model is based on the fact that electrons repel each other, and that it is reasonable to expect that the bonds and non-bonding valence electron pairs associated with a given atom will prefer to be as far apart as possible. The bonding configurations of carbon are easy to remember, since there are only three categories.

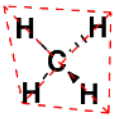
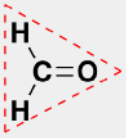
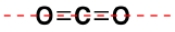
| Configuration | Bonding Partners | Bond Angles | Example |
|---|---|---|---|
| Tetrahedral | 4 | 109.5º |  |
| Trigonal Planar | 3 | 120º |  |
| Linear | 2 | 180º |  |

***Figure 1.4.3***

In the three examples shown above, the central atom (carbon) does not have any non-bonding valence electrons; consequently the configuration may be estimated from the number of bonding partners alone. However, for molecules of water and ammonia, the non-bonding electrons must be included in the calculation. In each case there are four regions of electron density associated with the valence shell so that a tetrahedral bond angle is expected. The measured bond angles of these compounds ($H_2O$ 104.5º & $NH_3$ 107.3º) show that they are closer to being tetrahedral than trigonal planar or linear. Of course, it is the configuration of atoms (not electrons) that defines the the shape of a molecule, and in this sense ammonia is said to be pyramidal (not tetrahedral). The compound boron trifluoride, $BF_3$, does not have non-bonding valence electrons and the configuration of its atoms is trigonal. Nice treatments of VSEPR theory have been provided by Oxford and Purdue. The best way to study the three-dimensional shapes of molecules is by using molecular models. Many kinds of model kits are available to students and professional chemists.

## Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, .

### $AX_2$: $BeH_2$

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is




Figure 1.4.4: Lewis Structure for $BeH_2$

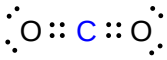
2. There are two electron groups around the central atom. We see from Figure 1.4.3 that the arrangement that minimizes repulsions places the groups 180° apart.

3. Both groups around the central atom are bonding pairs (BP). Thus $BeH_2$ is designated as $AX_2$.

4. From Figure 1.4.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in $BeH_2$ is *linear*.

### $AX_2$: $CO_2$

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like $BeH_2$, the arrangement that minimizes repulsions places the groups 180° apart.

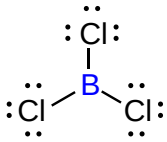
3. Once again, both groups around the central atom are bonding pairs (BP), so $CO_2$ is designated as $AX_2$.

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of $CO_2$ is linear (Figure 1.4.3).

## Three Electron Groups

### $AX_3$: $BCl_3$

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



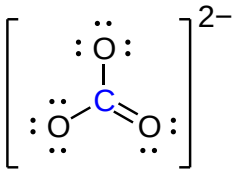
2. There are three electron groups around the central atom. To minimize repulsions, the groups are placed 120° apart (Figure 1.4.3).

3. All electron groups are bonding pairs (BP), so the structure is designated as $AX_3$.

4. From Figure 1.4.3 we see that with three bonding pairs around the central atom, the molecular geometry of $BCl_3$ is *trigonal planar*.

### $AX_3$: $CO_3^{2-}$

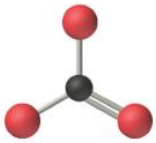
1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



2. The structure of $CO_3^{2-}$ is a resonance hybrid. It has three identical bonds, each with a bond order of 4/3. We minimize repulsions by placing the three groups 120° apart (Figure 1.4.3).

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as $AX_3$.

4. We see from Figure 1.4.3 that the molecular geometry of $CO_3^{2-}$ is trigonal planar.

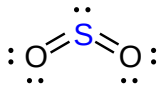


Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

- $AX_2E$: $SO_2$

  1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.



2. There are three electron groups around the central atom, two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Figure 1.4.3).

3. There are two bonding pairs and one lone pair, so the structure is designated as $AX_2E$. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 1.4.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In $SO_2$, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 1.4.2.1 and 1.4.3).

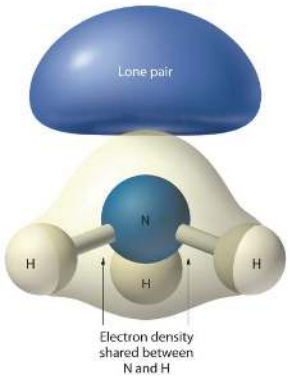
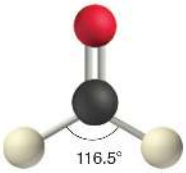



Figure 1.4.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair

As with $SO_2$, this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as $CH_2O$ ($AX_3$), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).

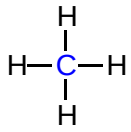



- ## Four Electron Groups

  One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

  ### $AX_4$: $CH_4$

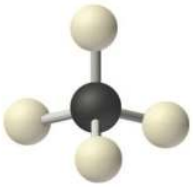
  1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is



2. There are four electron groups around the central atom. As shown in Figure 1.4.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

3. All electron groups are bonding pairs, so the structure is designated as $AX_4$.

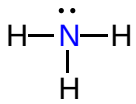
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 1.4.3).



Molecular geometry
(tetrahedral)

### $AX_3E$: $NH_3$

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



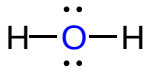
2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

3. With three bonding pairs and one lone pair, the structure is designated as $AX_3E$. This designation has a total of four electron pairs, three X and one E. We expect the LP–BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 1.4.3). However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsions.

### $AX_2E_2$: $H_2O$

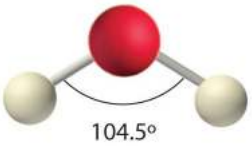
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



2. There are four groups around the central oxygen atom, two bonding pairs and two lone pairs. Repulsions are minimized by directing the bonding pairs and the lone pairs to the corners of a tetrahedron Figure 1.4.3.

3. With two bonding pairs and two lone pairs, the structure is designated as $AX_2E_2$ with a total of four electron pairs. Due to LP–LP, LP–BP, and BP–BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H–O–H angle that is even less than the H–N–H angles in $NH_3$, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one.. This molecular shape is essentially a tetrahedron with two missing vertices.




## Exercises

- ## Contributors and Attributions
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# 1.5: Describing Chemical Bonds - Valence Bond Theory

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- bond strength
- covalent bond
- bond length
- sigma (σ) bond
- pi ($\pi$) bond
- valence bond theory

## Valence Bond Theory

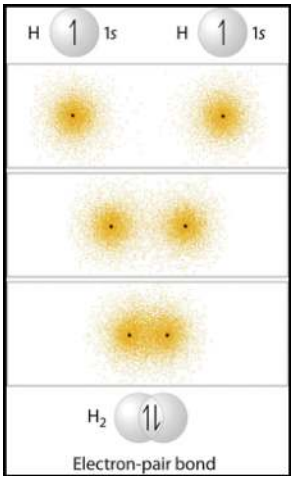
As we have been discussing how to use Lewis structures to depict the bonding in organic compounds, we have been very vague so far in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the 'sharing' of a pair of electrons between two atoms – but how does this happen, and how does it lead to the formation of a bond holding the two atoms together? Two main models have been developed to described how covalent bonds are formed: valence bond theory and molecularly orbital theory.

Valence bond theory is most often used to describe bonding in organic molecules. In this model, covalent bonds are considered to form from the overlap of two atomic orbitals on different atoms, each orbital containing a single electron. The electrons become paired in the orbital overlap bonding the atoms together.

The simplest example valence bond theory can be demonstrated by the $H_2$ molecule. We can see from the periodic table that each hydrogen atom has a single valence electron. If 2 hydrogen atoms come together to form a bond, then each hydrogen atom effectively has a share in both electrons and thus each resembles the noble gas helium and is more stable. The 2 electrons shared in the orbital overlap are represented by a single dash between the atoms.

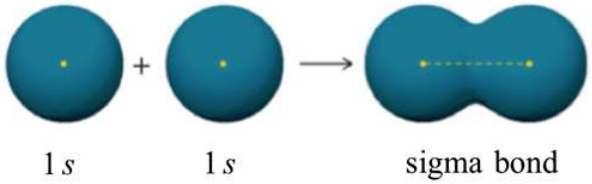



Valence bond theory describes a chemical bond as the overlap of atomic orbitals. In the case of the hydrogen molecule, the 1s orbital of one hydrogen atom overlaps with the 1s orbital of the second hydrogen atom to form a molecular orbital called a sigma bond which contains two electrons of opposite spin. The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.




ne more characteristic of the covalent bond in $H_2$ is important to consider at this point. The two overlapping 1*s* orbitals can be visualized as two spherical balloons being pressed together. This means that the bond has **cylindrical symmetry**: if we were to take

a cross-sectional plane of the bond at any point, it would form a circle. This type of bond is referred to as a **σ(sigma) bond**.




The energy of the system depends on how much the orbitals overlap. The energy diagram below illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is called the the bond lengths between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration.

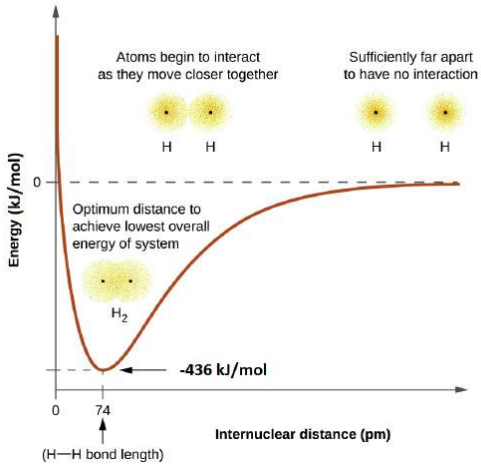



Figure 1.5.2 A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen **Atoms**

This optimal internuclear distance is the **bond length**. For the $H_2$ molecule, the distance is 74 pm (picometers, $10^{-12}$ meters). Likewise, the difference in potential energy between the lowest energy state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond dissociation energy,** or, more simply**, bond strength**. For the hydrogen molecule, the H-H bond strength is equal to about 435 kJ/mol. This means it would take 435 kJ to break one mole of H-H bonds.

Every covalent bond in a given molecule has a characteristic length and strength. In general, the length of a typical carbon-carbon single bond in an organic molecule is about 150 pm, while carbon-carbon double bonds are about 130 pm, carbon-oxygen double bonds are about 120 pm, and carbon-hydrogen bonds are in the range of 100 to 110 pm. The strength of covalent bonds in organic molecules ranges from about 234 kJ/mol for a carbon-iodine bond (in thyroid hormone, for example), about 410 kJ/mole for a typical carbon-hydrogen bond, and up to over 800 kJ/mole for a carbon-carbon triple bond.

## Representative Bond Energies and Lengths

| Bond | Length (pm) | Energy (kJ/mol) | | Bond | Length (pm) | Energy (kJ/mol) |
|---|---|---|---|---|---|---|
| H-H | 74 | 436 | | C-O | 140.1 | 358 |
| H-C | 106.8 | 413 | | C=O | 119.7 | 745 |

| Bond | Length (pm) | Energy (kJ/mol) | | Bond | Length (pm) | Energy (kJ/mol) |
|---|---|---|---|---|---|---|
| H-N | 101.5 | 391 | | C≡O | 113.7 | 1072 |
| H-O | 97.5 | 467 | | H-Cl | 127.5 | 431 |
| C-C | 150.6 | 347 | | H-Br | 141.4 | 366 |
| C=C | 133.5 | 614 | | H-I | 160.9 | 298 |
| C≡C | 120.8 | 839 | | O-O | 148 | 146 |
| C-N | 142.1 | 305 | | O=O | 120.8 | 498 |
| C=N | 130.0 | 615 | | F-F | 141.2 | 159 |
| C≡N | 116.1 | 891 | | Cl-Cl | 198.8 | 243 |

## Contributors and Attributions

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- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

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# 1.6: $sp^3$ Hybrid Orbitals and the Structure of Methane

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

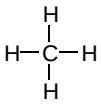
- bond angle
- hybridization
- $sp^3$ hybrid

**Study Notes**

The tetrahedral shape is a very important one in organic chemistry, as it is the basic shape of all compounds in which a carbon atom is bonded to four other atoms. Note that the tetrahedral bond angle of $\mathrm{H-C-H}$ is 109.5°.

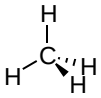
## Valence Bond Theory

Valence bond theory's use of overlapping atomic orbitals to explain how chemical bonds form works well in simple diatomic molecules such as $H_2$. However, when molecules with more than two atoms form stable bonds, we require a more detailed model. A good example is methane ($CH_4$). According to valence bond theory, the structure of a covalent species can be depicted using a Lewis structure.



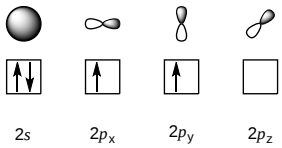
**1**

Experimentally, it has been shown that the four carbon-hydrogen bonds in the methane molecule are identical, meaning they have the same bond energy and the same bond length. Also, VSEPR theory suggests that the geometry at the carbon atom in the methane molecule is tetrahedral **(2)**, and there exists a large body of both theoretical and experimental evidence supporting this prediction.



**2**

According to valence bond theory, to form a covalent bond forms when an unpaired electron in one atom overlaps with an unpaired electron in a different atom. Now, consider the the electron configuration of the four valence electrons in carbon.




There is a serious mismatch between the electron configuration of carbon ($1s^2 2s^2 2p^2$) and the predicted structure of methane. The modern structure shows that there are only 2 unpaired electrons to share with hydrogens, instead of the 4 needed to create methane. Also, the $p_x$ and $p_y$ orbitals are at $90^o$ to each other. They would form perpendicular bonds instead of the tetrahedral $109.5^o$ bond angle predicted by VSEPR and experimental data. Lastly, there are two different orbitals, 2*s* and 2*p*, which would create different types of C-H bonds. As noted earlier, experimentally, the four carbon-hydrogen bonds in the methane molecule are identical.

### Hybrid Orbitals

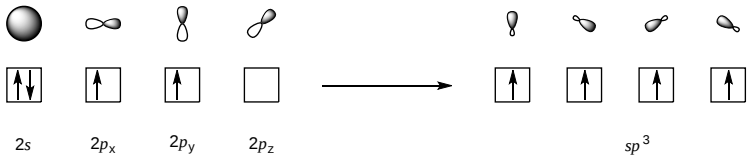
An answer to the problems posed above was offered in 1931 by Linus Pauling. He showed mathematically that an *s* orbital and three *p* orbitals on an atom can combine to form four equivalent hybrid atomic orbitals.

**Important Ideals in Understanding Hybridization**

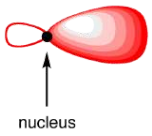
1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom create the molecular geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds.
7. Lone pair electrons are often contained in hybrid orbitals

## $sp^3$ Hybridization in Methane

In order to explain this observation, valence bond theory relies on a concept called **orbital hybridization**. In this picture, the four valence orbitals of the carbon (one 2*s* and three 2*p* orbitals) combine mathematically (remember: orbitals are described by equations) to form four equivalent **hybrid orbitals**, which are named ***sp*$^3$ orbitals** because they are formed from mixing one *s* and three *p* orbitals. In the new electron configuration, each of the four valence electrons on the carbon occupies a single $sp^3$ orbital creating four unpaired electrons.




The shape of an $sp^3$ hybridized orbital is a combination of *s* and *p* atomic orbitals.




Each $sp^3$-hybridized orbital bears an electron, and electrons repel each other. To minimize the repulsion between electrons, the four $sp^3$-hybridized orbitals arrange themselves around the carbon nucleus so that they are as far away as possible from each other, resulting in the tetrahedral arrangement predicted by VSPER. The carbon atom in methane is called an "$sp^3$-hybridized carbon atom." The larger lobes of the $sp^3$ hybrids are directed towards the four corners of a tetrahedron, meaning that the angle between any two orbitals is 109.5°.

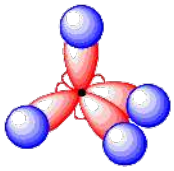


5

## Bonding in Methane

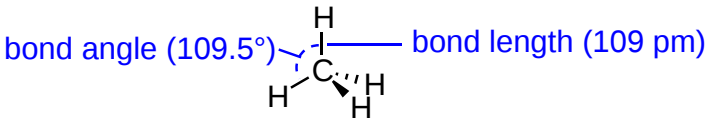
Each C-H bond in methane, then, can be described as an overlap between a half-filled 1*s* orbital in four hydrogen atoms and the larger lobe of one of the four half-filled $sp^3$ hybrid orbitals form a four equivalent sigma (σ) bond. This orbital overlap is often described using the notation: $sp^3$(C)-1*s*(H). The formation of $sp^3$ hybrid orbitals successfully explains the tetrahedral structure of methane and the equivalency of the the four C-H bonds.

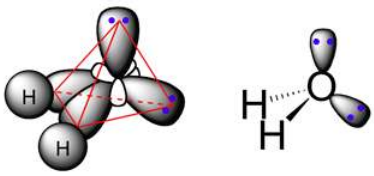
What remains is an explanation of why the $sp^3$ hybrid orbitals form. When the *s* and 3 *p* orbitals in carbon hybridize the resulting $sp^3$ hybrid orbital is unsymmetrical with one lobe larger than the other. This means the larger lobe can overlap more effectively with orbitals from other bonds making them stronger. Hybridizing allows for the carbon to form stronger bonds than it would with unhybridized *s* or *p* orbitals.



6

The four carbon-hydrogen bonds in methane are equivalent and all have a bond length of 109 pm (1.09 x 10-10 m), bond strength of of 429 kJ/mol. All of the H-C-H bond angles are 109.5°.



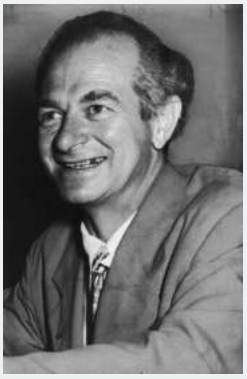




## Looking Closer: Linus Pauling

Arguably the most influential chemist of the 20th century, Linus Pauling (1901–1994) is the only person to have won two individual (that is, unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book *The Nature of the Chemical Bond* is one of the most significant books ever published in chemistry.

Pauling's big contribution to chemistry was valence bond theory, which combined his knowledge of quantum mechanical theory with his knowledge of basic chemical facts, like bond lengths and and bond strengths and shapes of molecules. Valence bond theory, like Lewis's bonding theory, provides a simple model that is useful for predicting and understanding the structures of molecules, especially for organic chemistry. .

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was very close to discovering the double helix structure of DNA when James Watson and James Crick announced their own discovery of its structure in 1953.) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.



*Linus Pauling was one of the most influential chemists of the 20th century.*

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal

## Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Gamini Gunawardena from the OChemPal site (Utah Valley University)
- Dr. Krista Cunningham

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# 1.7: sp² Hybrid Orbitals and the Structure of Ethylene

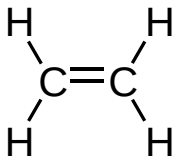
**Key Terms**

Make certain that you can define, and use in context, the key terms below.

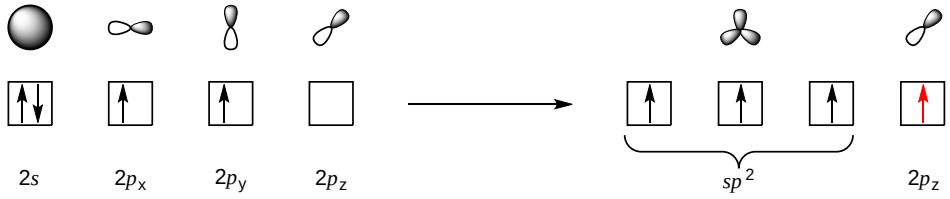
- pi (π) bond
- $sp^2$ hybrid

## Bonding in Ethylene

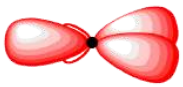
Thus far valence bond theory has been able to describe the bonding in molecules containing only single bonds. However, when molecules contain double or triple bonds the model requires more details. Ethylene (commonly knows as ethene), $CH_2CH_2$, is the simplest molecule which contains a carbon carbon double bond. The Lewis structure of ethylene indicates that there are one carbon-carbon double bond and four carbon-hydrogen single bonds. Experimentally, the four carbon-hydrogen bonds in the ethylene molecule have been shown to be identical. Because each carbon is surrounded by three electron groups, VSEPR theory says the molecule should have a trigonal planar geometry. Although each carbon has fulfilled its tetravalent requirement, one bond appears different. Clearly, a different type of orbital overlap is involved.



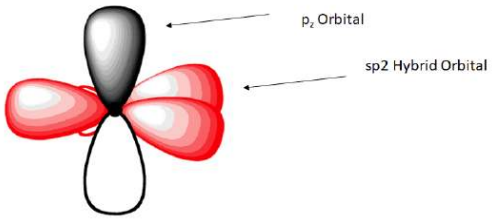

The sigma bonds formed in ethene is by the participation of a different kind of hybrid orbital. Three atomic orbitals on each carbon – the 2*s*, $2p_x$ and $2p_y$ – combine to form three $sp^2$ hybrids, leaving the $2p_z$ orbital unhybridized. Three of the four valence electrons on each carbon are distributed to the three $sp^2$ hybrid orbitals, while the remaining electron goes into the unhybridized $p_z$ orbital. Each carbon in ethene is said to be a "$sp^2$-hybridized carbon." The electron configuration of the $sp^2$ hybridized carbon shows that there are four unpaired electrons to form bonds. However, the unpaired electrons are contained in two different types of orbitals so it is to be expected that two different types of bonds will form.



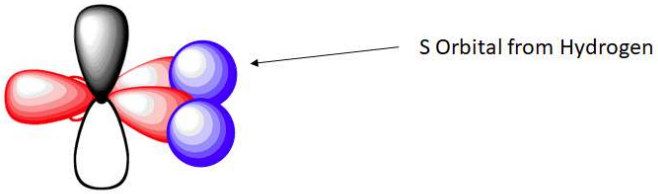

The shape of the $sp^2$-hybridized orbital has be mathematically shown to to be roughly the same as that of the $sp^3$-hybridized orbital. To minimize the repulsion between electrons, the three $sp^2$-hybridized orbitals are arranged with a trigonal planar geometry. Each orbital lobe is pointing to the three corners of an equilateral triangle, with angles of 120° between them. Again, geometry and hybrization can be tied together. Atoms surrounded by three electron groups can be said to have a trigonal planar geometry and $sp^2$ hybridization.



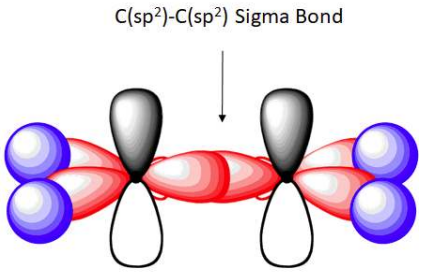
The unhybridized $2p_z$ orbital is *perpendicular* to the plane of the trigonal planar $sp^2$ hybrid orbtals.



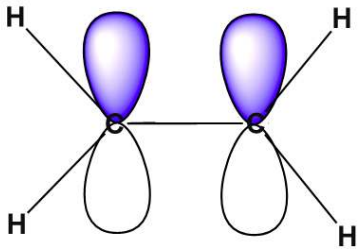

In the ethylene molecule, each carbon atom is bonded to two hydrogen atoms. Thus, overlap two $sp^2$-hybridized orbitals with the 1s orbitals of two hydrogen atoms for the C-H sigma bonds in ethylene ($sp^2$(C)-1s(H). Consequently, consistent with the observations, the four carbon-hydrogen bonds in ethylene are identical.



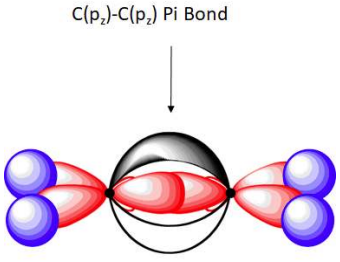

The C-C sigma bond in ethylene is formed by the overlap of an $sp^2$ hybrid orbital from each carbon.



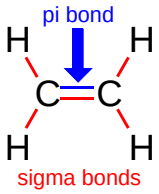

The overlap of hybrid orbitals or a hybrid orbital and a 1s orbtial from hydrogen creates the sigma bond framework of the ethylene molecule. However the unhybridized $p_z$ orbital on each carbon remains.



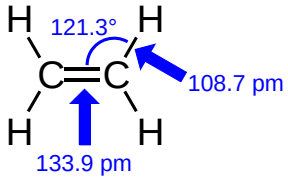

The unhybridized pz orbitals on each carbon overlap to a π bond (pi). The orbital overlap is commonly written as $p_z$(C)-1$p_z$(C). In general multiple bonds in molecular compound are formed by the overlap of unhybridized p orbitals. It should be noted that the carbon-carbon double bond in ethlene is made up of two different types of bond, a sigma and a pi.



Overall, ethylene is said to contain five sigma bonds and one pi bond. Pi bonds tend to be weaker than sigma bonds because the side-by-side overlap the p orbitals give a less effective orbital overlap when compared to the end-to-end orbital overlap of a sigma bond. This makes the pi much easier to break which is one of the most important ideas in organic chemistry reactions as we will see in Chapter 7 and subsequent chapters.

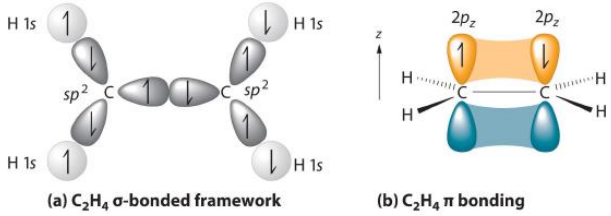



An ethylene molecule is said to be made up of five sigma bonds and one pi bond. The three $sp^2$ hybrid orbitals on each carbon orient to create the basic trigonal planer geometry. The H-C-C bond angle in ethylene is $121.3^o$ which is very close to the $120^o$ predicted by VSEPR. The four C-H sigma bonds in ethylene . The carbon-carbon double bond in ethylene is both shorter (133.9 pm) and almost twice as strong (728 kJ/mol) than the carbon- carbon single bond in ethylene (154 pm & 377 kJ/mol). Each of the four carbon-hydrogen bond in ethylene are equivalent has have a length of 108.7 pm




## Rigidity in Ethene

Because they are the result of side-by-side overlap (rather then end-to-end overlap like a sigma bond), *pi bonds are not free to rotate.* If rotation about this bond were to occur, it would involve disrupting the side-by-side overlap between the two $2p_z$ orbitals that make up the pi bond. If free rotation were to occur the p-orbitals would have to go through a phase where they are 90° from each other, which would break the pi bond because there would be no overlap. Since the pi bond is essential to the structure of ethene it must not break, so there can be not free rotation about the carbon-carbon sigma bond. The presence of the pi bond thus 'locks' the six atoms of ethene into the same plane.




(a) $C_2H_4$ σ-bonded framework (b) $C_2H_4$ π bonding

## Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Dr. Krista Cunningham

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# 1.8: sp Hybrid Orbitals and the Structure of Acetylene

**Key Terms**

Make certain that you can define, and use in context, the key term below.

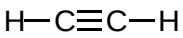
- *sp* hybrid orbital

**Study Notes**

The bond angles associated with $sp^3$-, $sp^2$- and *sp*-hybridized carbon atoms are approximately 109.5°, 120° and 180°, respectively.

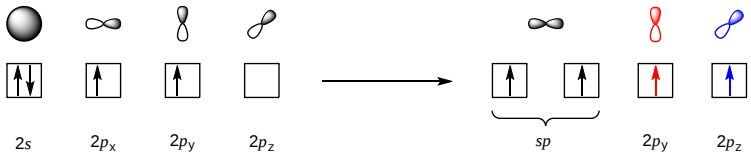
## Bonding in acetylene

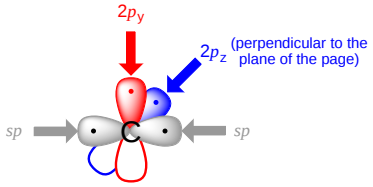
Finally, the hybrid orbital concept applies well to triple-bonded groups, such as alkynes and nitriles. Consider, for example, the structure of ethyne (another common name is acetylene), the simplest alkyne.



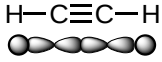
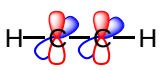
ethyne
(acetylene)

This molecule is linear: all four atoms lie in a straight line. The carbon-carbon triple bond is only 1.20Å long. In the hybrid orbital picture of acetylene, both carbons are ***sp*-hybridized**. In an *sp*-hybridized carbon, the 2*s* orbital combines with the $2p_x$ orbital to form two *sp* hybrid orbitals that are oriented at an angle of 180°with respect to each other (eg. along the x axis). The $2p_y$ and $2p_z$ orbitals remain non-hybridized, and are oriented perpendicularly along the y and z axes, respectively.

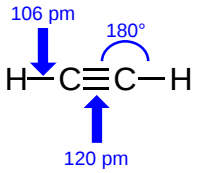



The C-C sigma bond is formed by the overlap of one *sp* orbital from each of the carbons, while the two C-H sigma bonds are formed by the overlap of the second *sp* orbital on each carbon with a 1*s* orbital on a hydrogen. Each carbon atom still has two half-filled $2p_y$ and $2p_z$ orbitals, which are perpendicular both to each other and to the line formed by the sigma bonds. These two perpendicular pairs of *p* orbitals form two pi bonds between the carbons, resulting in a triple bond overall (one sigma bond plus two pi bonds).

| | |
|---|---|
|  |  |
| sigma bonding in ethylene | pi bonding in ethylene |

Acetylene is said to have three sigma bonds and two pi bonds. The carbon-carbon triple bond in acetylene is the shortest (120 pm) and the strongest (965 kJ/mol) of the carbon-carbon bond types. Because each carbon in acetylene has two electron groups, VSEPR predicts a linear geometry and and H-C-C bond angle of 180°.

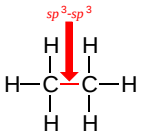
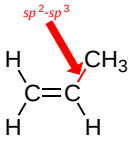
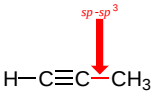



## Comparison of C-C bonds Ethane, Ethylene, and Acetylene

| Molecule | Bond | Bond Strength (kJ/mol) | Bond Length (pm) |
|---|---|---|---|
| **Ethane, $CH_3CH_3$** | **($sp^3$) C-C ($sp^3$)** | **376** | **154** |
| **Ethylene, $H_2C{=}CH_2$** | **($sp^2$) C=C ($sp^2$)** | **728** | **134** |
| **Acetylene, HC≡CH** | **($sp$) C≡C ($sp$)** | **965** | **120** |

Notice that as the bond order increases the bond length decreases and the bond strength increases.

The hybrid orbital concept nicely explains another experimental observation: single bonds adjacent to double and triple bonds are progressively shorter and stronger than 'normal' single bonds, such as the one in a simple alkane. The carbon-carbon bond in ethane (structure A below) results from the overlap of two $sp^3$ orbitals.

| | | |
|---|---|---|
|  |  |  |
| A | B | C |

In propene (B), however, the carbon-carbon single bond is the result of overlap between an $sp^2$ orbital and an $sp^3$ orbital, while in propyne (C) the carbon-carbon single bond is the result of overlap between an sp orbital and an $sp^3$ orbital. These are all single bonds, but the single bond in molecule C is shorter and stronger than the one in B, which is in turn shorter and stronger than the one in A.

The explanation here is relatively straightforward. An sp orbital is composed of one *s* orbital and one *p* orbital, and thus it has 50% *s* character and 50% *p* character. $sp^2$ orbitals, by comparison, have 33% *s* character and 67% *p* character, while $sp^3$ orbitals have 25% *s* character and 75% *p* character. Because of their spherical shape, 2*s* orbitals are smaller, and hold electrons closer and 'tighter' to the nucleus, compared to 2*p* orbitals. Consequently, bonds involving sp + $sp^3$ overlap (as in alkyne C) are shorter and stronger than bonds involving $sp^2$ + $sp^3$ overlap (as in alkene B). Bonds involving $sp^3$-$sp^3$overlap (as in alkane A) are the longest and weakest of the group, because of the 75% '*p*' character of the hybrids.

## Hybridization Summary

- A single bond is a sigma bond.
- A double bond is made up of a sigma bond and a pi bond.
- A triple bond is made up of a sigma bond and two pi bonds.
- Sigma bonds are made by the overlap of two hybrid orbitals or the overlap of a hybrid orbital and a s orbital from hydrogen.
- Pi bonds are made by the overlap of two unhybridized p orbitals.
- Lone pair electrons are usually contained in hybrid orbitals.

The hybrid orbitals used (and hence the hybridization) depends on how many electron groups are around the atom in question. An electron group can mean either a bonded atom or a lone pair. Molecular geometry is also decided by the number of electron groups so it is directly linked to hybridization.

| # of Electron Groups | Hybrid Orbital Used | Example | Basic Geometry | Basic Bond Angle |
|---|---|---|---|---|
| 2 | sp | —C≡ | Linear | 180º |

| | | | | |
|---|---|---|---|---|
| 3 | $sp^2$ |  | Trigonal Planar | 120º |
| 4 | $sp^3$ |  | Tetrahedral | 109.5º |

## Contributors and Attributions

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# 1.9: Noncovalent Interactions Between Molecules

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- dipole-dipole forces
- London dispersion forces
- hydrogen bond
- intermolecular forces
- noncovalent interaction
- van der Waals forces

**Study Notes**

Much of the material in this section should be familiar to you from your pre-requisite general chemistry course. Nonetheless, this section is important, as it covers some of the fundamental factors that influence many physical and chemical properties.

## Introduction

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

**Note**

The properties of liquids are intermediate between those of gases and solids but are more similar to solids.

Intermolecular forces determine bulk properties such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law.

In this section, we explicitly consider three kinds of intermolecular interactions: dipole-dipole forces, dispersion forces, and hydrogen bonds. These intermolecular interactions are also called van der Waals forces or noncovalent interactions. There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. These are less common with organic molecules, so will not be described further in this section.

## Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure 2.12.1 parts (a and b). Arrangements in which two

positive or two negative ends are adjacent (parts (c and d) in Figure 2.12.1) are higher energy as the similar charges would repel one another. Hence dipole–dipole interactions, such as those in parts (a and b) in Figure 2.12.1, are *attractive intermolecular interactions*, whereas those in part (c and d) are *repulsive intermolecular interactions*.

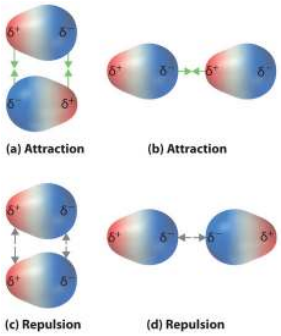



Figure 2.12.1 Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole ($\delta^+$) is near the negative end of another ($\delta^-$) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure 2.12.2. On average, however, the attractive interactions dominate.

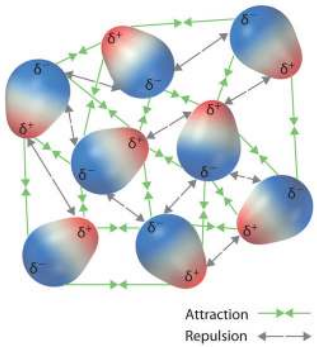
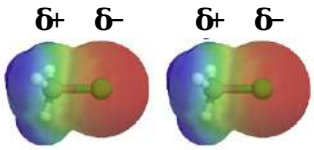



Figure 2.12.2 Both Attractive and Repulsive Dipole–Dipole Interactions Occur in a Liquid Sample with Many Molecules

Chloromethane is an example of a polar molecule. An electrostatic potential map shows a high electron density (seen in red) around the electronegative chlorine giving it a partial negative charge. The other end of the molecule has electron density pulled away from it giving it a partial positive charge seen in blue. The positive and negative ends of different chloromethane molecules are attracted to one another through this electrostatic interaction.






chloromethane
($\mu$ = 1.87 D)

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where $r$ is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^6$, so doubling the distance between the dipoles decreases the strength of the interaction by $2^6$, or 64-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure, whereas NaCl, which is held together by ionic interactions, is a

high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 2.12.1. Using what we learned about predicting relative bond polarities from the electronegativities of the bonded atoms, we can make educated guesses about the relative boiling points of similar molecules.

Table 2.12.1: Relationships between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

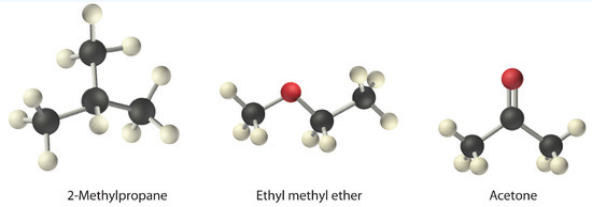
| Compound | Molar Mass (g/mol) | Dipole Moment (D) | Boiling Point (K) |
|---|---|---|---|
| $C_3H_6$ (cyclopropane) | 42 | 0 | 240 |
| $CH_3OCH_3$ (dimethyl ether) | 46 | 1.30 | 248 |
| $CH_3CN$ (acetonitrile) | 41 | 3.9 | 355 |

**Note**

The attractive energy between two ions is proportional to $1/r$, whereas the attractive energy between two dipoles is proportional to $1/r^6$.

**Example 2.12.1**

Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone ($CH_3COCH_3$) in order of increasing boiling points. Their structures are as follows:




**Strategy:**

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

**Solution:**

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds. The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativity values. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point. Ethyl methyl ether has a structure similar to $H_2O$; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point. Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point. Thus we predict the following order of boiling points: 2-methylpropane < ethyl methyl ether < acetone. This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

**Exercise 1.9.1**

Arrange carbon tetrafluoride ($CF_4$), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

**Answer**

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

## London Dispersion Forces

Thus far we have considered only interactions between polar molecules, but other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature, and others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both.

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 2.12.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

| Substance | Molar Mass (g/mol) | Melting Point (°C) | Boiling Point (°C) |
|---|---|---|---|
| Ar | 40 | −189.4 | −185.9 |
| Xe | 131 | −111.8 | −108.1 |
| $N_2$ | 28 | −210 | −195.8 |
| $O_2$ | 32 | −218.8 | −183.0 |
| $F_2$ | 38 | −219.7 | −188.1 |
| $I_2$ | 254 | 113.7 | 184.4 |
| $CH_4$ | 16 | −182.5 | −161.5 |

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 2.12.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by $2^6$, or 64-fold.

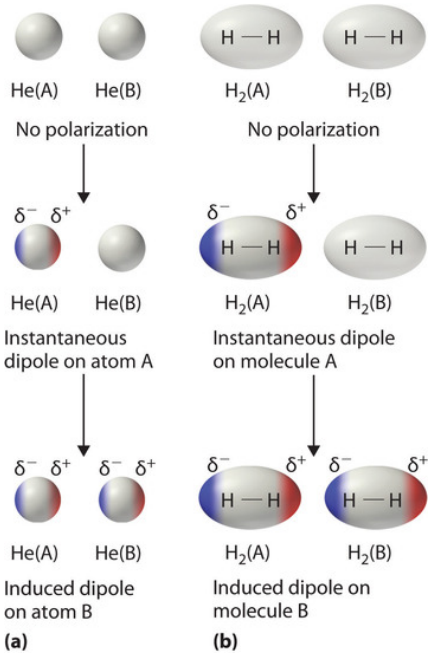



Figure 2.12.3 Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an $H_2$ molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two $H_2$ molecules in part (b) in Figure 2.12.3, tends to become more pronounced as atomic and molecular masses increase (Table 2.12.3). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

**Note**

For similar substances, London dispersion forces get stronger with increasing molecular size.

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 2.12.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 2.12.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula $C_5H_{12}$. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

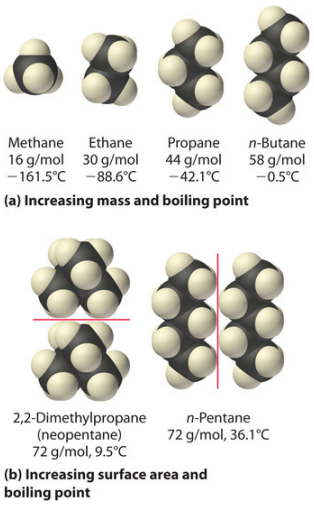



Figure 2.12.4 Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules and consequently higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

### ✔ Example 2.12.2

Arrange *n*-butane, propane, 2-methylpropane [isobutane], and *n*-pentane in order of increasing boiling points.

**Strategy:**

Determine the intermolecular forces in the compounds and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

**Solution:**

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

### Exercise 1.9.2

Arrange $GeH_4$, $SiCl_4$, $SiH_4$, $CH_4$, and $GeCl_4$ in order of decreasing boiling points.

**Answer**

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > $GeH_4$ (−88.5°C) > $SiH_4$ (−111.8°C) > $CH_4$ (−161°C)

## Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 2.12.5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted

on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for $H_2Te$ and $H_2Se$ to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

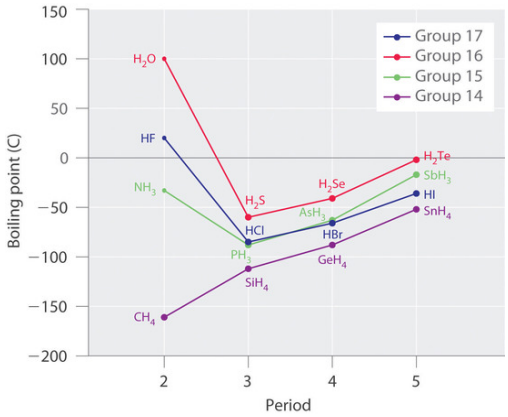



Figure 2.12.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, $NH_3$, and $H_2O$) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 2.12.6.

A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O···H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water rather than sinks.

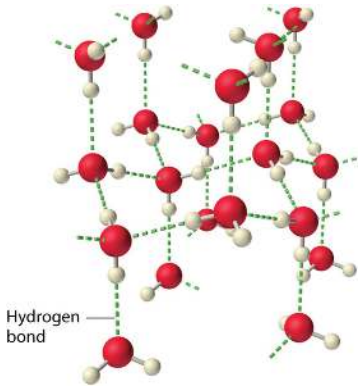



Figure 2.12.6: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cage-like structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

**Note**

Hydrogen bond formation requires *both* a hydrogen bond donor *and* a hydrogen bond acceptor.

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid $NH_3$. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

**Example 2.12.3**

Considering $CH_3OH$, $C_2H_6$, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

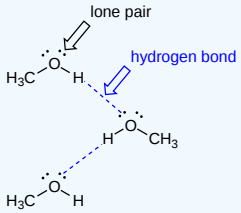
**Strategy:**

A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

**Solution:**

**A** Of the species listed, xenon (Xe), ethane ($C_2H_6$), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

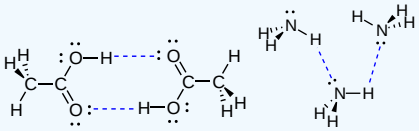
**B** The one compound that can act as a hydrogen bond donor, methanol ($CH_3OH$), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:




**Exercise 2.12.3**

Considering $CH_3CO_2H$, $(CH_3)_3N$, $NH_3$, and $CH_3F$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

**Answer:** $CH_3CO_2H$ and $NH_3$;



### Example 2.12.4

Arrange $C_{60}$ (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and $N_2O$ in order of increasing boiling points.

**Given:** compounds

**Asked for:** order of increasing boiling points

**Strategy:**

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

**Solution:**

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and $N_2O$ have very similar molar masses (40 and 44 g/mol, respectively), but $N_2O$ is polar while Ar is not. Consequently, $N_2O$ should have a higher boiling point. A $C_{60}$ molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or $N_2O$. Because the boiling points of nonpolar substances increase rapidly with molecular mass, $C_{60}$ should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses: He (−269°C) < Ar (−185.7°C) < $N_2O$ (−88.5°C) < $C_{60}$ (>280°C) < NaCl (1465°C).

### Exercise 2.12.4

Arrange 2,4-dimethylheptane, Ne, $CS_2$, $Cl_2$, and KBr in order of decreasing boiling points.

**Answer:** KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > $CS_2$ (46.6°C) > $Cl_2$ (−34.6°C) > Ne (−246°C)

## Summary

Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid or the liquid and gas phases are due to changes in intermolecular interactions but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^6$, where $r$ is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Like dipole–dipole interactions, their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O···Hhydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

## Key Takeaway

- Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds.

## Contributors and Attributions

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- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Electrostatic Potential Maps were made using ChemCompute (Mark Perri)
- Layne Morsch (University of Illinois Springfield)
- Dr. Krista Cunningham

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# 1.10: Drawing Chemical Structures

**Study Notes**

When drawing the structure of a neutral organic compound, you will find it helpful to remember that

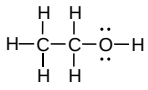
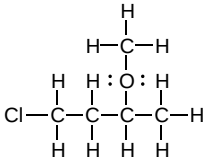
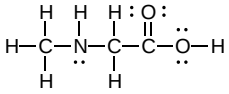
- each carbon atom has four bonds.
- each nitrogen atom has three bonds.
- each oxygen atom has two bonds.
- each hydrogen atom has one bond.

Through general chemistry, you may have already experienced looking at molecular structures using Lewis structures. Because organic chemistry can involve large molecules it would be beneficial if Lewis structures could be abbreviated. The three different ways to draw organic molecules include Kekulé Formulas, Condensed Formulas, and Skeletal structures (also called line-bond structures or line formulas). During this course, you will view molecules written in all three forms. It will be more helpful if you become comfortable going from one style of drawing to another, and look at drawings and understanding what they represent. Developing the ability to convert between different types of formulas requires practice, and in most cases the aid of molecular models. Many kinds of model kits are available to students and professional chemists, and the beginning student is encouraged to obtain one.

Simplification of structural formulas may be achieved without any loss of the information they convey. Kekule formulas is just organic chemistry's term for Lewis structures you have previously encountered. In **condensed structural formulas**, the bonds to each carbon are omitted, but each distinct structural unit (group) is written with subscript numbers designating multiple substituents, including the hydrogens. **Line formulas** omit the symbols for carbon and hydrogen entirely (unless the hydrogen is bonded to an atom other than carbon). Each straight line segment represents a bond, the ends and intersections of the lines are carbon atoms, and the correct number of hydrogens is calculated from the tetravalency of carbon. Non-bonding valence shell electrons are omitted in these formulas.

## Kekulé (a.k.a. Lewis Structures)

A Kekulé Formula or structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. All atom labels are shown and all lone pairs are shown.

| | | |
|---|---|---|
|  |  |  |
| **A** | **B** | **C** |

### Condensed Formula

A condensed formula is made up of the elemental symbols. Condensed structural formulas show the order of atoms like a structural formula but are written in a single line to save space and make it more convenient and faster to write out. The order of the atoms suggests the connectivity in the molecule. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together. Also, if more than one of the same substituent is attached to a given atom, it is show with a subscript number. An example is $CH_4$, which represents four hydrogens attached to the same carbon. Condensed formulas can be read from either direction and $H_3C$ is the same as $CH_3$, although the latter is more common.

Look at the examples below and match them with their identical molecule under the Kekulé structures and the line formulas.

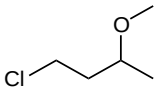
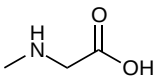
| | | |
|---|---|---|
| $CH_3CH_2OH$ | $ClCH_2CH_2CH(OCH_3)CH_3$ | $CH_3NHCH_2COOH$ |

| A | B | C |
|---|---|---|

Let's look closely at example B. As you go through a condensed formula, you want to focus on the carbons and other elements that aren't hydrogen. The hydrogen's are important, but are usually there to complete octets. Also, notice the -$OCH_3$ is in written in parentheses which tell you that it not part of the main chain of carbons. As you read through a a condensed formula, if you reach an atom that doesn't have a complete octet by the time you reach the next hydrogen, then it's possible that there are double or triple bonds. In example C, the carbon is double bonded to oxygen and single bonded to another oxygen. Notice how COOH means C(=O)-O-H instead of $CH_3$-C-O-O-H because carbon does not have a complete octet and oxygens.

## Line Formula

Because organic compounds can be complex at times, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by replacing the letter "C" with lines. A carbon atom is present wherever a line intersects another line. Hydrogen atoms are omitted but are assumed to be present to complete each of carbon's four bonds. Hydrogens that are attached to elements other than carbon are shown. Atom labels for all other elements are shown. Lone pair electrons are usually omitted. They are assumed to be present to complete the octet of non-carbon atoms. Line formulas help show the structure and order of the atoms in a compound.

|  |  |  |
|---|---|---|
| A | B | C |

These molecules correspond to the exact same molecules depicted for Kekulé structures and condensed formulas. Notice how the carbons are no longer drawn in and are replaced by the ends and bends of a lines. In addition, the hydrogens have been omitted, but could be easily drawn in (see practice problems). Although we do not usually draw in the H's that are bonded to carbon, we do draw them in if they are connected to other atoms besides carbon (example is the OH group above in example A) . This is done because it is not always clear if the non-carbon atom is surrounded by lone pairs or hydrogens. Also in example A, notice how the OH is drawn with a bond to the second carbon, but it does not mean that there is a third carbon at the end of that bond/ line.

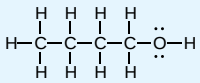
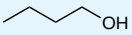
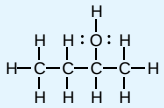
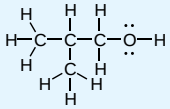
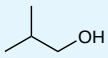
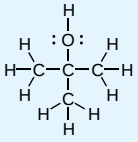
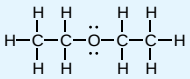
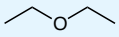
| Kekulé Formula | Condensed Formula | Line Formula |
|---|---|---|
|  | $CH_3(CH_2)_3OH$ |  |
|  | $CH_3CH_2CH(OH)CH_3$ |  |
|  | $(CH_3)_2CHCH_2OH$ |  |
|  | $(CH_3)_3COH$ |  |
|  | $CH_3CH_2OCH_2CH_3$ |  |

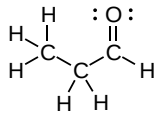
**Table 1.10.1 :** Structural Formulas for $C_4H_{10}O$ isomers

## Example: Converting between Structural Formulas

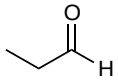
It is helpful to convert compounds into different structural formulas (Kekule, Line, and Condensed) depending on the type of question that is asked. Standardized exams frequently include a high percentage of condensed formulas because it is easier and cheaper to type letters and numbers than to import figures. Initially, it can be difficult writing a Line structure directly from a condensed formula. First, write the Kekule structure from the condensed formula and then draw the Line structure from the Kekule.

a) The condensed formula for propanal is $CH_3CH_2CHO$. Draw the Kekule structure.

The Kekule structure for propanal is shown below. Remember that every carbon will have four bonds and oxygens octet is filled with lone pairs.

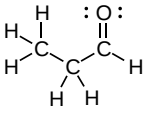


The bond-line structure for propanal is shown below. First, remove hydrogens. The hydrogen attached to the aldehyde group remains because it is part of a functional group. The remove the "C" labels from the structure and keep the lines in place. Lastly, remove any lone pairs.

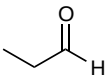


All three structures represent the same compound, propanal.

$CH_3CH_2CHO$ =



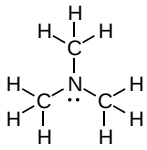
=



b) The following is the line structure of the molecule trimethyl amine.



To convert it to a Kekule structure first identify the carbons in the molecule. The will be at the corners and ends of line without an atom label. Trimethyl amine has three carbons. Next, add hydrogens to the carbons until four bonds are present. Each carbon in trimethyl amine is singly bonded to nitrogen. This means each carbon will need three additional C-H bonds to create its octet. Lastly, add lone pairs to other elements to fill their octets. The nitrogen in trimethyl amine is bonded to three carbons. This means it will require one of lone pair electrons to complete its octet.



## Exercises

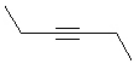
1. How many carbons are in the following drawing? How many hydrogens?



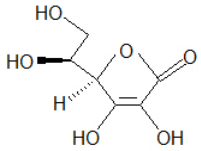
2. How many carbons are in the following drawing? How many hydrogens?



3. How many carbons are in the following drawing? How many hydrogens?

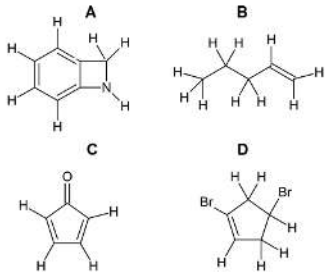


4. Look at the following molecule of vitamin A and draw in the hidden hydrogens and electron pairs.



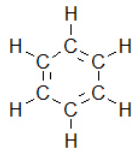

(hint: Do all of the carbons have 4 bonds? Do all the oxygens have a full octet?)

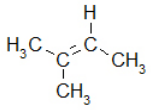
5. Draw $ClCH_2CH_2CH(OCH_3)CH_3$ in Kekulé and line form.
6. Write down the molecular formula for each of the compounds shown here.



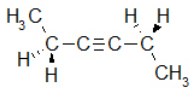

## Answers:

1. Remember the octet rule and how many times carbons and hydrogens are able to bond to other atoms.



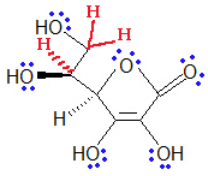



2.

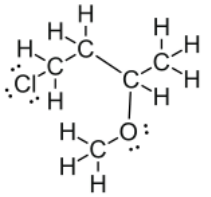


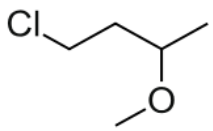

3.

4. Electron pairs drawn in blue and hydrogens draw in red.



5.





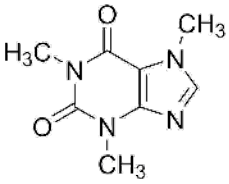
6.

A. $C_7H_7N$
B. $C_5H_{10}$
C. $C_5H_4O$
D. $C_5H_6Br_2$

## Questions

**Q1.12.1**

Below is the molecule for caffeine. Give the molecular formula for it.



## Solutions

**S1.12.1**

$C_8H_{10}O_2N_4$

## Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
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- Dr. Krista Cunningham

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# 1.11: Functional Groups

**Key Terms**

Make certain that you can define, and use in context, the key term below.

- functional group

**Study Notes**

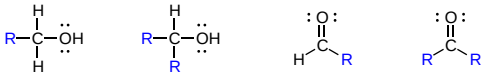
The concept of functional groups is a very important one. We expect that you will need to refer back to tables at the end of Section 3.1 quite frequently at first, as it is not really feasible to learn the names and structures of all the functional groups and compound types at one sitting. Gradually they will become familiar, and eventually you will recognize them automatically.

**Functional groups** are small groups of atoms that exhibit a characteristic reactivity. A particular functional group will almost always display its distinctive chemical behavior when it is present in a compound. Because of their importance in understanding organic chemistry, functional groups have specific names that often carry over in the naming of individual compounds incorporating the groups.

As we progress in our study of organic chemistry, it will become extremely important to be able to quickly recognize the most common functional groups, because they are the key structural elements that define how organic molecules react. For now, we will only worry about drawing and recognizing each functional group, as depicted by Lewis and line structures. Much of the remainder of your study of organic chemistry will be taken up with learning about how the different functional groups tend to behave in organic reactions.

## Drawing abbreviated organic structures

Often when drawing organic structures, chemists find it convenient to use the letter 'R' to designate part of a molecule outside of the region of interest. If we just want to refer in general to a functional group without drawing a specific molecule, for example, we can use 'R groups' to focus attention on the group of interest:




a primary alcohol | a secondary alcohol | an aldehyde | a ketone

The 'R' group is a convenient way to abbreviate the structures of large biological molecules, especially when we are interested in something that is occurring specifically at one location on the molecule.

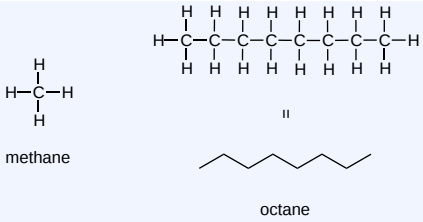
## Common Functional Groups

In the following sections, many of the common functional groups found in organic chemistry will be described. Tables of these functional groups can be found at the bottom of the page.

### Hydrocarbons

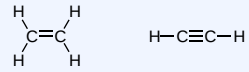
The simplest functional group in organic chemistry (which is often ignored when listing functional groups) is called an **alkane**, characterized by single bonds between two carbons and between carbon and hydrogen. Some examples of alkanes include methane, $CH_4$, is the natural gas you may burn in your furnace or on a stove. Octane, $C_8H_{18}$, is a component of gasoline.

**Alkanes**

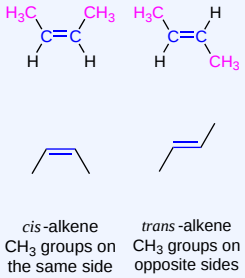



**Alkenes** (sometimes called **olefins**) have carbon-carbon double bonds, and **alkynes** have carbon-carbon triple bonds. Ethene, the simplest alkene example, is a gas that serves as a cellular signal in fruits to stimulate ripening. (If you want bananas to ripen quickly, put them in a paper bag along with an apple - the apple emits ethene gas, setting off the ripening process in the bananas). Ethyne, commonly called acetylene, is used as a fuel in welding blow torches.

**Alkenes and alkynes**



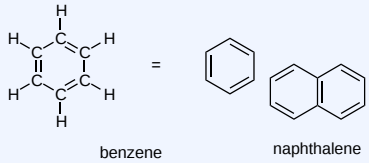

Alkenes have trigonal planar electron geometry (due to $sp^2$ hybrid orbitals at the alkene carbons) while alkynes have linear geometry (due to sp hybrid orbitals at the alkyne carbons). Furthermore, many alkenes can take two geometric forms: ***cis*** or ***trans*** *(or Z and E which will be explained in detail in Chapter 7)*. The *cis* and *trans* forms of a given alkene are different molecules with different physical properties there is a very high energy barrier to rotation about a double bond. In the example below, the difference between *cis* and *trans* alkenes is readily apparent.




Alkanes, alkenes, and alkynes are all classified as **hydrocarbons**, because they are composed solely of carbon and hydrogen atoms. Alkanes are said to be **saturated hydrocarbons**, because the carbons are bonded to the maximum possible number of hydrogens - in other words, they are *saturated* with hydrogen atoms. The double and triple-bonded carbons in alkenes and alkynes have fewer hydrogen atoms bonded to them - they are thus referred to as **unsaturated hydrocarbons**. As we will see in Chapter 7, hydrogen can be added to double and triple bonds, in a type of reaction called 'hydrogenation'.

The **aromatic** group is exemplified by benzene (which used to be a commonly used solvent on the organic lab, but which was shown to be carcinogenic), and naphthalene, a compound with a distinctive 'mothball' smell. Aromatic groups are planar (flat) ring structures, and are widespread in nature. We will learn more about the structure and reactions of aromatic groups in Chapter 15.

### Aromatics



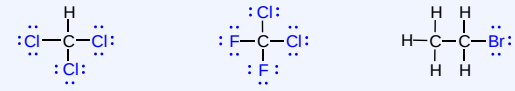


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## Functional Groups with Carbon Single Bonds to other Atoms

### Halides

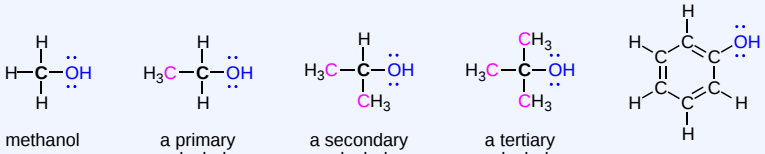
When the carbon of an alkane is bonded to one or more halogens, the group is referred to as a **alkyl halide** or **haloalkane**. The presence of a halogen atom (F, Cl, Br, or I), is often represented by X due to the similar chemistry of halogens. Chloroform is a useful solvent in the laboratory, and was one of the earlier anesthetic drugs used in surgery. Chlorodifluoromethane was used as a refrigerant and in aerosol sprays until the late twentieth century, but its use was discontinued after it was found to have harmful effects on the ozone layer. Bromoethane is a simple alkyl halide often used in organic synthesis. Alkyl halides groups are quite rare in biomolecules.



trichloromethane (chloroform) | dichlorodifluoromethane (Freon-12) | bromoethane

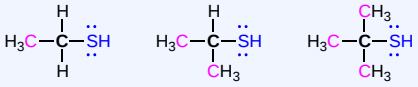
### Alcohols and Thiols

In the **alcohol** functional group, a carbon is single-bonded to an OH group (the OH group, by itself, is referred to as a **hydroxyl**). Except for methanol, all alcohols can be classified as primary, secondary, or tertiary. In a **primary alcohol**, the carbon bonded to the OH group is also bonded to only one other carbon. In a **secondary alcohol** and **tertiary alcohol,** the carbon is bonded to two or three other carbons, respectively. When the hydroxyl group is *directly* attached to an aromatic ring, the resulting group is called a **phenol**.



methanol | a primary alcohol | a secondary alcohol | a tertiary alcohol | a phenol

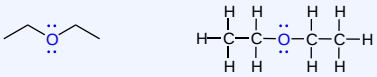
The sulfur analog of an alcohol is called a **thiol** (the prefix *thio*, derived from the Greek, refers to sulfur).



a primary thiol | a secondary thiol | a tertiary thiol

### Ethers and sulfides

In an **ether** functional group, a central oxygen is bonded to two carbons. Below are the line and Lewis structures of diethyl ether, a common laboratory solvent and also one of the first medical anaesthesia agents.

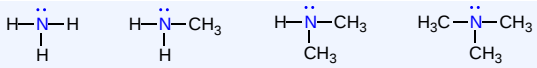


In **sulfides**, the oxygen atom of an ether has been replaced by a sulfur atom.



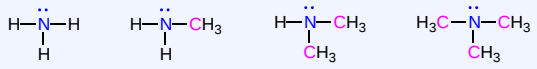
### Amines

**Amines** are characterized by nitrogen atoms with single bonds to hydrogen and carbon. Just as there are primary, secondary, and tertiary alcohols, there are primary, secondary, and tertiary amines. Ammonia is a special case with no carbon atoms.

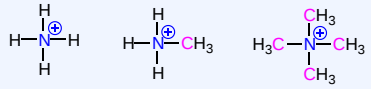


ammonia | a primary amine | a secondary amine | a tertiary amine

One of the most important properties of amines is that they are basic, and are readily protonated to form **ammonium** cations. In the case where a nitrogen has four bonds to carbon (which is somewhat unusual in biomolecules), it is called a quaternary ammonium ion.

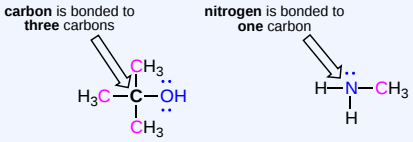


ammonia | a primary amine | a secondary amine | a tertiary amine



ammonium ion | a primary ammonium ion | a quaternary ammonium ion

**Note:** Do not be confused by how the terms 'primary', 'secondary', and 'tertiary' are applied to alcohols and amines - the definitions are different. In alcohols, what matters is how many other carbons the alcohol *carbon* is bonded to, while in amines, what matters is how many carbons the *nitrogen* is bonded to.

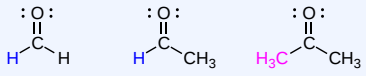



a tertiary alcohol | a primary amine

## Carbonyl Containing Functional Groups

### Aldehydes and Ketones

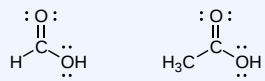
There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.



formaldehyde | an aldehyde | a ketone

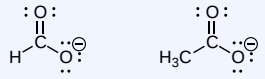
### Carboxylic acids and acid derivatives

If a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to a **heteroatom** (in organic chemistry, this term generally refers to oxygen, nitrogen, sulfur, or one of the halogens), the functional group is considered to be one of the '**carboxylic acid derivatives'**, a designation that describes a grouping of several functional groups. The eponymous member of this grouping is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl (OH) group.



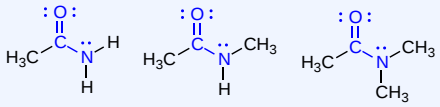
formic acid | acetic acid (vinegar)

As the name implies, carboxylic acids are acidic, meaning that they are readily deprotonated to form the conjugate base form, called a **carboxylate** (much more about carboxylic acids in Chapter 20).

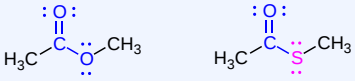


formate acetate

In **amides**, the carbonyl carbon is bonded to a nitrogen. The nitrogen in an amide can be bonded either to hydrogens, to carbons, or to both. Another way of thinking of an amide is that it is a carbonyl bonded to an amine.

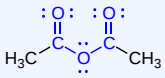


In **esters**, the carbonyl carbon is bonded to an oxygen which is itself bonded to another carbon. Another way of thinking of an ester is that it is a carbonyl bonded to an alcohol. **Thioesters** are similar to esters, except a sulfur is in place of the oxygen.



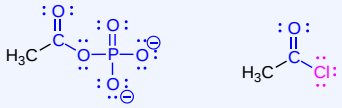
an ester a thioester

In an **acid anhydride**, there are two carbonyl carbons with an oxygen in between. An acid anhydride is formed from combination of two carboxylic acids with the loss of water (anhydride).



an anhydride

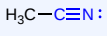
In an **acyl phosphate**, the carbonyl carbon is bonded to the oxygen of a phosphate, and in an **acid chloride**, the carbonyl carbon is bonded to a chlorine.



an acyl phosphate an acid chloride

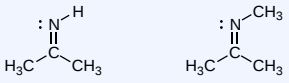
## Nitriles and Imines

In a **nitrile** group, a carbon is triple-bonded to a nitrogen. Nitriles are also often referred to as **cyano** groups.



a nitrile

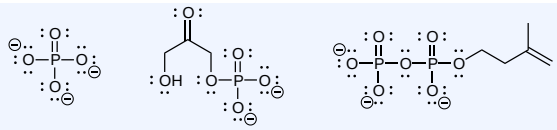
Molecules with carbon-nitrogen double bonds are called **imines**, or **Schiff bases**.



imines

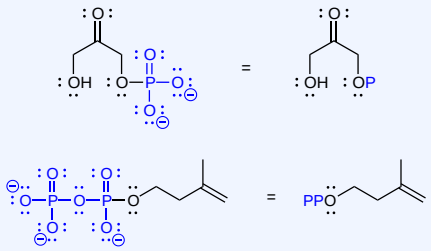
## Phosphates

Phosphorus is a very important element in biological organic chemistry, and is found as the central atom in the **phosphate** group. Many biological organic molecules contain phosphate, diphosphate, and triphosphate groups, which are linked to a carbon atom by the **phosphate ester** functionality.



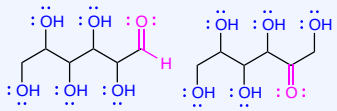
inorganic phosphate | an organic phosphate ester | an organic diphosphate ester

Because phosphates are so abundant in biological organic chemistry, it is convenient to depict them with the abbreviation 'P'. Notice that this 'P' abbreviation includes the oxygen atoms and negative charges associated with the phosphate groups.



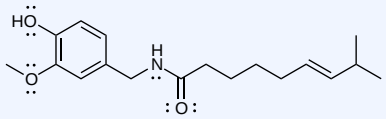
## Molecules with Multiple Functional Groups

A single compound may contain several different functional groups. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol**').



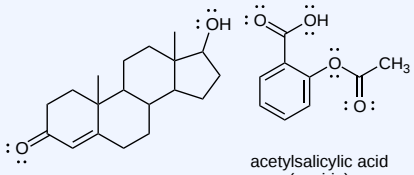
glucose | fructose

Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.



capsaicin

The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.

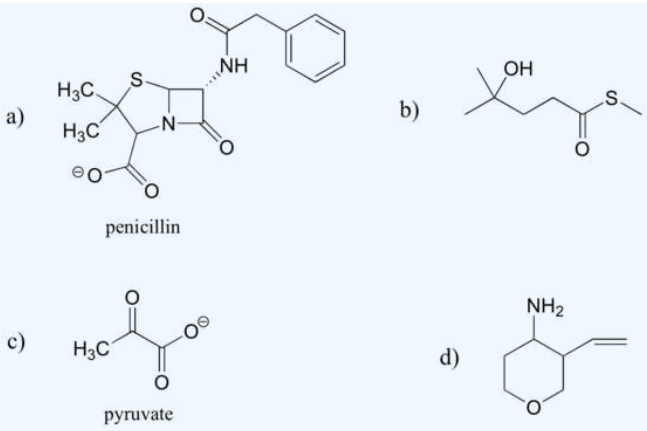


testosterone | acetylsalicylic acid (aspirin)

While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological and laboratory organic chemistry. The table found below provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

### Exercise 1.11.1

Identify the functional groups in the following organic compounds. State whether alcohols and amines are primary, secondary, or tertiary.




**Answer**

a) carboxylate, sulfide, aromatic, two amide groups (one of which is cyclic)

b) tertiary alcohol, thioester

c) carboxylate, ketone

d) ether, primary amine, alkene

2: Draw one example each (there are many possible correct answers) of compounds fitting the descriptions below, using line structures. Be sure to designate the location of all non-zero formal charges. All atoms should have complete octets (phosphorus may exceed the octet rule).

a) a compound with molecular formula $C_6H_{11}NO$ that includes alkene, secondary amine, and primary alcohol functional groups

b) an ion with molecular formula $C_3H_5O_6P^{2-}$ that includes aldehyde, secondary alcohol, and phosphate functional groups.

c) A compound with molecular formula $C_6H_9NO$ that has an amide functional group, and does *not* have an alkene group.

## Functional Group Tables

### Exclusively Carbon Functional Groups

| Group Formula | Class Name | Specific Example | IUPAC Name | Common Name |
|---|---|---|---|---|
|  | alkene | $H_2C{=}CH_2$ | ethene | ethylene |
|  | alkyne | $HC{\equiv}CH$ | ethyne | acetylene |
|  | arene | $C_6H_6$ | benzene | benzene |

### Functional Groups with Single Bonds to Heteroatoms

| Group Formula | Class Name | Specific Example | IUPAC Name | Common Name |
|---|---|---|---|---|
|  | halide | $H_3C$-I | iodomethane | methyl iodide |
|  | alcohol | $CH_3CH_2OH$ | ethanol | ethyl alcohol |
|  | ether | $CH_3CH_2OCH_2CH_3$ | diethyl ether | ether |

| Group Formula | Class Name | Specific Example | IUPAC Name | Common Name |
|---|---|---|---|---|
|  | amine | $H_3C\text{-}NH_2$ | aminomethane | methylamine |
|  | nitro compound | $H_3C\text{-}NO_2$ | nitromethane | |
|  | thiol | $H_3C\text{-}SH$ | methanethiol | methyl mercaptan |
|  | sulfide | $H_3C\text{-}S\text{-}CH_3$ | dimethyl sulfide | |

## Functional Groups with Multiple Bonds to Heteroatoms

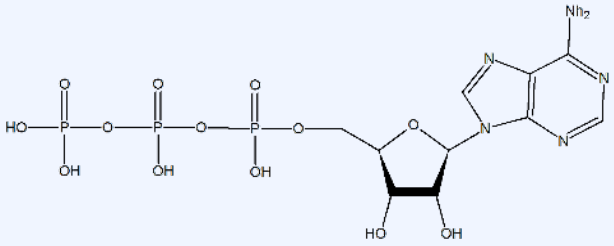
| Group Formula | Class Name | Specific Example | IUPAC Name | Common Name |
|---|---|---|---|---|
|  | nitrile | $H_3C\text{-}CN$ | ethanenitrile | acetonitrile |
|  | aldehyde | $H_3CCHO$ | ethanal | acetaldehyde |
|  | ketone | $H_3CCOCH_3$ | propanone | acetone |
|  | carboxylic acid | $H_3CCO_2H$ | ethanoic Acid | acetic acid |
|  | ester | $H_3CCO_2CH_2CH_3$ | ethyl ethanoate | ethyl acetate |
|  | acid halide | $H_3CCOCl$ | ethanoyl chloride | acetyl chloride |
|  | amide | $H_3CCON(CH_3)_2$ | N,N-dimethylethanamide | N,N-dimethylacetamide |
|  | acid Anhydride | $(H_3CCO)_2O$ | ethanoic anhydride | acetic anhydride |

## Exercises

## Questions

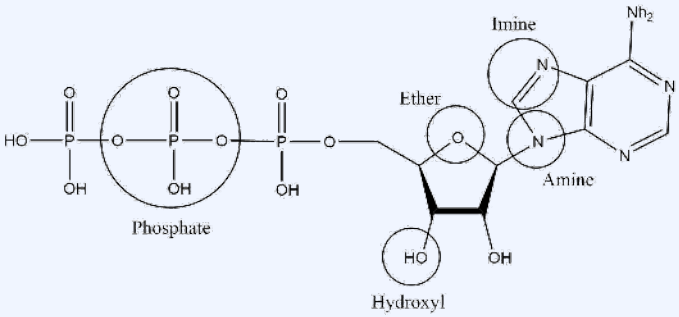
**Q3.1.1**

The following is the molecule for ATP, or the molecule responsible for energy in human cells. Identify the functional groups for ATP.



## Solutions

**S3.1.1**




## Contributors and Attributions

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- Layne Morsch (University of Illinois Springfield)
- Dr. Krista Cunningham

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# 1.12: Formal Charges

**Key Terms**

Make certain that you can define, and use in context, the key term below.

- valence electrons
- bonding and non-bonding electrons
- formal charge
- carbocations

**Study Notes**

It is more important that students learn to easily identify atoms that have formal charges of zero, than it is to actually calculate the formal charge of every atom in an organic compound. Students will benefit by memorizing the "normal" number of bonds and non-bonding electrons around atoms whose formal charge is equal to zero.

## Determining the Formal Charge on an Atom

A **formal charge** compares the number of electrons around a "neutral atom" (an atom not in a molecule) versus the number of electrons around an atom in a molecule. Formal charge is assigned to an atom in a molecule by assuming that electrons in all chemical bonds are shared equally between atoms, regardless of relative electronegativity. To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Non-bonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the two bonded atoms, so one electron from each bond goes to each atom.

The formal charge of each atom in a molecule can be calculated using the following equation:

**Formal Charge = (# of valence electrons in free atom) − (# of lone-pair electrons) − (1/2 # of bond pair electrons)** *Eqn. 2.3.1*

To illustrate this method, let's calculate the formal charge on the atoms in ammonia ($NH_3$) whose Lewis structure is as follows:



A neutral nitrogen atom has five valence electrons (it is in group 15). From the Lewis structure, the nitrogen atom in ammonia has one lone pair and three bonds with hydrogen atoms. Substituting into Equation 2.3.1, we obtain

*Formal Charge of N = (5 valence e-) − (2 lone pair e-) − (1/2 x 6 bond pair e-) = 0*

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule has no non-bonding electrons and one bond. Using Equation 2.3.1 to calculate the formal charge on hydrogen, we obtain

*Formal Charge of H = (1 valence e-) − (0 lone pair e-) − (1/2 x 2 bond pair e-) = 0*

The sum of the formal charges of each atom must be equal to the overall charge of the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall neutral charge of the $NH_3$ molecule.

Typically, the structure with the most formal charges of zero on atoms is the more stable Lewis structure. In cases where there MUST be positive or negative formal charges on various atoms, the most stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges for polyatomic ions.

## Example 2.3.1

Calculate the formal charges on each atom in the $NH_4^+$ ion.

**Given:** chemical species

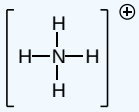
**Asked for:** formal charges

**Strategy:**

Identify the number of valence electrons in each atom in the $NH_4^+$ ion. Use the Lewis electron structure of $NH_4^+$ to identify the number of bonding and non-bonding electrons associated with each atom and then use Equation 2.3.1 to calculate the formal charge on each atom.

**Solution:**

The Lewis electron structure for the $NH_4^+$ ion is as follows:



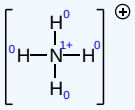
The nitrogen atom in ammonium has zero non-bonding electrons and 4 bonds. Using Equation 2.3.1, the formal charge on the nitrogen atom is therefore

$$\textit{Formal Charge of N} = \textit{(5 valence e-)} - \textit{(0 lone pair e-)} - \textit{(1/2 x 8 bond pair e-)} = 1+$$

Each hydrogen atom in has one bond and zero non-bonding electrons. The formal charge on each hydrogen atom is therefore

$$\textit{Formal Charge of H} = \textit{(1 valence e-)} - \textit{(0 lone pair e-)} - \textit{(1/2 x 2 bond pair e-)} = 0$$

The formal charges on the atoms in the $NH_4^+$ ion are thus

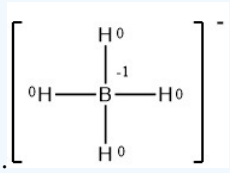


Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is 0 + 1 + 0 + 0 + 0 = 1+, which is the same as the overall charge of the ammonium polyatomic ion.

## Exercise 1.12.1

Write the formal charges on all atoms in $BH_4^-$.

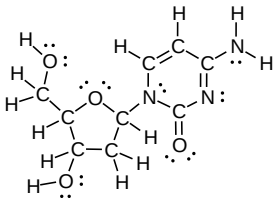
**Answer**



### Determining the Charge of Atoms in Organic Structures

The calculation method reviewed above for determining formal charges on atoms is an essential starting point for a novice organic chemist, and works well when dealing with small structures. But this method becomes unreasonably time-consuming when dealing with larger structures. It would be exceptionally tedious to determine the formal charges on each atom in 2'-deoxycytidine (one of

the four nucleoside building blocks that make up DNA) using equation 2.3.1. As you get more experience with organic structures, you will be able to quickly look at this type of complicated structure and determine charges on each atom.



*2'-deoxycytidine*

You need to develop the ability to quickly and efficiently draw large structures and determine formal charges. Fortunately, this only requires some practice with recognizing common bonding patterns.

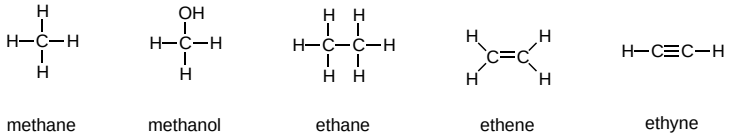
Organic chemistry only deals with a small part of the periodic table, so much so that it becomes convenient to be able to recognize the bonding forms of these atoms. The figure below contains the most important bonding forms. These will be discussed in detail below. An important idea to note is most atoms in a molecule are neutral. Pay close attention to the neutral forms of the elements below because that is how they will appear most of the time.

| Atom | Positive | Neutral | Negative |
|---|---|---|---|
| C |  |  |  |
| N |  |  |  |
| O |  |  |  |
| Cl (halogens) |  |  |  |

Figure 1.12.1: Structures of common organic atoms and ions.

## Carbon

Carbon, the most important element for organic chemists. In the structures of methane, methanol, ethane, ethene, and ethyne, there are four bonds to the carbon atom. And each carbon atom has a formal charge of zero. In other words, carbon is ***tetravalent***, meaning that it commonly forms four bonds.




*Carbon usually makes four bonds*

Carbon is tetravalent in most organic molecules, but there are exceptions. Later in this chapter and throughout this book are examples of organic ions called ‘carbocations’ and carbanions’, in which a carbon atom has a positive or negative formal charge, respectively. ***Carbocations*** occur when a carbon has only three bonds and no lone pairs of electrons. Carbocations have only 3 valence electrons and a formal charge of 1+. ***Carbanions*** occur when the carbon atom has three bonds plus one lone pair of electrons. Carbanions have 5 valence electrons and a formal charge of 1−.

| | | |
|---|---|---|
|  |  |  |

| carbocation: 3 bonds & no lone pair | carbanion: 3 bonds & one lone pair | carbon radical: 3 bonds & one unpaired electron |
|---|---|---|

Two other possibilities are carbon radicals and carbenes, both of which have a formal charge of zero. A ***carbon radical*** has three bonds and a single, unpaired electron. Carbon radicals have 4 valence electrons and a formal charge of zero. ***Carbenes*** are a highly reactive species, in which a carbon atom has two bonds and one lone pair of electrons, giving it a formal charge of zero. Though carbenes are rare, you will encounter them in section 8.10 Addition of Carbenes to Alkenes.

You should certainly use the methods you have learned to check that these formal charges are correct for the examples given above. More importantly, you will need, before you progress much further in your study of organic chemistry, to simply recognize these patterns (and the patterns described below for other atoms) and be able to identify carbons that bear positive and negative formal charges by a quick inspection.

## Hydrogen

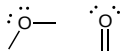
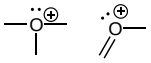
The common bonding pattern for hydrogen is easy: hydrogen atoms in organic molecules typically have only one bond, no unpaired electrons and a formal charge of zero. The exceptions to this rule are the proton, $H^+$, the hydride ion, $H^-$, and the hydrogen radical, $H^{\cdot}$. The ***proton*** is a hydrogen with no bonds and no lone pairs and a formal charge of 1+. The ***hydride ion*** is a is a hydrogen with no bonds, a pair of electrons, and a formal charge of 1−. The ***hydrogen radical*** is a hydrogen atom with no bonds, a single unpaired electron and a formal charge of 0. Because this book concentrates on organic chemistry as applied to living things, however, we will not be seeing 'naked' protons and hydrides as such, because they are too reactive to be present in that form in aqueous solution. Nonetheless, the *idea* of a proton will be very important when we discuss acid-base chemistry, and the *idea* of a hydride ion will become very important much later in the book when we discuss organic oxidation and reduction reactions. As a rule, though, all hydrogen atoms in organic molecules have one bond, and no formal charge.



*Neutral Hydrogen: one bond, no lone pair*

## Oxygen

The common arrangement of oxygen that has a formal charge of zero is when the oxygen atom has 2 bonds and 2 lone pairs. Other arrangements are oxygen with 1 bond and 3 lone pairs, that has a 1− formal charge, and oxygen with 3 bonds and 1 lone pair that has a formal charge of 1+. All three patterns of oxygen fulfill the octet rule.

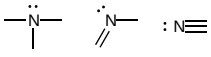
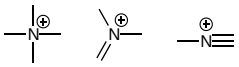
|  |  |  |
|---|---|---|
| neutral oxygen: 2 bonds & 2 lone pairs | negative oxygen: 1 bond & 3 lone pairs | positive oxygen: 3 bonds & one lone pair |

If it has two bonds and two lone pairs, as in water, it will have a formal charge of zero. If it has one bond and three lone pairs, as in hydroxide ion, it will have a formal charge of 1−. If it has three bonds and one lone pair, as in hydronium ion, it will have a formal charge of 1+.

Oxygen can also exist as a radical, such as where an oxygen atom has one bond, two lone pairs, and one unpaired (free radical) electron, giving it a formal charge of zero. For now, however, concentrate on the three main non-radical examples, as these will account for most oxygen containing molecules you will encounter in organic chemistry.

## Nitrogen

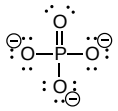
Nitrogen has two major bonding patterns, both of which fulfill the octet rule:

|  |  |  |
|---|---|---|
| neutral nitrogen: 3 bonds & 1 lone pair | positive nitrogen: 4 bonds | negative nitrogen: 2 bonds & 2 lone pairs |

If a nitrogen has three bonds and a lone pair, it has a formal charge of zero. If it has four bonds (and no lone pair), it has a formal charge of 1+. In a fairly uncommon bonding pattern, negatively charged nitrogen has two bonds and two lone pairs.

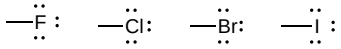
## Phosphorus and Sulfur

Two third row elements are commonly found in biological organic molecules: phosphorus and sulfur. Although both of these elements have other bonding patterns that are relevant in laboratory chemistry, in a biological context sulfur almost always follows the same bonding/formal charge pattern as oxygen, while phosphorus is present in the form of phosphate ion ($PO_4^{3-}$), where it has five bonds (almost always to oxygen), no lone pairs, and a formal charge of zero. Remember that elements in the third row of the periodic table have *d* orbitals in their valence shell as well as *s* and *p* orbitals, and thus are not bound by the octet rule.



## Halogens

The halogens (fluorine, chlorine, bromine, and iodine) are very important in laboratory and medicinal organic chemistry, but less common in naturally occurring organic molecules. Halogens in organic compounds usually are seen with one bond, three lone pairs, and a formal charge of zero. Sometimes, especially in the case of bromine, we will encounter reactive species in which the halogen has two bonds (usually in a three-membered ring), two lone pairs, and a formal charge of 1+.



*Common Neutral Bonding Patterns for Halogens*



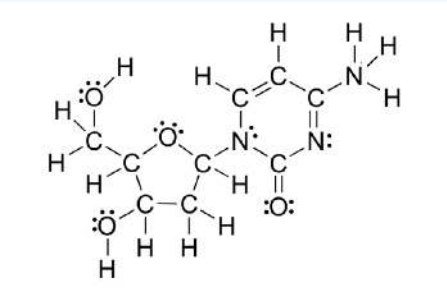
*Common Positive Bonding Pattern for Halogens*

These rules, if learned and internalized so that you don't even need to think about them, will allow you to draw large organic structures, complete with formal charges, quite quickly.

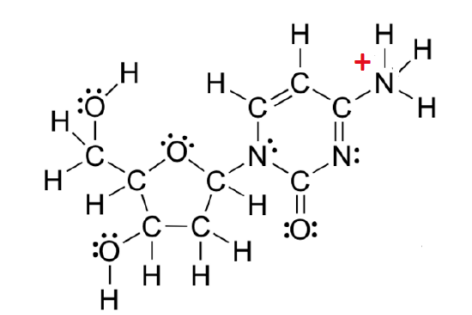
Once you have gotten the hang of drawing Lewis structures, it is not always necessary to draw lone pairs on heteroatoms, as you can assume that the proper number of electrons are present around each atom to match the indicated formal charge (or lack thereof). Occasionally, though, lone pairs are drawn if doing so helps to make an explanation more clear.

### Exercise 1.12.2

Please identify an atom with a non-neutral charge in the following atom:

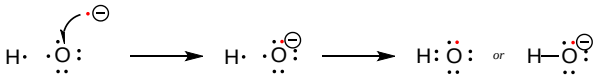


**Answer**

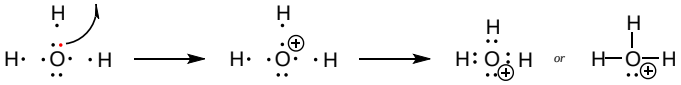


## Drawing the Lewis Structure of Ionic Molecular Compounds

The hydroxide ion, $OH^-$, is drawn simply by showing the oxygen atom with its six valence electrons, then adding one more electron to account for the negative charge. By changing the number of valence electrons the bonding characteristic of oxygen are now changed. Now the oxygen has three non-bonding lone pairs, and can only form one bond to a hydrogen.



To draw a Lewis structure of the hydronium ion, $H_3O^+$, you again start with the oxygen atom with its six valence electrons, then take one away to account for the positive charge to give oxygen five valence electrons. The oxygen has one non-bonding lone pair and three unpaired electrons which can be used to form bonds to three hydrogen atoms.



## Using Formal Charges to Distinguish between Lewis Structures

As an example of how formal charges can be used to determine the most stable Lewis structure for a substance, we can compare two possible structures for $CO_2$. Both structures conform to the rules for Lewis electron structures.

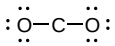
### $CO_2$

1. C is less electronegative than O, so it is the central atom.

2. C has 4 valence electrons and each O has 6 valence electrons, for a total of 16 valence electrons.

3. Placing one electron pair between the C and each O gives O–C–O, with 12 electrons left over.

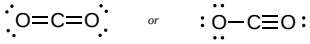
4. Dividing the remaining electrons between the O atoms gives three lone pairs on each atom:



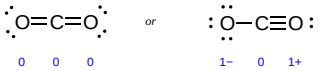
This structure has an octet of electrons around each O atom but only 4 electrons around the C atom.

5. No electrons are left for the central atom.

6. To give the carbon atom an octet of electrons, we can convert two of the lone pairs on the oxygen atoms to bonding electron pairs. There are, however, two ways to do this. We can either take one electron pair from each oxygen to form a symmetrical structure or take both electron pairs from a single oxygen atom to give an asymmetrical structure:



Both Lewis electron structures give all three atoms an octet. How do we decide between these two possibilities? The formal charges for the two Lewis electron structures of $CO_2$ are as follows:




Both Lewis structures have a net formal charge of zero, but the structure on the right has a 1+ charge on the more electronegative atom (O). Thus the symmetrical Lewis structure on the left is predicted to be more stable, and it is, in fact, the structure observed experimentally. Remember, though, that formal charges do *not* represent the actual charges on atoms in a molecule or ion. They are used simply as a bookkeeping method for predicting the most stable Lewis structure for a compound.

**Note**

The Lewis structure with the set of formal charges closest to zero is usually the most stable.

**Example 2.3.2**

The thiocyanate ion ($SCN^-$), which is used in printing and as a corrosion inhibitor against acidic gases, has at least two possible Lewis electron structures. Draw two possible structures, assign formal charges on all atoms in both, and decide which is the preferred arrangement of electrons.

**Given:** chemical species

**Asked for:** Lewis electron structures, formal charges, and preferred arrangement

**Strategy:**

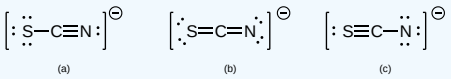
**A** Use the step-by-step procedure to write two plausible Lewis electron structures for $SCN^-$.

**B** Calculate the formal charge on each atom using Equation 2.3.1.

**C** Predict which structure is preferred based on the formal charge on each atom and its electronegativity relative to the other atoms present.

**Solution:**

**A** Possible Lewis structures for the $SCN^-$ ion are as follows:



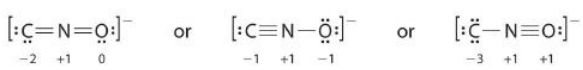

**B** We must calculate the formal charges on each atom to identify the more stable structure. If we begin with carbon, we notice that the carbon atom in each of these structures shares four bonding pairs, the number of bonds typical for carbon, so it has a formal charge of zero. Continuing with sulfur, we observe that in (a) the sulfur atom shares one bonding pair and has three lone pairs and has a total of six valence electrons. The formal charge on the sulfur atom is therefore 6 - (6 + 2/2) = 1−. In (b), the sulfur atom has a formal charge of 0. In (c), the sulfur atom has a formal charge of 1+. Continuing with the nitrogen, we observe that in (a) the nitrogen atom shares three bonding pairs and has one lone pair and has a total of 5 valence electrons. The formal charge on the nitrogen atom is therefore 5 - (2 + 6/2) = 0. In (b), the nitrogen atom has a formal charge of 1−. In (c), the nitrogen atom has a formal charge of 2−.

**C** Which structure is preferred? Structure (b) is preferred because the negative charge is on the more electronegative atom (N), and it has lower formal charges on each atom as compared to structure (c): 0, 1− versus 1+, 2−.

**Exercise 1.12.2**

Salts containing the fulminate ion ($CNO^-$) are used in explosive detonators. Draw three Lewis electron structures for $CNO^-$ and use formal charges to predict which is more stable. (Note: N is the central atom.)

**Answer**



The second structure is predicted to be the most stable.

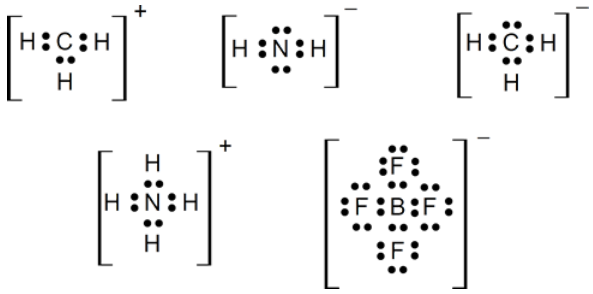
## Exercises

1. Draw the Lewis structure of each of the molecules listed below.

   $CH_3^+$, $NH_2^-$, $CH_3^-$, $NH_4^+$, $BF_4^-$

   In each case, use the method of calculating formal charge described to satisfy yourself that the structures you have drawn do in fact carry the charges shown.

Answer

1. 

## Contributors and Attributions

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- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Layne Morsch (University of Illinois Springfield)
- Dr. Krista Cunningham

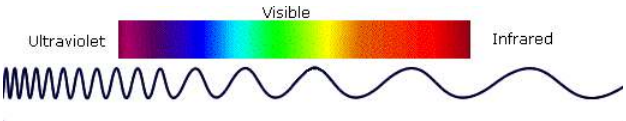
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# 1.13: Infrared (IR) Spectroscopy

## Introduction

Photon energies associated with the infrared (from 1 to 15 kcal/mole) are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups.

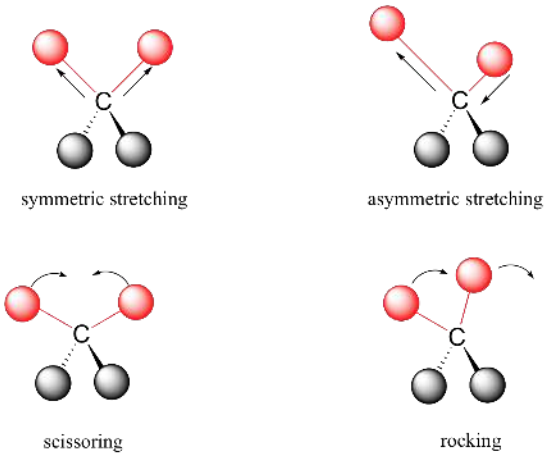



The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and bent. The mobile nature of organic molecules was noted in the chapter concerning conformational isomers. We must now recognize that, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations. Infrared spectrometers, similar in principle to the UV-Visible spectrometer described elsewhere, permit chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure.

## Vibrational Spectroscopy

A molecule composed of n-atoms has 3n degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves 3n-6 degrees of vibrational freedom (3n-5 if the molecule is linear). Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting. The four-atom molecule of formaldehyde, the gas phase spectrum of which is shown below, provides an example of these terms. If a ball & stick model of formaldehyde is not displayed to the right of the spectrum, press the **view ball&stick model** button on the right. We expect six fundamental vibrations (12 minus 6), and these have been assigned to the spectrum absorptions. To see the formaldehyde molecule display a vibration, click one of the buttons under the spectrum, or click on one of the absorption peaks in the spectrum.

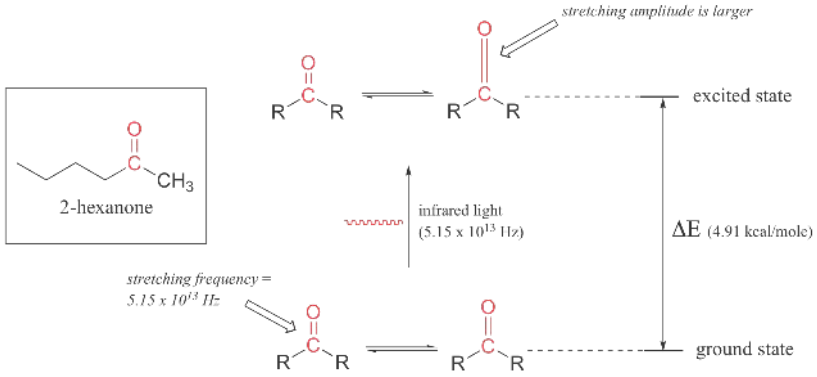
Covalent bonds in organic molecules are not rigid sticks – rather, they behave more like springs. At room temperature, organic molecules are always in motion, as their bonds stretch, bend, and twist. These complex vibrations can be broken down mathematically into individual **vibrational modes**, a few of which are illustrated below.




The energy of molecular vibration is *quantized* rather than continuous, meaning that a molecule can only stretch and bend at certain 'allowed' frequencies. If a molecule is exposed to electromagnetic radiation that matches the frequency of one of its vibrational modes, it will in most cases absorb energy from the radiation and jump to a higher vibrational energy state - what this means is that the *amplitude* of the vibration will increase, but the vibrational *frequency* will remain the same. The difference in energy between the two vibrational states is equal to the energy associated with the wavelength of radiation that was absorbed. It turns out that it is the *infrared* region of the electromagnetic spectrum which contains frequencies corresponding to the vibrational frequencies of organic bonds.

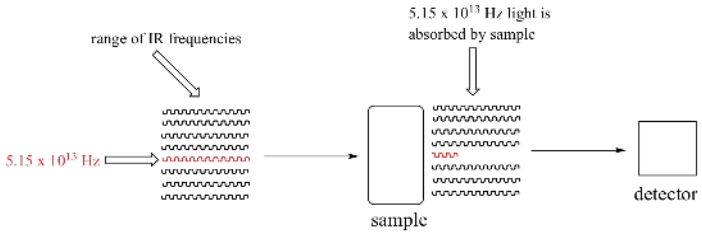
An IR Spectrum

We will use a ketone sample to illustrate this process. The sample is irradiated with infrared light and the carbonyl bond will specifically absorb light with this same frequency, which by equations 4.1 and 4.2 corresponds to a wavelength of 5.83 x $10^{-6}$ m and an energy of 4.91 kcal/mol. When the carbonyl bond absorbs this energy, it jumps up to an excited vibrational state.




The value of **Δ**E - the energy difference between the low energy (ground) and high energy (excited) vibrational states - is equal to 4.91 kcal/mol, the same as the energy associated with the absorbed light frequency. The molecule does not remain in its excited vibrational state for very long, but quickly releases energy to the surrounding environment in form of heat, and returns to the ground state.

With an instrument called an infrared spectrophotometer, we can 'see' this vibrational transition. In the spectrophotometer, infrared light with frequencies ranging from about $10^{13}$ to $10^{14}$ Hz is passed though our sample of cyclohexane. Most frequencies pass right through the sample and are recorded by a detector on the other side.

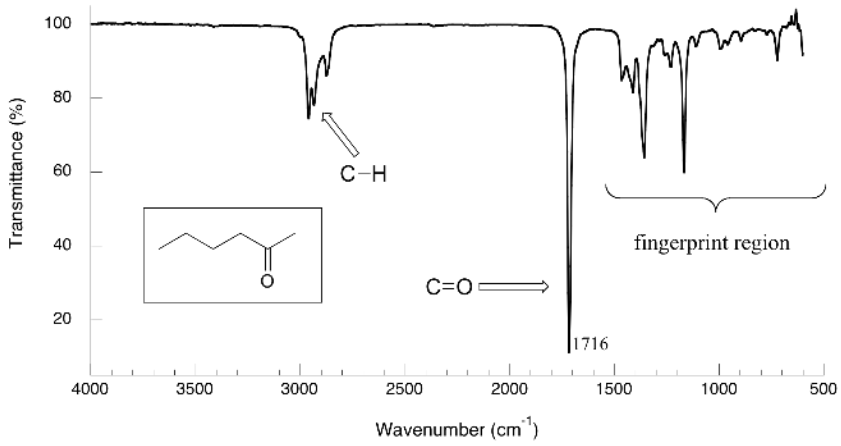



Our 5.15 x $10^{13}$ Hz carbonyl stretching frequency, however, is absorbed by the 2-hexanone sample, and so the detector records that the intensity of this frequency, after having passed through the sample, is something less than 100% of its initial intensity.

The vibrations of a 2-hexanone molecule are not, of course, limited to the simple stretching of the carbonyl bond. The various carbon-carbon bonds also stretch and bend, as do the carbon-hydrogen bonds, and all of these vibrational modes also absorb different frequencies of infrared light.

The power of infrared spectroscopy arises from the observation that *different functional groups have different characteristic absorption frequencies*. The carbonyl bond in a ketone, as we saw with our 2-hexanone example, typically absorbs in the range of 5.11 - 5.18 x $10^{13}$ Hz, depending on the molecule. The carbon-carbon triple bond of an alkyne, on the other hand, absorbs in the range 6.30 - 6.80 x $10^{13}$ Hz. The technique is therefore very useful as a means of identifying which functional groups are present in a molecule of interest. If we pass infrared light through an unknown sample and find that it absorbs in the carbonyl frequency range but not in the alkyne range, we can infer that the molecule contains a carbonyl group but not an alkyne.

Now, let's look at some actual output from IR spectroscopy experiments. Below is the IR spectrum for 2-hexanone.




There are a number of things that need to be explained in order for you to understand what it is that we are looking at. On the horizontal axis we see IR wavelengths expressed in terms of a unit called **wavenumber** ($cm^{-1}$), which tells us how many waves fit into one centimeter. On the vertical axis we see '**% transmittance**', which tells us how strongly light was absorbed at each frequency (100% transmittance means no absorption occurred at that frequency). The solid line traces the values of % transmittance for every wavelength – the 'peaks' (which are actually pointing down) show regions of strong absorption. For some reason, it is typical in IR spectroscopy to report wavenumber values rather than wavelength (in meters) or frequency (in Hz). The 'upside down' vertical axis, with absorbance peaks pointing down rather than up, is also a curious convention in IR spectroscopy. We wouldn't want to make things too easy for you!

A calculator for interconverting these frequency and wavelength values is provided on the right. Simply enter the value to be converted in the appropriate box, press "Calculate" and the equivalent number will appear in the empty box.
Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent). If solvents are used to dissolve solids, care must be taken to avoid obscuring important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used. Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates.

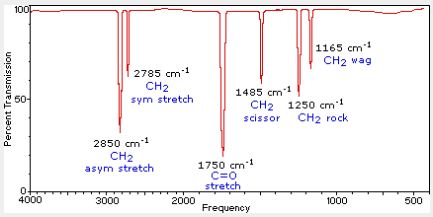
## Frequency - Wavelength Converter

**Frequency in $cm^{-1}$**

Calculate

**Wavelength in µ**

## Gas Phase Infrared Spectrum of Formaldehyde, $H_2C=O$




1. View CH2 Asymmetric Stretch
   View CH2 Symmetric Stretch
   View C=O Stretch
   View CH2 Scissoring
   View CH2 Rocking
   View CH2 Wagging

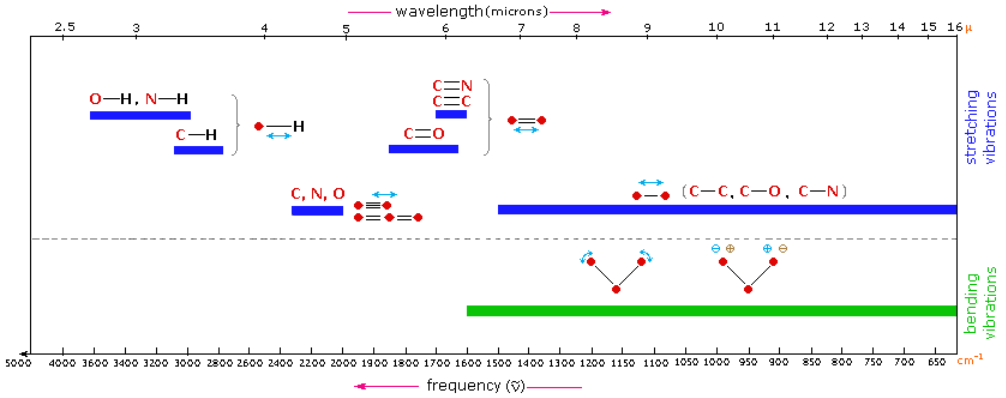
O Ball&Stick Model
O Spacefill Model
O Stick Model
O Motion Off

The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. For a more detailed discussion of these factors Click Here. In practice, infrared spectra do not normally display separate absorption signals for each of the 3n-6 fundamental vibrational modes of a molecule. The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact. Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules. One selection rule that influences the intensity of infrared absorptions, is that a change in dipole moment should occur for a vibration to absorb infrared energy. Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode.

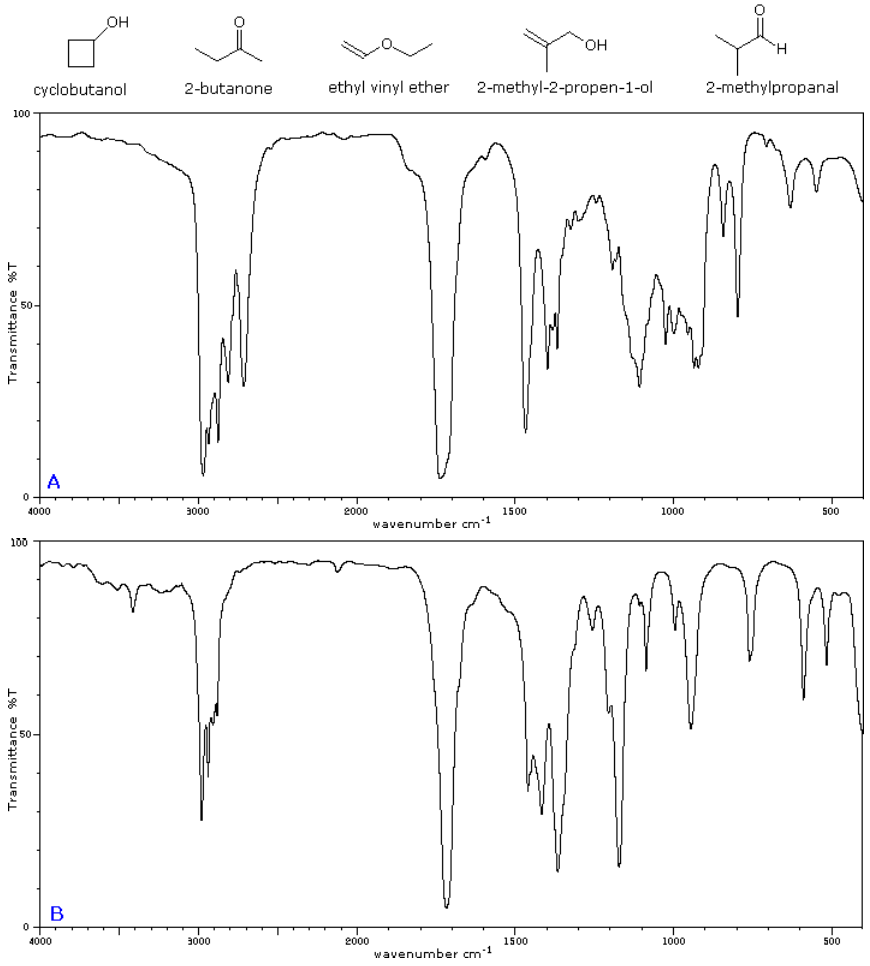
**Some General Trends:**

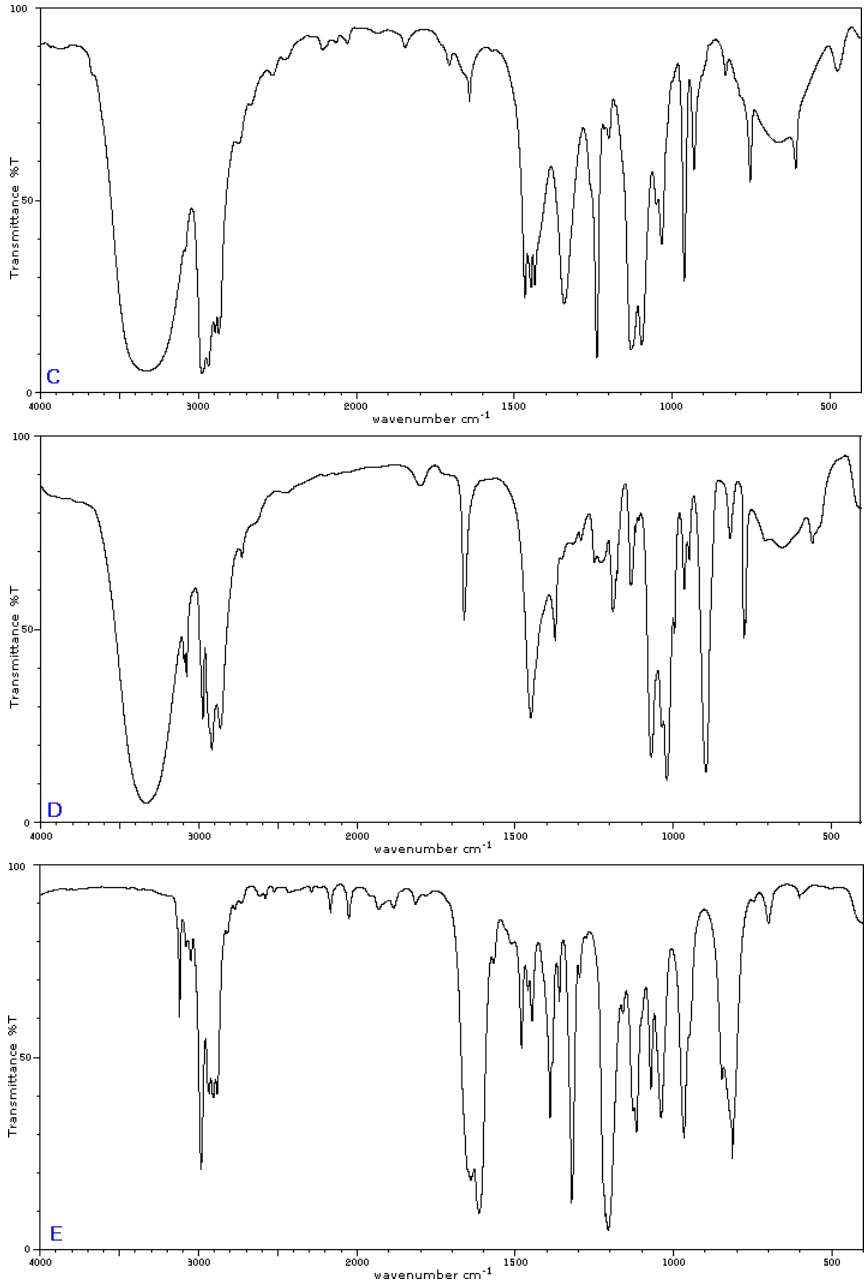
1. Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it.)
2. Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.
3. Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds.(Except for bonds to hydrogen).

The general regions of the infrared spectrum in which various kinds of vibrational bands are observed are outlined in the following chart. Note that the blue colored sections above the dashed line refer to stretching vibrations, and the green colored band below the line encompasses bending vibrations. The complexity of infrared spectra in the 1450 to 600 $cm^{-1}$ region makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the **fingerprint** region. Absorption bands in the 4000 to 1450 $cm^{-1}$ region are usually due to stretching vibrations of diatomic units, and this is sometimes called the **group frequency** region.




To illustrate the usefulness of infrared absorption spectra, examples for five $C_4H_8O$ isomers are presented below their corresponding structural formulas. Try to associate each spectrum (A - E) with one of the isomers in the row above it.






Answers

## Internal Links

- Organic Chemistry With a Biological Emphasis

### Contributors

- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry

## Contributors and Attributions

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- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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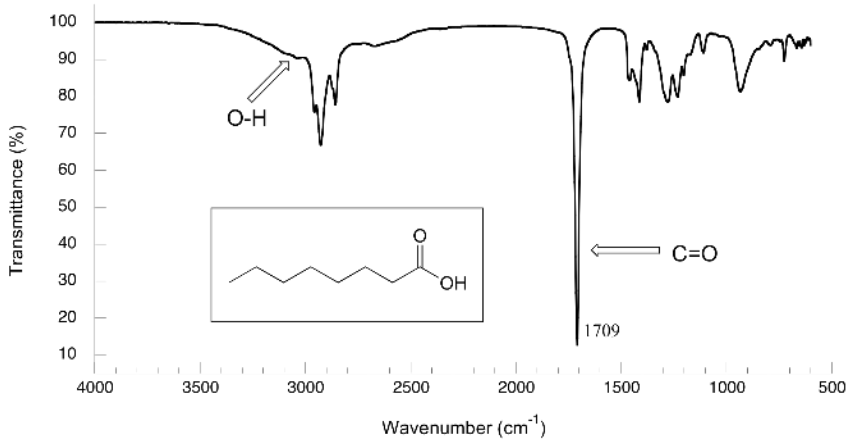
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# 1.14: Interpreting IR Spectra

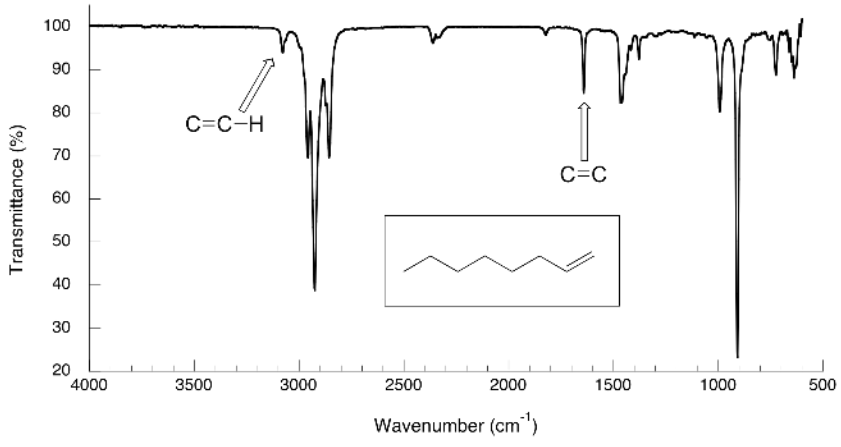
## Guided IR Spectrum Interpretation

Now, let's take a look at the IR spectrum for 1-hexanol. There is a very broad 'mountain' centered at about 3400 $cm^{-1}$. This signal is characteristic of the O-H stretching mode of alcohols, and is a dead giveaway for the presence of an alcohol group. The breadth of this signal is a consequence of hydrogen bonding between molecules.

In the spectrum of octanoic acid we see, as expected, the characteristic carbonyl peak, this time at 1709 $cm^{-1}$. We also see a low, broad absorbance band that looks like an alcohol, except that it is displaced slightly to the right (long-wavelength) side of the spectrum, causing it to overlap to some degree with the C-H region. This is the characteristic carboxylic acid O-H single bond stretching absorbance.




The spectrum for 1-octene shows two peaks that are characteristic of alkenes: the one at 1642 $cm^{-1}$ is due to stretching of the carbon-carbon double bond, and the one at 3079 cm-1 is due to stretching of the s bond between the alkene carbons and their attached hydrogens.



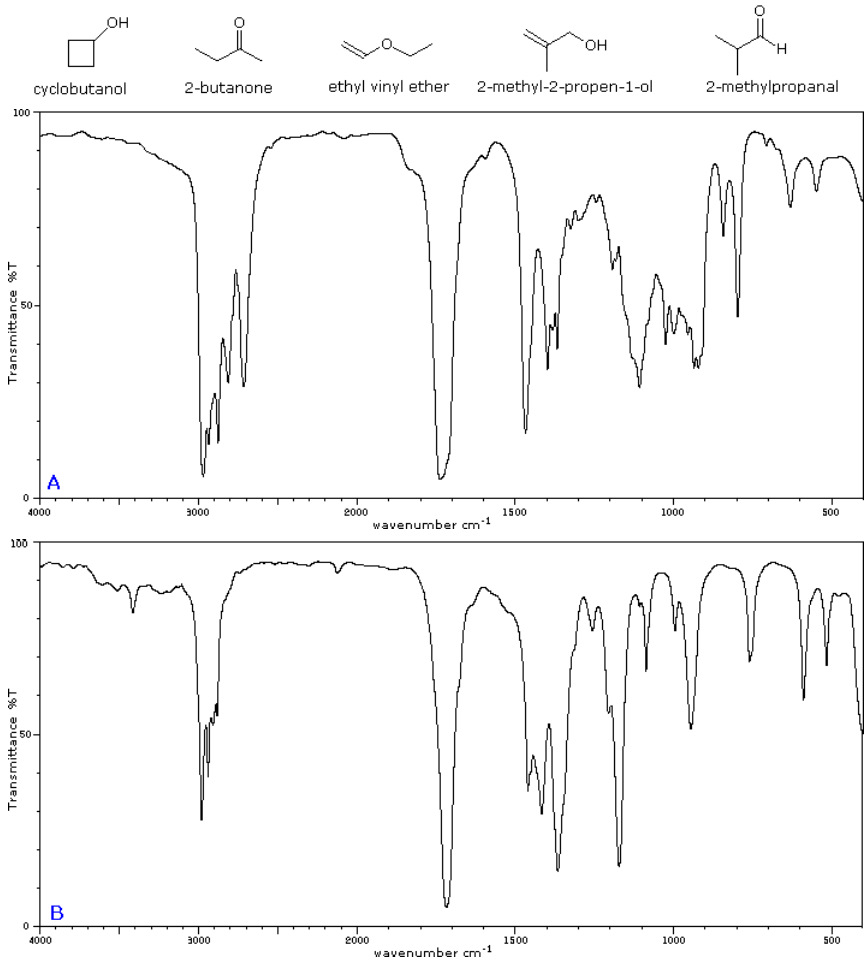

Alkynes have characteristic IR absorbance peaks in the range of 2100-2250 $cm^{-1}$ due to stretching of the carbon-carbon triple bond, and terminal alkenes can be identified by their absorbance at about 3300 cm-1, due to stretching of the bond between the sp-hybridized carbon and the terminal hydrogen.

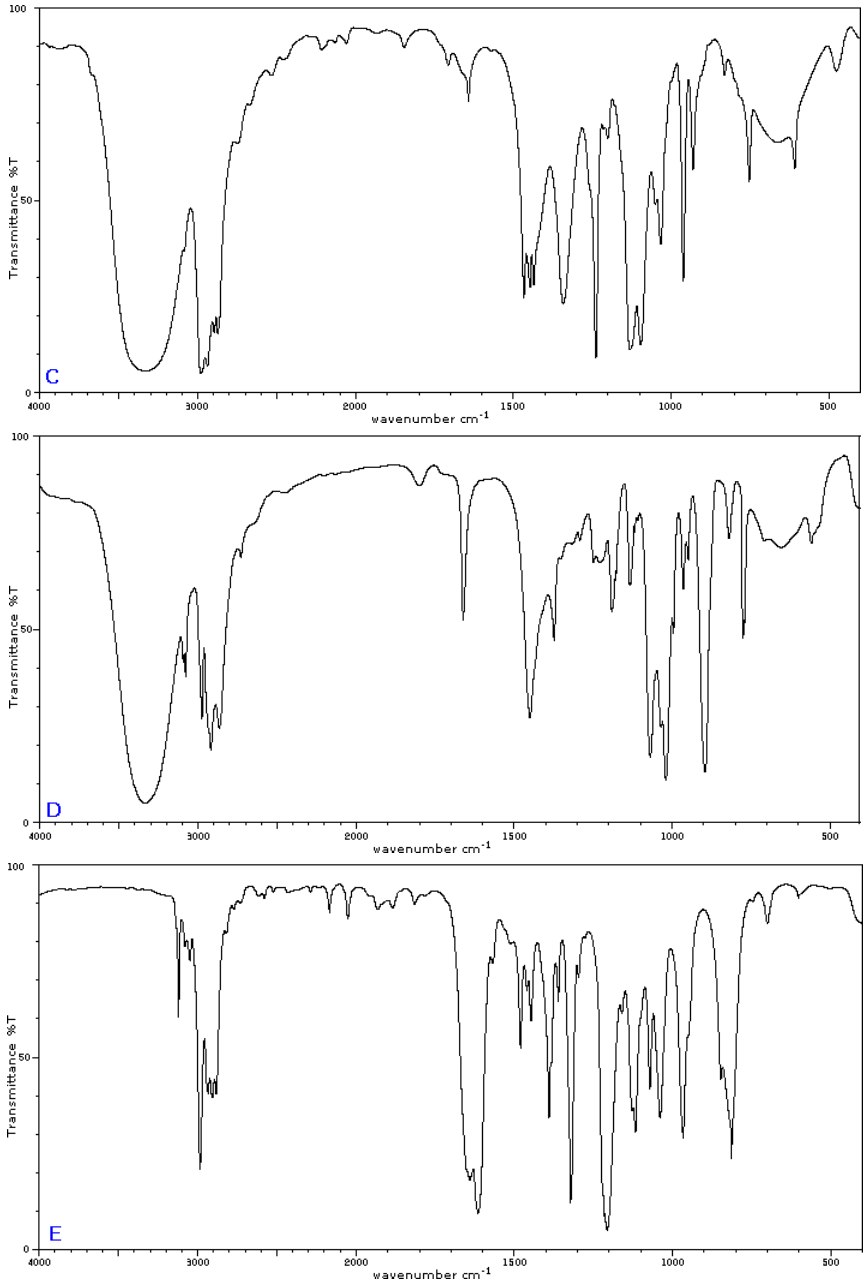
It is possible to identify other functional groups such as amines and ethers, but the characteristic peaks for these groups are considerably more subtle and/or variable, and often are overlapped with peaks from the fingerprint region. For this reason, we will limit our discussion here to the most easily recognized functional groups, which are summarized in this table.

As you can imagine, obtaining an IR spectrum for a compound will not allow us to figure out the complete structure of even a simple molecule, unless we happen to have a reference spectrum for comparison. In conjunction with other analytical methods, however, IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups. IR can also be a quick and convenient way for a chemist to check to see if a reaction has proceeded as planned. If we were to run a reaction in which we wished to convert cyclohexanone to cyclohexanol, for example, a quick comparison of the IR spectra of starting compound and product would tell us if we had successfully converted the ketone group to an alcohol.

## More examples of IR spectra

To illustrate the usefulness of infrared absorption spectra, examples for five $C_4H_8O$ isomers are presented below their corresponding structural formulas. Try to associate each spectrum with one of the isomers in the row above it.






## Exercises

## Contributors and Attributions

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# CHAPTER OVERVIEW

## 2: Arrow Pushing


2.1: Polar Covalent Bonds - Electronegativity
2.2: Polar Covalent Bonds - Dipole Moments
2.3: Kinds of Organic Reactions
2.4: Using Curved Arrows in Polar Reaction Mechanisms
2.5: An Example of a Polar Reaction - Addition of HBr to Ethylene
2.6: Resonance
2.7: Rules for Resonance Forms
2.8: Drawing Resonance Forms


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# 2.1: Polar Covalent Bonds - Electronegativity

## Key Terms

Make certain that you can define, and use in context, the key terms below.

- electronegativity inductive effect
- polar covalent bond

## Study Notes

Students often wonder why it is important to be able to tell whether a given bond is polar or not, and why they need to know which atoms carry a partial positive charge and which a partial negative charge. Consider the chloromethane ($CH_3Cl$) molecule. The carbon atom is shown as carrying a partial positive charge. Now, recall that opposite charges attract. Thus, it seems reasonable that the slightly positive carbon atom in chloromethane should be susceptible to attack by a negatively charged species, such as the hydroxide ion, $OH^-$. This theory is borne out in practice: hydroxide ions react with chloromethane by attacking the slightly positive carbon atom in the latter. It is often possible to rationalize chemical reactions in this manner, and you will find the knowledge of bond polarity indispensible when you start to write reaction mechanisms.

**Note:** Because of the small difference in electronegativity between carbon and hydrogen, the **C-H** bond is normally assumed to be nonpolar.

### Electronegativity

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called **electronegativity** (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), which is defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by the neighboring atoms in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. ***Figure* 2.1.1** shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In this scale a value of 4.0 is arbitrarily given to the most electronegative element, fluorine, and the other electronegativities are scaled relative to this value. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0 as previously noted). It is important to notice that the elements most important to organic chemistry, carbon, nitrogen, and oxygen have some of the highest electronegativites in the periodic table (EN = 2.5, 3.0, 3.5 respectively). Metals, on the left, tend to be less electronegative elements, with cesium having the lowest (EN = 0.7). Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell.

> *Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The **larger** the electronegativity value, the **greater** the attraction.*

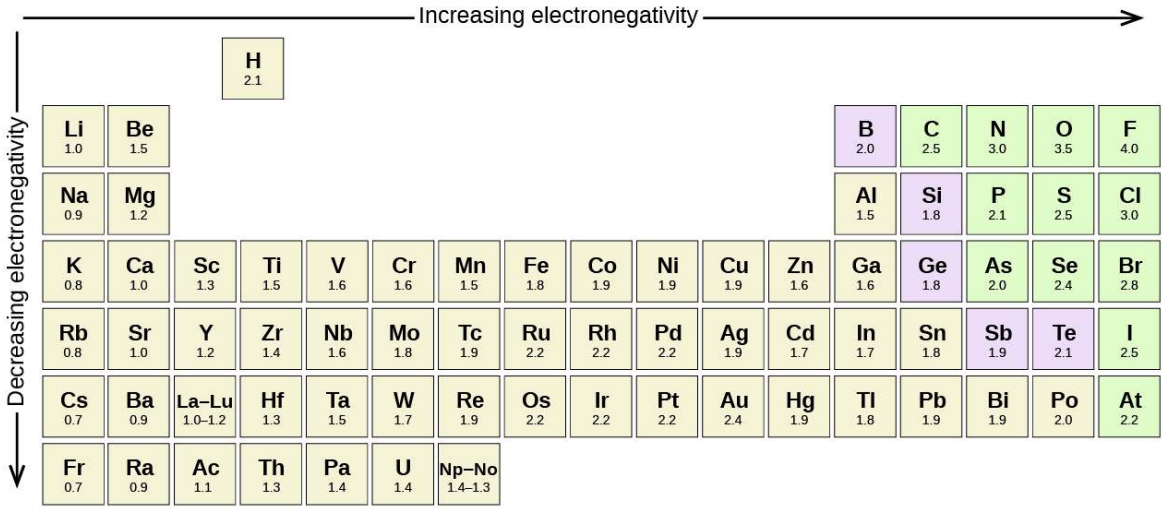



Figure 2.1.1: Pauling scale electronegativities of elements

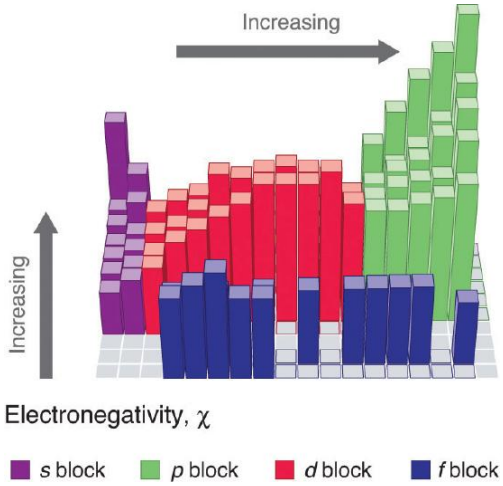



Figure 2.1.2: Visual representation of electronegativities.

## Electronegativity and Bond Type

The two idealized extremes of chemical bonding: (1) **ionic bonding**—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) **covalent bonding**, in which electrons are shared equally between two atoms. Most compounds, however, have **polar covalent bonds**, which means that electrons are shared unequally between the bonded atoms. Electronegativity determines how the shared electrons are distributed between the two atoms in a polar covalent bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms. Recall that a lowercase Greek delta ( $\delta$ ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by $\delta^+$ , or a partial negative charge, indicated by $\delta^-$ , and a bond between two atoms that possess partial charges is a polar bond.

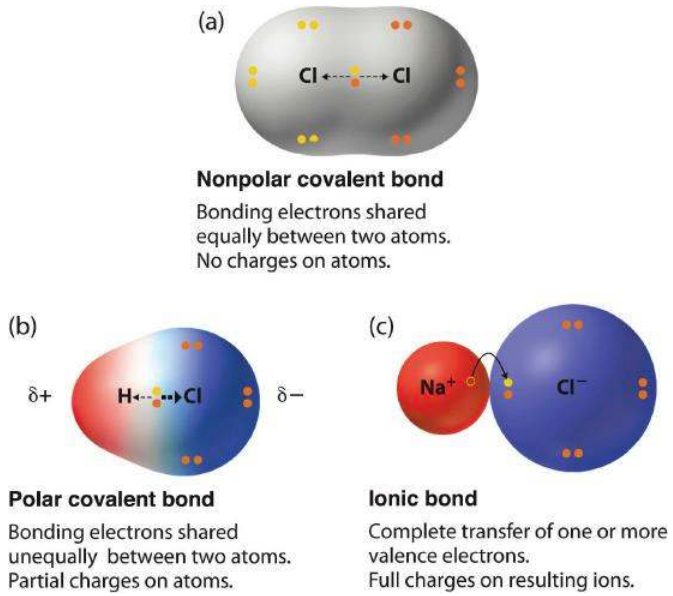
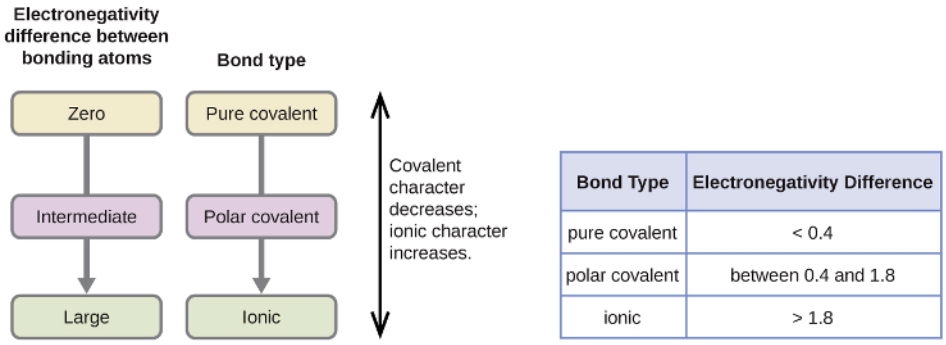



Figure 2.1.3: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Whether a bond is **ionic**, **nonpolar covalent**, or **polar covalent** can be estimated by by calculating the absolute value of the difference in electronegativity (ΔEN) of two bonded atoms. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 7.2.4 shows the relationship between electronegativity difference and bond type. This table is just a general guide, however, with many exceptions. The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.




| Bond Type | Electronegativity Difference |
|---|---|
| pure covalent | < 0.4 |
| polar covalent | between 0.4 and 1.8 |
| ionic | > 1.8 |

Figure 2.1.4: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as $OH^-$, $NO_3^-$, and $NH_4^+$, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, $KNO_3$, contains the $K^+$ cation and the polyatomic $NO_3^-$ anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions $K^+$ and $NO_3^-$, as well as covalent between the nitrogen and oxygen atoms in $NO_3^-$.

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Table A2, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

**Solution**

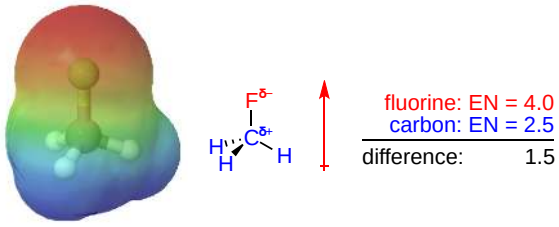
The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 2.1.1 shows these bonds in order of increasing polarity.

Table 2.1.1: Bond Polarity and Electronegativity Difference

| Bond | ΔEN | Polarity |
|---|---|---|
| C–H | 0.4 | $\overset{\delta-}{\mathrm{C}}-\overset{\delta+}{\mathrm{H}}$ |
| S–H | 0.4 | $\overset{\delta-}{\mathrm{S}}-\overset{\delta+}{\mathrm{H}}$ |
| C–N | 0.5 | $\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{N}}$ |
| N–H | 0.9 | $\overset{\delta-}{\mathrm{N}}-\overset{\delta+}{\mathrm{H}}$ |
| C–O | 1.0 | $\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{O}}$ |
| O–H | 1.4 | $\overset{\delta-}{\mathrm{O}}-\overset{\delta+}{\mathrm{H}}$ |

## Visualizing Bonding

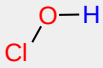
Calculated charge distributions in molecules can easily be visualized by using electrostatic potential maps. The color red is used to indicate electron-rich regions of a molecule while the color blue is used to indicated electron-poor regions. An easier method for visually representing electron displacement in a molecule uses a crossed arrow. By convention the arrow point in the direction of the electron-rich region of a molecule and away from the electron-poor. An example is shown in the molecule fluoromethane. The C-F bond is polarized drawing the bonding electrons toward the more electronegative fluorine giving it a partial negative charge. Consequently, the bonding electrons are drawn away from the less electronegative carbon giving it a partial positive charge. The the electron-rich fluorine is shown as red in the electrostatic potential map and while the electron-poor carbon is shown as blue. The crossed arrow points in the direction of the electron-rich fluorine.




*Electrostatic Potential Map and Dipole Moment of Fluoromethane*

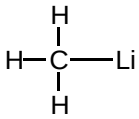
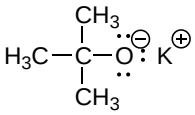
Chemists often use the term, **inductive effect**, to describe the shifting of electrons in a sigma by the electronegativity of atoms. Relatively electronegative atoms, such as fluorine, tend to inductively draw electrons towards themselves and away from nearby atoms. The inductive effect will be used to explain chemical reactivity in many situations in organic chemistry. An excellent example of the inductive effect is seen when comparing the O-H bond polarities of water ($H_2O$) and hypochlorous acid (ClOH). Replacing the less electronegative hydrogen (EN = 2.1) in water with the more electronegative chlorine (EN = 3.0) in hypochlorous acid creates a greater bond polarity. The chlorine draws electrons away giving the hydrogen a greater partial positive charge. This is shown in the electrostatic potential map as an increase in the blue color around hydrogen.



| | |
|---|---|
|  |  |
| water | hypochlorous acid |

### A "spectrum" of bonds

There is no clear-cut division between covalent and ionic bonds. In a pure non-polar covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end. How far does this dragging have to go before the bond counts as ionic? There is no real answer to that. Sodium chloride is typically considered an ionic solid, but even here the sodium has not completely lost control of its electron. Because of the properties of sodium chloride, however, we tend to count it as if it were purely ionic. Lithium iodide, on the other hand, would be described as being "ionic with some covalent character". In this case, the pair of electrons has not moved entirely over to the iodine end of the bond. Lithium iodide, for example, dissolves in organic solvents like ethanol - not something which ionic substances normally do. Many bonds between metals and non-metal atoms, are considered ionic, however some of these bonds cannot be simply identified as one type of bond. Examples of this are the lithium - carbon bond in methyllithium which is usually considered as polar covalent (somewhat between covalent and ionic) and the potassium - oxygen bond in potassium *tert*-butoxide which is considered more ionic than covalent.

| | |
|---|---|
|  |  |
| methyllithium | potassium *tert*-butoxide |

## Summary

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

- No electronegativity difference between two atoms leads to a non-polar covalent bond.
- A small electronegativity difference leads to a polar covalent bond.
- A large electronegativity difference leads to an ionic bond.

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- Jim Clark (Chemguide.co.uk)
- Dr. Krista Cunningham

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# 2.2: Polar Covalent Bonds - Dipole Moments

**Key Terms**

Make certain that you can define, and use in context, the key term below.

- dipole moment

**Study Notes**

You must be able to combine your knowledge of molecular shapes and bond polarities to determine whether or not a given compound will have a dipole moment. Conversely, the presence or absence of a dipole moment may also give an important clue to a compound's structure. $BCl_3$, for example, has no dipole moment, while $NH_3$ does. This suggests that in $BCl_3$ the chlorines around boron are in a trigonal planar arrangement, while the hydrogens around nitrogen in $NH_3$ have a less symmetrical arrangement - trigonal pyramidal.

Remember that the C-H bond is assumed to be non-polar.

## Molecular Dipole Moments

In molecules containing more than one polar bond, the molecular dipole moment is just the vector combination of what can be regarded as individual "**bond dipole moments**". Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for $CO_2$, a linear molecule (Figure 2.2.1*a*). Each C–O bond in $CO_2$ is polar, yet experiments show that the $CO_2$ molecule has no dipole moment. Because the two C–O bond dipoles in $CO_2$ are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the $CO_2$ molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the $H_2O$ molecule is not linear (Figure 2.2.1*b*); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as $H_2O$ has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows $H_2O$ to hydrogen-bond to other polarized or charged species, including other water molecules.

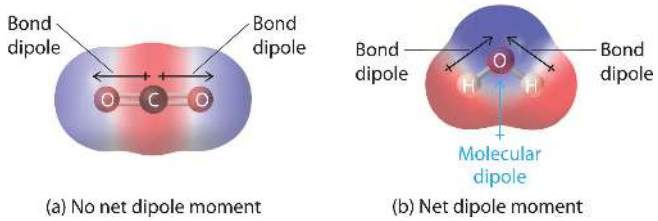



Figure 2.2.1: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In $CO_2$, the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so $CO_2$ therefore has no net dipole. (b) In $H_2O$, the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and $H_2O$ has a net dipole moment.

The following is a simplified equation for a simple separated two-charge system that is present in diatomic molecules or when considering a bond dipole within a molecule.

$$\mu_{diatomic} = Q \times r \tag{2.2.1}$$

This bond dipole, μ (Greek mu) is interpreted as the dipole from a charge separation over a distance $r$ between the partial charges $Q^+$ and $Q^-$ (or the more commonly used terms $\delta^+$ - $\delta^-$); the orientation of the dipole is along the axis of the bond. The units on dipole moments are typically debyes (D) where one debye is equal to 3.336 x $10^{30}$ coulomb meters (C · m) in SI units. Consider a simple system of a single electron and proton separated by a fixed distance. The unit charge on an electron is 1.60 X 1019 C and the proton & electron are 100 pm apart (about the length of a typical covalent bond), the dipole moment is calculated as:

$$\begin{aligned} \mu &= Qr \\ &= (1.60 \times 10^{-19}\ C)(1.00 \times 10^{-10}\ m) \\ &= 1.60 \times 10^{-29}\ C \cdot m \end{aligned} \tag{2.2.2}$$

$$\mu = (1.60 \times 10^{-29}\ C \cdot m)\left(\frac{1\ D}{3.336 \times 10^{-30}\ C \cdot m}\right)$$

$$= 4.80\ D \tag{2.2.3}$$

$4.80\ D$ is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. However, if the charge separation were increased then the dipole moment increases (linearly):

- If the proton and electron were separated by 120 pm:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\ D \tag{2.2.4}$$

- If the proton and electron were separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\ D \tag{2.2.5}$$

- If the proton and electron were separated by 200 pm:

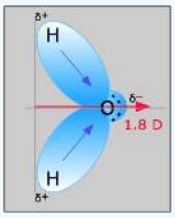
$$\mu = \frac{200}{100}(4.80\ D) = 9.60\ D \tag{2.2.6}$$

**Example 2.2.1: Water**

The water molecule in Figure 2.2.1 can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5˚).

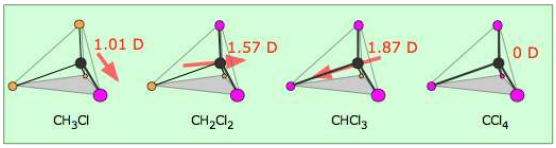
The bond moment of O-H bond =1.5 D, so the net dipole moment is

$$\mu = 2(1.5)\cos\left(\frac{104.5^{\circ}}{2}\right) = 1.84\ D$$




## Dipoles with Differing Atoms

In more complex molecules with more than one polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether the molecule has a net dipole moment. The manner in which the individual bonds contribute to the dipole moment of the molecule is nicely illustrated by the series of chloromethanes shown below. The electronegative chlorine draws electrons towards itself.




Consider $CCl_4$, (left panel in figure below), which as a molecule is not polar - in the sense that it doesn't have an end (or a side) which is slightly negative and one which is slightly positive. The whole of the outside of the molecule is somewhat negative, but there is no overall separation of charge from top to bottom, or from left to right. In contrast, $CHCl_3$ is a polar molecule (right panel in figure above). However, although a molecule like $CHCl_3$ has a tetrahedral geometry, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments do not cancel one another, and the result is a molecule which has a dipole moment. The hydrogen at the top of the molecule is less electronegative than carbon and so is slightly positive. This means that the molecule now has a slightly positive "top" and a slightly negative "bottom", and so is overall a polar molecule.

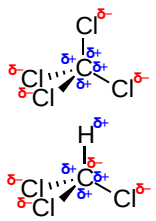



Figure 2.2.3: Bond polarities for $CCl_4$ (left) and $CHCl_3$(right)

Electron densities in a molecule (and the dipole moments that unbalanced electron distributions can produce) are easily visualized with electrostatic potential maps. In this example, $CHCl_3$, the blue area centered on carbon represents a electron-deficient positive area, of the molecule, the red area centered on the chlorine, represents a electron-abundant negative area. This charge separation creates a net dipole moment of 1.87 D which points in

the direction of the chlorine. In, $CCl_4$ the evenly spaced red areas represent that there is no separation of charge in the molecule. $CCl_4$ has a net dipole moment of zero which makes it a nonpolar molecule.

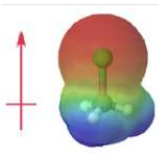
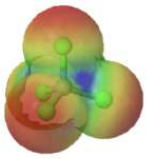
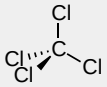
| | |
|---|---|
|  |  |
|  |  |
| chloromethane | tetrachloromethane |
| (μ = 1.87 D) | (μ = 0 D) |

***Figure 2.2.4:*** Electrostatic potential maps and dipole moments for chloromethane and tetrachloromethane (carbon tetrachloride).

## Molecules with asymmetrical charge distributions have a net dipole moment

Other examples of molecules with polar bonds are shown in Figure 2.2.2. In molecules like $BCl_3$ and $CCl_4$, that have only one type of bond and a molecular geometries that are highly symmetrical (trigonal planar and tetrahedral), the individual bond dipole moments completely cancel, and there is no net dipole moment. However, although a molecule like $CHCl_3$ has a tetrahedral geometry, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments do not cancel one another, and the result is a molecule which has a dipole moment.

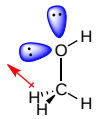
| | | | | | | | |
|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  |
| net dipole | no net dipole | net dipole | net dipole | no net dipole | net dipole | no net dipole | no net dipole |
| HCl | $BCl_3$ | $CH_2O$ | $NH_3$ | $CCl_4$ | $CHCl_3$ | $PF_5$ | $SF_6$ |

***Figure 2.2.5****: Molecules with Polar Bonds. Individual bond dipole moments are indicated in black. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl, $CH_2O$, $NH_3$, and $CHCl_3$), indicated in red, whereas others do not because the bond dipole moments cancel ($BCl_3$, $CCl_4$, $PF_5$, and $SF_6$).*

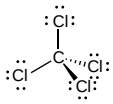
**Table 2.2.1:** Dipole Moments of Some Compounds

| Compound | Dipole Moment (Debyes) |
|---|---|
| NaCl | 9.0 (measured in the gas phase) |
| $CH_2O$ | 2.33 |
| $CH_3Cl$ | 1.87 |
| $H_2O$ | 1.85 |
| $CH_3OH$ | 1.70 |
| $NH_3$ | 1.47 |
| $CH_3NH_2$ | 1.31 |
| $CO_2$ | 0 |
| $CCl_4$ | 0 |
| $CH_4$ | 0 |
| $CH_3CH_3$ | 0 |

The table above give the dipole moment of some common substances. Sodium chloride has the largest dipole listed (9.00 D) because it is an ionic compounds. Even small organic compounds such as formaldehyde ($CH_2O$, 2.33 D) and methanol ($CH_3OH$, 1.70 D) have significant dipole moments. Both of these molecules contain the strongly electronegative oxygen atom lone pair electrons which gives rise to considerable dipole moments.

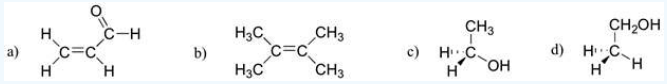
| | |
|---|---|
|  |  |
| methanol | formaldehyde |
| (μ = 1.70 D) | (μ = 2.33 D) |

In contrast many organic molecule have a zero dipole moment despite the fact that they are made up of polar covalent bonds. In, structures with highly symmetrical molecular geometries, the polar bonds and the lone pair electrons can can exactly cancel leaving no overall charge separation.

| | | |
|---|---|---|
|  |  |  |
| carbon dioxide | carbon tetrachloride | ethane |
| (μ = 0 D) | (μ = 0 D) | (μ = 0 D) |

**Exercise 2.2.1**

Which of the molecules below have molecular dipole moments?



**Answer**

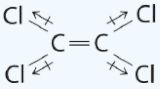
Only molecule (b) does *not* have a molecular dipole, due to its symmetry (bond dipoles are equal and in opposite directions). Add texts here.

**Exercise 2.2.2**

Draw out the line structure of the molecule with a molecular formula of $C_2Cl_4$. Indicate all of the individual bond polarities and predict if the molecule is polar or nonpolar.

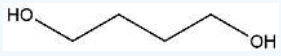
**Answer**

Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and Cl2C=CCl2" id="MathJax-Element-47-Frame" role="presentation" style="position:relative;" tabindex="0">does not have a net dipole moment.



**Exercise 2.2.3**

The following molecule has no net dipole moment, explain.

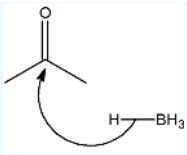


**Answer**

The hydroxyl groups are oriented opposite of one another and therefore the dipole moments would “cancel” one another out. Therefore having a zero net-dipole.

**Exercise 2.2.4**

Within reactions with carbonyls, such as a hydride reduction reaction, the carbonyl is attacked from the carbon side and not the oxygen side. Using knowledge of electronegativity explain why this happens.




**Answer**

The oxygen is more electronegative than the carbon and therefore creates a dipole along the bond. This leads to having a partial positive charge on the carbon and the reduction can take place.



## Exercise 2.2.1

Which molecule(s) has a net dipole moment?

a. $H_2S$
b. $NHF_2$
c. $BF_3$

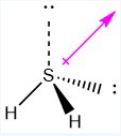
**Answer**

**Strategy:**

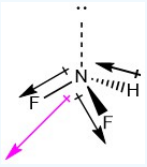
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

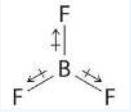
**Solution:**

The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of $H_2S$ is bent. The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.




Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of $NHF_2$ cannot cancel one another. This means that $NHF_2$ has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.




- The molecular geometry of $BF_3$ is trigonal planar. Because all the B–F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus $BF_3$ has a net dipole moment of zero:

## Contributors and Attributions


- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Dr. Krista Cunningham

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# 2.3: Kinds of Organic Reactions

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- addition reaction
- elimination reaction
- rearrangement reaction
- substitution reaction

**Study Notes**

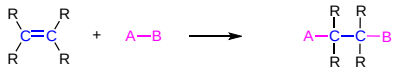
It is sufficient that you know the general form of each kind of reaction. However, given a chemical equation, you should be able to recognize which kind of reaction it involves.

If you scan any organic textbook you will encounter what appears to be a very large, often intimidating, number of reactions. These are the "tools" of a chemist, and to use these tools effectively, we must organize them in a sensible manner and look for patterns of reactivity that permit us make plausible predictions. Most of these reactions occur at special sites of reactivity known as functional groups, and these constitute one organizational scheme that helps us catalog and remember reactions.

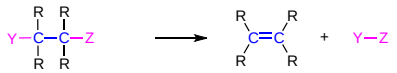
> *Ultimately, the best way to achieve proficiency in organic chemistry is to understand how reactions take place, and to recognize the various factors that influence their course.*

First, we identify four broad classes of reactions based solely on the **structural change** occurring in the reactant molecules. This classification does not require knowledge or speculation concerning reaction paths or mechanisms. The four main reaction classes are additions, eliminations, substitutions, and rearrangements.

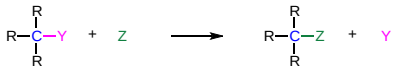
**Addition Reaction**



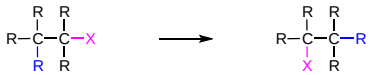
**Elimination Reaction**



**Substitution Reaction**



**Rearrangement Reaction**

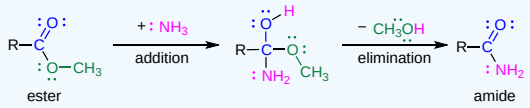


In an **addition** reaction the number of σ-bonds in the substrate molecule increases, usually at the expense of one or more π-bonds. The reverse is true of **elimination** reactions, *i.e.*the number of σ-bonds in the substrate decreases, and new π-bonds are often formed. **Substitution** reactions, as the name implies, are characterized by replacement of an atom or group (Y) by another atom or group (Z). Aside from these groups, the number of bonds does not change. A **rearrangement** reaction generates an isomer, and again the number of bonds normally does not change.

The examples illustrated above involve simple alkyl and alkene systems, but these reaction types are general for most functional groups, including those incorporating carbon-oxygen double bonds and carbon-nitrogen double and triple bonds. Some common reactions may actually be a combination of reaction types.

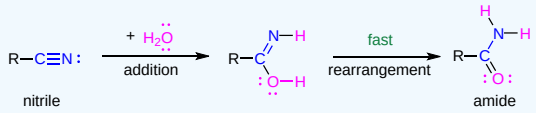
### Example 2.3.1: Reaction of an Ester with Ammonia

The reaction of an ester with ammonia to give an amide, as shown below, appears to be a substitution reaction ( Y = $CH_3O$ & Z = $NH_2$ ); however, it is actually two reactions, an addition followed by an elimination.




### Example 2.3.2: The Addition of water to a Nitrile

The addition of water to a nitrile does not seem to fit any of the above reaction types, but it is simply a slow addition reaction followed by a rapid rearrangement, as shown in the following equation. Rapid rearrangements of this kind are called **tautomerizations**.




## Exercises

## Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Dr. Krista Cunningham

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# 2.4: Using Curved Arrows in Polar Reaction Mechanisms

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- electrophilic
- nucleophilic

## Pushing Electrons and Curved Arrows

Understanding the location of electrons and being able to draw the curved arrows that depict the mechanisms by which the reactions occur is one of the most critical tools for learning organic chemistry since they allow you to understand what controls reactions, and how reactions proceed.

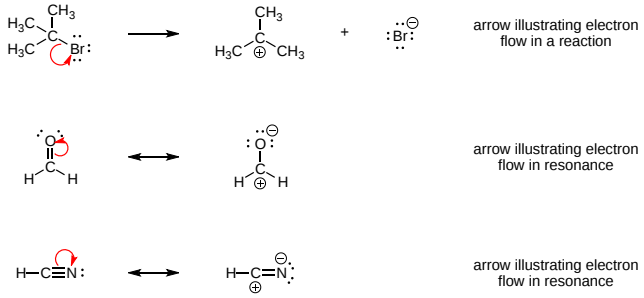
Before you can do this you need to understand that a **bond** is due to a pair of electrons shared between atoms.

When asked to draw a mechanism, curved arrows should be used to show all the bonding changes that occur.

A few simple lessons that illustrate these concepts can be found below.

# Lesson 1

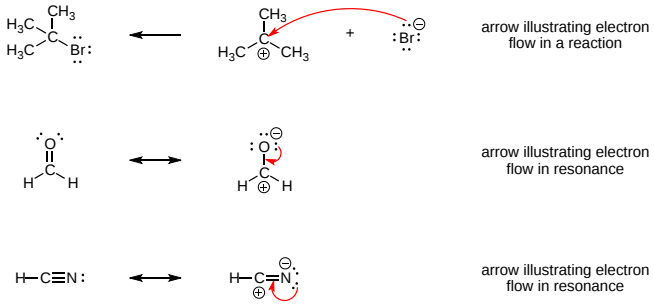
If we remove the pair of electrons in a bond, then we BREAK that bond. This is true for single and multiple bonds as shown below:




Notice that since the starting materials were *neutral*, the products are also *neutral*. In general terms, the *sum of the charges* on the starting materials MUST equal the *sum of the charges* on the products since we have the **same number of electrons**.

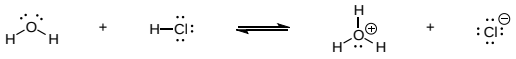
The first example is a REACTION since we broke a sigma bond. In the second two examples, we moved pi electrons into long pairs. This is RESONANCE.

If we move electrons between two atoms, then we MAKE a new bond:

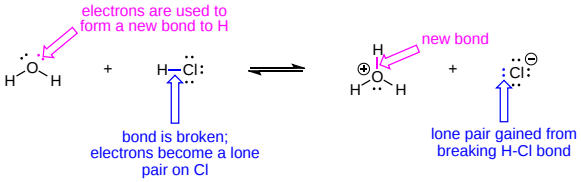



We always show electrons moving from **electron rich** to **electron poor**.

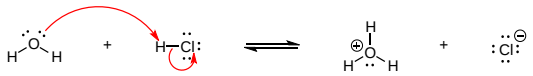
## Lesson 2



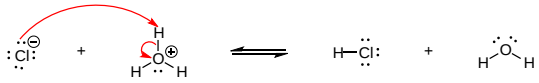
This is a simple acid/base reaction, showing the formation of the hydronium ion produced when hydrochloric acid is dissolved in water. It is useful to analyze the bond changes that are occurring. Water is functioning as a **base** and hydrochloric acid as an **acid**. Consider the differences in bonding between the starting materials and the products:




One of the lone pairs on the oxygen atom of water was used to form a bond to a hydrogen atom, creating the hydronium ion ($H_3O^+$) seen in the products. The hydrogen-chlorine bond of HCl was broken, and the electrons in this bond became a lone pair on the chlorine atom, thus generating a chloride ion. We can illustrate these changes in bonding using the curved arrows shown below.



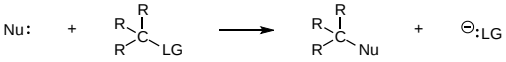
Note that in this diagram, the overall charge of the reactants is the same as the overall charge of the products. We can also show the curved arrows for the reverse reaction:



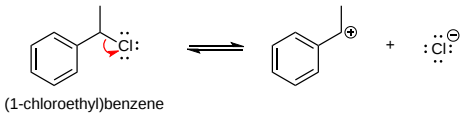
This shows the formation of the new H-Cl bond by using a lone pair of electrons from the electron-rich chloride ion to form a bond to an electron poor hydrogen atom of the hydronium ion. Because hydrogen can only form one bond, the oxygen-hydrogen bond is broken and its electrons become a lone pair on the electron-poor oxygen atom. Notice that the charges balance!

## Lesson 3

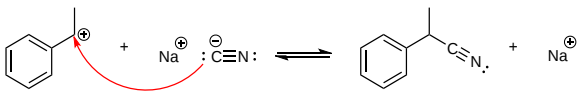
In this section, we will look at the curved arrows for some nucleophilic substitution reactions. Overall, the processes involved are similar to those for the acid/base reactions described above. In a nucleophilic substitution reaction, an electron-rich nucleophile (Nu) becomes bonded to an electron-poor carbon atom, and a leaving group (LG) is displaced. In bonding terms, we must *make* a Nu-C bond and *break* a C-LG bond.



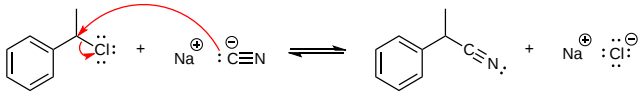
Let's consider the stepwise $S_N1$ reaction between (1-chloroethyl)benzene and sodium cyanide. The first step of this process is breaking the C-Cl bond, where the electrons in that bond become a lone pair on the chlorine atom. The carbon atom has lost electrons and therefore becomes positive, generating a secondary carbocation. Because the chlorine atom gained an additional lone pair of electrons, it becomes a negatively charged chloride ion.




In the second step, the electron-rich nucleophile donates electrons to form a new C-C bond with the electron-poor secondary carbocation.



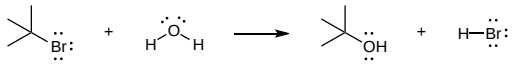
In an $S_N2$ reaction, the bond forming and breaking processes occur simultaneously. The scheme below shows the Nu donating electrons to form a new C-C bond at the same time that the C-Cl bond is breaking. The electrons in the C-Cl bond become a long pair on the chlorine atom, generating a chloride ion. Forming and breaking the bonds simultaneously allows carbon to obey the octet rule throughout this process.



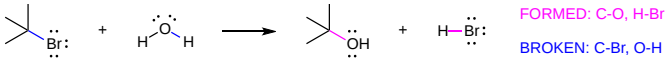
Notice that in all steps for the processes above, the overall charges of the starting materials match those of the products.

## Lesson 4

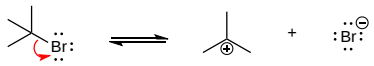
This section will dissect another substitution reaction, although it is more involved. Let's consider the $S_N1$ reaction of *tert*-butyl bromide with water.



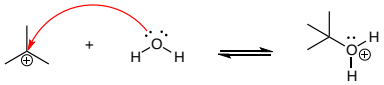
It can be helpful to take inventory of which bonds have been formed, and which bonds have been broken.



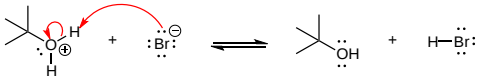

The curved arrows we draw must account for ALL of these bonding changes. Since we are dealing with an $S_N1$ reaction process, the first step will be cleavage of the C-Br bond to give a carbocation and and a bromide anion.



Water then acts as a nucleophile, using one of its lone pairs to form a bond to the electron-poor *t*-butyl cation. This generates an oxonium ion, where oxygen has three bonds and a positive formal charge.

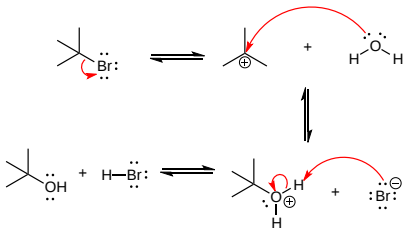


The final step is an acid/base reaction between the bromide anion generated in step 1 and the oxonium product of step 2. The bromide anion acts as a base, using a lone pair to form a bond to one of the hydrogen atoms. The O-H bond then breaks, and its electrons become a lone pair on oxygen. This gives the final products of HBr and *t*-butyl alcohol.

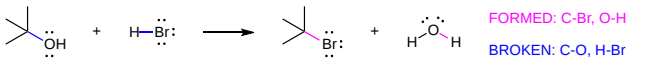


Notice that in each of the mechanistic steps above, the overall charge of the reactant side balances with the overall charge of the product side.

While the above process was broken down into distinct steps, however it is important to note that mechanisms are almost always shown as a continuous process. The overall mechanism for this processes can be found below:

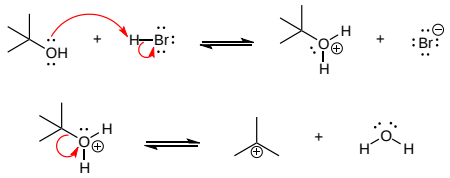


Now consider the reverse reaction, i.e. the reaction of *t*-butyl alcohol with hydrobromic acid to generate *t*-butyl bromide and water. The scheme is shown below, along with an analysis of the bonds formed and broken in this process:

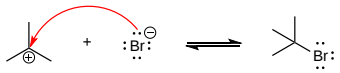



The mechanism must occur via the same pathway as shown above (Law of Macroscopic Reversibility), however this mechanism can still be deduced without knowing that. First, it is known that HBr is a strong acid and can donate a proton to a base. The most basic sites in the whole system are the lone pairs on the oxygen atom of *t*-butanol. Since the lone pairs are the electron-rich area of

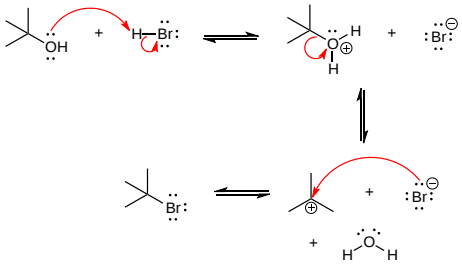
the molecule, the arrow starts at a lone pair and ends at the proton of HBr. The H-Br bond breaks, pushing its electrons onto the bromine atom and generating a bromide ion.



The bromide ion generated in the first step can then react with the *t*-butyl cation to generate *t*-butyl bromide.



Once again, the above the overall process is broken down into individual steps, however it is more common to illustrate this as one overall process:



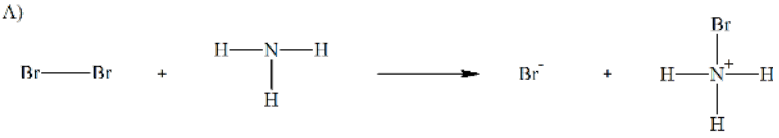
# Curved Arrow Summary

- Curved arrows flow from electron rich to electron poor.
- Therefore they start from lone pairs or bonds.
- The charges in any particular step should always be balanced.
- Remember to obey the rules of valence (*eg*. octet rule for C,N,O,F *etc*.)
- If electrons are taken out of a bond, then that bond is broken.
- If electrons are placed between two atoms then it implies a bond is being made.

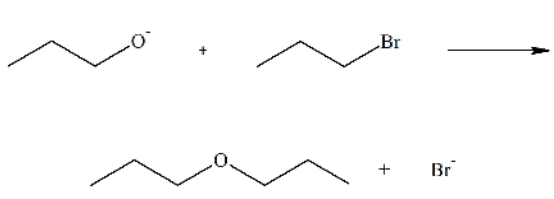
## Exercises

Draw curved arrows to indicate mechanisms for the following reactions:

A)



B)

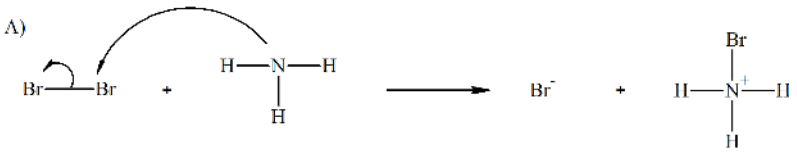


C)

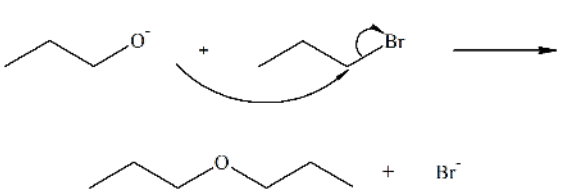


## Solutions

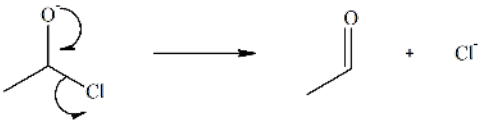
A)



B)



C)



## Contributors and Attributions

- Dr. Ian Hunt, Department of Chemistry, University of Calgary
- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Layne A. Morsch (University of Illinois Springfield)
- Dr. Krista Cunningham

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# 2.5: An Example of a Polar Reaction - Addition of HBr to Ethylene

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- electrophilic addition
- carbocation

**Study Notes**

The curved arrows introduced in this section are used throughout the course to indicate the movement of electron pairs. It takes practice for the beginning student to feel comfortable using these arrows. Remember that the head of the arrow indicates where the electron pair moves to; its tail shows where the electron pair comes from. (Chemists often refer to the use of curved arrows as “electron pushing.")

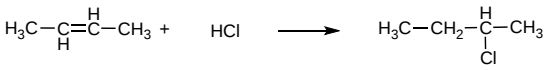
This page looks at the reaction of the carbon-carbon double bond in alkenes such as ethene with hydrogen halides such as hydrogen chloride and hydrogen bromide. Symmetrical alkenes (like ethene or but-2-ene) are dealt with first. These are alkenes where identical groups are attached to each end of the carbon-carbon double bond.

## Addition to symmetrical alkenes

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond, and a halogen atom to the other. For example, with ethene and hydrogen chloride, you get chloroethane:




With but-2-ene you get 2-chlorobutane:

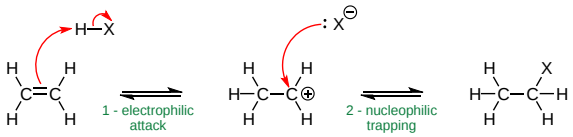



What happens if you add the hydrogen to the carbon atom at the right-hand end of the double bond, and the chlorine to the left-hand end? You would still have the same product. The chlorine would be on a carbon atom next to the end of the chain - you would simply have drawn the molecule flipped over in space. That would be different of the alkene was unsymmetrical - that's why we have to look at them separately.

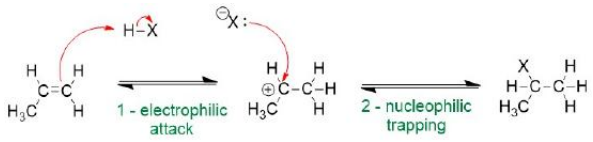
## Mechanism

The addition of hydrogen halides is one of the easiest electrophilic addition reactions because it uses the simplest electrophile: the proton. Hydrogen halides provide both an electrophile (proton) and a nucleophile (halide). First, the electrophile will attack the double bond and take up a set of pi electrons, attaching it to the molecule (1). This is basically the reverse of the last step in the E1 reaction (deprotonation step). The resulting molecule will have a single carbon-carbon bond with a positive charge on one of them (carbocation). The next step is when the nucleophile (halide) bonds to the carbocation, producing a new molecule with both the original hydrogen and halide attached to the organic reactant (2). The second step will only occur if a good nucleophile is used.

*Mechanism of Electrophilic Addition of Hydrogen Halide to Ethene*




*Mechanism of Electrophilic Addition of Hydrogen Halide to Propene*




All of the halides (HBr, HCl, HI, HF) can participate in this reaction and add on in the same manner. Although different halides do have different rates of reaction, due to the H-X bond getting weaker as X gets larger (poor overlap of orbitals)s.

## Reaction rates

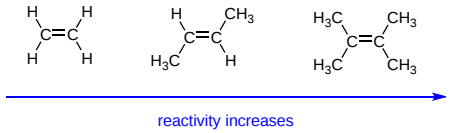
**Variation of rates when you change the halogen**

Reaction rates increase in the order HF - HCl - HBr - HI. Hydrogen fluoride reacts much more slowly than the other three, and is normally ignored in talking about these reactions. When the hydrogen halides react with alkenes, the hydrogen-halogen bond has to be broken. The bond strength falls as you go from HF to HI, and the hydrogen-fluorine bond is particularly strong. Because it is difficult to break the bond between the hydrogen and the fluorine, the addition of HF is bound to be slow.

**Variation of rates when you change the alkene**

This applies to unsymmetrical alkenes as well as to symmetrical ones. For simplicity the examples given below are all symmetrical ones- but they don't have to be. Reaction rates increase as the alkene gets more complicated - in the sense of the number of alkyl groups (such as methyl groups) attached to the carbon atoms at either end of the double bond.

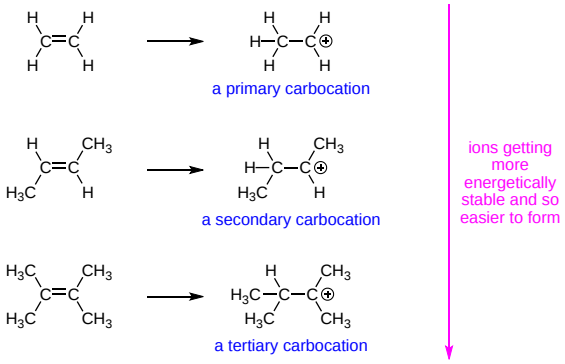
For example:




There are two ways of looking at the reasons for this - both of which need you to know about the mechanism for the reactions.

Alkenes react because the electrons in the pi bond attract things with any degree of positive charge. Anything which increases the electron density around the double bond will help this. Alkyl groups have a tendency to "push" electrons away from themselves towards the double bond. The more alkyl groups you have, the more negative the area around the double bonds becomes.

The more negatively charged that region becomes, the more it will attract molecules like hydrogen chloride. The more important reason, though, lies in the stability of the intermediate ion formed during the reaction. The three examples given above produce these carbocations (carbonium ions) at the half-way stage of the reaction:



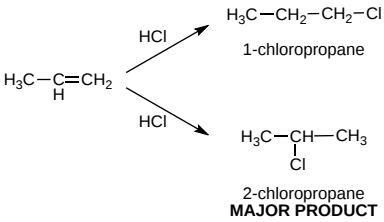

The stability of the intermediate ions governs the activation energy for the reaction. As you go towards the more complicated alkenes, the activation energy for the reaction falls. That means that the reactions become faster.

## Addition to unsymmetrical alkenes

In terms of reaction conditions and the factors affecting the rates of the reaction, there is no difference whatsoever between these alkenes and the symmetrical ones described above. The problem comes with the orientation of the addition - in other words, which way around the hydrogen and the halogen add across the double bond.

### Orientation of addition

If HCl adds to an unsymmetrical alkene like propene, there are two possible ways it could add. However, in practice, there is only one major product.




This is in line with Markovnikov's Rule which says:

> When a compound HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.

In this case, the hydrogen becomes attached to the $CH_2$ group, because the $CH_2$ group has more hydrogens than the CH group. Notice that only the hydrogens directly attached to the carbon atoms at either end of the double bond count. The ones in the $CH_3$ group are totally irrelevant.

## Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)
- Dr. Krista Cunningham
- John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

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# 2.6: Resonance

**Key Terms**

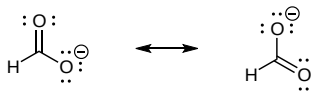
Make certain that you can define, and use in context, the key term below.

- resonance form
- delocalization

## Resonance Delocalization

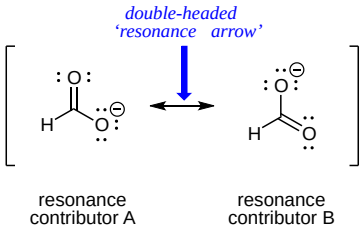
Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. **Resonance** is a way of describing **delocalized** electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance contributors or canonical forms). Resonance contributors involve the 'imaginary movement' of pi-bonded electrons or of lone-pair electrons that are adjacent to pi bonds. Note, sigma bonds cannot be broken during resonance – if you show a sigma bond forming or breaking, you are showing a chemical reaction taking place. Likewise, the positions of atoms in the molecule **cannot change** between resonance contributors.

When looking at the structure of the molecule, formate, we see that there are two equivalent structures possible. Which one is correct? There are two simple answers to this question: 'both' and 'neither one'. Both ways of drawing the molecule are equally acceptable approximations of the bonding picture for the molecule, but neither one, by itself, is an accurate picture of the delocalized pi bonds. The two alternative drawings, however, when considered together, give a much more accurate picture than either one on its own. This is because they imply, together, that the carbon-carbon bonds are not double bonds, not single bonds, but about halfway in between.

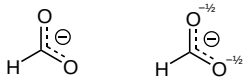


*Formate Ion*
*Structures are Equivalent in Energy*

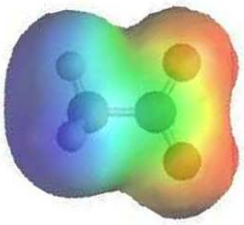
When it is possible to draw more than one valid structure for a compound or ion, we have identified **resonance contributors**: two or more different Lewis structures depicting the same molecule or ion that, when considered together, do a better job of approximating delocalized pi-bonding than any single structure. By convention, resonance contributors are linked by a double-headed arrow, and are sometimes enclosed by brackets:



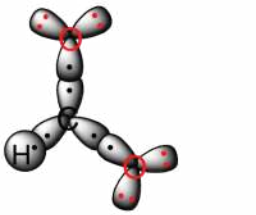

The depiction of formate using the two resonance contributors A and B in the figure above does *not* imply that the molecule at one moment looks like structure A, then at the next moment shifts to look like structure B. Rather, at all moments, the molecule is a combination, or **resonance hybrid** of both A and B. Each individual resonance contributor of the formate ion is drawn with one carbon-oxygen double bond (120 pm) and one carbon-oxygen single bond (135 pm), with a negative formal charge located on the single-bonded oxygen. However, the two carbon-oxygen bonds in formate are actually the same length (127 pm) which implies that neither resonance contributor is correct. Although there is an overall negative formal charge on the formate ion, it is shared equally between the two oxygens. Therefore, the formate ion can be more accurately depicted by a *pair* of resonance contributors. Alternatively, a single structure can be used, with a dashed line depicting the resonance-delocalized pi bond and the negative charge located in between the two oxygens.



The electrostatic potential map of formate shows that there is an equal amount of electron density (shown in red) around each oxygen.

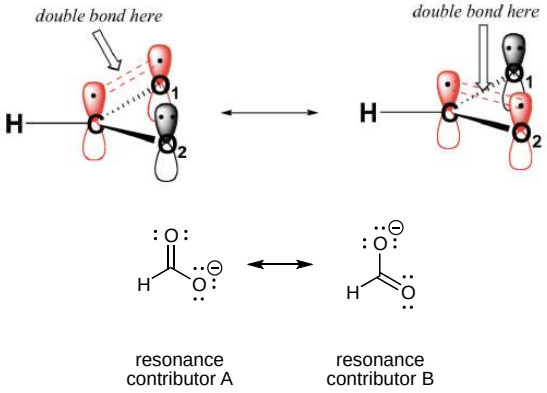


Valence bond theory can be used to develop a picture of the bonding in a carboxylate group. We know that the carbon must be $sp^2$-hybridized, (the bond angles are close to 120˚, and the molecule is planar), and we will treat both oxygens as being $sp^2$-hybridized as well. Both carbon-oxygen sigma bonds, then, are formed from the overlap of carbon $sp^2$ orbitals and oxygen $sp^2$ orbitals.



the σ-bonding framework of formate

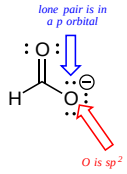
In addition, the carbon and both oxygens each have an un-hybridized $2p_z$ orbital situated perpendicular to the plane of the sigma bonds. These three $2p_z$ orbitals are parallel to each other, and can overlap in a side-by-side fashion to form a delocalized pi bond.



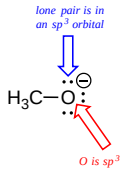

Overall, the situation is one of *three parallel, overlapping $2p_z$ orbitals sharing four delocalized pi electrons*. Because there is one more electron than there are $2p_z$ orbitals, the system has an overall charge of 1–. Resonance contributors are used to approximate overlapping $2p_z$ orbitals and delocalized pi electrons. Molecules with resonance are usually drawn showing only one resonance contributor for the sake of simplicity. However, identifying molecules with resonance is an important skill in organic chemistry.

This example shows an important exception to the general rules for determining the hybridization of an atom. The oxygen with the negative charge appears to be $sp^3$ hybridized because it is surrounded by four electron groups. However, this representation of the oxygen atom is not correct because it is actually part of a resonance hybrid. A pair of lone pair of electrons on the negatively charged oxygen are not localized in an $sp^3$ orbital, rather, they are delocalized as part of a

conjugated pi system. The stability gained though resonance is enough to cause the expected $sp^3$ to become $sp^2$. The $sp^2$ hybridization gives the oxygen a p orbital allowing it to participate in conjugation. As a general rule $sp^3$ hybridized atoms with lone pair electrons tend to become $sp^2$ hybridized when adjacent to a conjugated system.




oxygen is *conjugated*




oxygen is *not conjugated*

## Example: Carbonate ($CO_3^{2-}$)

Like formate, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike $O_3$, though, the Lewis structures describing $CO_3^{2-}$ has *three* equivalent representations.

1. Because carbon is the least electronegative element, we place it in the central position:

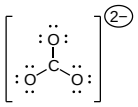


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the 2− charge. This gives 4 + (3 × 6) + 2 = 24 valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

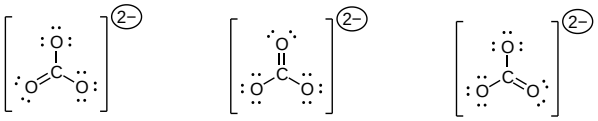


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the 2− charge:

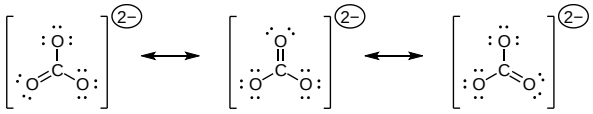



5. There are no electrons left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:




As with formate, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:




As the case for formate, the actual structure involves the formation of a molecular orbital from $p_z$ orbitals centered on each atom and sitting above and below the plane of the $CO_3^{2-}$ ion.

## Example 2.4.1

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule ($C_6H_6$) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

**Given:** molecular formula and molecular geometry

**Asked for:** resonance structures

**Strategy:**

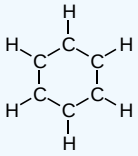
**A** Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.

**B** Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.

**C** Draw the resonance structures for benzene.

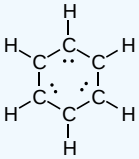
**Solution:**

**A** Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



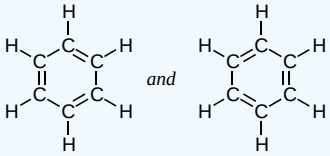
Each carbon atom in this structure has only 6 electrons and has a formal charge of 1+, but we have used only 24 of the 30 valence electrons.

**B** If the 6 remaining electrons are uniformly distributed pair-wise on alternate carbon atoms, we obtain the following:

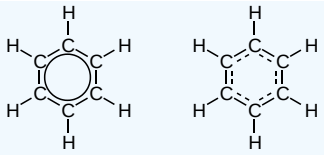


Three carbon atoms now have an octet configuration and a formal charge of 1−, while three carbon atoms have only 6 electrons and a formal charge of 1+. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

**C** There are, however, two ways to do this:

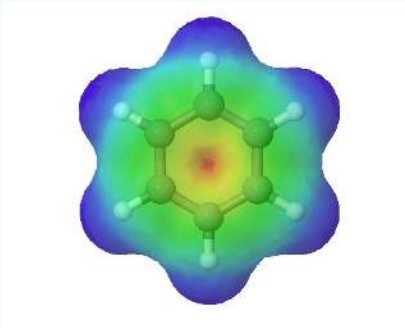



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



benzene

This combination of *p* orbitals for benzene can be visualized as a ring with a node in the plane of the carbon atoms. As can be seen in an electrostatic potential map of benzene, the electrons are distributed symmetrically around the ring.



## ? Exercise 2.6.1

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion ($NO_2^-$).

**Answer**



## Exercises

## Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Layne Morsch (University of Illinois Springfield)
- Dr. Krista Cunningham

### Extra example - $O_3$

A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone ($O_3$), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

1. We know that ozone has a V-shaped structure, so one O atom is central:



2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

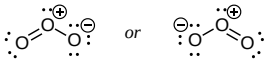


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:



6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either

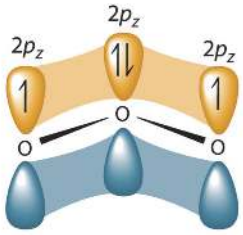



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. If the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in $O_2$ (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called resonance structures . The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



Figure 2.4.1).




*The resonance structure of ozone involves a molecular orbital extending all three oxygen atoms.In ozone, a molecular orbital extending over all three oxygen atoms is formed from three atom centered $p_z$ orbitals. Similar molecular orbitals are found in every resonance structure.*

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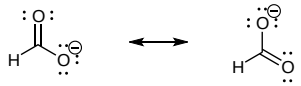
- **2.3: Resonance** by Dietmar Kennepohl, Krista Cunningham, Layne Morsch, Steven Farmer, Tim Soderberg is licensed CC BY-SA 4.0.

# 2.7: Rules for Resonance Forms

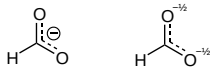
## Rules for Drawing and Working with Resonance Contributors

Recognizing, drawing, and evaluating the relative stability of resonance contributors is essential to understanding organic reaction mechanisms. When learning to draw and interpret resonance structures, there are a few basic guidelines to help. .

1) There is ONLY ONE REAL STRUCTURE for each molecule or ion. This real structure (the **resonance hybrid**) takes its character from the average of all the individual **resonance contributors**. When looking at a resonance contributors, we are seeing the exact same molecule or ion depicted in different ways. Resonance hybrids are really a single, unchanging structure.



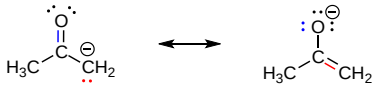
*Major resonance contributors of the formate ion*



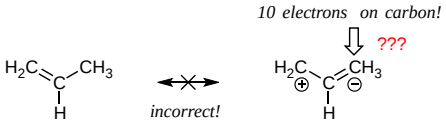
*Representations of the formate resonance hybrid*

2) The resonance hybrid is more stable than any individual resonance structures. Often, resonance structures represent the movement of a charge between two or more atoms. The charge is spread out amongst these atoms and therefore more stabilized. When looking at the picture above the resonance contributors represent the negative charge as being on one oxygen or the other. The resonance hybrid shows the negative charge being shared equally between two oxygens. In the resonance hybrid, the negative charge is spread out over a larger part of the molecule and is therefore more stable.

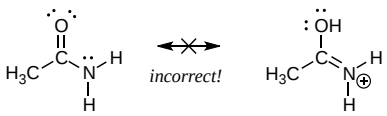
3) Resonance contributors do not have to be equivalent. Because of this, resonance structures do necessarily contribute equally to the resonance hybrid. The two resonance structures shown below are not equivalent because one show the negative charge on an oxygen while the other shows it on a carbon. Later, we will show that the contributor with the negative charge on the oxygen is the more stable of the two. Also, this means that the resonance hybrid will not be an exact mixture of the two structures.



4) All resonance contributors must be correct Lewis structures. Each atom should have a complete valence shell and be shown with correct formal charges. A carbocation (carbon with only 6 valence electrons) is the only allowed exception to the valence shell rules. The structure below is an invalid resonance structure even though it only shows the movement of a pi bond. The resulting structure contains a carbon with ten electrons, which violates the octet rule, making it invalid.




5) All resonance contributors must have the same molecular formula, the same number of electrons, and same net charge. The molecules in the figure below are not resonance structures of the same molecule because then have different molecular formulas ($C_2H_5NO$ Vs. $C_2H_6NO$). Also, the two structures have different net charges (neutral Vs. positive).

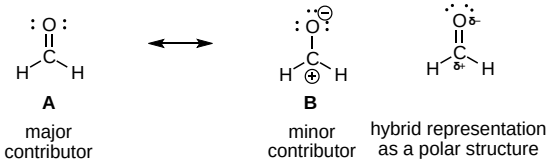



6) Resonance contributors only differ by the positions of pi bond and lone pair electrons. Sigma bonds are never broken or made, because of this atoms must maintain their same position. The molecules in the figure below are not resonance structures of the same molecule even though they have the same molecular formula ($C_3H_6O$). These molecules are considered structural isomers because their difference involves the breaking of a sigma bond and moving a hydrogen atom.



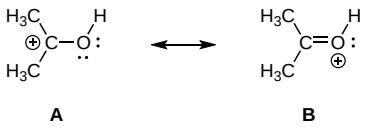

## Major and Minor Resonance Contributors

As previously state the true structure of a resonance hybrid is the combination of all the possible resonance structures. If the resonance structures are equal in stability they the contribute equally to the structure of the hybrid. However, if the resonance structures have different stabilities they contribute to the hybrid's structure in proportions related to their relative stabilities. It can be said the the resonance hybrid's structure resembles the most stable resonance structure. Because of this it is important to be able to compare the stabilities of resonance structures. In the example below, structure **B** is much less important in terms of its contribution to the hybrid because it contains the violated octet of a carbocation. The relative stabilities of the two structures are so vastly different that molecules which contain a C=O bond are almost exclusively written in a form like structure **A**. However, as will learn in chapter 19, the positively charged carbon created by structure **B** will explain how the C=O bond will react with electron rich species.

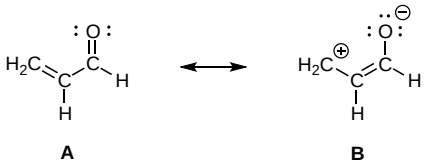



## Rules for Estimating Stability of Resonance Structures

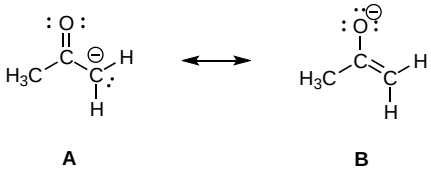
1. The resonance structures in which all atoms have complete valence shells is more stable. This means most atoms have a full octet. In the example below structure **A** has a carbon atom with a positive charge and therefore an incomplete octet. Based on this criterion, structure **A** is less stable and is a more minor contributor to the resonance hybrid than structure **B**.




2. The structures with the **least number of formal charges** is more stable. Based on this, structure **B** is less stable because is has two atoms with formal charges while structure **A** has none. Structure **A** would be the major resonance contributor.

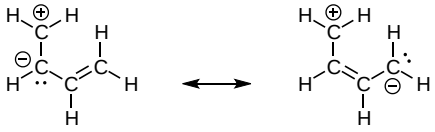



3. The structures with a **negative charge on the more electronegative atom** will be more stable. The difference between the two resonance structures is the placement of a negative charge. Structure **B** is the more stable and the major resonance contributor, because it places the negative charge on the more electronegative oxygen.



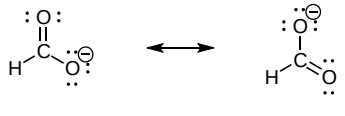

4. The structures with a **positive charges on the least electronegative atom** (most electropositive) is more stable.

5. The structures with the **least separation of formal charges** is more stable. The only difference between the two structures below are the relative positions of the positive and negative charges. In structure **A** the charges are closer together making it more stable.



**A** **B**

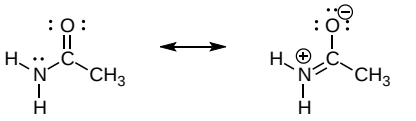
6. **Resonance forms that are equivalent have no difference in stability**. When looking at the two structures below no difference can be made using the rules listed above. This means the two structures are equivalent in stability and would make equal structural contributions to the resonance hybrid.



**A** **B**

## Examples of major and minor contributors

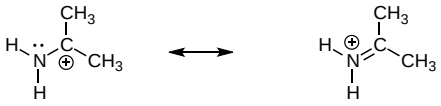
**Example 1:**



major contributor
(neutral structure)

minor contributor
(charge separation)

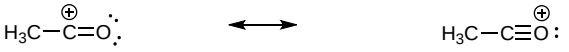
**Example 2:**



minor contributor
(Incomplete octet on carbon.)

major contributor
(All atoms have octets, even though there is a positive charge on nitrogen.)

**Example 3:**

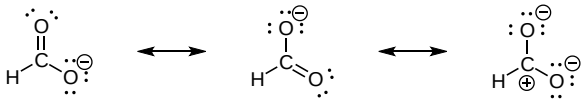


minor contributor
(Incomplete octet on carbon, but more important in terms of reactivity.)

major contributor
(All atoms have octets, even though there is a positive charge on oxygen.)

## Carboxylate example

In the case of carboxylates, contributors **A** and **B** below are equivalent in terms of their relative contribution to the hybrid structure. However, there is also a third resonance contributor **C**, in which the carbon bears a positive formal charge (a carbocation) and both oxygens are single-bonded and bear negative charges.



A B C

minor contributor
(separation of charge)

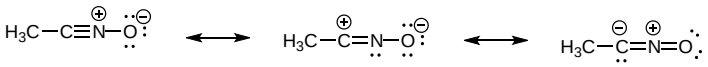
Structure **C** makes a less important contribution to the overall bonding picture of the group relative to **A** and **B**. How do we know that structure **C** is the 'minor' contributor? Apply the rules below

- The carbon in contributor **C** does not have an octet. In general, resonance contributors in which a carbon does not fulfill the octet rule are relatively less important. (rule #1)
- In structure **C**, there are only three bonds, compared to four in **A** and **B**. In general, a resonance structure with a lower number of total bonds is relatively less important. (rule #2)
- Structure **C** also has more formal charges than are present in **A** or **B**. In general, resonance contributors in which there is more/greater separation of charge are relatively less important. (rule #3)
- Structures **A** and **B** are equivalent and will be equal contributors to the resonance hybrid. (rule #5).
- The resonance contributor in which a negative formal charge is located on a more electronegative atom, usually oxygen or nitrogen, is more stable than one in which the negative charge is located on a less electronegative atom such as carbon. An example is in the upper left expression in the next figure. (rule #4)

## Example with 3 resonance structures

Molecules with more than 2 resonance structures can also be considered using the rules listed above. Of the resonance structures listed below, structure **A** would be the most stable because all the non-hydrogen atoms have a full octet and the negative charge is on the more electronegative atom (oxygen). Structure **C** would be next in stability because all of the non-hydrogen atoms have full octets, though now the negative charge is on carbon rather than oxygen. Structure **B** would be the least stable of the three because it has the carbocation does not have an octet. Of the three, structure **A** would be the major resonance structure and would most resemble the structure of the structure of the true resonance hybrid. Structure **B** is considered a minor resonance contributor and would have very little effect on the structure of the resonance hybrid.

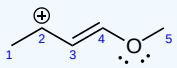

- **2.4: Rules for Resonance Forms** by Dietmar Kennepohl, Krista Cunningham, Steven Farmer, Tim Soderberg, William Reusch is licensed CC BY-SA 4.0.

A B C

### Example 2.7.1

Draw the major resonance contributor of the structure below. Include in your figure the appropriate curved arrows showing how you got from the given structure to your structure. Explain why your contributor is the major one. In what kind of orbitals are the two lone pairs on the oxygen?



**Solution**

In the structure above, the carbon with the positive formal charge does not have a complete octet of valence electrons. Using the curved arrow convention, a lone pair on the oxygen can be moved to the adjacent bond to the left, and the electrons in the double bond shifted over to the left (see the rules for drawing resonance contributors to convince yourself that these are 'legal' moves).

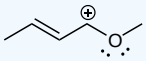


minor
(Carbon does not have a complete octet.)

major
(All atoms have a complete octet.)

The resulting resonance contributor, in which the oxygen bears the formal charge, is the major one because all atoms have a complete octet, and there is one additional bond drawn (resonance rules #1 and #2 both apply). This system can be thought of as four parallel *2p* orbitals (one each on $C_2$, $C_3$, and $C_4$, plus one on oxygen) sharing four pi electrons. One lone pair on the oxygen is in an unhybridized *2p* orbital and is part of the conjugated pi system, and the other is located in an $sp^2$ orbital.

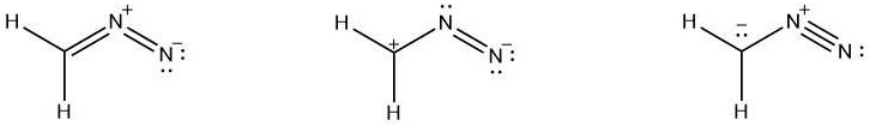
Also note that one additional contributor can be drawn, but it is also minor because it has a carbon with an incomplete octet:



minor

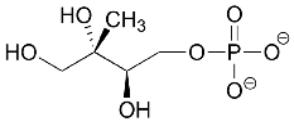
## Exercises

1) For the following resonance structures please rank them in order of stability. Indicate which would be the major contributor to the resonance hybrid.



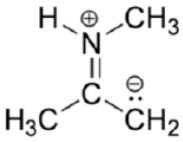
I II III

2) Draw four additional resonance contributors for the molecule below. Label each one as major or minor (the structure below is of a major contributor).

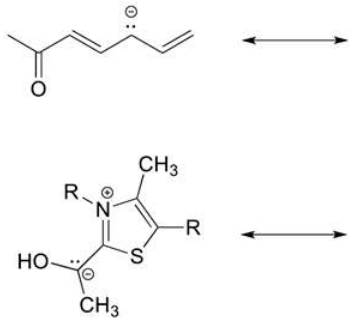


3) Draw three resonance contributors of methyl acetate (an ester with the structure $CH_3COOCH_3$), and order them according to their relative importance to the bonding picture of the molecule. Explain your reasoning.

4) Below is a minor resonance contributor of a species known as an 'enamine', which we will study more in Section 19.8 (formation of enamines) Section 23.12 (reactions of enamines). Draw the major resonance contributor for the enamine, and explain why your contributor is the major one.



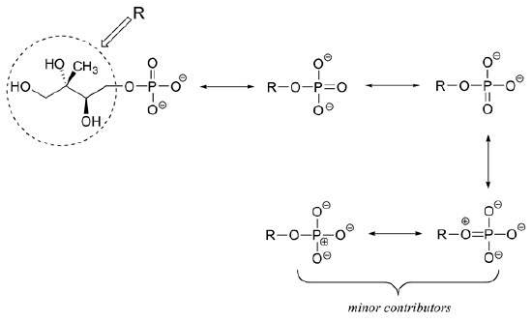
5) Draw the major resonance contributor for each of the anions below:



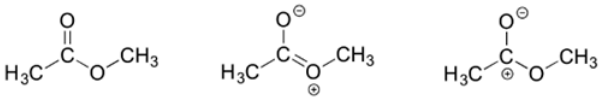
## Solutions

1) Structure I would be the most stable because all the non-hydrogen atoms have a full octet and the negative charge is on the more electronegative nitrogen. Structure III would be the next in stability because all of the non-hydrogen atoms have full octets. Structrure II would be the least stable because it has the violated octet of a carbocation.

2)




3)

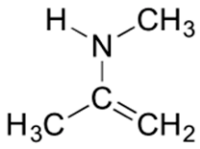


The contributor on the left is the most stable: there are no formal charges.

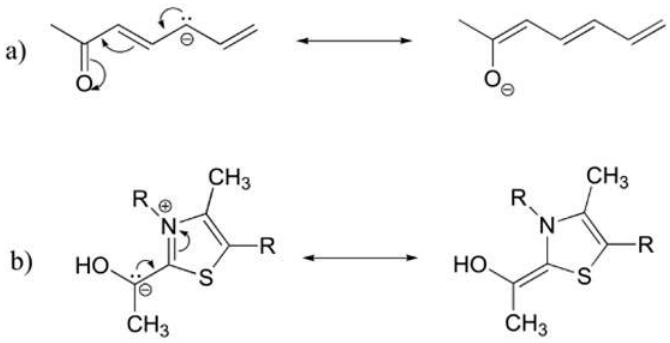
The contributor on the right is least stable: there are formal charges, and a carbon has an incomplete octet.

The contributor in the middle is intermediate stability: there are formal charges, but all atoms have a complete octet.

4) This contributor is major because there are no formal charges.



5)




## Exercises

## Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Layne Morsch (University of Illinois Springfield)
- Dr. Krista Cunningham

### Additional resonance topics

## Recognizing Resonance

Resonance contributors involve the ‘imaginary movement’ of pi-bonded electrons or of lone-pair electrons that are adjacent to (i.e. conjugated to) pi bonds. You can never shift the location of electrons in sigma bonds – if you show a sigma bond forming or breaking, you are showing a chemical reaction taking place. Likewise, the positions of atoms in the molecule cannot change between two resonance contributors.

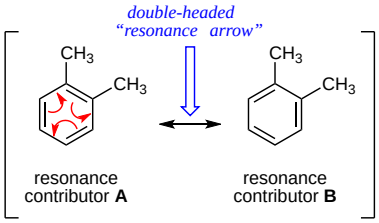
Because benzene will appear throughout this course, it is important to recognize the stability gained through the resonance delocalization of the six pi electrons throughout the six carbon atoms. Benzene also illustrates one way to recognize resonance - when it is possible to draw two or more equivalent Lewis structures. If we were to draw the structure of an aromatic molecule such as 1,2-dimethylbenzene, there are two ways that we could draw the double bonds:




*Is this correct…* *…or is this?*

Which way is correct? There are two simple answers to this question: 'both' and 'neither one'. Both ways of drawing the molecule are equally acceptable approximations of the bonding picture for the molecule, but neither one, by itself, is an accurate picture of the delocalized pi bonds. The two alternative drawings, however, when considered together, give a much more accurate picture than either one on its own. This is because they imply, together, that the carbon-carbon bonds are not double bonds, not single bonds, but about halfway in between.

When it is possible to draw more than one valid structure for a compound or ion, we have identified **resonance contributors**: two or more different Lewis structures depicting the same molecule or ion that, when considered together, do a better job of approximating delocalized pi-bonding than any single structure. By convention, resonance contributors are linked by a double-headed arrow, and are sometimes enclosed by brackets:

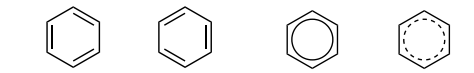



In order to make it easier to visualize the difference between two resonance contributors, small, curved arrows are often used. Each of these arrows depicts the 'movement' of two pi electrons. In the drawing of resonance contributors, however, this electron 'movement' occurs only in our minds, as we try to visualize delocalized pi bonds. Nevertheless, use of the curved arrow notation is an essential skill that you will need to develop in drawing resonance contributors.

The depiction of benzene using the two resonance contributors A and B in the figure above does *not* imply that the molecule at one moment looks like structure A, then at the next moment shifts to look like structure B. Rather, at all moments, the molecule is a combination, or **resonance hybrid** of both A and B.

**Caution**! It is very important to be clear that in drawing two (or more) resonance contributors, we are not drawing two different molecules: they are simply *different depictions of the exact same molecule*. Furthermore, the double-headed resonance arrow does NOT mean that a chemical reaction has taken place.

Benzene is often drawn as only one of the two possible resonance contributors (it is assumed that the reader understands that resonance hybridization is implied). However, sometimes benzene will be drawn with a circle inside the hexagon, either solid or dashed, as a way of drawing a resonance hybrid.




## Examples of Resonance

*Molecules with a Single Resonance Configuration*

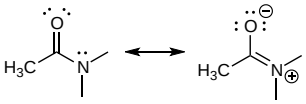
**Example 1:**



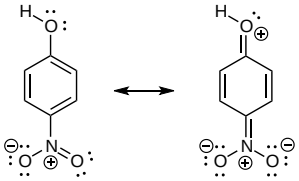
**Example 2:**



**Example 3:**




**Example 4:**



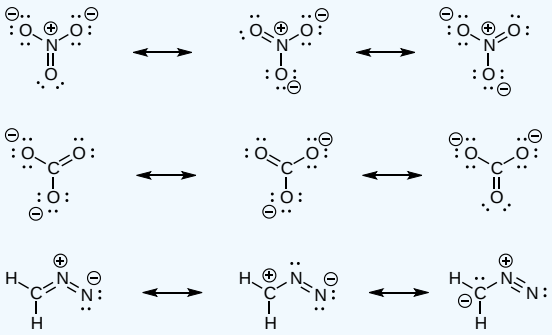

The above resonance structures show that the electrons are delocalized within the molecule and through this process the molecule gains extra stability. Ozone with both of its opposite formal charges creates a neutral molecule and through resonance it is a stable

molecule. The extra electron that created the negative charge one terminal oxygen can be delocalized by resonance through the other terminal oxygen.

Benzene is an extremely stable molecule due to its geometry and molecular orbital interactions, but most importantly, due to its resonance structures. The delocalized electrons in the benzene ring make the molecule very stable and with its characteristics of a nucleophile, it will react with a strong electrophile only and after the first reactivity, the substituted benzene will depend on its resonance to direct the next position for the reaction to add a second substituent.

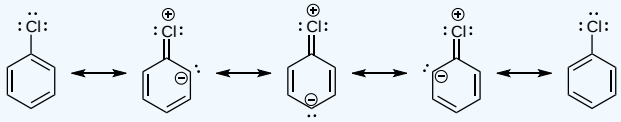
### Example 2.5.1: Multiple Resonance of other Molecules

Molecules and ions with more than one resonance form:



Some structural resonance conformations are the major contributor or the dominant forms that the molecule exists. For example, if we look at the above rules for estimating the stability of a molecule, we see that for the third molecule the first and second forms are the major contributors for the overall stability of the molecule. The nitrogen is more electronegative than carbon so, it can handle the negative charge more than carbon. A carbon with a negative charge is the least favorable conformation for the molecule to exist, so the last resonance form contributes very little for the stability of the Ion.

**Hybrid Resonance**



*The different resonance forms of the molecule help predict the reactivity of the molecule at specific sites.*

The Hybrid Resonance forms show the different Lewis structures with the electron been delocalized. This is very important for the reactivity of chloro-benzene because in the presence of an electrophile it will react and the formation of another bond will be directed and determine by resonance. The lone pair of electrons delocalized in the aromatic substituted ring is where it can potentially form a new bond with an electrophile, as it is shown there are three possible places that reactivity can take place, the first to react will take place at the *para* position with respect to the chloro- substituent and then to either *ortho*- position.

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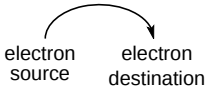
# 2.8: Drawing Resonance Forms

**Key words**

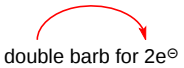
- resonance structure
- resonance hybrid

## Curved Arrows Communicate Electron Flow (movement)

Organic chemistry has developed a system to show how electrons move between resonance structures. This system will also be used to help describe how electrons from in reactions. Curved double barbed arrows indicates the flow of two electrons. The base of the curved arrow is placed at the source of the electrons that are moving. The head of the arrow is placed at the destination of the

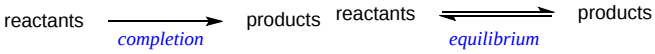



electrons.

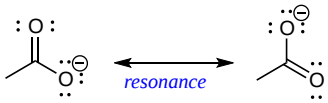



It is also important to consciously use the correct type of arrow. There are four primary types of arrows used by chemists to communicate one of the following: completion reaction, equilibrium reaction, electron movement, and resonance forms. The three other types of arrows are shown below to build discernment between them. Note, the electron movement arrows are the only ones that are curved.

### Reaction Arrows




### Resonance Arrows

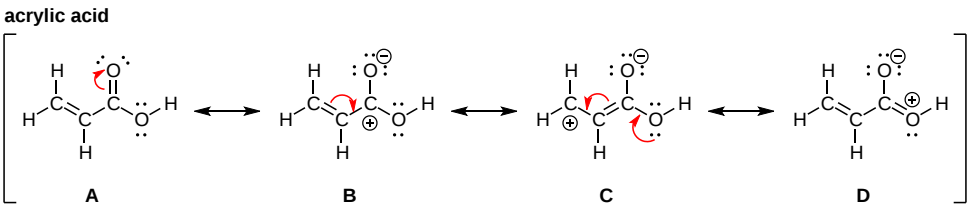



## Using Curved Arrows to Show Electron Movement

Because the double barbed arrow represents the movement of two electrons, they usually involve lone pair electrons or pi bonds. There are only three types of electron "motion" in resonance. They are:

1. **A lone pair forms a pi bond to an adjacent atom**
2. **A pi bond forms a new pi bond to an adjacent atom**
3. **A pi bond forms a lone pair on adjacent atom**

Let's look at the resonance within acrylic acid to demonstrate these three types of resonance.

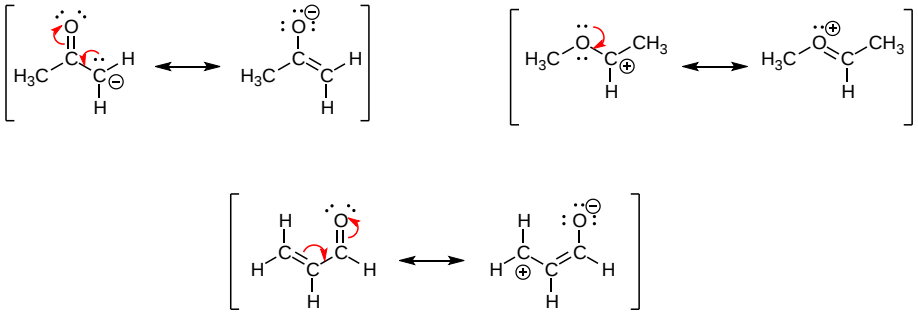



The curved arrow in structure A represents the type 3 resonance "motion" - the pi bond between the carbon and oxygen breaks to form another lone pair on the oxygen. The curved arrow in structure B represents type 2 resonance "motion" - the pi bond breaks to form a new pi bond to the carbocation carbon. In structure C, there are two curved arrows. The curved arrow from the oxygen lone

pair is type 1 resonance motion - the lone pairs forms a new pi bond between the oxygen and carbon. The other arrow in structure C moves the pi bond to the end of the chain and represents resonance type 2. By combining these three basic types of electron movement we can describe virtually any type of resonance.

## Example:

Below are a few more examples of 'legal' resonance expressions. Confirm for yourself that the octet rule is not exceeded for any atoms, that formal charges are correct, and identify which type of electron movement is being represented by each arrow.

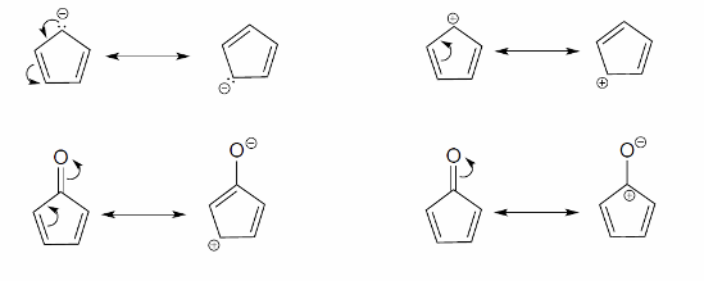


### Exercise 2.8.1

Draw the resonance contributors that correspond to the curved, two-electron movement arrows in the resonance expressions below. Then identify the type of resonance motion in each structure below.

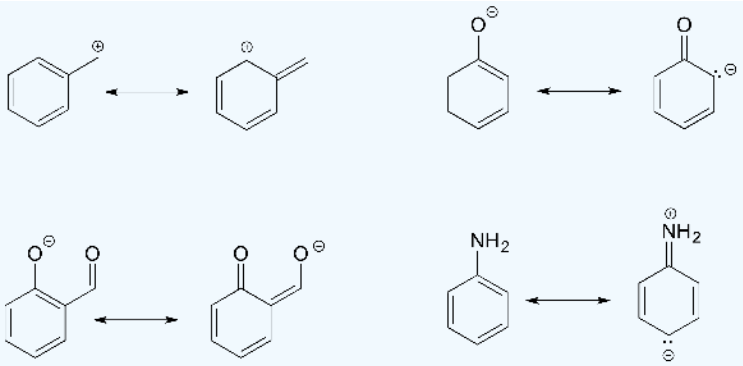


**Answer**

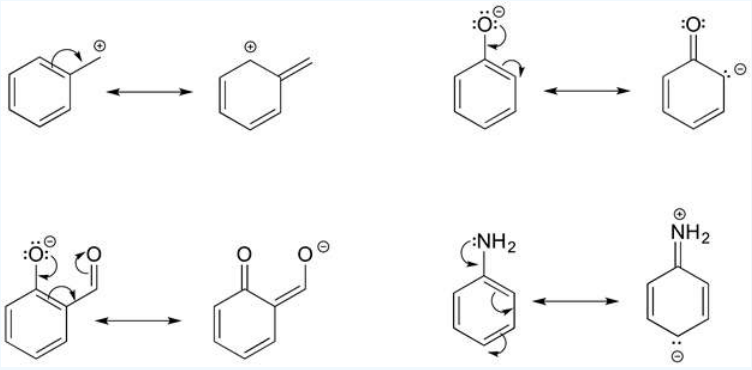


### Exercise 2.8.2

In each resonance expression, identify the type of resonance motion. Then draw curved arrows on the left-side contributor that shows how we get to the right-side contributor.



**Answer**



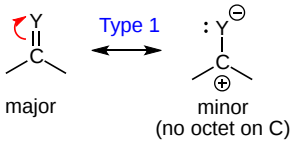
## Recognizing Common Patterns of Resonance

If you examine a large number of resonance examples, you will begin to notice that they nearly always match common patterns, of which there are only three. It is important to be able to identify atoms that participate in resonance. In complex resonance cases, multiple types of resonance may occur simultaneously.

## Type I - Neutral Species

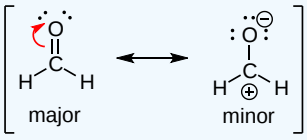
The electrons of a pi bond move to become a set of lone pair electrons on a electronegative atom. The resonance structure made has a carbon with a violated octet which make it a minor contributor. This type of resonance is commonly used to the polarity in certain double bonds.

*Neutral Species*




Note: Y is an electronegative atom, usually N, O, or S.

### ✔ Type I Example

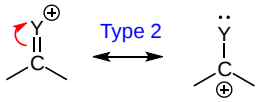



## Type II - Charged Species

Type II resonance is only seen with a + charge, and usually involves a positive charge on oxygen or nitrogen being shared onto a carbon; the carbocation form has only six valence electrons on the carbon, so it is a less stable form than the major form (which has

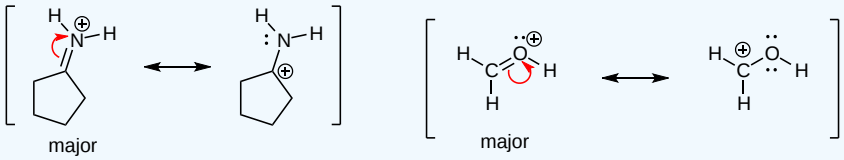
complete octets).

*Charged Species*



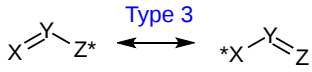

Note: Y is an electronegative atom, usually N, O, S, sometimes halogen

**Type II Example**




## Type III - Allylic Resonance

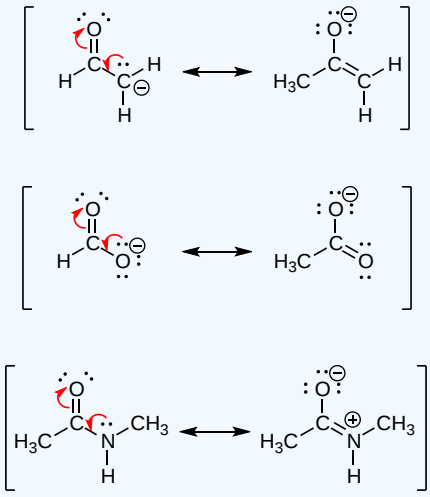
Type III resonance is very common and important because is serves to stabilize positive charges, negative charges, or lone pairs. It is sometimes referred to as “allylic” resonance, especially in cases with all carbon. This type of resonance can be identified by a three-atom group of atoms each with $sp^2$ hybridization and a *p* orbital.




* represents a charge or an unpaired electron

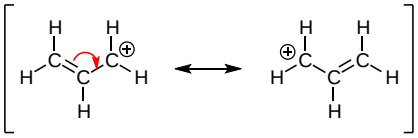
**Type III Example**

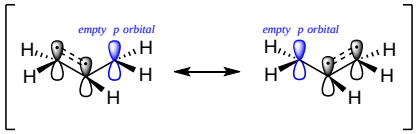
Atoms with lone pair electrons next to a pi bond can be $sp^2$ hybridized and have the lone pair of electrons in a p orbital despite the fact that they are surrounded by four electron groups. The lone pair electrons contained in the p orbital cause the ion to be stabilized due to resonance.



Similarly, carbocations are $sp^2$-hybridized, with an empty *2p* orbital oriented perpendicular to the plane formed by three sigma bonds. If a carbocation is adjacent to a double bond, then three *2p* orbitals can overlap and share the two pi electrons - another kind of conjugated pi system in which the positive charge is shared over two carbons.

*charge is delocalized over two carbons*

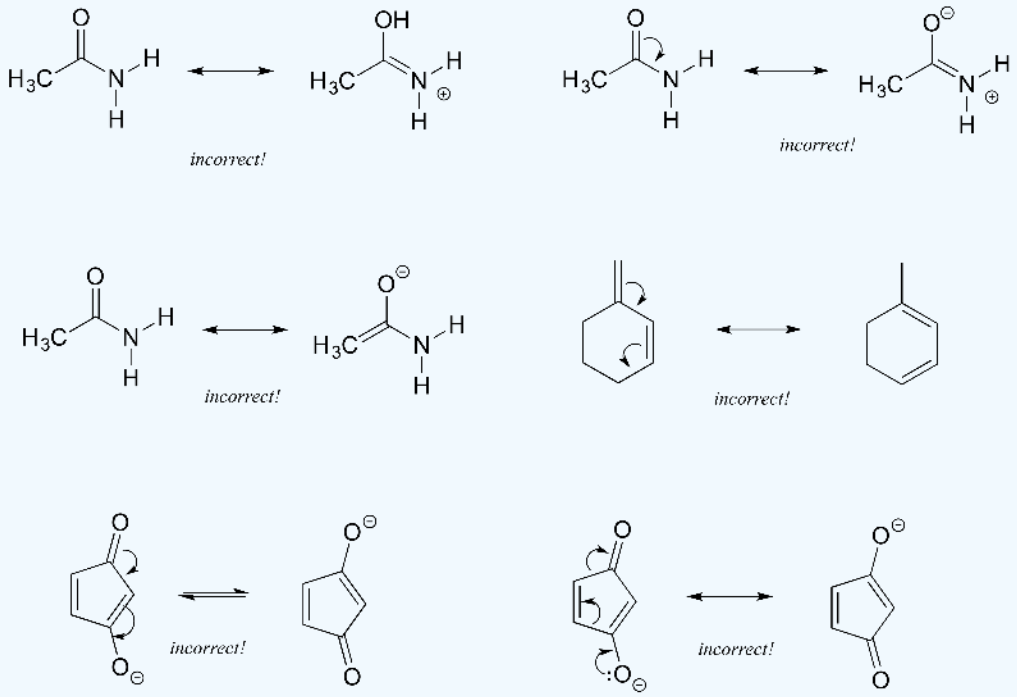





three *p* orbitals sharing two pi electrons

## Exercise 2.8.3

Each of the 'illegal' resonance expressions below contains one or more mistakes. Explain what is incorrect in each.

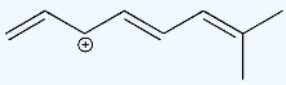



**Answer**

The first pair are not resonance structures since there is an additional hydrogen on the second structure oxygen. The second pair pushed electrons toward nitrogen which already has a lone pair and would exceed its octet. The third pair includes a structure with 5 bonds to carbon. The fourth pair requires moving carbon-hydrogen bonds, therefore is not resonance. The fifth pair show electrons moving toward the negatively charged oxygen which would exceed an octet. The fifth pair shows a sigma bond breaking on the ring, rather than pi bond.

## Exercise 2.8.4

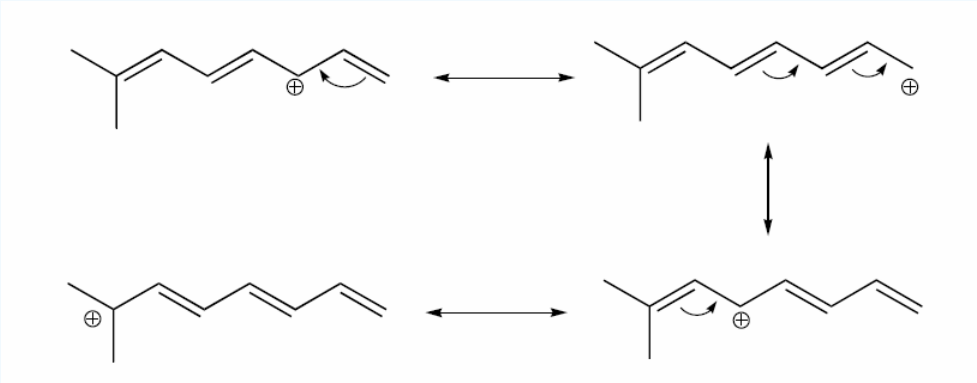
a) Draw three additional resonance contributors for the carbocation below. Include in your figure the appropriate curved arrows showing how one contributor is converted to the next.



b) Fill in the blanks: the conjugated pi system in this carbocation is composed of _____ *2p* orbitals sharing _____ delocalized pi electrons.

**Answer**

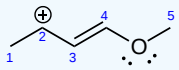
a)



b) The conjugated pi system in this carbocation is composed of seven p orbitals containing six delocalized pi electrons.

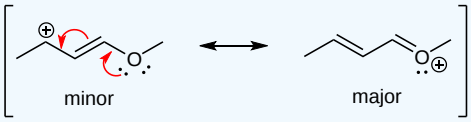
## Example 2.8.1

Draw the major resonance contributor of the structure below. Include in your figure the appropriate curved arrows showing how you got from the given structure to your structure. Explain why your contributor is the major one. In what kind of orbitals are the two lone pairs on the oxygen?



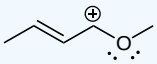

**Solution**

In the structure above, the carbon with the positive formal charge does not have a complete octet of valence electrons. Using the curved arrow convention, a lone pair on the oxygen can be moved to the adjacent bond to the left, and the electrons in the double bond shifted over to the left (see the rules for drawing resonance contributors to convince yourself that these are 'legal' moves).




The resulting resonance contributor, in which the oxygen bears the formal charge, is the major one because all atoms have a complete octet, and there is one additional bond drawn (resonance rules #1 and #2 both apply). This system can be thought of as four parallel *2p* orbitals (one each on $C_2$, $C_3$, and $C_4$, plus one on oxygen) sharing four pi electrons. One lone pair on the oxygen is in an unhybridized *2p* orbital and is part of the conjugated pi system, and the other is located in an $sp^2$ orbital.

Also note that one additional contributor can be drawn, but it is also minor because it has a carbon with an incomplete octet:



## Exercise 2.8.5

The figure below shows how the negative formal charge on an oxygen (of an enol) can be delocalized to the carbon indicated by an arrow. More resonance contributors can be drawn in which negative charge is delocalized to three other atoms on the molecule.

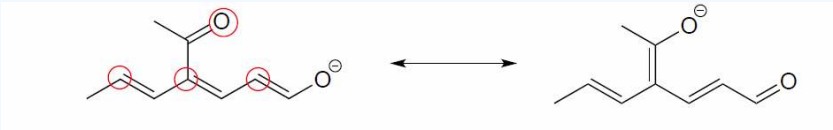
a) Circle these atoms that can also have a resonance structure with a negative charge.

b) Draw the two most important resonance contributors for the enolate ion.



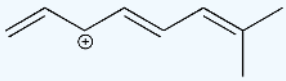
**Answer**

The two major contributors are those in which the negative formal charge is located on an oxygen rather than on a carbon.



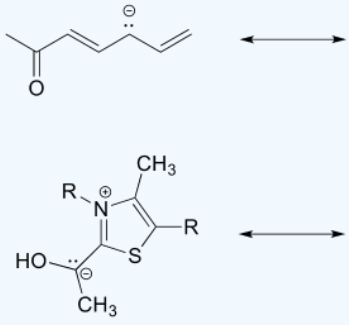
**Exercise 2.6.5:**

a) Draw three additional resonance contributors for the carbocation below. Include in your figure the appropriate curved arrows showing how one contributor is converted to the next.



b) Fill in the blanks: the conjugated pi system in this carbocation is composed of _____ *2p* orbitals sharing _____ delocalized pi electrons.

**Exercise 2.6.6:** Draw the major resonance contributor for each of the anions below.



c) Fill in the blanks: the conjugated pi system in part (a) is composed of _____ *2p* orbitals containing _____ delocalized pi electrons.

**Exercise 2.6.7:** The figure below shows how the negative formal charge on the oxygen can be delocalized to the carbon indicated by an arrow. More resonance contributors can be drawn in which negative charge is delocalized to three other atoms on the molecule.

a) Circle these atoms.

b) Draw the two most important resonance contributors for the molecule.



## A word of advice

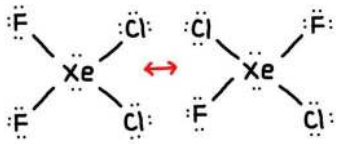
Becoming adept at drawing resonance contributors, using the curved arrow notation to show how one contributor can be converted to another, and understanding the concepts of conjugation and resonance delocalization are some of the most challenging but also most important jobs that you will have as a beginning student of organic chemistry. If you work hard now to gain a firm grasp of these ideas, you will have come a long way toward understanding much of what follows in your organic chemistry course. Conversely, if you fail to come to grips with these concepts now, a lot of what you see later in the course will seem like a bunch of mysterious and incomprehensible lines, dots, and arrows, and it will be difficult to be successful in organic chemistry.

### References


1. Petrucci, Ralph H., et al. *General Chemistry: Principles and Modern Applications*. New Jersey: Pearson Prentice Hall, 2007. Print.
2. Ahmad, Wan-Yaacob and Zakaria, Mat B. "Drawing Lewis Structures from Lewis Symbols: A Direct Electron Pairing Approach." Journal of Chemical Education: Journal 77.3: n. pag. Web. March 2000. Link to this journal: pkukmweb.ukm.my/~mbz/c_penerb...83%29/p329.pdf


### Problems

1. True or False, The picture below is a resonance structure?

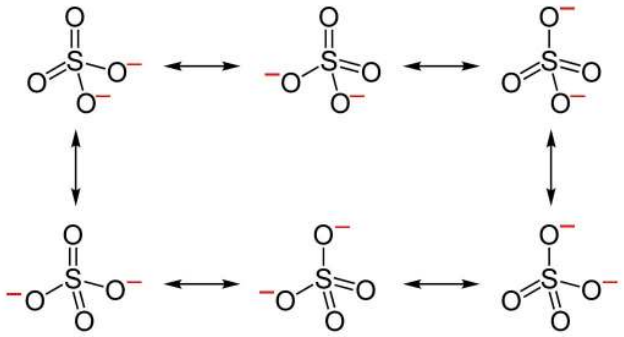


2. Draw the Lewis Dot Structure for $\mathbf{SO_4^{2-}}$ and all possible resonance structures. Which of the following resonance structure is not favored among the Lewis Structures? Explain why. Assign Formal Charges.
3. Draw the Lewis Dot Structure for $\mathbf{CH_3COO^-}$ and all possible resonance structures. Assign Formal Charges. Choose the most favorable Lewis Structure.
4. Draw the Lewis Dot Structure for $\mathbf{HPO_3^{2-}}$ and all possible resonance structures. Assign Formal Charges.
5. Draw the Lewis Dot Structure for $\mathbf{CHO_2^{1-}}$ and all possible resonance structures. Assign Formal Charges.
6. Draw the Resonance Hybrid Structure for $\mathbf{PO_4^{3-}}$.
7. Draw the Resonance Hybrid Structure for $\mathbf{NO_3^-}$.

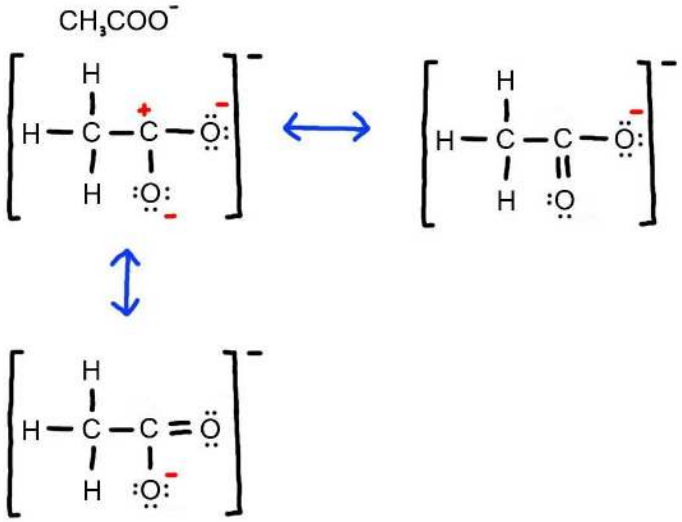
#### Answers

1. False, because the electrons were not moved around, only the atoms (this violates the Resonance Structure Rules).

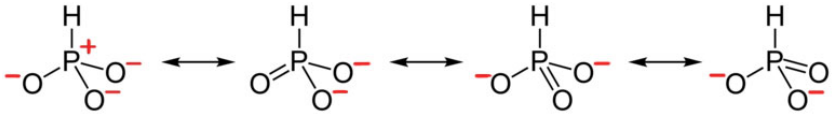
2. Below are the all Lewis dot structure with formal charges (in red) for Sulfate ($\mathbf{SO_4^{2-}}$). There isn't a most favorable resonance of the Sulfate ion because they are all identical in charge and there is no change in Electronegativity between the Oxygen atoms.



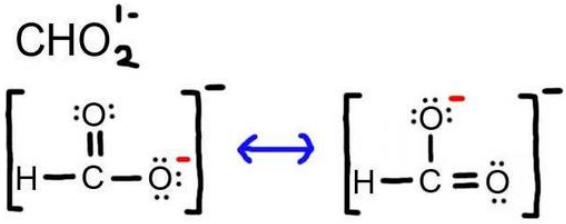
3. Below is the resonance for **$CH_3COO^-$**, formal charges are displayed in red. The Lewis Structure with the most formal charges is not desirable, because we want the Lewis Structure with the least formal charge.



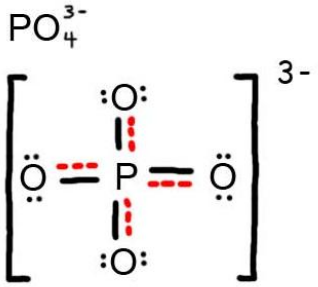

4. The resonance for **$HPO_3^{2-}$**, and the formal charges (in red).



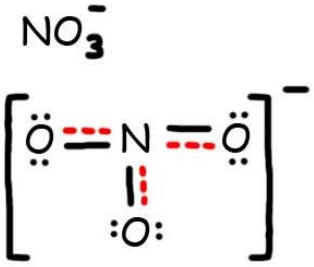
5. The resonance for **$CHO_2^{1-}$**, and the formal charges (in red).




6. The resonance hybrid for **$PO_4^{3-}$**, hybrid bonds are in red.




7. The resonance hybrid for $\mathbf{NO_3^-}$, hybrid bonds are in red.




## Contributors and Attributions

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# CHAPTER OVERVIEW

## 3: Acids and Bases


3.1: Acids and Bases - The Brønsted-Lowry Definition
3.2: Acids and Bases - The Lewis Definition
3.3: Acid and Base Strength
3.4: Predicting Acid-Base Reactions from pKa Values
3.5: Organic Acids and Organic Bases
3.6: Keto-Enol Tautomerism


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# 3.1: Acids and Bases - The Brønsted-Lowry Definition

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- Brønsted-Lowry acid
- Brønsted-Lowry base
- conjugate acid
- conjugate base

**Study Notes**

You should already be familiar with the Brønsted-Lowry concept of acidity and the differences between strong and weak acids. You may wish to review this topic before proceeding.

In 1923, chemists Johannes Brønsted and Martin Lowry independently developed definitions of acids and bases based on compounds abilities to either donate or accept protons ($H^+$ ions). Here, acids are defined as being able to donate protons in the form of hydrogen ions; whereas bases are defined as being able to accept protons. This took the Arrhenius definition one step further as water is no longer required to be present in the solution for acid and base reactions to occur.

## Brønsted-Lowry Definition

J.N. Brønsted and T.M. Lowry independently developed the theory of proton donors and proton acceptors in acid-base reactions, coincidentally in the same region and during the same year. The Arrhenius theory where acids and bases are defined by whether the molecule produces hydrogen ion or hydroxide ion when dissolved in water was too limiting, because not all chemical reactions, especially organic reactions, occur in water. The Brønsted-Lowry Theory defines an acid a proton donor, while a base is a proton acceptor. This is illustrated in the following reactions:

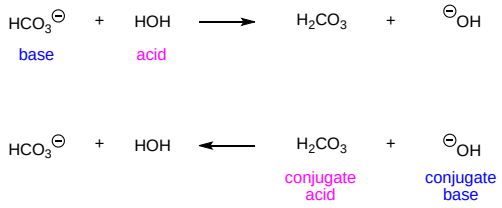
$$HCl + HOH \rightarrow H_3O^+ + Cl^- \tag{3.1.1}$$

$$HOH + NH_3 \rightarrow NH_4^+ + OH^- \tag{3.1.2}$$

| Acid | Base | |
|---|---|---|
| **Donates hydrogen ions** | **Accepts hydrogen ions.** | |
| HCl | HOH → | $H_3O^+ + Cl^-$ |
| HOH | $NH_3$→ | $NH_4^+ + {}^-OH$ |

The determination of a substance as a Brønsted-Lowry acid or base can only be done by examining the reaction, since many chemicals can be either an acid or a base. For example, HOH is a base in the first reaction and an acid in the second reaction.

**Bronsted-Lowry Acids and Bases**

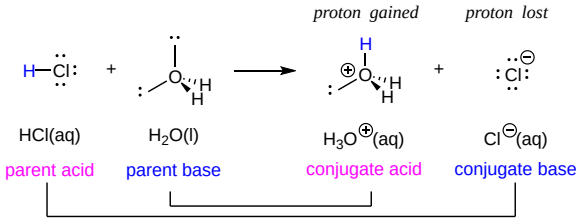



To determine whether a substance is an acid or a base, count the hydrogens on each substance before and after the reaction. If the number of hydrogens has decreased, then that substance is the acid (donates hydrogen ions). If the number of hydrogens has increased, then that substance is the base (accepts hydrogen ions). These definitions are normally applied to the reactants on the left. If the reaction is viewed in reverse a new acid and base can be identified. The substances on the right side of the equation are

called the conjugate acid and conjugate base compared to those on the left. Also note that an acid turns into a conjugate base, and the base turns into the conjugate acid after the reaction is over.

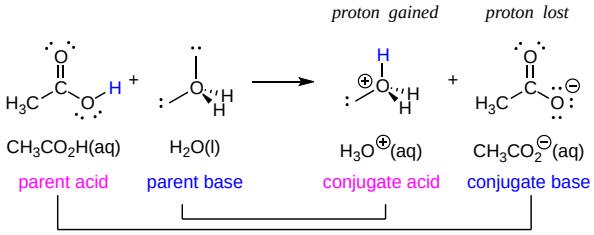
## Conjugate Acid–Base Pairs

In aqueous solutions, acids and bases can be defined in terms of the transfer of a proton from an acid to a base. Thus for every acidic species in an aqueous solution, there exists a species derived from the acid by the loss of a proton. These two species that differ by only a proton constitute a conjugate acid–base pair. For example, in the reaction of HCl with water shown below, HCl , the parent acid, donates a proton to a water molecule, the parent base, thereby forming Cl-. Thus HCl and Cl- constitute a conjugate acid–base pair. By convention, we always write a conjugate acid–base pair as the acid followed by its conjugate base. In the reverse reaction, the Cl- ion in solution acts as a base to accept a proton from $H_3O^+$, forming $H_2O$ and HCl. Thus $H_3O^+$ and $H_2O$ constitute a second conjugate acid–base pair. In general, any acid–base reaction must contain two conjugate acid–base pairs, which in this case are HCl/Cl- and $H_3O^+/H_2O$.

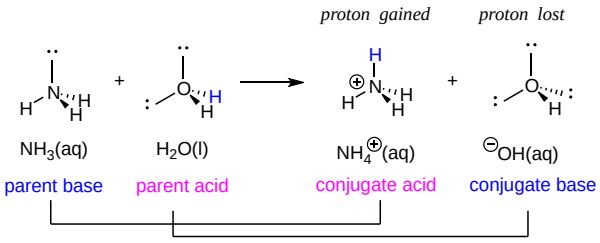



> *All acid–base reactions contain two conjugate acid–base pairs.*

Similarly, in the reaction of acetic acid with water, acetic acid donates a proton to water, which acts as the base. In the reverse reaction, $H_3O^+$ is the acid that donates a proton to the acetate ion, which acts as the base. Once again, we have two conjugate acid–base pairs: the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and the parent base and its conjugate acid ($H_3O^+/H_2O$).




In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are $NH_4^+/NH_3$ and $H_2O/OH^-$.




### Example 3.1.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

**Solution**

$C_6H_5NH_2$ and $H_2O$ are the reactants. When $C_6H_5NH_2$ accepts a proton from $H_2O$, it gains an extra H and a positive charge and leaves an $OH^-$ ion behind. The reaction is as follows:

$$C_6H_5NH_2(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The $H_2O$ molecule, because it donates a proton, is the Brønsted-Lowry acid.

**Example 3.1.1**

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

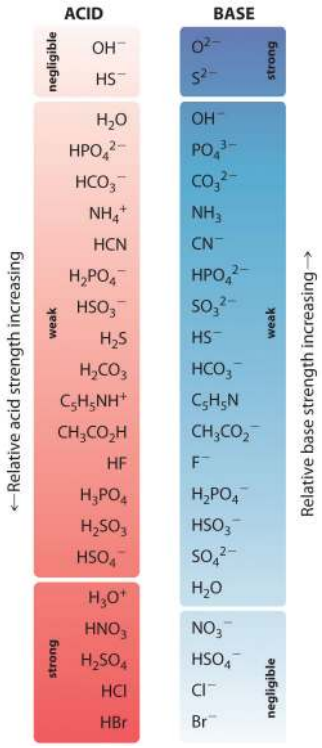
**Solution**

One pair is $H_2O$ and $OH^-$, where $H_2O$ has one more $H^+$ and is the conjugate acid, while $OH^-$ has one less $H^+$ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

Some common conjugate acid–base pairs are shown in Figure 2.7.1. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

***Figure 2.7.1*** *The Relative Strengths of Some Common Conjugate Acid–Base Pairs*




## Contributors and Attributions

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# 3.2: Acids and Bases - The Lewis Definition

**Objectives**

After completing this section, you should be able to

1. state the Lewis definition of an acid and a base.
2. identify a given compound as being a Lewis acid or Lewis base, given its Lewis structure or its Kekulé structure.
3. identify an organic molecule or ion in a reaction as either an electrophile or nucleophile.

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- Lewis acid
- Lewis base
- Electrophile
- Nucleophile

**Study Notes**

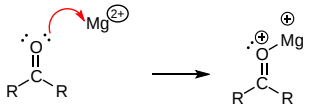
The Lewis concept of acidity and basicity will be of great use to you when you study reaction mechanisms. The realization that an ion such as



is electron deficient, and is therefore a Lewis acid, should help you understand why this ion reacts with substances which are Lewis bases (e.g., $H_2O$).

## Introduction to Lewis Acid-Base Theory

The Brønsted acid-base theory has been used throughout the history of acid and base chemistry. However, this theory is very restrictive and focuses primarily on acids and bases acting as proton donors and acceptors. Sometimes conditions arise where the theory doesn't necessarily fit, such as in solids and gases. In 1923, G.N. Lewis from UC Berkeley proposed an alternate theory to describe acids and bases. His theory gave a generalized explanation of acids and bases based on structure and bonding. Through the use of the Lewis definition of acids and bases, chemists are now able to predict a wider variety of acid-base reactions. Lewis' theory used electrons instead of proton transfer and specifically stated that an acid is a species that accepts an electron pair while a base donates an electron pair.



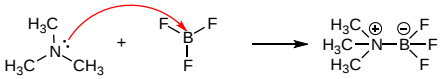
Example of Lewis base (oxygen atom from carbonyl) reacting with Lewis Acid ($Mg^{2+}$ ion).

The reaction of a Lewis acid and a Lewis base will produce a coordinate covalent bond. A coordinate covalent bond is just a type of covalent bond in which one reactant donates both electrons to form the bond. In this case the Lewis base donates its electrons to form a bond to the Lewis acid. The resulting product is called an addition compound, or more commonly a complex. The electron-pair flow from Lewis base to Lewis acid is shown using curved arrows much like those used for resonance structures in Section 2.5. Curved arrows always mean that an electron pair moves from the atom at the tail of the arrow to the atom at the head of the arrow. In this case the lone pair on the Lewis base attacks the Lewis acid forming a bond. This new type of electron pair movement, along with those described in Section 2.5 will be used throughout this text to describe electron flow during reactions.

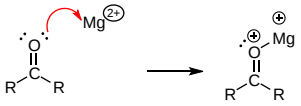
- Lewis Acid: a species that accepts an electron pair and will typically either have vacant orbitals or a polar bond involving hydrogen such that it can donate $H^+$ (which has an empty 1s orbital)
- Lewis Base: a species that donates an electron pair and will have lone-pair electrons of pi bonding electrons.

## Lewis Acids

Neutral compounds of boron, aluminum, and the other Group 13 elements, ($BF_3$, $AlCl_3$), which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Because these compounds are only surrounded by three electron groups, they are $sp^2$ hybridized, contained a vacant p orbital, and are potent Lewis acids. Trimethylamine's lone pair elections are contained in an $sp^3$ hybrid orbital making it a Lewis base. These two orbitals overlap, creating a covalent bond in a boron trifluoride-trimethylamine complex. The movement of electrons during this interaction is show by by an arrow.



Positive ions are often Lewis acids because they have an electrostatic attraction for electron donors. Examples include alkali and alkaline earth metals in the group IA and IIA columns. $K^+$, $Mg^{2+}$ and $Ca^{2+}$ are sometimes seen as Lewis acidic sites in biology, for example. These ions are very stable forms of these elements because of their low electron ionization potentials. However, their positive charges do attract electron donors.The interaction between a magnesium cation ($Mg^{+2}$) and a carbonyl oxygen is a common example of a Lewis acid-base reaction. The carbonyl oxygen (the Lewis base) donates a pair of electrons to the magnesium cation (the Lewis acid). As we will see in Chapter 19 when we begin the study of reactions involving carbonyl groups, this interaction has the very important effect of increasing the polarity of the carbon-oxygen double bond.



The eight-electron rule does not hold throughout the periodic table. In order to obtain noble gas configurations, some atoms may need eighteen electrons in their valence shell. Transition metals such as titanium, iron and nickel may have up to eighteen electrons and can frequently accept electron pairs from Lewis bases. Transition metals are often Lewis acids. For example, titanium has four valence electrons and can form four bonds in compounds such as titanium tetrakis (isopropoxide), below, or titanium tetrachloride, $TiCl_4$. However, the titanium atom in that compound has only eight valence electrons, not eighteen. It can easily accept electrons from donors.

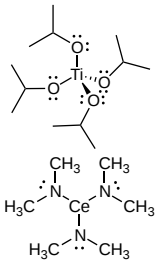


Figure 3.2.1: *Although titanium has eight electrons in this molecule, titanium tetrakis(isopropoxide), it can accommodate up to eighteen. It is a Lewis acid. The cerium atom in cerium tris(dimethylamide) comes from a similar part of the periodic table and is also a Lewis acid.*

For example, when THF and $TiCl_4$ are combined, a Lewis acid-base complex is formed, $TiCl_4(THF)_2$. $TiCl_4(THF)_2$ is a yellow solid at room temperature.

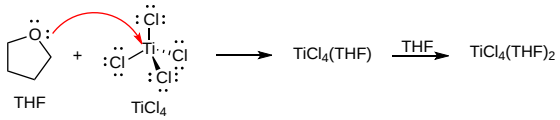


Figure 3.2.2: *A Lewis acid-base complex between tetrahydrofuran (THF) and titanium tetrachloride.*

## The Proton as a Common Lewis Acid

Perhaps the most common example of a Lewis acid is also the simplest. It is the hydrogen cation ($H^+$) or proton. It is called a proton because, in most hydrogen atoms, the only particle in the nucleus is a proton. If an electron is removed to make a cation, a proton is all that is left. A proton is a Lewis acid for a number of reasons. It has a positive charge, and so it will attract electrons, which are negative. Also, it lacks the electron configuration of its noble gas neighbor, helium. Helium has two electrons. If a Lewis base or nucleophile donates a pair of electrons to a proton, the proton will obtain a helium noble gas configuration.

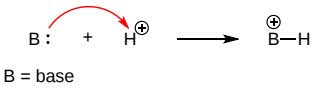



Figure 3.2.3: *Proton reacting as a Lewis acid.*

There is something about hydrogen cations that is not so simple, however. They are actually not so common. Instead, protons are generally always bound to a Lewis base. Hydrogen is almost always covalently (or coordinately) bonded to another atom. Many of the other elements commonly found in compounds with hydrogen are more electronegative than hydrogen. As a result, hydrogen often has a partial positive charge making is still act as a Lewis Acid.

A acid-base reaction involving protons might better be expressed as:

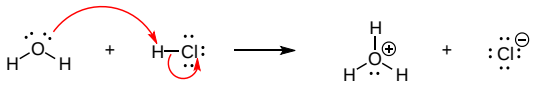


Figure 3.2.4: *Proton transfer from one site to another.*

The Lewis acid-base interactions we have looked at so far are slightly different here. Instead of two compounds coming together and forming a bond, we have one Lewis base replacing another at a proton. Two specific movements of electrons are shown in the reaction both of which are show by arrows. Lone pair electrons on oxygen attack the hydrogen to form an O-H bond in the product. Also, the electrons of the H-Cl bond move to become a lone pair on chlorine as the H-Cl bond breaks. These two arrows together are said to represent the mechanism of this acid-base reaction.

## Lewis Bases

What makes a molecule (or an atom or ion) a Lewis base? It must have a pair of electrons available to share with another atom to form a bond. The most readily available electrons are those that are not already in bonds. Bonding electrons are low in energy. Non-bonding electrons are higher in energy and may be stabilized when they are delocalized in a new bond. Lewis bases usually have non-bonding electrons or lone pairs this makes oxygen and nitrogen compounds common Lewis bases. Lewis bases may be anionic or neutral. The basic requirement is that they have a pair of electrons to donate.

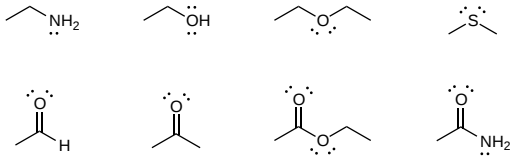


Figure 3.2.5: Some common organic examples of Lewis bases. Most oxygen, nitrogen and sulfur containing compounds can act as Lewis Bases.

### Note 1: Ammonia

Ammonia, $NH_3$, has a lone pair and is a Lewis base. It can donate to compounds that will accept electrons.



*Ammonia donating to an electron acceptor or Lewis acid.*

Not all compounds can act as a Lewis base. For example, methane, $CH_4$, has all of its valence electrons in bonding pairs. These bonding pairs are too stable to donate under normal conditions therefore methane is not a Lewis base. Neutral boron compounds also have all electrons in bonding pairs. For example, borane, $BH_3$ has no lone pairs; all its valence electrons are in bonds. Boron compounds are not typically Lewis bases.

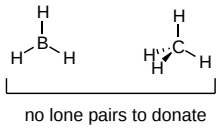



Figure 3.2.6: *Carbon and boron compounds with all sigma bonds do not have lone pairs, and do not act as Lewis bases.*

## Exercise 3.2.1

Which of the following compounds would you expect to be Lewis bases?

a) $SiH_4$ b) $AlH_3$ c) $PH_3$ d) $SH_2$ e) $^-SH$

**Answer**

a) No, silicon has 4 valence electrons (like carbon) and all 4 are involved in sigma bonds

b) No, aluminum has 3 valence electrons and all 3 are involved in sigma bonds

c) Yes, phosphorus has 5 valence electrons, so there is one lone pair available

d) Yes, sulfur has 6 valence electrons, so there are two lone pairs available

e) Yes, this ion has 3 lone pairs available

### Lewis Acid-Base Complexes

What happens when a Lewis base donates a pair of electrons to a Lewis acid? The electron pushing formalism (arrows) we have been using to illustrate the behavior of Lewis acids and Lewis bases is meant to show the direction of electron movement from the donor to the acceptor. However, given that a bond can be thought of as a pair of electrons that are shared between two atoms (in this case, between the donor and the acceptor), these arrows also show where bonds are forming.

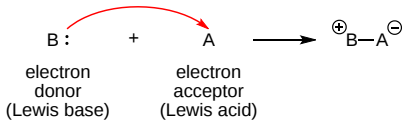



Figure 3.2.7: Donation of electrons from a Lewis base to a Lewis acid.

The electrons donated from a Lewis base to a Lewis acid form a new bond. A new, larger compound is formed from the smaller Lewis acid and Lewis base. This compound is called a Lewis acid-base complex. A simple example of Lewis acid-base complexation involves ammonia and boron trifluoride. The nitrogen atom has a lone pair and is an electron donor. The boron has no octet and is an electron acceptor. The two compounds can form a Lewis acid-base complex or a coordination complex together.

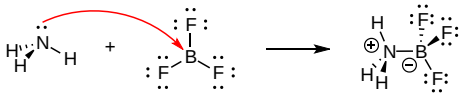


Figure 3.2.8: *Formation of a Lewis acid-base complex from ammonia and boron trifluoride.*

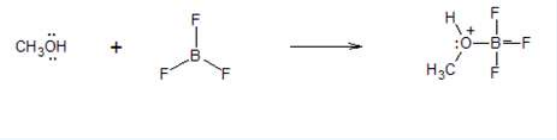
When the nitrogen donates a pair of electrons to share with the boron, the bond that forms is sometimes called a coordinate bond. A coordinate bond is any covalent bond that arose because one atom brought a pair of its electrons and donated them to another.

In organic chemistry terminology, the electron donor is called a **nucleophile** and the electron acceptor is called an **electrophile**. Ammonia is a nucleophile and boron trifluoride is an electrophile.

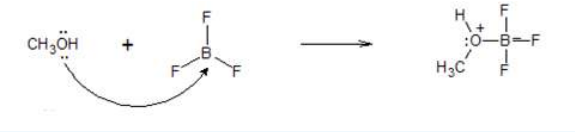
- Because Lewis bases are attracted to electron-deficient atoms, and because positive charge is generally associated with the nucleus of an atom, Lewis bases are sometimes refered to as "nucleophiles". Nucleophile means nucleus-loving.
- Because Lewis acids attract electron pairs, Lewis acids are sometimes called "electrophiles". Electrophile means electron-loving.

## Exercise 3.2.2

For the following reaction, add curved arrows (electron pushing formalism) to indicate the electron flow.



**Answer**



## Exercise 3.2.3

A Lewis acid-base complex is formed between THF (tetrahyrofuran) and borane, $BH_3$.

a) Which compound is the Lewis acid? Which one is the Lewis base?

b) Which atom in the Lewis acid is the acidic site? Why?

c) Which atom in the Lewis base is the basic site? Why?

d) How many donors would be needed to satisfy the acidic site?

e) Show, using arrow notation, the reaction to form a Lewis acid-base complex.

f) Borane is highly pyrophoric; it reacts violently with air, bursting into flames. Show, using arrow notation, what might be happening when borane contacts the air.

g) Borane-THF complex is much less pyrophoric than borane. Why do you suppose that is so?

Add exercises text here.

**Answer**

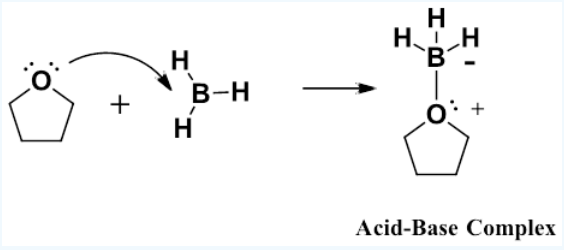
a) Borane is the Lewis acid. THF has lone pair electrons so it is the Lewis base.

b) The Boron atom has an unfilled octet so it has an empty p orbital that can accept electrons.

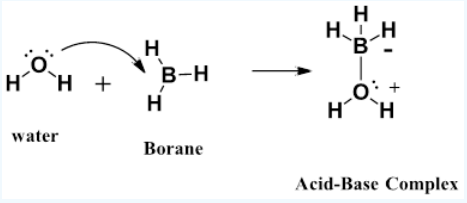
c) The oxygen atom in THF has lone pair electrons contained in a $sp^3$ hybridized orbital.

d) The boron in borane has six electrons around it so it would only need one lone pair donor to reach an octet.

e) Show, using arrow notation, the reaction to form a Lewis acid-base complex.




f) The Borane initially reacts with water in air.



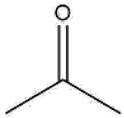

g) After the Borane-THF complex is formed, the boron atom has a complete octet making it less reactive.

## Exercises

### Questions

**Q2.11.1**

For the following molecules state wither they are Lewis acid or base and wither or not they are a Brønsted acid or base.



$NH_4^+$

## Solutions

**S2.11.1**

Acetone is a Lewis base and a Brønsted base. Ammonium cation is both a Lewis acid and a weak Brønsted acid.

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# 3.3: Acid and Base Strength

**Key Terms**

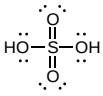
Make certain that you can define, and use in context, the key terms below.

- acidity constant, $K_a$
- equilibrium constant, $K_{eq}$

**Study Notes**

Calculations and expressions involving $K_a$ and p$K_a$ were covered in detail in your first-year general chemistry course. Note that acidity constant is also known as the acid dissociation constant.

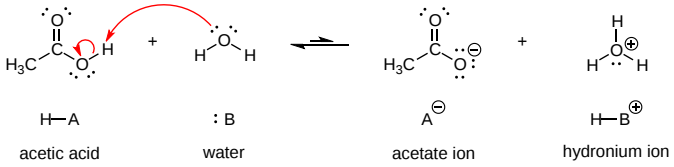
You are no doubt aware that some acids are stronger than others. Sulfuric acid is strong enough to be used as a drain cleaner, as it will rapidly dissolve clogs of hair and other organic material.



Not surprisingly, concentrated sulfuric acid will also cause painful burns if it touches your skin, and permanent damage if it gets in your eyes (there's a good reason for those safety goggles you wear in chemistry lab!). Acetic acid (vinegar), will also burn your skin and eyes, but is not nearly strong enough to make an effective drain cleaner. Water, which we know can act as a proton donor, is obviously not a very strong acid. Even hydroxide ion could *theoretically* act as an acid – it has, after all, a proton to donate – but this is not a reaction that we would normally consider to be relevant in anything but the most extreme conditions.

The relative acidity of different compounds or functional groups – in other words, their relative capacity to donate a proton to a common base under identical conditions – is quantified by a number called the **acid dissociation constant**, abbreviated $\mathbf{K_a}$. The common base chosen for comparison is water.

We will consider acetic acid as our first example. When a small amount of acetic acid is added to water, a proton-transfer event (acid-base reaction) occurs to some extent.




Notice the phrase 'to some extent' – this reaction does *not* run to completion, with all of the acetic acid converted to acetate, its conjugate base. Rather, a *dynamic equilibrium* is reached, with proton transfer going in both directions (thus the two-way arrows) and finite concentrations of all four species in play. The nature of this equilibrium situation, as you recall from General Chemistry, is expressed by an equilibrium constant, K.

The equilibrium constant is actually a ratio of activities (represented by the symbol $a$), but activities are rarely used in courses other than analytical or physical chemistry. To simplify the discussion for general chemistry and organic chemistry courses, the activities of all of the solutes are replaced with molarities, and the activity of the solvent (usually water) is defined as having the value of 1.

In our example, we added a small amount of acetic acid to a large amount of water: water is the *solvent* for this reaction. Therefore, in the course of the reaction, the concentration of water changes very little, and the water can be treated as a pure solvent, which is always assigned an activity of 1. The acetic acid, acetate ion and hydronium ion are all *solutes*, and so their activities are approximated with molarities. The acid dissociation constant, or $K_a$, for acetic acid is therefore defined as:

$$K_{eq} = \frac{a_{CH_3COO^-} \cdot a_{H_3O^+}}{a_{CH_3COOH} \cdot a_{H_2O}} \approx \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][1]} \tag{3.3.1}$$

Because dividing by 1 does not change the value of the constant, the "1" is usually not written, and $K_a$ is written as:

$$K_{eq} = K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.75 \times 10^{-5} \tag{3.3.2}$$

In more general terms, the dissociation constant for a given acid is expressed as:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \tag{3.3.3}$$

or

$$K_a = \frac{[A][H_3O^+]}{[HA^+]} \tag{3.3.4}$$

Equation 3.3.3 applies to a neutral acid such as like HCl or acetic acid, while Equation 3.3.4 applies to a cationic acid like ammonium ($NH_4^+$).

The value of $K_a$ = 1.75 x $10^{-5}$ for acetic acid is very small - this means that very little dissociation actually takes place, and there is much more acetic acid in solution at equilibrium than there is acetate ion. Acetic acid is a relatively weak acid, at least when compared to sulfuric acid ($K_a = 10^9$) or hydrochloric acid ($K_a = 10^7$), both of which undergo essentially complete dissociation in water.

A number like 1.75 x $10^{-5}$ is not very easy either to say or to remember. Chemists often use **$pK_a$** values as a more convenient term to express relative acidity. **$pK_a$** is related to **$K_a$** by the following equation

$$pK_a = -\log K_a \tag{3.3.5}$$

Doing the math, we find that the $pK_a$ of acetic acid is 4.8. The use of $pK_a$ values allows us to express the acidity of common compounds and functional groups on a numerical scale of about –10 (very strong acid) to 50 (not acidic at all). Table 3.3.1 at the end of the text lists exact or approximate $pK_a$ values for different types of protons that you are likely to encounter in your study of organic and biological chemistry. Looking at Table 3.3.1, you see that the $pK_a$ of carboxylic acids are in the 4-5 range, the $pK_a$ of sulfuric acid is –10, and the $pK_a$ of water is 14. Alkenes and alkanes, which are not acidic at all, have $pK_a$ values above 30. *The lower the $pK_a$ value, the stronger the acid.*

***Table* 3.3.1*:*** *Representative acid constant*

| | | | | |
|---|---|---|---|---|
|  sulfuric acid $pK_a$ −10 |  hydrochloric acid $pK_a$ −7 |  hydronium $pK_a$ 0.00 |  protonated ketone $pK_a$ ~ −7 |  protonated alcohol $pK_a$ ~ −3 |
|  phosphate monoester $pK_a$ ~ 1 |  phosphate diester $pK_a$ ~ 1.5 |  phosphoric acid $pK_a$ 2.2 |  protonated aniline $pK_a$ ~ 4.6 |  carboxylic acid $pK_a$ ~ 4-5 |
|  pyridinium $pK_a$ 5.3 |  carbonic acid $pK_a$ 6.4 |  hydrogen cyanide $pK_a$ ~ 9.2 |  ammonium $pK_a$ 9.2 |  phenol $pK_a$ 9.9 |
|  thiol $pK_a$ ~ 10-11 |  water $pK_a$ ~ 14.0 |  amide $pK_a$ ~ 17 |  alcohol $pK_a$ ~ 16-18 |  alpha-proton $pK_a$ ~ 18-20 |
| |  terminal alkyne $pK_a$ ~ 25 |  terminal alkene $pK_a$ ~ 35 |  ammonia $pK_a$ ~ 35 | |

It is important to realize that $pK_a$ is *not* the same thing as pH: $pK_a$ is an inherent property of a compound or functional group, while pH is the measure of the hydronium ion concentration in a particular aqueous solution:

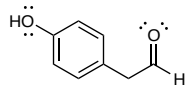
$$pH = -\log[H_3O^+] \tag{3.3.6}$$

Any particular acid will always have the same $pK_a$ (assuming that we are talking about an aqueous solution at room temperature) but different aqueous solutions of the acid could have different pH values, depending on how much acid is added to how much water.

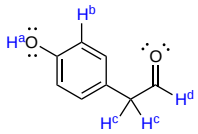
Our table of $pK_a$ values will also allow us to compare the strengths of different bases by comparing the $pK_a$ values of their conjugate acids. The key idea to remember is this: *the stronger the conjugate acid, the weaker the conjugate base*. Sulfuric acid is the strongest acid on our list with a $pK_a$ value of –10, so $HSO_4^-$ is the weakest conjugate base. You can see that hydroxide ion is a stronger base than ammonia ($NH_3$), because ammonium ($NH_4^+$, $pK_a$ = 9.2) is a stronger acid than water ($pK_a$ = 14.0).

> *The stronger the conjugate acid, the weaker the conjugate base.*

While Table 3.3.1 provides the $pK_a$ values of only a limited number of compounds, it can be very useful as a starting point for estimating the acidity or basicity of just about any organic molecule. Here is where your familiarity with organic functional groups will come in very handy. What, for example, is the $pK_a$ of cyclohexanol? It is not on the table, but as it is an alcohol it is probably somewhere near that of ethanol ($pK_a$ = 16). Likewise, we can use Table 3.3.1 to predict that para-hydroxyphenyl acetaldehyde, an intermediate compound in the biosynthesis of morphine, has a $pK_a$ in the neighborhood of 10, close to that of our reference compound, phenol.




Notice in this example that we need to evaluate the potential acidity at *four* different locations on the molecule.




$pK_a$ $H^a$ ~ 10
$pK_a$ $H^b$ = not on table (not acidic)
$pK_a$ $H^c$ ~ 19
$pK_a$ $H^d$ = not on table (not acidic)

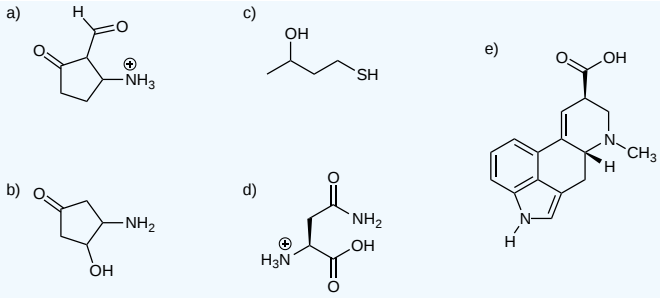
Aldehyde and aromatic protons are not at all acidic ($pK_a$ values are above 40 – not on our table). The two protons on the carbon next to the carbonyl are slightly acidic, with $pK_a$ values around 19-20 according to the table. The most acidic proton is on the phenol group, so if the compound were to be reacted with a single molar equivalent of strong base, this is the proton that would be donated first.

As you continue your study of organic chemistry, it will be a very good idea to commit to memory the approximate $pK_a$ ranges of some important functional groups, including water, alcohols, phenols, ammonium, thiols, phosphates, carboxylic acids and carbons next to carbonyl groups (so-called a-carbons). These are the groups that you are most likely to see acting as acids or bases in biological organic reactions.

A word of caution: when using the pKa table, be absolutely sure that you are considering the correct conjugate acid/base pair. If you are asked to say something about the basicity of ammonia ($NH_3$) compared to that of ethoxide ion ($CH_3CH_2O^-$), for example, the relevant $pK_a$ values to consider are 9.2 (the $pK_a$ of ammonium ion) and 16 (the $pK_a$ of ethanol). From these numbers, you know that ethoxide is the stronger base. Do not make the mistake of using the $pK_a$ value of 38: this is the $pK_a$ of ammonia *acting as an acid*, and tells you how basic the $NH_2^-$ ion is (very basic!)

### Example 3.3.1: Acidic Groups

Using the $pK_a$ table, estimate $pK_a$ values for the most acidic group on the compounds below, and draw the structure of the conjugate base that results when this group donates a proton. Use the pKa table above and/or from the Reference Tables.




**Answer**

a. The most acidic group is the protonated amine, pKa ~ 5-9

b. Alpha proton by the C=O group, pKa ~ 18-20

c. Thiol, pKa ~ 10

d. Carboxylic acid, pKa ~ 5

e. Carboxylic acid, pKa ~ 5

## Example 3.3.2

Acetic acid ($CH_3COOH$) is known to have a $pK_a$ of 4.76. Please determine the Ka for acetic acid.

**Solution**

Solving for $K_a$ algebraically you get the following:

$pK_a = -Log(K_a)$

$-pK_a = Log(K_a)$

$10^{-pK_a} = K_a$

Using a calculator first enter in the value for the $pK_a$ (4.76). The make the number negative (-4.76). Next, use the inverse log function. All calculators are slightly different so this function may appear as: ANTILOG, INV LOG, or $10^X$. Often it is the second function of the LOG button.

$K_a$ for acetic acid = $10^{-pK_a} = 1.74 \times 10^{-5}$

## Contributors and Attributions

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# 3.4: Predicting Acid-Base Reactions from pKa Values

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**Key Terms**

Make certain that you can define, and use in context, the key term below.

- p$K_a$

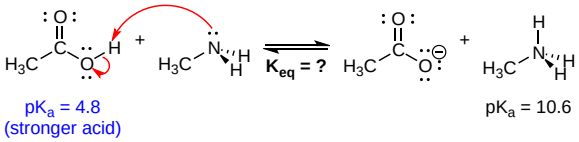
## Using $pK_a$ values to predict reaction Equilibria

By definition, the $pK_a$ value tells us the extent to which an acid will react with water as the base, but by extension, we can also calculate the equilibrium constant for a reaction between any acid-base pair. Mathematically, it can be shown that:

$$K_{eq} \text{ (for the acid base reaction in question)} = 10^{\Delta pKa}$$

where $\Delta pK_a$ is the $pK_a$ of product acid minus $pK_a$ of reactant acid

Consider a reaction between methylamine and acetic acid:




First, we need to identify the acid species on either side of the equation. On the left side, the acid is of course acetic acid, while on the right side the acid is methyl ammonium. The specific $pK_a$ values for these acids are not on our very generalized $pK_a$ table, but are given in the figure above. Without performing any calculations, you should be able to see that this equilibrium lies far to the right-hand side: acetic acid has a lower $pK_a$, is a stronger acid, and thus it wants to give up its proton more than methyl ammonium does. Doing the math, we see that

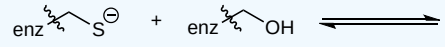
$$K_{eq} = 10^{\Delta pK_a} = 10^{10.6-4.8} = 10^{5.8} = 6.3 \times 10^5 \tag{3.4.1}$$

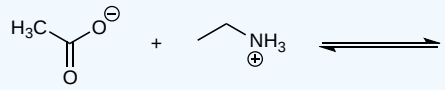
So $K_{eq}$ is a very large number (much greater than 1) and the equilibrium lies far to the right-hand side of the equation, just as we had predicted.

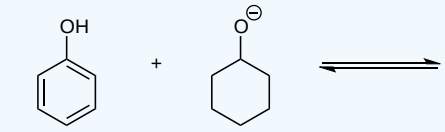
If you had just wanted to approximate an answer without bothering to look for a calculator, you could have noted that the difference in $pK_a$ values is approximately 6, so the equilibrium constant should be somewhere in the order of $10^6$, or one million. Using the $pK_a$ table in this way, and making functional group-based $pK_a$ approximations for molecules for which we don't have exact values, we can easily estimate the extent to which a given acid-base reaction will proceed.

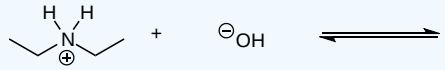
**Example 3.4.1**

Show the products of the following acid-base reactions, and estimate the value of $K_{eq}$. Use the $pK_a$ table from Section 2.8 and/or from the Reference Tables.

a) 

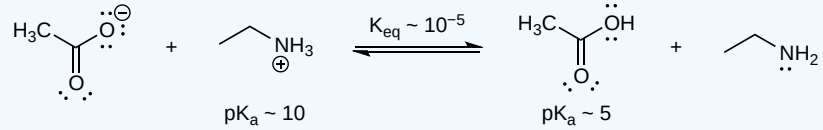
b) 

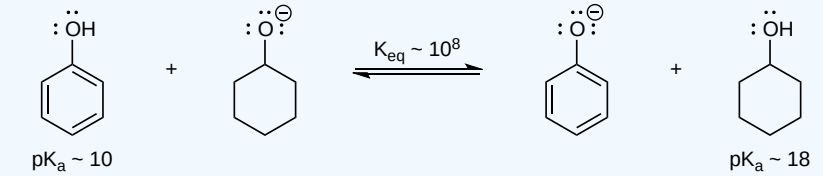
c) 

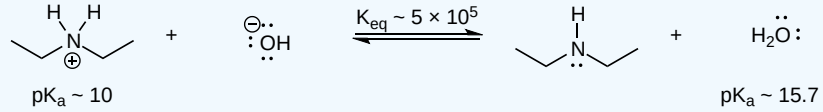
d) 

**Answer**

a) 


b) 

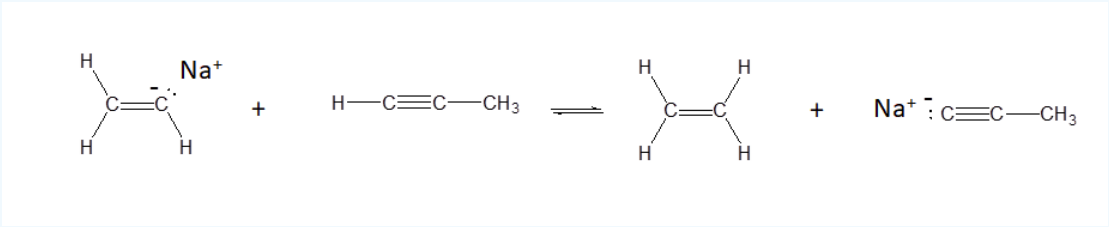

c) 


d) 

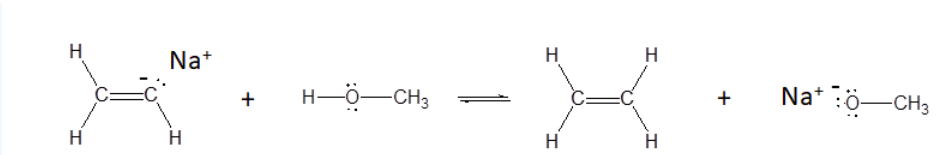

## Exercises

### Exercise 3.4.1

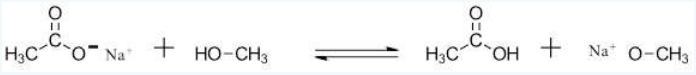
Use the pKa table from Section 2.8 and/or from the Reference Tables to determine if the following reactions would be expected to occur:

a) 

b)



c)



**Answer**

a) Yes - alkenes have $pK_a$ values of ~35 while alkynes have $pK_a$ values of ~25. This means that alkynes are more acidic and more likely to donate a proton.

b) Yes - alkenes have $pK_a$ values of ~35 while alcohols have $pK_a$ values of ~16-18. This means that alcohols are more acidic and more likely to donate a proton.

c) No - carboxylic acids have $pK_a$ values of ~4-5 while alcohols have $pK_a$ values of ~16-18. This means that carboxylic acids are more acidic and more likely to donate a proton (so the reverse reaction would be expected to occur).

## Contributors and Attributions

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- Prof. Steven Farmer (Sonoma State University)
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3.4: Predicting Acid-Base Reactions from pKa Values is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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# 3.5: Organic Acids and Organic Bases

## Organic acids as weak acids

For the purposes of this topic, we are going to take the definition of an acid as "a substance which donates hydrogen ions (protons) to other things". We are going to get a measure of this by looking at how easily the acids release hydrogen ions to water molecules when they are in solution in water.

An acid in solution sets up this equilibrium:

$$AH_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)} \tag{3.5.1}$$

A hydronium ion is formed together with the anion (negative ion) from the acid. This equilibrium is sometimes simplified by leaving out the water to emphasize the ionization of the acid.

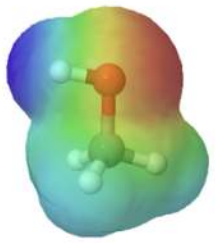
$$AH_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)} \tag{3.5.2}$$

If you write it like this, you must include the state symbols - "(aq)". Writing $H^+_{(aq)}$ implies that the hydrogen ion is attached to a water molecule as $H_3O^+$. Hydrogen ions are always attached to something during chemical reactions.

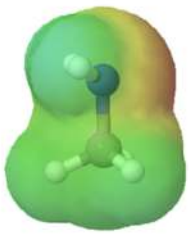
The organic acids are weak in the sense that this ionization is very incomplete. At any one time, most of the acid will be present in the solution as un-ionized molecules. For example, in the case of dilute ethanoic acid, the solution contains about 99% of ethanoic acid molecules - at any instant, only about 1% have actually ionized. The position of equilibrium therefore lies well to the left.

### Weak acid polarization

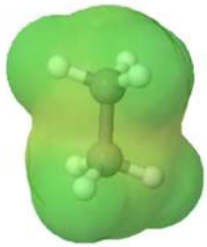
Organic acids can usually can be characterized in electrostatic potential maps by the presence of of a positively polarized hydrogen atom shown in blue. When looking at the maps below, methanol has a slightly polarized O-H bond and is considered very weakly acidic. The O-H bond in methyl amine is less polarized, as shown by the lighter blue color around the hydrogen, making it less acidic than methanol. However, the C-H bond in ethane lack virtually any polarity, as shown by the lack of a blue color, making it non-acidic. The following discussion will explain the difference in acidity of these and other organic molecules molecules.



methanol



methylamine



ethane

## Comparing the strengths of acids

Acid strength is strongly correlated to stability of the conjugate base that will form by removing a proton. In order to analyze how acidic a molecule is likely to be, then you need to estimate the stability of its conjugate base.

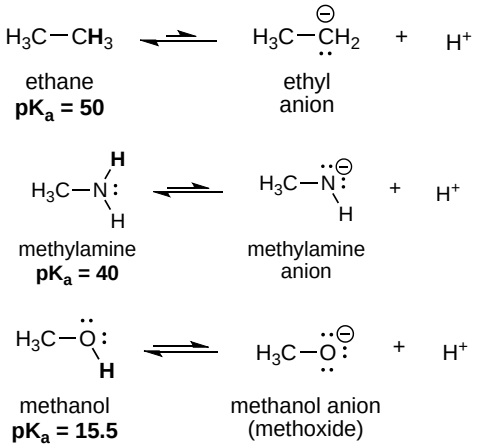
### Stabilization of the Conjugate Base - Four Main Considerations:

1. Electronegativity of the atom bonded to the acidic hydrogen
2. Inductive stabilization of the conjugate base
3. Size of the atom bonded to the acidic hydrogen
4. Can the charge be delocalized by resonance?

These considerations are explained individually, but must be looked at collectively. Note that sometimes two of the above considerations will suggest different conclusions when comparing acidity of two different acids. In the end, we have to do our best to apply these qualitative factors to try to predict a quantitative outcome.

## 1. Electronegativity Effects in Acidity

When comparing elements, it depends on the positional relationship of the elements on the periodic table. When moving a period (aka across a row) of the main group elements, the valence electrons all occupy orbitals in the same shell. These electrons have comparable energy, so this factor does not help us discern differences relative stability. Differences in electronegativity are now the dominant factor. This trend is shown when comparing the pKa values of ethane, methyl amine, and methanol which reflects the relative electronegativities of the C < N < O. The key to understanding this trend is to consider the hypothetical conjugate base in each case*: the more stable the conjugate base, the stronger the acid*. In general, the more electronegative an atom, the better it is able to bear a negative charge. In the ethyl anion, the negative charge is borne by carbon, in the methylamine anion by nitrogen, and in the methoxide anion by an oxygen. Remember the periodic trend in electronegativity: it also increases as we move from left to right along a row, meaning that oxygen is the most electronegative of three elements being considered. This makes the negative charge on the methoxide anion the most stable of the three conjugate bases and methanol the strongest of the three acids. Likewise, carbon is the least electronegative making ethane the weakest of the three acids.




### 1. a. Orbital Hybridization

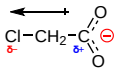
The hybridization of an orbital affects its electronegativity. Within a shell, the s orbitals occupy the region closer to the nucleus than the p orbitals. Therefore, the spherical s orbitals are more electronegative than the lobed p orbitals. The relative electronegativity of hybridized orbitals is sp > $sp^2$ > $sp^3$ since the percentage of s-character is decreasing as more p-orbitals are added to the hybrids. This trend indicates the sp hybridized orbitals are more stable with a negative charge than $sp^3$ hybridized orbitals. The table below shows how orbital hybridization influences relative acidity.

| compound | conjugate base | hybridization | *s* character | $pK_a$ | |
|---|---|---|---|---|---|
|  |  | $sp^3$ | 25% | 50 | weakest acid |
|  |  | $sp^2$ | 33% | 44 | ↓ |
|  |  | | | 36 | ↓ |
|  |  | sp | 50% | 25 | ↓ |
|  |  | | | 16 | strongest acid |

## 2. Inductive Effects

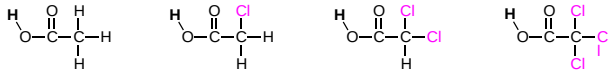
The inductive effect is an experimentally observed effect of the transmission of charge through a chain of atoms in a molecule, resulting in a permanent dipole in a bond. For example, in a carboxylic acid group the presence of chlorine on adjacent carbons increases the acidity of the carboxylic acid group. A chlorine atom is more electronegative than hydrogen, and thus is able to 'induce', or 'pull' electron density towards itself, away from the carboxylate group. This further spreads out the electron density of the conjugate base, which has a stabilizing effect. In this context, the chlorine substituent is called an **electron-withdrawing group**. Notice that the $pK_a$-lowering effect of each chlorine atom, while significant, is not as dramatic as the delocalizing resonance

effect illustrated by the difference in $pK_a$ values between an alcohol and a carboxylic acid. In general, *resonance effects are more powerful than inductive effects*.



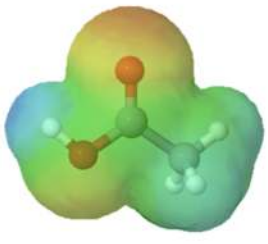
*negative charge is delocalized by being pulled out onto chlorine atom*

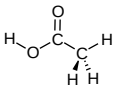
Compare the $pK_a$ values of acetic acid and its mono-, di-, and tri-chlorinated derivatives:



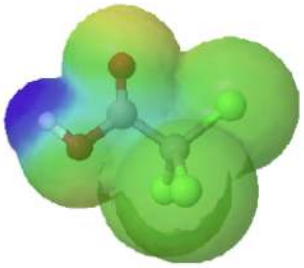
**$pK_a$ = 4.8** **$pK_a$ = 2.8** **$pK_a$ = 1.3** **$pK_a$ = 0.64**

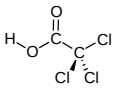
The inductive effects of chlorine can be clearly seen when looking at the electrostatic potential maps of acetic acid (Left) and trichloroacetic acid (Right). The O-H bond in trichloroacetic acid is highly polarized as shown by the dark blue color. This illustrates that tricholoracetic acid is a much stronger acid than acetic acid.





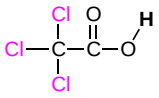
acetic acid



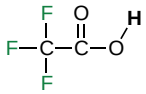


trichloroacetic acid

Because the inductive effect depends on electronegativity, fluorine substituents have a more pronounced $pK_a$-lowering effect than chlorine substituents.

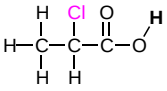


trichloroacetic acid
**$pK_a$ = 0.64**

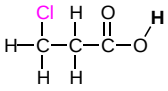


trifluoroacetic acid
**$pK_a$ = −0.25**

In addition, the inductive takes place through covalent bonds, and its influence decreases markedly with distance – thus a chlorine two carbons away from a carboxylic acid group has a decreased effect compared to a chlorine just one carbon away. 2-chloropropanoic acid has a $pK_a$ of 2.8 while for 3-chloropropanoic acid, the $pK_a$ is 4.0.

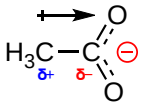


2-chloropropanoic acid
**$pK_a$ = 2.8**
*stronger acid*



3-chloropropanoic acid
**$pK_a$ = 4.0**

Alkyl groups (hydrocarbons) are weak inductive electron donators. In this case the inductive effect pushes electron density onto the conjugate base, causing the electron density to become more concentrated and producing a destabilizing effect.



*more negative charge pushed towards already negative end*

The inductive effects of alkyl groups causes a significant variation in the acidities of different carboxylic acids. Notice that the inductive effect drops off after the alkyl chain is about three carbons long.

| | $pK_a$ |
|---|---|
| HCOOH (Methanoic Acid or Formic Acid) | 3.75 |
| $CH_3COOH$ (Ethanoic Acid or Acetic Acid) | 4.76 |
| $CH_3CH_2COOH$ (Propanoic Acid) | 4.87 |
| $CH_3CH_2CH_2COOH$ (Butanoic Acid) | 4.82 |

### 3. Size of the atom bonded to the acidic hydrogen

Within a Group (aka down a column) As we move down the periodic table, the electrons are occupying higher energy subshells creating a larger atomic size and volume. As the volume of an element increases, any negative charge present tends to become more spread out which decreases electron density and increases stability. The figure below shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

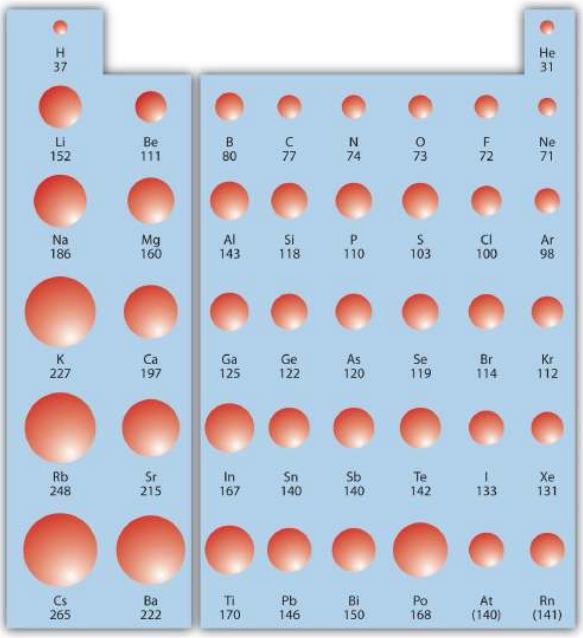
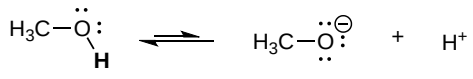
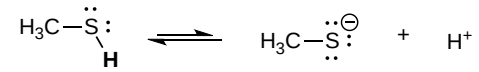



Figure 3.5.1: Atomic Radii Trends on the Periodic Table. Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.

This relationship of atomic size and electron density is illustrated when we compare the relative acidities of methanol, $CH_3OH$, with methanethiol, $CH_3SH$. The lower pKa value of 10.4 for methanethiol indicates that it is a stronger acid than methanol with a pKa value of 15.5. It is important to remember that neither compound is considered an acid. These relationships become useful when trying to deprotonate compounds to increase their chemical reactivity in non-aqueous reaction conditions.

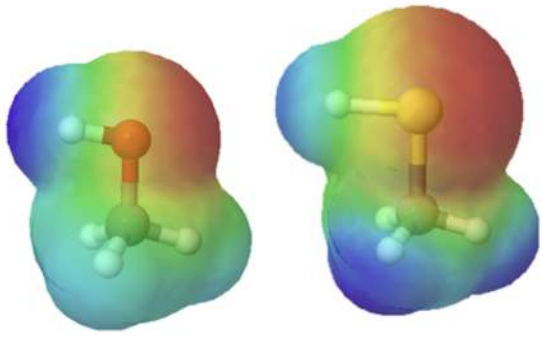


methanol
**$pK_a$ = 15.5**



methanethiol
**$pK_a$ = 10.4**

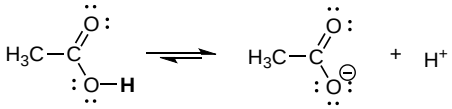
The difference in size can easily be seen when looking at the electrostatic potential maps for methanol (Left) and methanethiol (Right). The sulfur atom methanethiol is larger than the oxygen atom in methanol. The larger size of sulfur will be better able to delocalize and stabilize the negative charge in its conjugate base metanethiolate.



In addition to decreased charge density, the strength of the bond between the atom and acidic proton is also important. The larger the *n* value for the valence shell of the atom, then the weaker the bond will be to the acidic hydrogen owing to the worse orbital overlap between the other atom and the proton. We will explore this factor more later on when looking at Leaving Groups. For now, it is sufficient to say that the large orbitals on atoms with valence electrons in a higher valence shell will be much larger, so the electron density is not shared very effectively with the small *1s* orbital in the valence shell of the hydrogen.

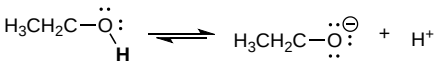
4. Resonance Effects in Acidity

This section will focus on how the resonance structures of different organic groups contributes to their relative acidity even though the same element acts as the proton donor. When evaluating conjugate bases for the presence of resonance contributors, remember to look for movable electrons (lone pairs and pi bonding electrons). Delocalizing electrons over two or more atoms spreads out the electron density, increasing the stability of the conjugate base, and increasing the acidity of the corresponding acid. A classic example compares the relative acidity of ethanol and acetic acid, but the conclusions we reach will be equally valid for all alcohol and carboxylic acid groups. Despite the fact that they are both oxygen acids, the $pK_a$ values of ethanol and acetic acid are very different.



acetic acid
**$pK_a$ = 4.8**

acetate anion



ethanol
**$pK_a$ = 16**

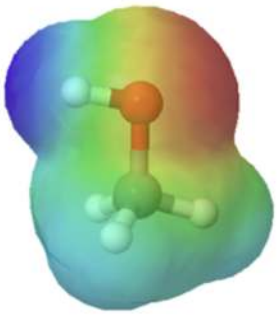
ethoxide anion

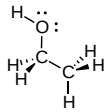
In both species, the negative charge on the conjugate base is held by an oxygen, so periodic trends cannot be invoked. For acetic acid, however, there is a key difference: a resonance contributor can be drawn in which the negative charge is drawn on the second oxygen of the group. The two resonance forms for the conjugate base are equal in energy, according to our 'rules of resonance' (Section 2.5). What this means is that the negative charge on the acetate ion is not located on one oxygen or the other: rather it is shared between the two. Chemists use the term 'delocalization of charge' to describe this situation. In the ethoxide ion, by contrast, the negative charge is 'locked' on the single oxygen. This stabilization leads to a markedly increased acidity.

The delocalization of charge by resonance has a very powerful effect on the reactivity of organic molecules, enough to account for the difference of nearly 12 $pK_a$ units between ethanol and acetic acid (and remember, $pK_a$ is a log expression, so we are

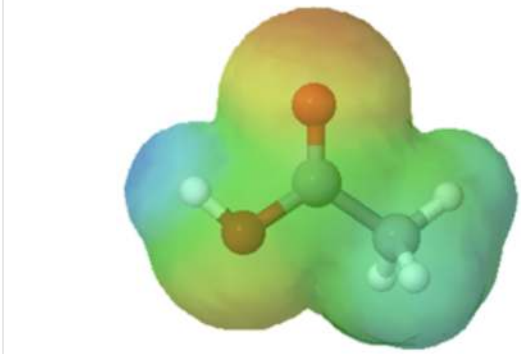
talking about a difference of over $10^{12}$ between the acidity constants for the two molecules). The acetate ion is much more stable than the ethoxide ion, due to the effects of resonance delocalization.

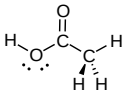
The effects of conjugation can be seen when comparing the electrostatic potential maps of ethanol and acetic acid. Conjugation creates a greater polarization in the O-H bond in acetic acid as shown by its darker blue color.





ethanol

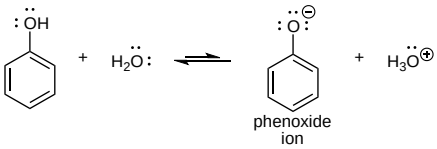




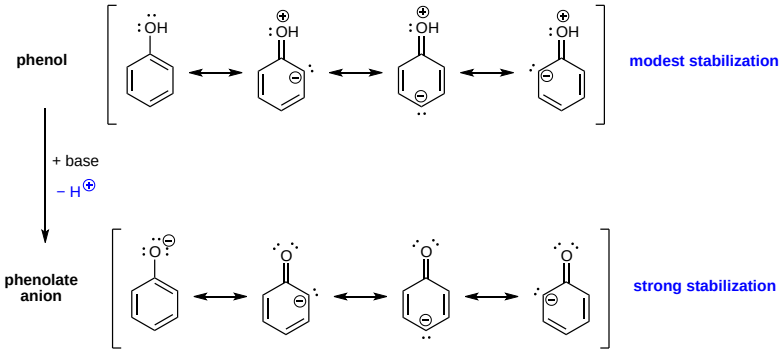
acetic acid

## Why is Phenol Acidic?

Compounds like alcohols and phenol which contain an -OH group attached to a hydrocarbon are very weak acids. Alcohols are so weakly acidic that, for normal lab purposes, their acidity can be virtually ignored. However, phenol is sufficiently acidic for it to have recognizably acidic properties - even if it is still a very weak acid. A hydrogen ion can break away from the -OH group and transfer to a base. For example, in aqueous solution:

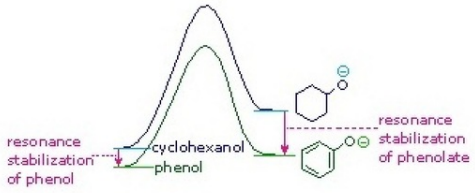



Since phenol is a very weak acid, the position of equilibrium lies well to the left. However, phenol can lose a hydrogen ion because the phenoxide ion (or phenolate ion - the two terms can be used interchangeably) formed is stabilized due to resonance. The negative charge on the oxygen atom is delocalized around the ring since one of the lone pairs on the oxygen atom can be in a p orbital and overlap with the pi electrons on the benzene ring.



This overlap leads to a delocalization which extends from the ring out over the oxygen atom. As a result, the negative charge is no longer entirely localized on the oxygen, but is spread out around the whole ion. Spreading the charge around makes the ion more stable than it would be if all the charge remained on the oxygen. However, oxygen is the most electronegative element in the ion and the delocalized electrons will be drawn towards it. That means that there will still be a lot of charge around the oxygen which will tend to attract the hydrogen ion back again. That is why phenol is only a very weak acid.

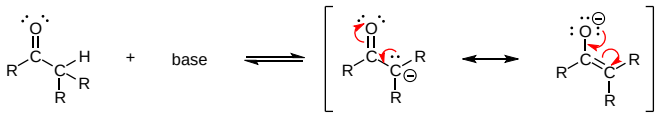
This explains why phenol is a much stronger acid than cyclohexanol. As can be seen in the following energy diagram, resonance stabilization is increased for the conjugate base of phenol vs. cyclohexanol after removal of a proton.




The resonance stabilization in these two cases is very different. An important principle of resonance is that charge separation diminishes the importance of contributors to the resonance hybrid. The contributing structures to the phenol hybrid all suffer charge separation, resulting in very modest stabilization of this compound. On the other hand, the phenolate anion is already charged, and the canonical contributors act to disperse the charge, resulting in a substantial stabilization of this species. The conjugate bases of simple alcohols are not stabilized by charge delocalization, so the acidity of these compounds is similar to that of water. An energy diagram showing the effect of resonance on cyclohexanol and phenol acidities is shown on the right. Since the resonance stabilization of the phenolate conjugate base is much greater than the stabilization of phenol itself, the acidity of phenol relative to cyclohexanol is increased. Supporting evidence that the phenolate negative charge is delocalized on the ortho and para carbons of the benzene ring comes from the influence of electron-withdrawing substituents at those sites.

### Acidity of hydrogen α (alpha) to carbonyl

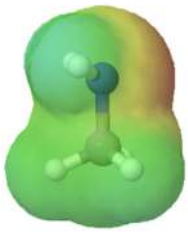
Alkyl hydrogen atoms bonded to a carbon atom in a α (alpha) position (directly adjacent) relative to a C=O group display unusual acidity. While the pKa values for alkyl C-H bonds in is typically on the order of 40-50, pKa values for these alpha hydrogens is more on the order of 19-20. This is almost exclusively due to the resonance stabilization of the product carbanion, called an enolate, as illustrated in the diagram below. The effect of the the stabilizing C=O is seen when comparing the pKa for the α hydrogens of aldehydes (~16-18), ketones (~19-21), and esters (~23-25).




enolate ion

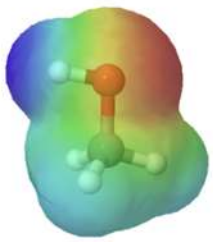
## Comparing the Strengths of Weak Bases

Technically, organic bases are characterized by the presence of an atom with lone pair electrons. These lone pairs contain a high electron density, which is shown red in the electrostatic potential maps, and can bond to $H^+$. Below are the maps of methanol, methyl amine, and acetone. All three compounds can be protonated with a sufficiently strong acid. Note, that all three of these compounds also have the ability to donate a proton when reacted with a strong enough base. Whether these compounds act as a acid or base depends on the conditions.



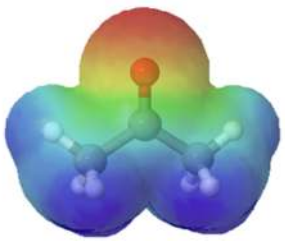


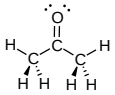
methylamine





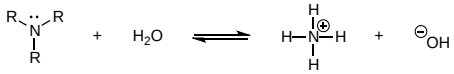
methanol



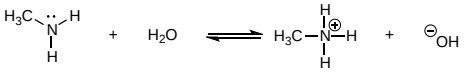


acetone

It is common to compare basicity's quantitatively by using the pK$_a$'s of their conjugate acids rather than their pK$_b$'s. Since pK$_a$ + pK$_b$ = 14, **the higher the pK$_a$ the stronger the base**, in contrast to the usual inverse relationship of pK$_a$ with acidity. Recall that ammonia ($NH_3$) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. The conjugate acid of most simple alkyl amines have pK$_a$'s in the range 9.5 to 11.0, and their water solutions are basic (have a pH of 11 to 12, depending on concentration). This can be illustrated by the reaction below where an amine removes a proton from water to form substituted ammonium (e.g. $NH_4^+$) ions and hydroxide ($OH^-$) ions:



Amines are one of the only neutral functional groups which are considered basic. This is a direct consequence of the presence of the unshared electron pair on the nitrogen. The unshared electron pair is less tightly held by the nitrogen of an amine than the corresponding oxygen of an alcohol, which makes it more available to act as a base. As a specific example, methylamine reacts with water to form the methylammonium ion and the $OH^-$ ion.



**Example: Ammonia**

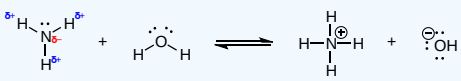
All of the have similarities to ammonia and so we'll start by looking at the reason for its basic properties. For the purposes of this topic, we are going to take the definition of a base as "a substance which combines with hydrogen ions (protons)". We are going to get a measure of this by looking at how easily the bases take hydrogen ions from water molecules when they are in solution in water.

Ammonia in solution sets up this equilibrium:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \tag{2.10.1}$$

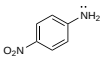
An ammonium ion is formed together with hydroxide ions. Because the ammonia is only a weak base, it doesn't hang on to the extra hydrogen ion very effectively and so the reaction is reversible. At any one time, about 99% of the ammonia is present as unreacted molecules. The position of equilibrium lies well to the left.

The ammonia reacts as a base because of the active lone pair on the nitrogen. Nitrogen is more electronegative than hydrogen and so attracts the bonding electrons in the ammonia molecule towards itself. That means that in addition to the lone pair, there is a build-up of negative charge around the nitrogen atom. That combination of extra negativity and active lone pair attracts the new hydrogen from the water.



When looking at the table below, it is clear that the basicity of nitrogen containing compounds is greatly influenced by their structures. The variance in the basicity of these compounds can mostly be explained by the effects of electron delocalization discussed above.

Table 3.5.1: pKa of conjugate acids of a series of amines.

| Compound |  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
| $pK_a$ | 11.0 | 10.7 | 10.7 | 9.3 | 5.2 | 4.6 | 1.0 | 0.0 | -1.0 | -10.0 |

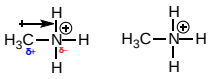
## Inductive Effects in Nitrogen Basicity

Alkylamines are more basic than ammonia since alkyl groups donate electrons to the more electronegative nitrogen. This inductive effect makes the electron density on the alkylamine nitrogen greater than the nitrogen of ammonium. That means that there will be a small amount of extra negative charge built up on the nitrogen atom. That extra negativity around the nitrogen makes the lone pair even more attractive towards hydrogen ions. Correspondingly, primary, secondary, and tertiary alkyl amines are more basic than ammonia.



*methyl group pushes electron density toward the nitrogen, making it more basic*

Making the nitrogen more negative helps the lone pair to pick up a hydrogen ion. What about the effect on the positive methylammonium ion formed? Is this more stable than a simple ammonium ion? Compare the methylammonium ion with an ammonium ion:



$CH_3$ group pushes electron density toward nitrogen

In the methylammonium ion, the positive charge is spread around the ion by the "electron-pushing" effect of the methyl group. The more you can spread charge around, the more stable an ion becomes. In the ammonium ion there is not any way of spreading the charge.

To summarize:

- The nitrogen is more negative in methylamine than in ammonia, and so it picks up a hydrogen ion more readily.
- The ion formed from methylamine is more stable than the one formed from ammonia, and so is less likely to shed the hydrogen ion again.

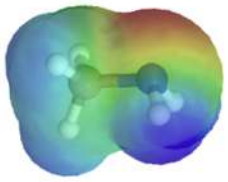
Taken together, these mean that methylamine is a stronger base than ammonia.

| Compound | $pK_a$ |
|---|---|
| $NH_3$ | 9.3 |
| $CH_3NH_2$ | 10.66 |
| $(CH_3)_2NH$ | 10.74 |
| $(CH_3)_3N$ | 9.81 |

## Resonance Effects in Nitrogen Basicity

The resonance effect also explains why a nitrogen atom is basic when it is in an amine, but *not* significantly basic when it is part of an amide group. While the lone pair of electrons in an amine nitrogen is localized in one place, the lone pair on an amide nitrogen

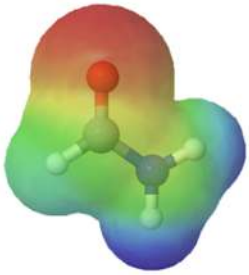
is delocalized by resonance. The lone pair is stabilized by resonance delocalization. Here's another way to think about it: the lone pair on an amide nitrogen is not available for bonding with a proton – these two electrons are too stable being part of the delocalized pi-bonding system. The electrostatic potential map show the effect of resonance on the basicity of an amide. The map shows that the electron density, shown in red, is almost completely shifted towards the oxygen. This greatly decreases the basicity of the lone pair electrons on the nitrogen in an amide.





amine

*$pK_a$ of conjugate acid ~ 11*





amide

*$pK_a$ of conjugate acid ~ −1*

Aniline, the amine analog of phenol, is substantially less basic than an amine (as evidenced by the $pK_a$ of the conjugate acids).



cyclohexylamine

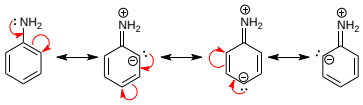
*$pK_a$ of conjugate acid ~ 10*



aniline

*$pK_a$ of conjugate acid ~ 5*

We can use the same reasoning that we used when comparing the acidity of a phenol to that of an alcohol. In aniline, the lone pair on the nitrogen atom is stabilized by resonance with the aromatic pi system, making it less available for bonding and thus less basic.



*lone pair is stabilized through resonance*

In these cases, you seem to be breaking the same oxygen-hydrogen bond each time, and so you might expect the strengths to be similar. The most important factor in determining the relative acid strengths of these molecules is the nature of the ions formed. You always get a hydronium ion - so that's constant - but the nature of the anion (the negative ion) varies markedly from case to case.

## Exercises

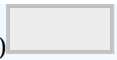
### Exercise 3.5.1

Select the more basic from each of the following pairs of compounds.

(a)

(b)

**Answer**

a)  The lone pair of electrons on the amide nitrogen are less available to react with a proton.

(b) NaOH -- The hydroxide has a negative charge with three lone pairs of electrons that can react with a proton.

**Exercise 3.5.2**

The 4-methylbenzylammonium ion has a $pK_a$ of 9.51, and the butylammonium ion has a $pK_a$ of 10.59. Which is more basic? What's the $pK_b$ for each compound?

**Answer**

The butylammonium is more basic. Remember that $pK_a+pK_b = 14$. The $pK_b$ for butylammonium is 3.41, the $pK_b$ for 4-methylbenzylammonium is 4.49.

## Contributors and Attributions

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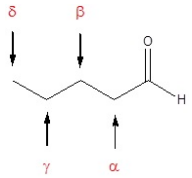
# 3.6: Keto-Enol Tautomerism

**Key Terms**

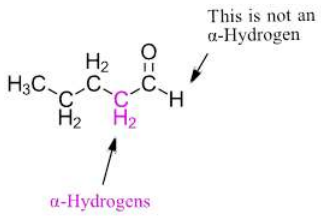
Make certain that you can define, and use in context, the key terms below.

- enol
- keto
- tautomerism
- tautomers
- enolate ion

Often, the position of carbon atoms near a carbonyl group are designated by Greek letters. The atom adjacent to the carbonyl is alpha, the next removed is beta and so on. The carbon in the carbonyl group is used as reference point and is not assigned a Greek letter. Likewise, hydrogens bare the same Greek letter as the carbon atoms to which they are attached. α Hydrogens are bonded to α carbons and β hydrogens are bonded to β carbons etc.



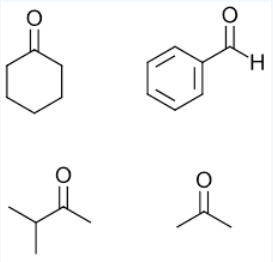

The presence of α hydrogens in a molecule provides the possibility of certain chemical reactions, which will be discussed in this chapter and Chapter 23. Because of this, the ability to identify α hydrogens is an important skill. As shown below, pentanal has two α hydrogens. Note that aldehyde hydrogens are not given a Greek letter, they are referred to simply as an aldehyde hydrogen.



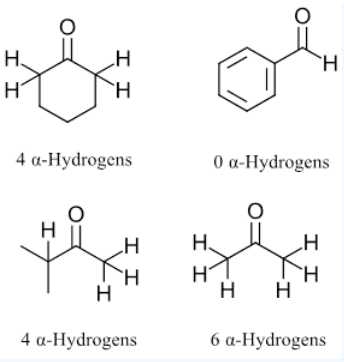

**Pentanal**

**Example 3.6.1**

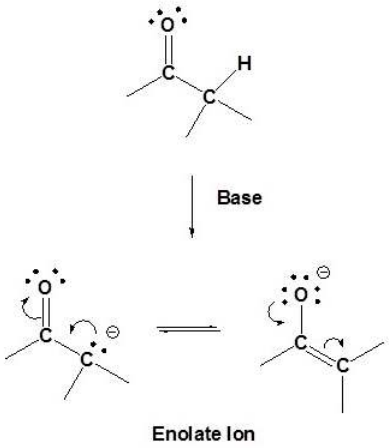
Indicate any α hydrogens contained in the following molecules:



**Solution**



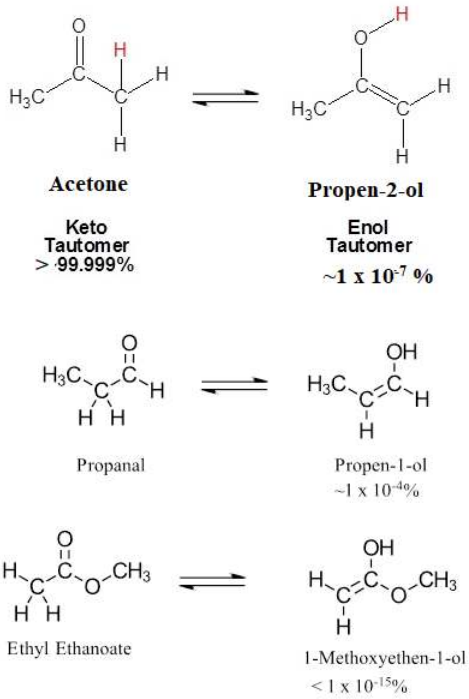

α hydrogens, which are directly adjacent to a carbonyl group, display unusual acidity. This is almost exclusively due to the resonance stabilization of the carbanion conjugate base, called an enolate, as illustrated in the diagram below. The effect of the the stabilizing C=O is seen when comparing the $pK_a$ for the α hydrogens of aldehydes (~16-18), ketones (~19-21), and esters (~23-25) to that of a typical alkyl C-H bond (~40-50).



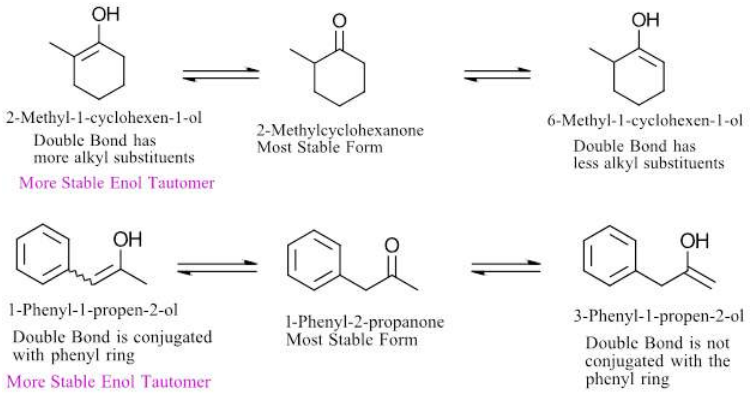

## Keto-enol Tautomerization

Because of the acidity of α hydrogens, many carbonyl containing molecules undergo a proton-transfer equilibrium called tautomerism. Tautomers are readily interconverted constitutional isomers, usually distinguished by a different location for an atom or a group. Because tautomers involve the rearrangement of atoms they are distinctly different than resonance forms, which only differ in the position of pi bonds and lone pair electrons. This discussion will focus on carbonyl group with alpha hydrogen, which undergo keto-enol tautomerism. Keto implies that the tautomer contains a carbonyl bond while enol implies the presence of a double bond and a hydroxyl group.

The keto-enol tautomerization equilibrium is dependent on stabilization factors of both the keto tautomer and the enol tautomer. For simple carbonyl compounds under normal conditions, the equilibrium usually strongly favors the keto tautomer (acetone, for example, is >99.999% keto tautomer). The keto tautomer is preferred because it is usually more stable the the enol tautomer by about 45–60 kJ/mol, mainly due to the C=O double bond (-749 kJ/mol) being stronger than the C=C double bond (-611 kJ/mol). Because ketones have two alky groups donating electron density into the carbonyl carbon, they tend to be more stable and therefore less apt to form the enol tautomer than aldehydes. Propanal is 1000 times more likely to be in its enol tautomer than acetone.

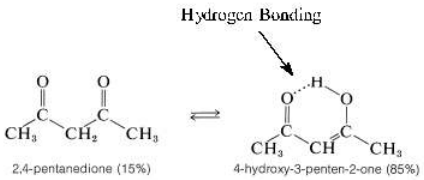


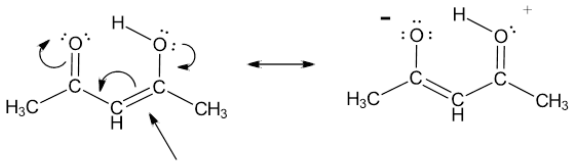

Alkehydes and symmetrical ketones typically only have one possible enol tautomer while asymmetrical ketones have two or more. The preferred enol tautomer form can be predicted by considering effects which stabilize alkenes, such as conjugation and alkyl group substitution.



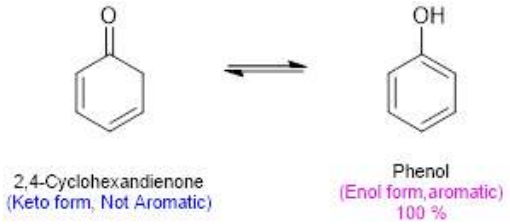

## 1,3- Dicarbonyls

In certain cases additional stabilizing effects allow the enol tautomer to be preferred in the tautomeization equilibrium. In particular, the 1,3 arrangement of two carbonyl groups can work synergistically to stabilize the enol tautomer, increasing the amount present at equilibrium. The diketone, 2,4-pentanedione, is in its enol form 85% of the time under normal conditions. The positioning of the carbonyl groups allows for the formation of a stabilizing intramolecular hydrogen bond between the hydroxyl group of the enol and the carbonyl oxygen. The alkene group of the enol tautomer is also conjugated with the carbonyl double bond which provides additional stabilization. Both of these stabilizing effects are not possible in the keto tautomer.





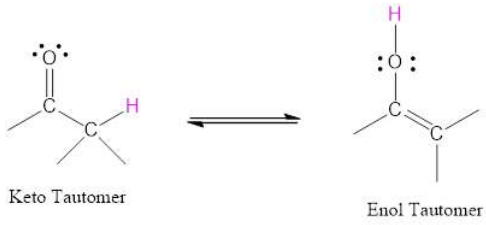

Another effect which can stabile an enol tautomer is aromaticity. When considering the molecule 2,4-cyclohexadienone, the enol tautomer is the aromatic molecule phenol. The stabilization gained by forming an aromatic ring is sufficient to make phenol the exclusive tautomer present in the equilibrium.




## Mechanism for Catalyzed Keto-Enol Tautomerization

The enol tautomer has valuable nucleophilic characteristics. In neutral medial, tautomerization is slow but it can be speed up by catalysis with acids or bases. Both pathways involve two separate proton transfer steps. Because enols are a key reactive intermediate, these mechanistic steps will be used repeatedly in later reactions. The following mechanistic steps represent the continuous interconversion between the keto and enol tautomers.

**Overall Process**

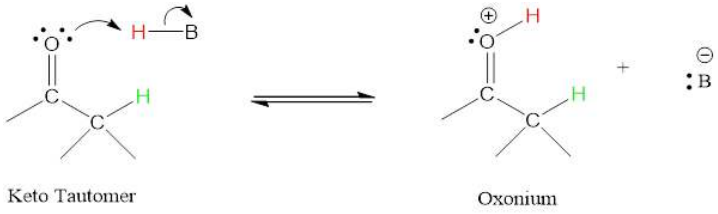



## Acidic Conditions

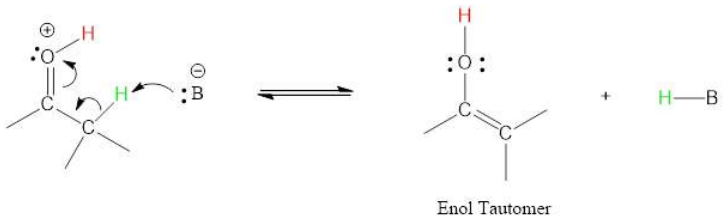
**Keto Tautomer → Enol Tautomer**

In the first step, the carbonyl oxygen is protonated by an acid to form an intermediate oxonium compound. A base removes an α-hydrogen during the second step forming a double bond by an E2 type reaction. This causes the pi electrons of the protonated cabonyl to move to the oxygen forming the hydroxyl group of the enol product and regenerating the acid catalyst.

1) Protonation of the carbonyl to form an oxonium compound



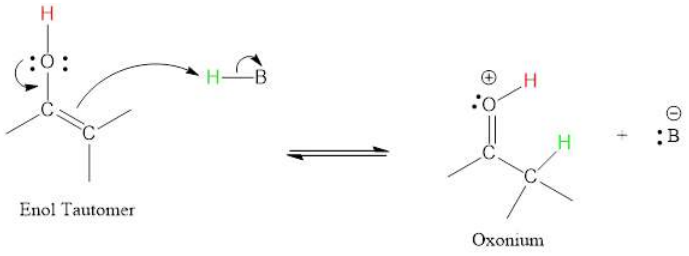

2) Deprotonation of an *α* hydrogen to form an enol



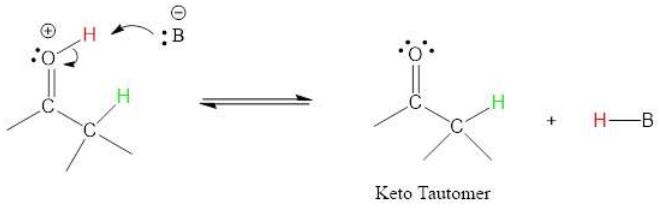

**Enol Tautomer → Keto Tautomer**

First, pi bond electrons from the carbon in the alpha position attack the electrophilic $H^+$ provided by acid catalyst causing one of the lone pairs of electrons on the oxygen to form a pi bond to carbon generating a carbonyl. This produces an oxonium intermediate with is subsequently deprotonated to form the neutral ketone and regenerates the acid catalyst.

1) Protonation at the alpha carbon




2) Deprotonation

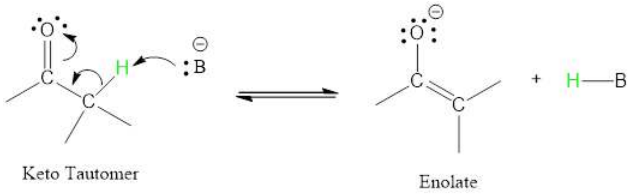



## Under Basic Conditions

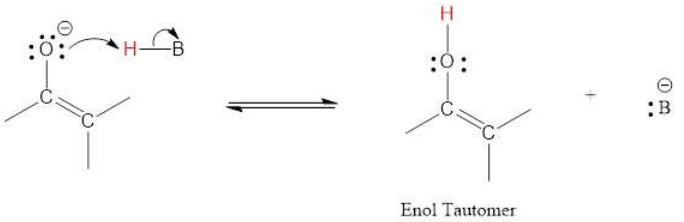
**Keto Tautomer → Enol Tautomer**

In the first step, a base removes an α hydrogen to form an alkene by an E2 type process. The causes the pi electrons of the carbonyl to move onto the oxygen forming an enolate anion. The oxygen of the enolate anion is protonated in the second step to create a neutral enol and regenerate the base catalyst.

1) Deprotonation *α* to the carbonyl to form an enolate ion



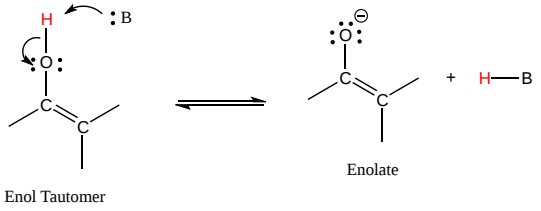

2) Protonation the enolate ion to form an enol



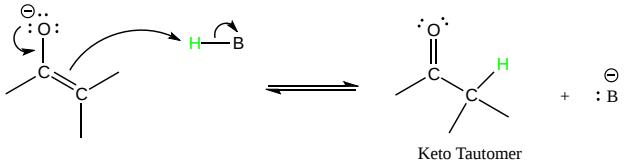
**Enol Tautomer → Keto Tautomer**

The mechanistic return to the keto tautomer begins with deprotonnation of the hydroxyl hydrogen producing an enolate. Then lone pair electrons from the enolate anion attack an electrophilic $H^+$ through conjugation with the double bond. This simultaneously forms the carbonyl double bond, adds an alpha hydrogen, and regenerates the base catalyst.

1)



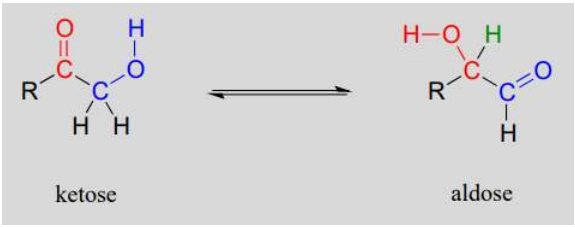

2)




## Biological Enol Forming Reactions

**Carbonyl Isomerization**

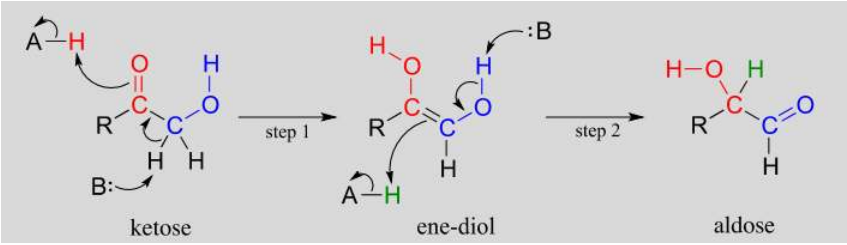
One very important family of isomerase enzymes catalyzes the shifting of a carbonyl group in sugar molecules, often converting between a ketose and an aldose in a process called carbonyl isomerization (recall that the terms ketose and aldose refer to sugar molecules containing ketone and aldehyde groups, respectively).




**Carbonyl Isomerization**

**Mechanism**

Carbonyl isomerization can only occur if there is an OH group adjacent to the carbonyl. This forms an ene-diol intermediate which has both OH hydrogens available to be removed to reform the carbonyl. If the hydrogen from the original OH group is removed a new carbonyl bond is formed.




Carbonyl isomerization is involved in the metabolism of carbohydrates (starches and sugars) to their eventual conversion to $CO_2$ and $H_2O$. First, starches are broken down into glucose in the digestive tract. In the cells, the first step of the glycolysis pathway involves an enzyme converting glucose to glucose-6-phosphate. This is followed by the enzyme-catalzyed tautomerization of glucose-6-phosphate (an aldose) to fructose-6-phosphate (a ketose) through an enediol intermediate. Notice how the carbonyl has moved from the 1-carbon (terminal) to the 2-carbon.




glucose-6-phosphate fructose-6-phosphate

## Contributors and Attributions

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- Prof. Steven Farmer (Sonoma State University)
- Layne Morsch (University of Illinois Springfield)

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# CHAPTER OVERVIEW

## 4: Conformations


- 4.1: Conformational Analysis of Alkanes
- 4.2: Cycloalkanes and Their Relative Stabilities
- 4.3: Cyclohexane Conformations
- 4.4: Conformations of Disubstituted Cyclohexanes


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# 4.1: Conformational Analysis of Alkanes

## 4.1.1 Conformation

At a molecular level, a property of σ (sigma) bonds in alkane is that the bonds keep on rotating. For the example of ethane ($CH_3CH_3$), one methyl ($CH_3$) group is able to rotate around the C-C bond freely without any obstacles.

It is highly recommended that the molecular model is used here to "see" the bond rotation. With a molecular model on hand, you can hold one methyl group steady, and rotate the other methyl group.

The C-C bond is formed by the $sp^3$-$sp^3$ orbitals overlapping and the bond is cylindrically symmetrical, so rotation about the bond can occur easily and the molecule does not seem to change. However, a closer look indicates that the rotation of the C-C bond **does** result in a different spatial arrangement of hydrogen atoms in the molecule, as shown below:

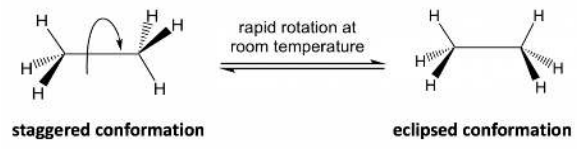



Figure 4.1a Two conformers of ethane in perspective formulas

The different spatial arrangements of the atoms/groups that result from the single bond rotation are called **conformations**. Molecules with different conformations are called **conformational isomers** or **conformers**. The two extreme conformations of ethane coming from the C-C rotation shown above are: the ***staggered conformation*** with all of the H atoms spread out, and the ***eclipsed conformation*** with all of the H atoms overlapped.

In the study of conformation, it is convenient to use certain types of structural formulas. The formula used in the drawing above is the **perspective formula** (see **section 2.1.1**) that shows the side-view of the molecule. In perspective formulas, solid and dashed wedges are used to show the spatial arrangement of atoms (or groups) around the $sp^3$ carbons.

Another structural formula is the **sawhorse formula** that shows the tilted top-view of the molecule.

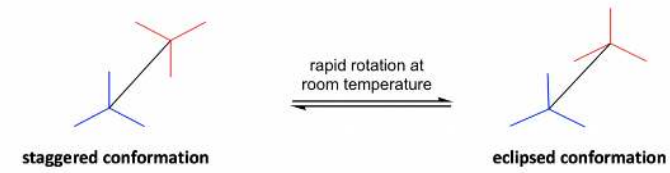



Figure 4.1b Two conformers of ethane in sawhorse formulas

The most commonly applied formula in conformation analysis is the **Newman projection** formula.

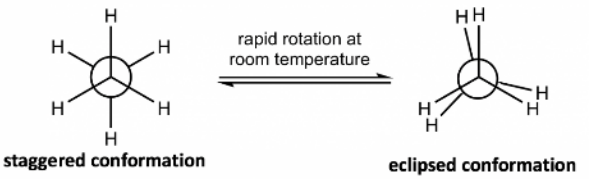



Figure 4.1c Two conformers of ethane in Newman projections

### How to draw a Newman projection

To draw a **Newman projection,** we will imagine **viewing** the molecule *from one carbon to the next carbon atom directly along a selected C–C bond*, as shown below, and follow the rules:

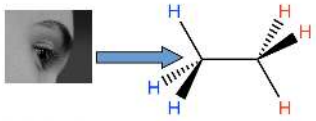


Figure 4.1d Viewing of the molecule

- The front carbon atom is shown as a point with three other bonds:



- The rear carbon atom is shown as a circle with three other bonds:



- Put the two carbons together to get the Newman projection of the staggered conformation:



- From the staggered conformation, fix the front carbon in place, and rotate the rear carbon by 60° to get the eclipsed conformation:



Note: In eclipsed conformers, **the C-H bonds are supposed to be completed overlapped; however, to make the** rear *groups still visible, the bonds on the* rear carbon are intentionally drawn slightly tilted.

## 4.1.2 Conformation Analysis of Ethane

Next, we will do a conformation analysis of ethane by using the Newman projections. **A conformation analysis** is an investigation of energy differences and relative stabilities of the different conformations of a compound.

The two conformations of ethane, staggered and eclipsed, are different and have energies. It turns out that the staggered conformation is lower in energy than the eclipsed conformation by ~4 kJ/mol in ethane. In eclipsed conformations, the H atoms on the front carbon are overlapping with the H atoms on the rear carbon, and this arrangement causes something called the **torsional strain**. Due to the torsional strain, the eclipsed conformer is in the energy level that is 12 kJ/mol (or about 2.9 kcal/mol) higher than the staggered one (because there are three of these eclipsing interactions). This can be represented graphically in a potential energy diagram as shown in Figure 4.1f.

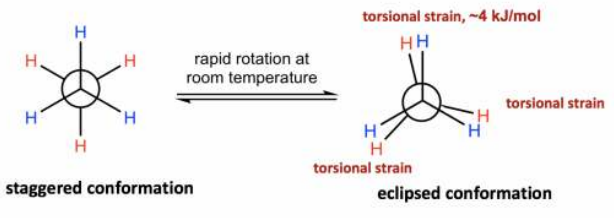



Figure 4.1e Staggered vs. eclipsed conformation

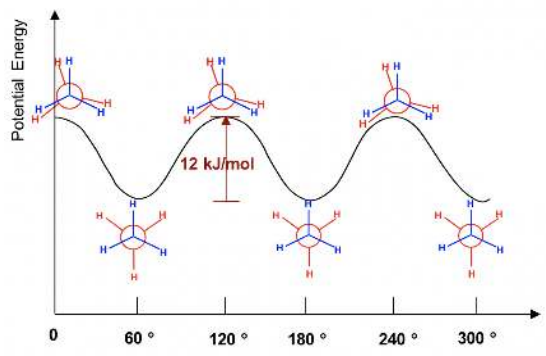



Fig. 4.1f Potential Energy of Ethane vs the Angle of Rotation about the C-C bond

Because of this energy difference, an energy barrier must be overcome when the rotation about the C-C bond occurs. However, this energy difference in ethane is rather small, and the kinetic energy of molecules at room temperature is high enough to cover it. So

at room temperature, the changes from staggered to eclipsed conformers occur millions of times per second. Because of these continuous interconversions, these two conformers cannot be separated from each other. However, at any given moment, about 99% of the ethane molecules will be in a staggered conformation because of their higher stability.

The origin of **why** this torsional strain arises requires an understanding of a concept known as Molecular Orbital Theory, which is beyond the scope of what we have encountered so far. For the time being, if we accept that there is a type of strain known as **torsional strain** that leads to staggered conformations being lower in energy than eclipsed conformations, then we have everything we need for the time being. This concept of **torsional strain** will be revisted once we have learned more about Molecular Orbital Theory.

### 4.1.3 Conformation Analysis of Propane

A similar analysis can be applied to propane as well. We will find that there are still two types of conformations, staggered and eclipsed, resulting from the rotation. The difference between propane and ethane is that there is a methyl ($CH_3$) group connected on the rear carbon for propane. However, that does not affect the relative amounts of torsional strain, and the staggered conformer is still more stable and in lower energy.

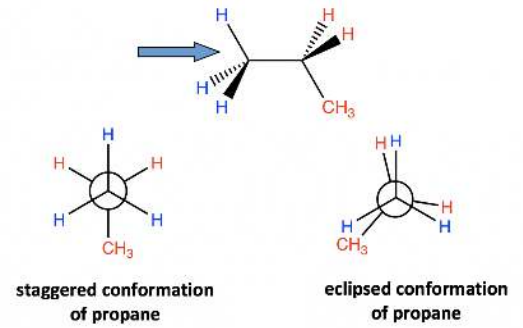



Figure 4.1g Staggered and eclipsed conformation of propane

### 4.1.4 **Conformation Analysis of Butane**

There are three C-C bonds in butane, and rotation can occur about each of them. If we pick up C1-C2 (or C3-C4) for the study, the situation is almost the same as propane, with the ethyl $CH_2CH_3$ group replace the $CH_3$ group. However, if we consider the rotation about the C2-C3 bond, the situation will be much more complex.

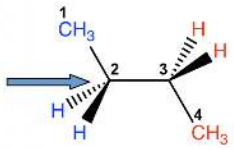


Figure 4.1h Conformation analysis of butane by viewing along C2-C3 bond

For both carbon atoms, C2 and C3, there are two hydrogen atoms and one methyl $CH_3$ group bonded with. We can start with the conformer in which the two $CH_3$ groups are **opposite** to each other, then fix the front carbon and do 60° rotations of the rear carbon to investigate **all** the possible conformations.

Exercises 4.1: Draw all the possible conformers of butane from viewing along the C2-C3 bond. Finish this practice by yourself before continue reading!

**Tips** for drawing all the possible conformers about a certain C-C bond:

- View along that C-C bond; circle and decide what atoms/groups are connected on each carbon;
- Start with the staggered conformation in which the largest groups on each carbon are opposite (far away) to each other (this is called the "*anti*"conformation as we will learn later);
- Keep the groups on one carbon "fixed", and rotate the groups on the other carbon at 60° angles. Repeat the rotation five times, and you should get total of six conformers.

Answers to Practice Questions Chapter 4

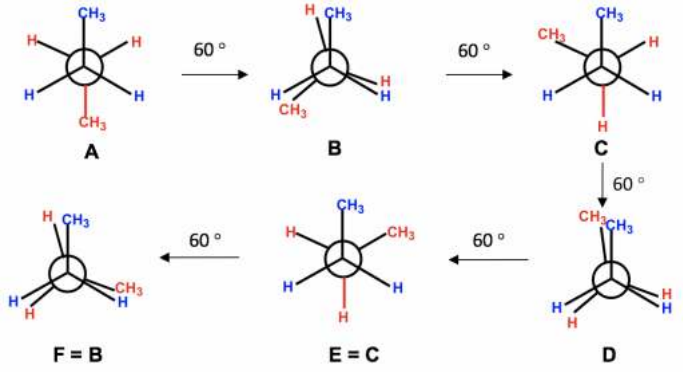



Figure 4.1i All the conformers of butane by viewing along C2-C3 bond

Among all the six conformers obtained, there are three staggered and three eclipsed. Staggered conformations **C** and **E** should be in the same energy level because the groups are arranged in equivalent way between these two conformers. Similarly, eclipsed conformations **F** and **B** are also in the same energy level. So our studies can be focused on the four conformers, **A, B, C** and **D**, that are different in terms of energy and stability.

Between the two staggered conformers **A** and **C**, **A** is more stable than **C** because the two methyl $CH_3$ groups in **A** are as far apart as possible. This most stable staggered conformation is called the **anti** conformation (*anti* is Greek for "opposite"). In **anti** conformations, the largest groups on the front and rear carbon are 180° opposite to each other. The other staggered conformation **C** is called a **gauche** conformation, in which the two large groups are adjacent and are 60° to each other. With the large groups being close to each other in gauche conformers, the molecule experiences **steric strain**. **Steric strain** is the strain that is caused when atoms (or groups) are close enough together that their electron clouds repel each other. Steric strain only matters when the groups are close to each other (less or equal to 60°), so steric strain does not apply in anti conformations. The magnitude of steric strain also depends on the size of group; the larger the size, the higher the steric strain. As a result, there is no steric strain between two small hydrogen atoms, even if they are close to each other. That is why no steric strain is observed when considering the rotation around the central C-C bonds in either ethane or propane (discussed above).

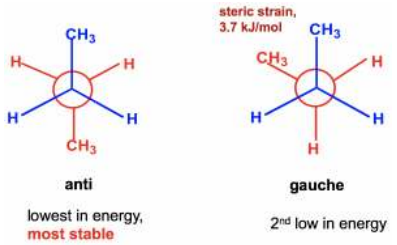



Figure 4.1j Anti and gauche conformations

Between the two eclipsed conformers **B** and **D** , **D** is less stable than **B** , because the two $CH_3$ groups are eclipsing (overlapping) each other in **D** , causing both torsional and steric strains.

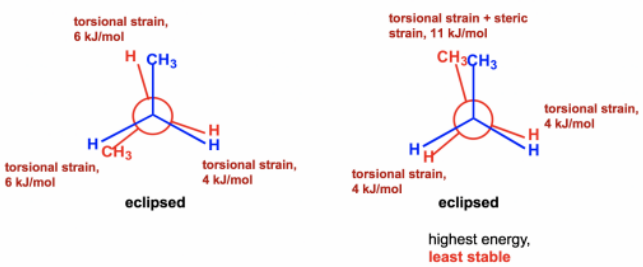



Figure 4.1k Comparison between the two eclipsed conformations

The energy difference of all the conformers obtained from the rotation about the C2-C3 bond are shown in the potential energy diagram **Fig. 4.1l** . The curve is more complex than that of ethane since there are four different energy levels corresponding to four conformers with different stabilities. Even the energy barriers for the rotations are larger than that of ethane, but they are still not high enough to stop rotation at room temperature.

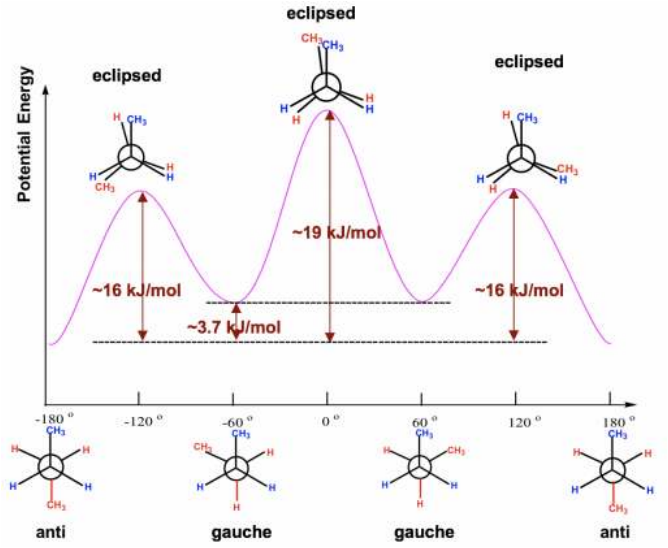



Figure 4.1l Potential Energy of Butane vs the Angle of Rotation about the C2-C3 bond

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# 4.2: Cycloalkanes and Their Relative Stabilities

While the open chain alkanes have conformational isomers because of bond rotation, will this apply to cycloalkanes as well? In this section, we will take a look at properties of cycloalkanes first, and then investigate how the different conformers of cycloalkanes contribute to the different stabilities.

The short line structural formulas of cycloalkenes simply look like shapes such as a triangle, square etc. The internal angles of the shapes can be calculated with geometry, as shown below.

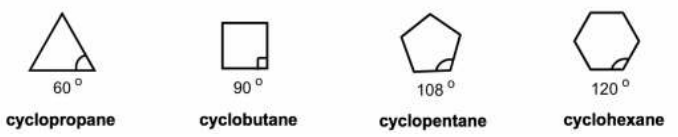



Figure 4.2a Short line structural formula of cycloalkanes

An interesting fact about the cycloalkanes is that they have different relative stabilities, and the stability depends on the size of the ring. It has been observed that cyclic compounds found in nature usually are in 5- or 6-membered rings, and the 3- or 4-membered rings are rather rare.

To explain this stability difference, German chemist Adolf von Baeyer proposed the "Bayer Strain Theory". By assuming all the rings are in a *flat* (or planar) shape, Bayer Theory suggests that the difference between the ideal bond angle (which is 109.5° for $sp^3$ carbon) and the angle in the planer cycloalkane causes the strain, which is called **angle (or ring) strain**. According to the Bayer Theory, cyclopentane would be the most stable because its bond angles, 108°, are closest to the ideal angle of 109.5°. Cyclopropane would be the least stable one since it has the largest angle deviation of 49.5° (60° vs 109.5°). It was also predicted that cyclohexane would be less stable than cyclopentane because of the larger angle deviation (10.5° deviation for cyclohexane vs 1.5° for cyclopentane), and as the number of sides in the cycloalkanes increases beyond six the stability would decrease.

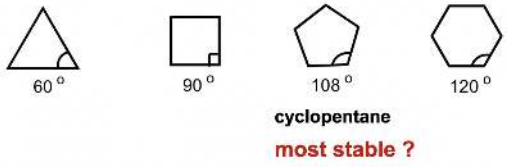



Figure 4.2b Which cyclo is stable?

However, experimental results show a different trend. It turns out that **cyclohexane** is the most stable ring that is strain-free, and is as stable as an open-chain alkane. Furthermore, cyclic compounds do not become less and less stable as the number of rings increases.

To measure the relative stability of cycloalkanes, the heat of combustion ($\Delta H_{comb}$) for each cycloalkane was measured. The heat of combustion is the amount of heat released when the compounds burns completely with oxygen. The cycloalkanes will be in higher energy levels than corresponding chain alkanes because of strain energy. Therefore, when cycloalkane burns, more heat will be released, so the difference of $\Delta H_{comb}$ between cycloalkane vs the "strainless" chain alkane is just the amount of strain energy, as shown below. The larger the difference, the higher the strain energy of the cycloalkane. The strain energy for different cycloalkanes measured by this method are listed in **Table 4.1**.

combustion reaction: $(CH_2)_n + 3n/2\ O_2 \rightarrow n\ CO_2 + n\ H_2O$ + heat

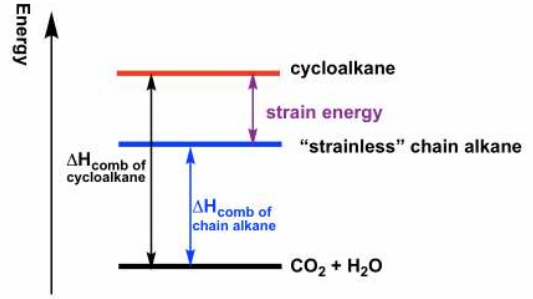



Figure 4.2c The relationship between heat of combustion and strain energy

| | cyclopropane | cyclobutane | cyclopentane | cyclohexane |
|---|---|---|---|---|
| Strain Energy (KJ/mol) | 114 | 110 | 25 | 0 |

**Table 4.1 Strain Energies of Cycloalkanes**

The major drawback of the Baeyer Theory was that we must assume that all the rings are flat. The highest stability of cyclohexane from experimental results indicate that the rings may not be in a planar shape. We will have a closer look at the actual shape and conformation of 3-, 4-, 5- and 6-membered cycloalkanes.

## Cyclopropane

With three carbons for the ring, cyclopropane must be planar.

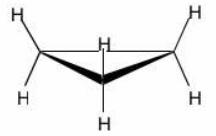
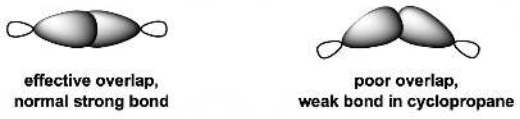


Figure 4.2d Cyclopropane

The bond angle in cyclopropane is 60°, derived significantly from the optimal angle of 109.5°, so it has very high angle strains. The $sp^3$-$sp^3$ orbitals can only overlap partially because of the angle deviation, so the overlapping is not as effective as it should be, and as a result the C-C bond in cyclopropane is relatively weak.

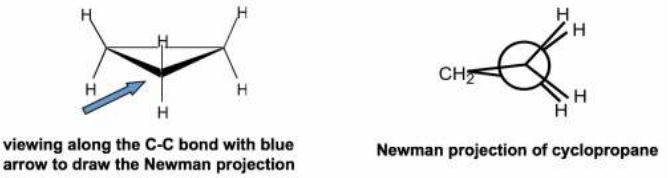



Because of the poor overlapping of $sp^3$-$sp^3$orbitals, the bonds formed in cyclopropane resemble the shape of a banana, and are sometimes called banana bonds.



Figure 4.2e “Banana bonds” of cyclopropane

Other than the angle strains, all the adjacent C-H bonds are eclipsed in cyclopropane, therefore the torsional strains are applied as well. Such a strain can be “viewed” more clearly from the Newman projection of cyclopropane.



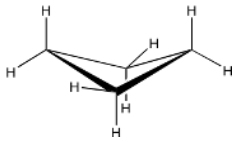

The Newman projection of cyclopropane might seems weird at first glance. For cyclopropane, there are three carbons, so the **$CH_2$ group connects with both front and rear carbons** of the Newman projection.

Because of the high level of angle strains and torsional strains, 3-membered rings are unstable. They rarely exist in nature and undergo ring-opening reaction easily to release the strains.

## Cyclobutane

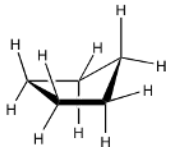
Cyclobutane is not planar. The ring puckers (or folds) slightly due to the efforts of releasing some torsional strain. Meanwhile, cyclobutane still has a considerable amount of angle strains as the internal angles become about 88° with the folded shape. Overall,

cyclobutane is an unstable structure with rather high level of strains.

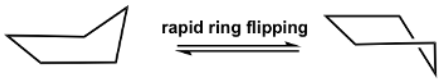


## Cyclopentane

Cyclopentane is not planar as well and the total level of strain is lowered quite a lot. It also puckers and adopts a bent conformation where one carbon atom sticks out of the plane of the others, which helps to release the torsional strain by allowing some hydrogen atoms to become almost staggered.



This bent shape of cyclopentane is also called the “envelope” conformation. The envelope conformation can undergo a process called “ring flipping” as a result of C-C bond rotation. More discussions about ring flipping will be included in the section of cyclohexane, which we will take a look at later on.




## Cyclohexane

It turns out that cyclohexane rings end up adopting a conformation called a chair conformation that reduces both torsional and angle (ring) strain. The conformations of cyclohexane rings are very well-studied and warrant a full discussion on their own. For the time being, we shall simply accept that the conformation adopted by cyclohexane rings represents a beautiful balance that minimizes both torsional and angle strain.

## Rings Larger than cyclohexane

Rings larger than six-membered rings tend not to adopt conformations as well-defined as cyclohexane or cyclopentane. As the number of atoms in a ring gets >6, these rings tend to get "floppy" and adopt a large number of less well-defined conformations as the molecules seek to find the lowest energy conformations that minimize both torsional and angle strain as best they can. Because they don't adopt clearly-understandable conformations, organic chemists tend to spend less effort defining the conformations of rings with >6 atoms in them so we shall simply accept that these rings do adopt conformations to minimize the strain (and thus energy) of the system, and leave it at that.

---

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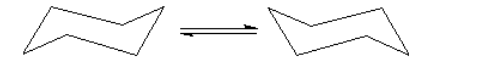
# 4.3: Cyclohexane Conformations

## Introduction

Rings larger than cyclopentane would have angle strain if they were planar. However, this strain, together with the eclipsing strain inherent in a planar structure, can be relieved by puckering the ring. Cyclohexane is a good example of a carbocyclic system that virtually eliminates eclipsing and angle strain by adopting non-planar conformations. Cycloheptane and cyclooctane have greater strain than cyclohexane, in large part due to transannular crowding (steric hindrance by groups on opposite sides of the ring).

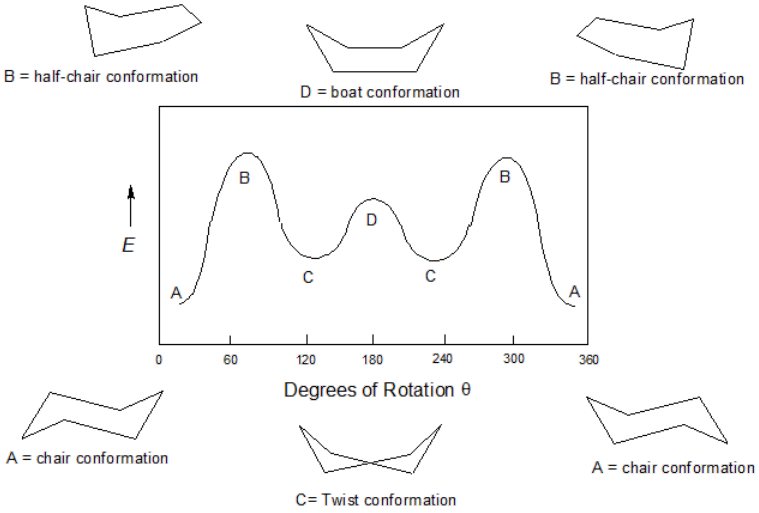
## Cyclohexane Conformations (aka Chair Flips)

Cyclohexane is rapidly rotating between the two most stable conformations known as the chair conformations in what is called the "Chair Flip" shown below.



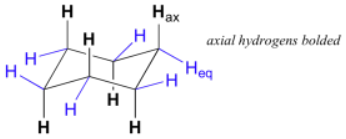
The "Chair Flip" describes the rapid equilibrium of cyclohexane rings between the two chair conformations.

Several other notable cyclohexane conformations occur during the transition from one chair conformer to the other - the boat, the twist, and the half-chair. The relative energies of the conformations is a direct reflection of their relative stabilities. These structural and energetic relationships are summarized in the conformational energy diagram for cyclohexane below.

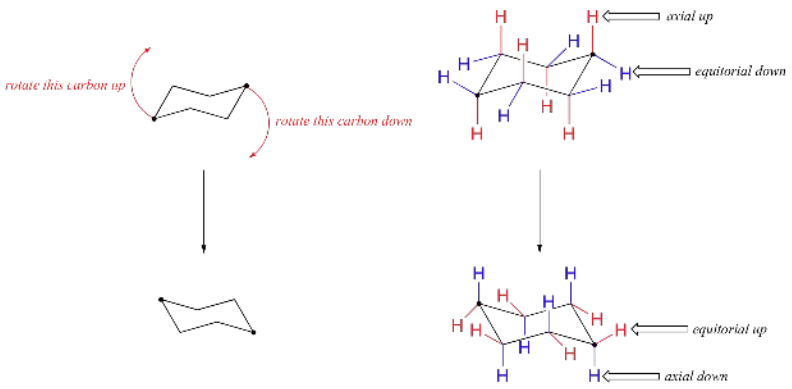



## The Chair Conformation - a closer look

Since the chair conformation has the lowest potential energy, it is the most relevant to the conformation of cyclohexane. On careful examination of a chair conformation of cyclohexane, we find that the twelve hydrogens are not structurally equivalent. Six of them are located about the periphery of the carbon ring, and are termed equatorial. The other six are oriented above and below the approximate plane of the ring (three in each location), and are termed axial because they are aligned parallel to the symmetry axis of the ring.




In the figure above, the equatorial hydrogens are colored blue, and the axial hydrogens are in bold. Since there are two equivalent chair conformations of cyclohexane in rapid equilibrium, all twelve hydrogens have 50% equatorial and 50% axial character. The figure below illustrates how to convert a molecular model of cyclohexane between two different chair conformations - this is something that you should practice with models. Notice that a 'ring flip' causes equatorial hydrogens to become axial, and vice-versa.

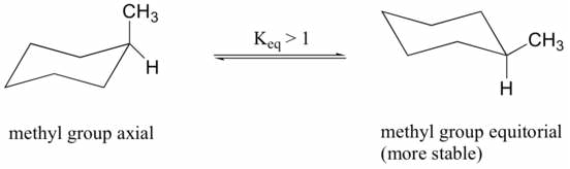



## How to Draw chairs

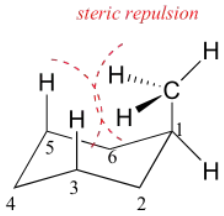
When drawing the basic chair conformation, the key points in adding substituents are:

- Axial groups alternate up and down, and are shown "vertical".
- Equatorial groups are approximately horizontal, but actually somewhat distorted from that, so that the angle from the axial group is a bit more than a right angle -- reflecting the common 109 degree bond angle.
- As cautioned before, it is usually easier to draw and see what is happening at the four corners of the chair than at the two middle positions.

Because axial bonds are parallel to each other, substituents larger than hydrogen generally suffer greater steric crowding when they are oriented axial rather than equatorial. Consequently, ***substituted cyclohexanes will preferentially adopt conformations in which the larger substituents assume equatorial orientation***.




When the methyl group in the structure above occupies an axial position it suffers steric crowding by the two axial hydrogens located on the same side of the ring.




The conformation in which the methyl group is equatorial is more stable, and thus the equilibrium lies in this direction

## Contributors and Attributions

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Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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# 4.4: Conformations of Disubstituted Cyclohexanes

**Learning Objective**

- draw di-substituted cyclohexane conformers (chair only)
- correlate energies of conformations with rotational energy diagrams and predict the most stable conformations for disubstituted cyclohexanes

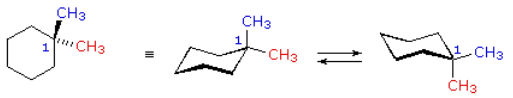
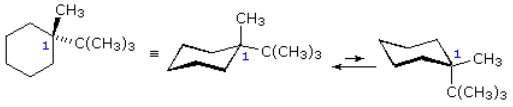
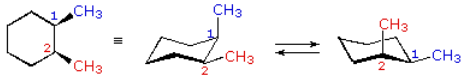
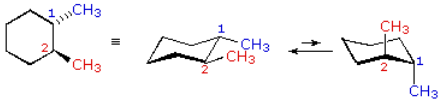
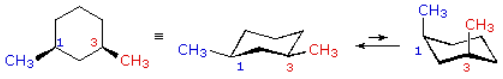
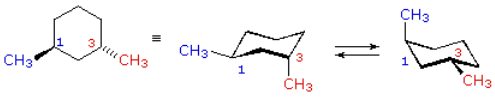
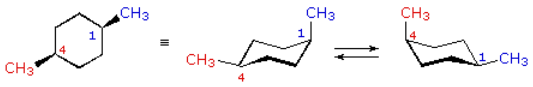
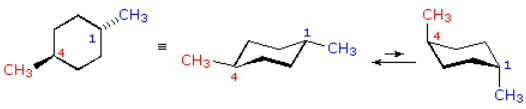
Conformational Structures of Disubstituted Cyclohexanes

In a sample of cyclohexane, the two identical chair conformers are present in equal concentration, and the hydrogens are all equivalent (50% equatorial & 50% axial) due to rapid interconversion of the conformers. When the cyclohexane ring bears a substituent, the two chair conformers are not the same. In one conformer the substituent is axial, in the other it is equatorial. Due to steric hindrance in the axial location, substituent groups prefer to be equatorial and that chair conformer predominates in the equilibrium.

When cycloalkanes have two substituents on different ring carbon atoms, then a pair of configurational stereoisomers exist. Now we must examine the way in which favorable ring conformations influence the properties of the configurational isomers. Remember, configurational stereoisomers are stable, unique chemical compounds, whereas, conformational isomers are different rotations of the same compound. In examining possible structures for disubstituted cyclohexane, it is useful to follow two principles:

1. Substituents on chair conformers prefer to occupy equatorial positions due to the increased steric hindrance of axial locations.

The following equations and formulas illustrate how the presence of two or more substituent on a cyclohexane ring perturbs the interconversion of the two chair conformers in ways that can be predicted. When there is a potential energy difference between the conformers, then the lower energy conformation is favored as indicated by the equilibrium reaction arrows.

| | |
|---|---|
| 1,1-dimethylcyclohexane |  |
| 1-t-butyl-1-methylcyclohexane |  |
| cis-1,2-dimethylcyclohexane |  |
| trans-1,2-dimethylcyclohexane |  |
| cis-1,3-dimethylcyclohexane |  |
| trans-1,3-dimethylcyclohexane |  |
| cis-1,4-dimethylcyclohexane |  |
| trans-1,4-dimethylcyclohexane |  |

In the case of 1,1-disubstituted cyclohexanes, one of the substituents must necessarily be axial and the other equatorial, regardless of which chair conformer is considered. Since the substituents are the same in 1,1-dimethylcyclohexane, the two conformers are identical and present in equal concentration. In 1-t-butyl-1-methylcyclohexane the t-butyl group is much larger than the methyl, and that chair conformer in which the larger group is equatorial will be favored in the equilibrium( > 99%). Consequently, the methyl group in this compound is almost exclusively axial in its orientation.

In the cases of 1,2-, 1,3- and 1,4-disubstituted compounds the analysis is a bit more complex. It is always possible to have both groups equatorial, but whether this requires a cis-relationship or a trans-relationship depends on the relative location of the substituents. As we count around the ring from carbon #1 to #6, the uppermost bond on each carbon changes its orientation from equatorial (or axial) to axial (or equatorial) and back. It is important to remember that the **bonds on a given side of a chair ring-conformation always alternate in this fashion**. Therefore, it should be clear that for cis-1,2-disubstitution, one of the substituents must be equatorial and the other axial; in the trans-isomer both may be equatorial. Because of the alternating nature of equatorial and axial bonds, the opposite relationship is true for 1,3-disubstitution (cis is all equatorial, trans is equatorial/axial). Finally, 1,4-disubstitution reverts to the 1,2-pattern.

The conformations of some substituted cyclohexanes may be examined as interactive models by Clicking Here.

It can be helpful to add the hydrogen atoms at the axial positions to help recognize the equatorial position.

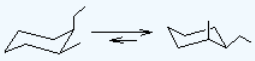
## Exercise

1. Draw the two chair conformations for cis-1-ethyl-2-methylcyclohexane using bond-line structures and indicate the more energetically favored conformation.

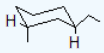
2. Draw the most stable conformation for trans-1-ethyl-3-methylcyclohexane using bond-line structures.

3. Draw the most stable conformation for trans-1-t-butyl-4-methylcyclohexane using bond-line structures.

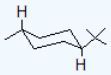
**Answer**

1. 

larger ethyl group in equatorial position is favored

2. 


larger ethyl group in equatorial position is favored

3. 


both alkyl groups in equatorial position

## Contributors

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# CHAPTER OVERVIEW

## 5: Stereochemistry

This chapter introduces the concept of chirality, and discusses the structure of compounds containing one or two chiral centers. A convenient method of representing the three-dimensional arrangement of the atoms in chiral compounds is explained; furthermore, throughout the chapter , considerable emphasis is placed on the use of molecular models to assist in the understanding of the phenomenon of chirality. The chapter continues with an examination of stereochemistry—the three-dimensional nature of molecules. The subject is introduced using the experimental observation that certain substances have the ability to rotate plane-polarized light. Finally, certain reactions of alkenes are re-examined in the light of the new material encountered in this chapter.


5.1: The Reason for Handedness in Molecules - Chirality
5.2: Enantiomers and the Tetrahedral Carbon
5.3: Optical Activity
5.4: Sequence Rules for Specifying Configuration
5.5: Diastereomers
5.6: Meso Compounds
5.7: A Review of Isomerism



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# 5.1: The Reason for Handedness in Molecules - Chirality

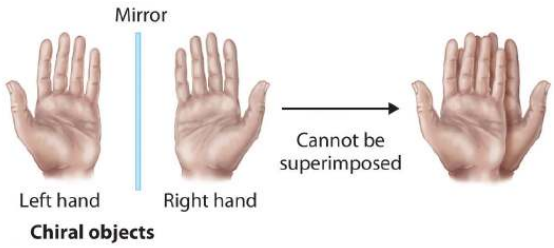
**Key Terms**

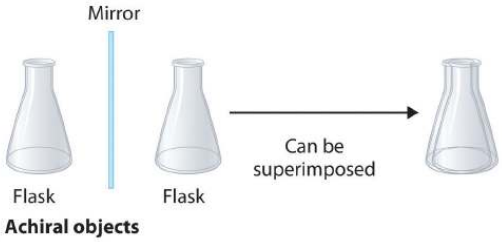
Make certain that you can define, and use in context, the key terms below.

- achiral
- chiral
- chiral (stereogenic) centre
- plane of symmetry

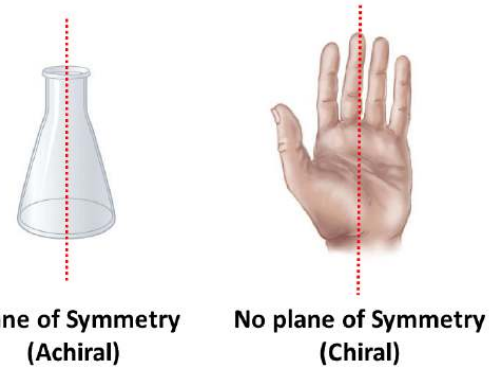
## Symmetry and Chirality

Molecules that are nonsuperimposable mirror images of each other are said to be chiral (pronounced “ky-ral,” from the Greek cheir, meaning “hand”). Examples of some familiar chiral objects are your hands. Your left and right hands are nonsuperimposable mirror images. (Try putting your right shoe on your left foot—it just doesn’t work.) An achiral object is one that can be superimposed on its mirror image, as shown by the superimposed flasks in the figure below.




An an important questions is why is one chiral and the other not? The answer is that the flask has a plane of symmetry and your hand does not. A plane of symmetry is a plane or a line through an object which divides the object into two halves that are mirror images of each other. When looking at the flask, a line can be drawn down the middle which separates it into two mirror image halves. However, a similar line down the middle of a hand separates it into two non-mirror image halves. This idea can be used to predict chirality. If an object or molecule has a plane of symmetry it is achiral. If if lacks a plane of symmetry it is chiral.

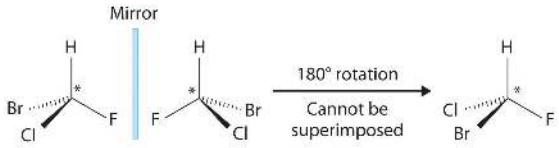


Symmetry can be used to explain why a carbon bonded to four different substituents is chiral. When a carbon is bonded to fewer than four different substituents it will have a plane of symmetry making it achiral. A carbon atom that is bonded to four different substituents loses all symmetry, and is often referred to as an asymmetric carbon. The lack of a plane of symmetry makes the carbon chiral. The presence of a single chiral carbon atom sufficient to render the molecule chiral, and modern terminology refers to such groupings as chiral centers or stereo centers.

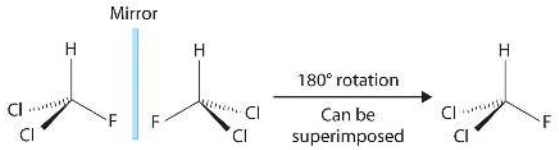
## A Special Note on Molecular Models

This entire chapter will be **MUCH** easier to learn by using molecular models. Trying to represent a three-dimensional idea on a two-dimensional screen is much more difficult than using a three-dimensional model. Pull out your molecular models and try to actually build the molecules shown below to follow along. The time invested in building the models will be less than time spent puzzling over the screen.

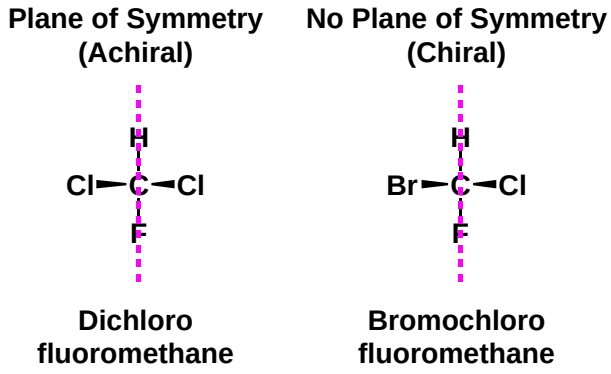
An example is shown in the bromochlorofluoromethane molecule shown in part (a) of the figure below. This carbon, is attached to four different substituents making it chiral. which is often designated by an asterisk in structural drawings. If the bromine atom is replaced by another chlorine to make dichlorofluoromethane, as shown in part (b) below, the molecule and its mirror image can now be superimposed by simple rotation. Thus the carbon is no longer a chiral center. Upon comparison, bromochlorofluoromethane lacks a plane of symmetry while dichlorofluoromethane has a plane of symmetry.




**(a) Bromochlorofluoromethane**




**(b) Dichlorofluoromethane**

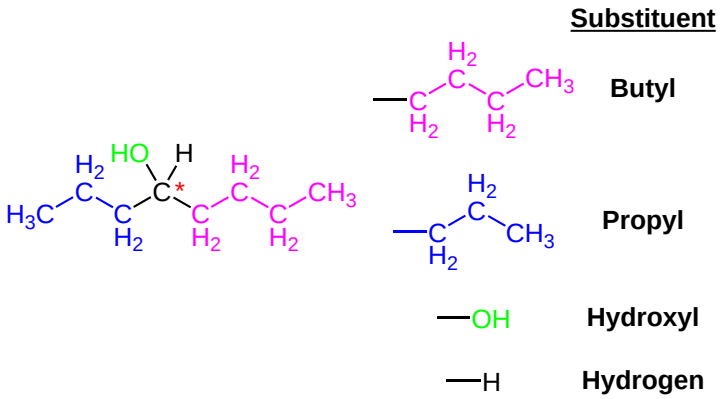



## Identifying Chiral carbons

Identifying chiral carbons in a molecule is an important skill for organic chemists. The presence of a chiral carbon presents the possibility of a molecule having multiple stereoisomers. Most of the chiral centers we shall discuss in this chapter are asymmetric carbon atoms, but it should be recognized that other tetrahedral or pyramidal atoms may become chiral centers if appropriately substituted. Also, when more than one chiral center is present in a molecular structure, care must be taken to analyze their relationship before concluding that a specific molecular configuration is chiral or achiral. This aspect of stereoisomerism will be treated later. Because an carbon requires four different substituents to become asymmetric, it can be said, with few exceptions, that $sp^2$ and sp hybridized carbons involved in multiple bonds are achiral. Also, any carbon with more than one hydrogen, such as a -$CH_3$ or -$CH_2$- group, are also achiral.

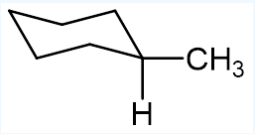
Looking for planes of symmetry in a molecule is useful, but often difficult in practice. It is difficult to illustrate on the two dimensional page, but you will see if you build models of these achiral molecules that, in each case, there is at least one **plane of symmetry**, where one side of the plane is the mirror image of the other. In most cases, the easiest way to decide whether a molecule is chiral or achiral is to look for one or more stereocenters - with a few rare exceptions, the general rule is that molecules with at least one stereocenter are chiral, and molecules with no stereocenters are achiral.

Determining if a carbon is bonded to four distinctly different substituents can often be difficult to ascertain. Remember even the slightest difference makes a substituent unique. Often these difference can be distant from the chiral carbon itself. Careful consideration and often the building of molecular models may be required. A good example is shown below. It may appear that the molecule is achiral, however, when looking at the groups directly attached to the possible chiral carbon, it is clear that they all different. The two alkyl groups are differ by a single -$CH_2$- group which is enough to consider them different.



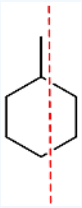

## Example 5.1.1

Predict if the following molecule would be chiral or achiral:



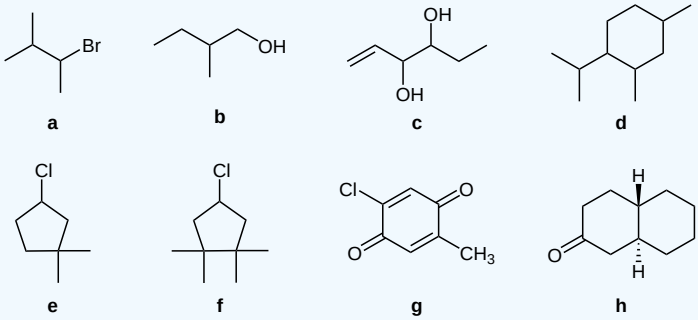
**Answer**

Achiral. When determinig the chirality of a molecule, it best to start by locating any chiral carbons. An obvious candidate is the ring carbon attached to the methyl substituent. The question then becomes: does the ring as two different substituents making the substituted ring carbon chiral? With an uncertantity such as this, it is then helpful try to identify any planes of symmetry in the molecule. This molecule does have a plane of symmetry making the molecul achiral. The plane of symmetry would be easier see if the molecule were view from above. Typically, monosubstitued cycloalkanes have a similar plane of symmetry making them all achiral.

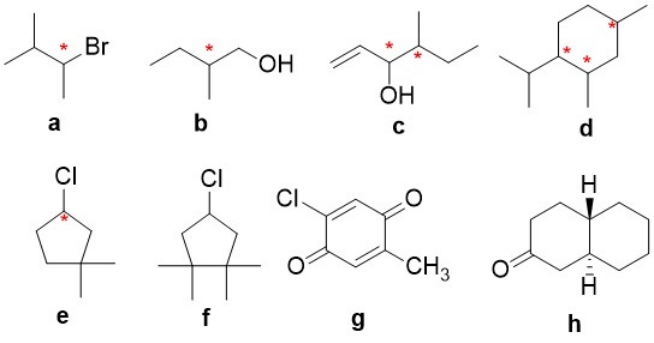


## Exercise 5.2.1

Determine if each of the following molecules are chiral or achiral. For chiral molecules indicate any chiral carbons.




**Answer**

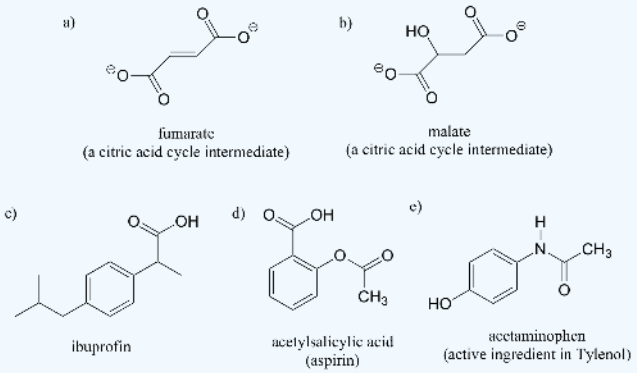



**Explanation**

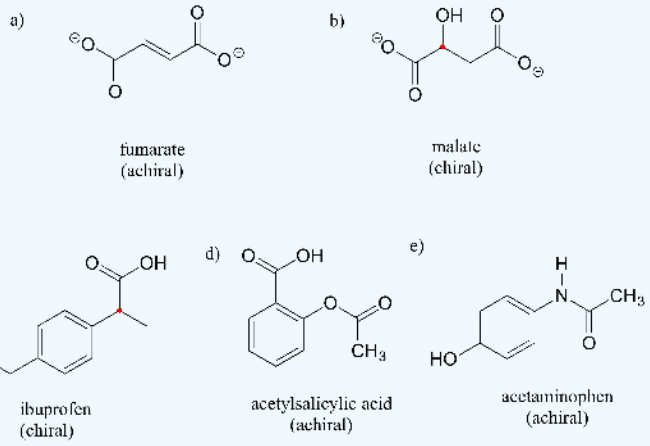
Structures F and G are achiral. The former has a plane of symmetry passing through the chlorine atom and bisecting the opposite carbon-carbon bond. The similar structure of compound E does not have such a symmetry plane, and the carbon bonded to the chlorine is a chiral center (the two ring segments connecting this carbon are not identical). Structure G is essentially flat. All the carbons except that of the methyl group are $sp^2$ hybridized, and therefore trigonal-planar in configuration. Compounds C, D & H have more than one chiral center, and are also chiral.

## Example 5.2.2

Label the molecules below as chiral or achiral, and locate all stereocenters.

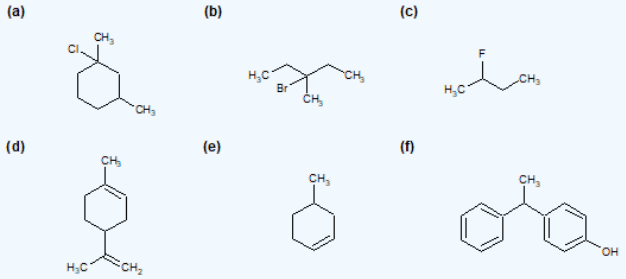



**Answer**

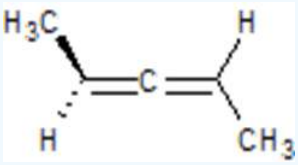



## Exercise 5.2.2

1) For the following compounds, star (*) each chiral center, if any.




2) Explain why the following compound is chiral.



3) Determine which of the following objects is chiral.

a) A Glove.

b) A nail.

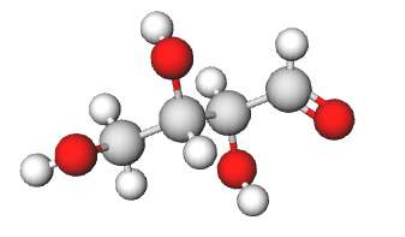
c) A pair of sunglasses.

d) The written word "Chiral".

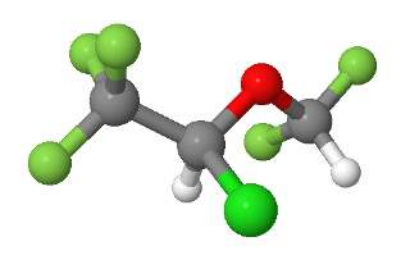
4) Place an "*" by all of the chrial carbons in the following molecules.

a)

Erythrose, a four carbon sugar.

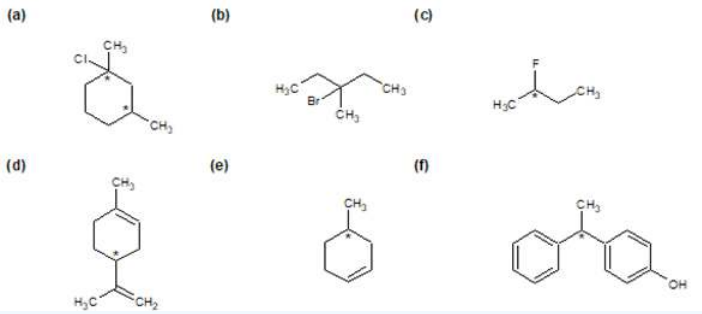


b) Isoflurane, an anestetic. Bright green = Chlorine, Pale green = Fluorine.



**Answer**

1)




2) Though the molecule does not contain a chiral carbon, it is chiral as it is non-superimposable on its mirror image due to its twisted nature (the twist comes from the structure of the double bonds needing to be at 90° angles to each other, preventing the molecule from being planar).

3)

a) Just as hands are chiral a glove must also be chiral.

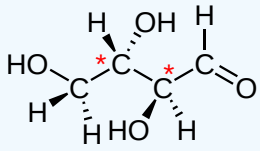
b) A nail has a plane of symmetry which goes down the middle making it a achiral.

c) A pair of sunglasses has a plane of symmetry which goes through the nose making it achiral.

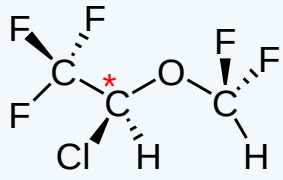
d) Most written words are chiral. Look one in a mirror to confirm this.

4

a)

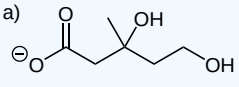



b)

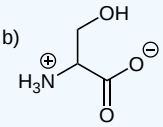


## Exercise 5.2.3

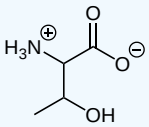
Circle all of the carbon stereocenters in the molecules below.

a) 

mevalonate

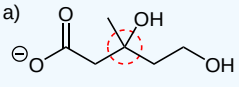
b) 

serine

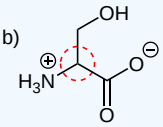
c) 

threonine

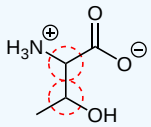
**Answer**

a) 

mevalonate

b) 

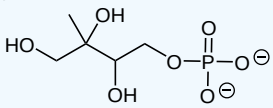
serine

c) 

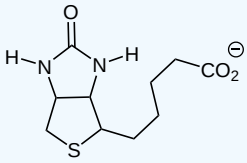
threonine

## Exercise 5.2.4

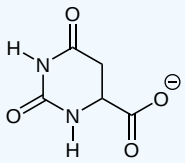
Circle all of the carbon stereocenters in the molecules below.

a) 

2-methylerythritol-4-phopshate

b) 

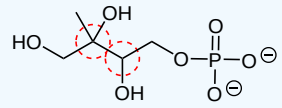
biotin

c) 

dihydroorotate

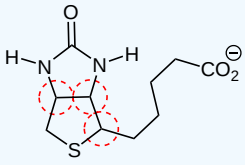
**Answer**

a)



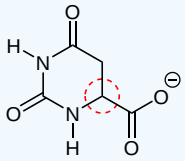
2-methylerythritol-4-phopshate

b)



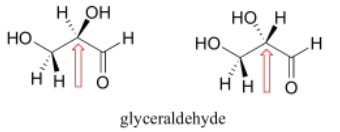
biotin

c)

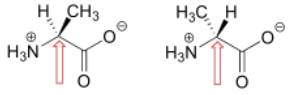


dihydroorotate

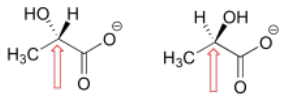
Here are some more examples of chiral molecules that exist as pairs of enantiomers. In each of these examples, there is a single stereocenter, indicated with an arrow. (Many molecules have more than one stereocenter, but we will get to that that a little later!)



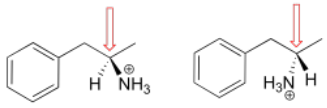
glyceraldehyde



alanine

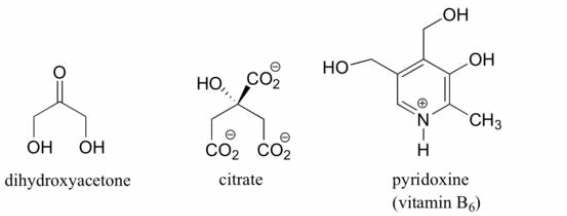


lactate



amphetamine

Here are some examples of molecules that are **achiral** (*not* chiral). Notice that none of these molecules has a stereocenter.



dihydroxyacetone

citrate

pyridoxine (vitamin $B_6$)

pyruvate

glycine (amino acid)

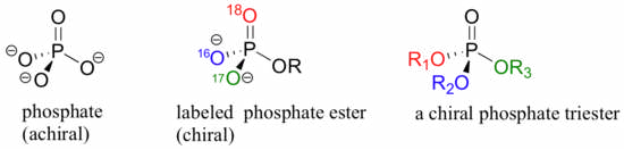
dopamine (neurotransmitter)

It is difficult to illustrate on the two dimensional page, but you will see if you build models of these achiral molecules that, in each case, there is at least one **plane of symmetry**, where one side of the plane is the mirror image of the other. Chirality is tied conceptually to the idea of asymmetry, and *any molecule that has a plane of symmetry cannot be chiral*. When looking for a plane of symmetry, however, we must consider all possible conformations that a molecule could adopt. Even a very simple molecule like ethane, for example, is asymmetric in many of its countless potential conformations – but it has obvious symmetry in both the eclipsed and staggered conformations, and for this reason it is achiral.

Looking for planes of symmetry in a molecule is useful, but often difficult in practice. In most cases, the easiest way to decide whether a molecule is chiral or achiral is to look for one or more stereocenters - with a few rare exceptions, the general rule is that molecules with at least one stereocenter are chiral, and molecules with no stereocenters are achiral. Carbon stereocenters are also referred to quite frequently as **chiral carbons**.

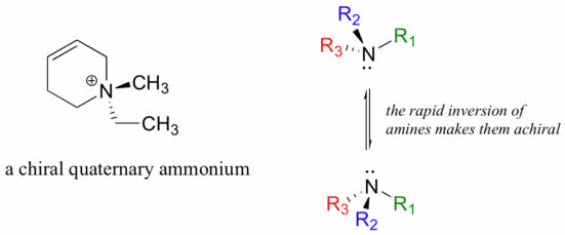
When evaluating a molecule for chirality, it is important to recognize that the question of whether or not the dashed/solid wedge drawing convention is used is irrelevant. Chiral molecules are sometimes drawn without using wedges (although obviously this means that stereochemical information is being omitted). Conversely, wedges may be used on carbons that are not stereocenters – look, for example, at the drawings of glycine and citrate in the figure above. Just because you see dashed and solid wedges in a structure, do not automatically assume that you are looking at a stereocenter.

Other elements in addition to carbon can be stereocenters. The phosphorus center of phosphate ion and organic phosphate esters, for example, is tetrahedral, and thus is potentially a stereocenter.




In order to investigate phosphate transfer reactions in living systems, especially involving ATP, researchers have incorporated sulfur and/or $^{17}O$ and $^{18}O$ isotopes of oxygen (the 'normal' isotope is $^{16}O$) to create chiral phosphate groups. Phosphate triesters are chiral if the three substituent groups are different.

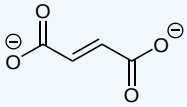
Asymmetric quaternary ammonium groups are also chiral. Amines, however, are not chiral, because they rapidly invert, or turn 'inside out', at room temperature.



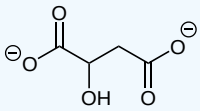

## Exercise 5.2.5

Label the molecules below as chiral or achiral, and circle all stereocenters.

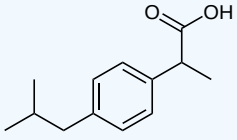
a) fumarate (a citric acid cycle intermediate)



b) malate (a citric acid cycle intermediate)

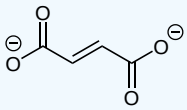


b) malate (a citric acid cycle intermediate)

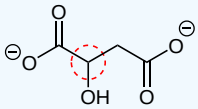


**Answer**

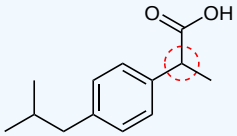
a) achiral (no stereocenters)



b) chiral



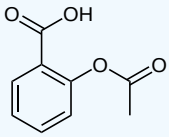
c) chiral



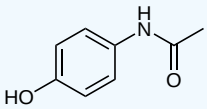
## Exercise 5.2.6

Label the molecules below as chiral or achiral, and circle all stereocenters.

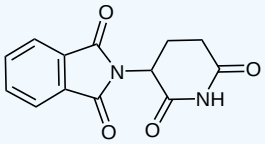
a) acetylsalicylic acid (aspirin)



b) acetaminophen (active ingredient in Tylenol)

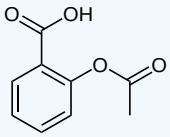


c) thalidomide (drug that caused birth defects in pregnant mothers in the 1960's)

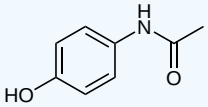


**Answer**

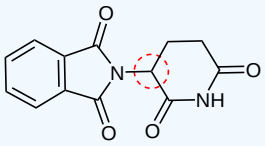
a) achiral (no stereocenters)



b) achiral (no stereocenters)

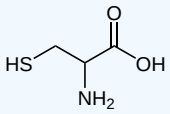


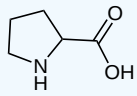
c) chiral



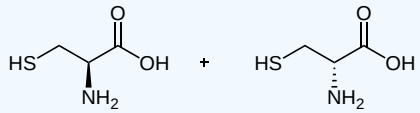
## Exercise 5.2.7

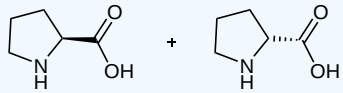
Draw both enantiomers of the following chiral amino acids.

a) Cysteine 

b) Proline 

**Answer**

a) 

b) 

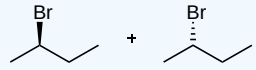
## Exercise 5.2.8

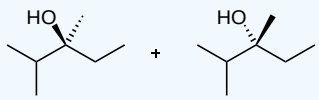
Draw both enantiomers of the following compounds from the given names.

a) 2-bromobutane

b) 2,3-dimethyl-3-pentanol

**Answer**

a) 

b) 

## Exercise 5.2.9

Which of the following body parts are chiral?

a) Hands b) Eyes c) Feet d) Ears

**Answer**

a) Hands- chiral since the mirror images cannot be superimposed (think of the example in the beginning of the section)

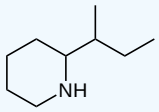
b) Eyes- achiral since mirror images that are superimposable

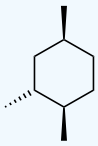
c) Feet- chiral since the mirror images cannot be superimposed (Does your right foot fit in your left shoe?)

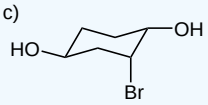
d) Ears- chiral since the mirror images cannot be superimposed

## Exercise 5.2.10

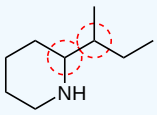
Circle the chiral centers in the following compounds.

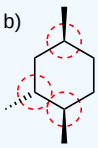
a) 

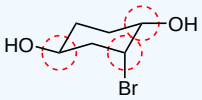

b) 

c) 


**Answer**

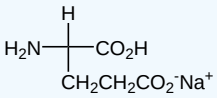
a) 

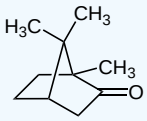

b) 

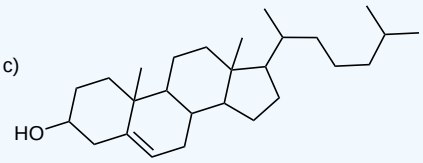
c) 


## Exercise 5.2.11

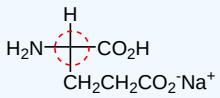
Identify the chiral centers in the following compounds.

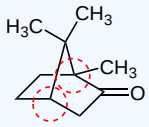
a) 

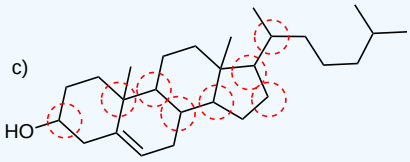

b) 


c) 


**Answer**

a) 

b) 

c) 

## Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)
- Dr. Zachary Sharrett (Sonoma State University)
- Layne Morsch (University of Illinois Springfield)

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# 5.2: Enantiomers and the Tetrahedral Carbon

**Key Terms**

Make certain that you can define, and use in context, the key term below.

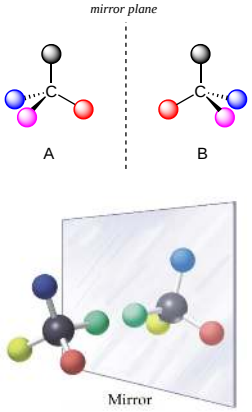
- enantiomer

**Study Notes**

Stereoisomers are isomers that differ in spatial arrangement of atoms, rather than order of atomic connectivity. One of the most interesting types of isomer is the mirror-image stereoisomer, a non-superimposable set of two molecules that are mirror images of one another. The existence of these molecules are determined by a a concept known as **chirality**. The word “chiral” was derived from the Greek word for hand, because our hands are a good example of chirality since they are non-superimposable mirror images of each other.

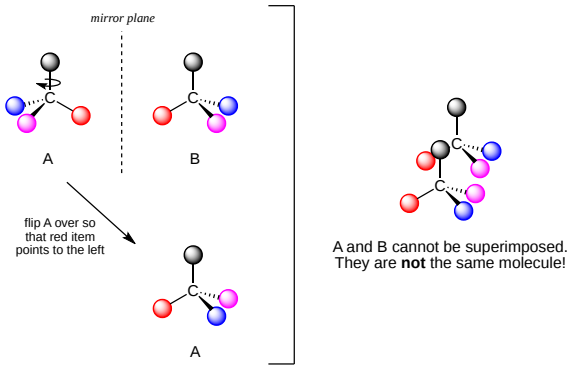
## Chiral Molecules

The term **chiral**, from the Greek work for 'hand', refers to anything which cannot be superimposed on its own mirror image. Certain organic molecules are chiral meaning that they are not superimposable on their mirror image. Chiral molecules contain one or more **stereocenters**, which are almost always tetrahedral ($sp^3$-hybridized) carbons with four different substituents. Consider the molecule A below: a tetrahedral carbon, with four different substituents denoted by balls of four different colors. Try to build these molecules exactly as they are drawn using your molecular models. It will be much easier to see the mirror plane as well as see their chiral nature using molecular models.




The mirror image of A, which we will call B, is drawn on the right side of the figure, and an imaginary mirror is in the middle. Notice that every point on A lines up through the mirror with the same point on B: in other words, if A looked in the mirror, it would see B looking back.

Now, if we flip compound A over and try to superimpose it point for point on compound B, we find that we cannot do it: if we superimpose any two colored balls, then the other two are misaligned.




A is not superimposable on its mirror image (B), thus by definition A is a chiral molecule. It follows that B also is not superimposable on *its* mirror image (A), and thus it is also a chiral molecule.

A and B are called **stereoisomers or optical isomers**: molecules with the same molecular formula and the same bonding arrangement, but *a different arrangement of atoms in space*. **Enantiomers** are pairs of stereoisomers which are mirror images of each other: thus, A and B are enantiomers. It should be self-evident that a chiral molecule will always have one (and *only* one) enantiomer: enantiomers come in pairs. Enantiomers have identical physical properties (melting point, boiling point, density, and so on). However, enantiomers do differ in how they interact with polarized light (we will learn more about this soon) and they may also interact in very different ways with other chiral molecules - proteins, for example. We will begin to explore this last idea in later in this chapter, and see many examples throughout the remainder of our study of biological organic chemistry.

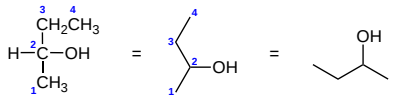
### The Many Synonyms of the Stereocenter

Be aware - all of the following terms can be used to describe a stereocenter:

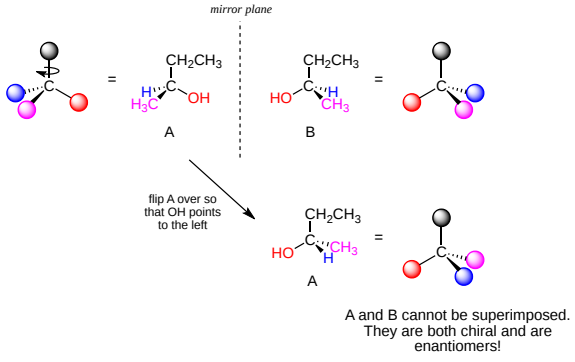
chiral carbon = asymmetric carbon = optically active carbon = stereo carbon = stereocenter = chiral center

Let's apply our chirality discussion to real molecules.

Consider 2-butanol, drawn in two dimensions below.

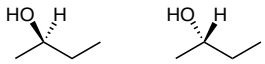



Carbon #2 is a stereocenter: it is $sp^3$-hybridized and tetrahedral (even though it is not drawn that way above), and the four substituents attached to is are different: a hydrogen (H) , a methyl ($-CH_3$) group, an ethyl ($-CH_2CH_3$) group, and a hydroxyl (OH) group. If the bonding at $C_2$ of 2-butanol is drawn in three dimensions and this structure called A. Then the mirror image of A can be drawn to form structure B.

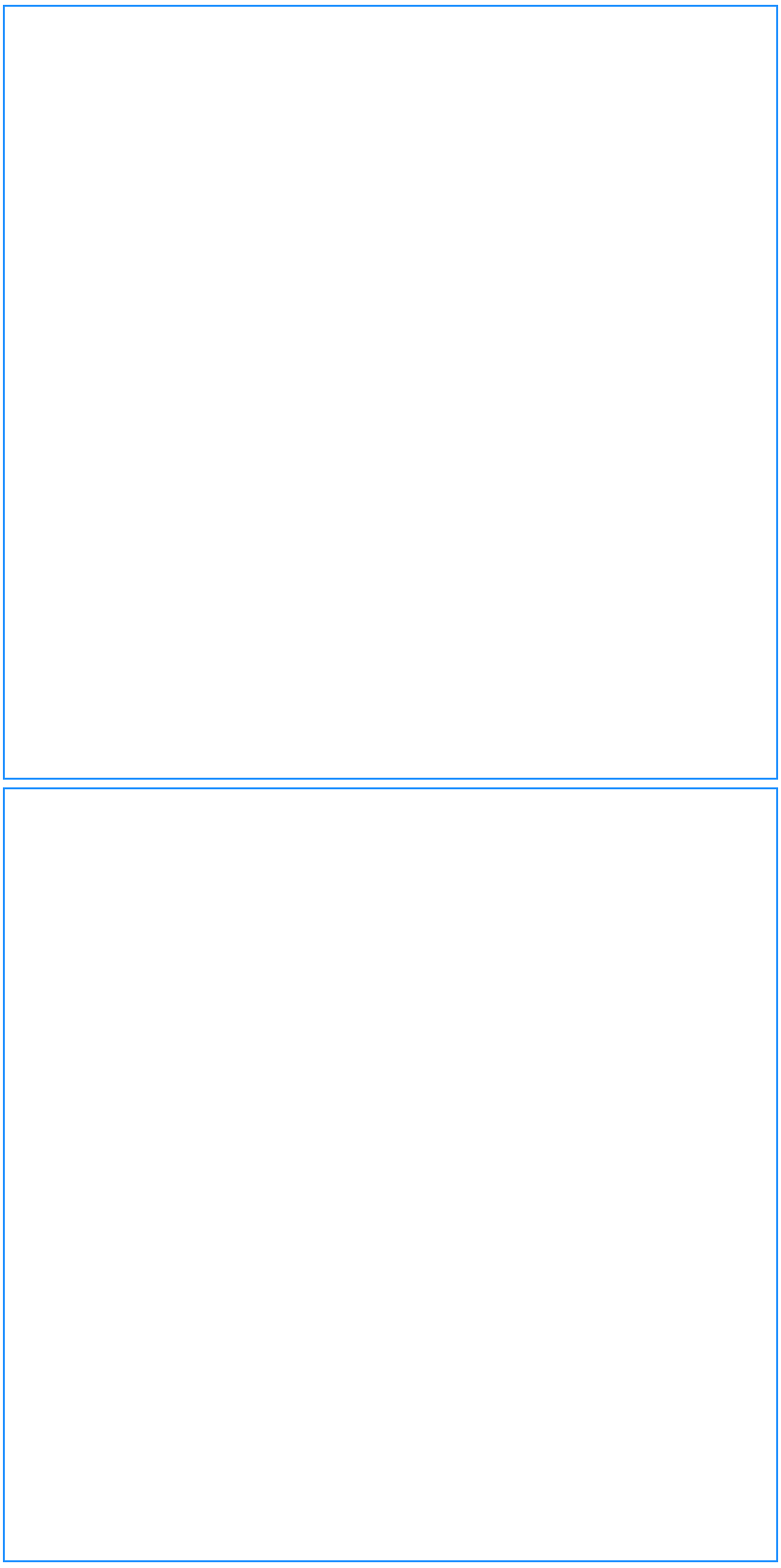



When we try to superimpose A onto B, we find that we cannot do it. Because structure A and B are not superimposable on their mirror image they are both chiral molecules. Because A and B are different due only to the arrangement of atoms in space they are

stereoisomers. Because A and B are mirror images of each other they are also enantiomers. When looking at simplified line structures is clear that there are two distinct ways of drawing 2-butanol which only differ in their spatial arrangement around a chiral carbon.




two enantiomers of 2-butanol

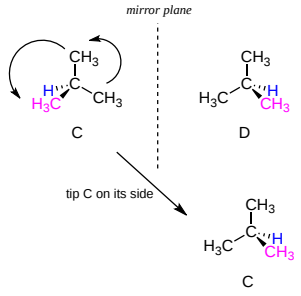


**The 3D Structures of the Two Enantiomers of 2-Butanol**

For comparison, 2-propanol, is an achiral molecule because is lacks a stereocenter. Carbon #2 is bonded to two identical substituents (methyl groups), and so it is not a stereocenter. Being achiral means that 2-propanol should be superimposable on its

mirror image which is shown in the figure below. A more detailed explanation on why 2-propanol is achiral will be given in the next section.

**2-propanol is achiral:**




## Stereoisomers

Stereoisomers have been defined as molecules with the same connectivity but different arrangements of the atoms in space. It is important to note that there are two types of stereoisomers: geometric and optical.

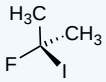
**Optical isomers** are molecules whose structures are mirror images but cannot be superimposed on one another in any orientation. Optical isomers have identical physical properties, although their chemical properties may differ in asymmetric environments. Molecules that are nonsuperimposable mirror images of each other are said to be chiral.

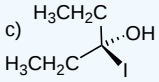
**Geometric isomers** differ in the relative position(s) of substituents in a rigid molecule. Simple rotation about a C–C σ bond in an alkene, for example, cannot occur because of the presence of the π bond. The substituents are therefore rigidly locked into a particular spatial arrangement. Thus a carbon–carbon multiple bond, or in some cases a ring, prevents one geometric isomer from being readily converted to the other. The members of an isomeric pair are identified as either cis or trans, and interconversion between the two forms requires breaking and reforming one or more bonds. Because their structural difference causes them to have different physical and chemical properties, cis and trans isomers are actually two distinct chemical compounds.mers have the same connectivity, but different arrangements of atoms in space.

### ? Exercise 5.2.1

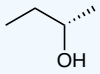
Identify the following molecules as chiral or achiral.

a) 

b) 

c) 

d) 

e) 

f) 

**Answer**

a) chiral (4 different groups off C)

b) achiral (2 identical -$CH_3$ substituents off central C)

c) achiral (2 identical -$CH_2CH_3$ substituents off central C)

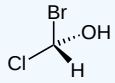
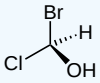
d) achiral (2 identical $CH_3$ substituents off carbon 2)

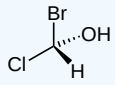
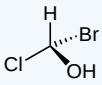
e) chiral (4 different groups off carbon 2)

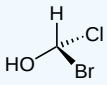
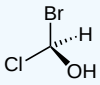
f) achiral (2 identical $CH_3$ substituents off central C)

## Exercise 5.2.2

Determine if the following sets of compounds in each group are enantiomers or the same compound.

a)  & 

b)  & 

c)  & 

d)  & 

**Answer**

a) enantiomers – non superimposable mirror images

b) same compound – when you rotate the molecule on the right it is identical to the one on the left

c) enantiomers – non superimposable mirror images

d) enantiomers – non superimposable mirror images

## Contributors and Attributions

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- Jim Clark (Chemguide.co.uk)
- Dr. Zachary Sharrett (Sonoma State University)
- Dr. Krista Cunningham

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# 5.3: Optical Activity

**Key Terms**

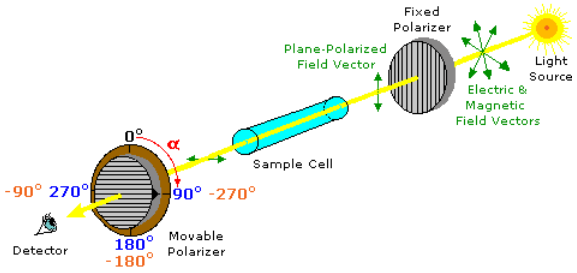
Make certain that you can define, and use in context, the key terms below.

- analyzer
- dextrorotatory
- levorotatory
- optically active
- plane-polarized light
- polarimeter
- polarizer
- specific rotation

Identifying and distinguishing enantiomers is inherently difficult, since their physical and chemical properties are largely identical. Fortunately, a nearly two hundred year old discovery by the French physicist Jean-Baptiste Biot has made this task much easier. This discovery disclosed that the right- and left-handed enantiomers of a chiral compound perturb plane-polarized light in opposite ways. This perturbation is unique to chiral molecules, and has been termed **optical activity**.

## Polarimetry

Plane-polarized light is created by passing ordinary light through a polarizing device, which may be as simple as a lens taken from polarizing sun-glasses. Such devices transmit selectively only that component of a light beam having electrical and magnetic field vectors oscillating in a single plane. The plane of polarization can be determined by an instrument called a **polarimeter**, shown in the diagram below.




Monochromatic (single wavelength) light, is polarized by a fixed polarizer next to the light source. A sample cell holder is located in line with the light beam, followed by a movable polarizer (the analyzer) and an eyepiece through which the light intensity can be observed. In modern instruments an electronic light detector takes the place of the human eye. In the absence of a sample, the light intensity at the detector is at a maximum when the second (movable) polarizer is set parallel to the first polarizer ($\alpha = 0^o$). If the analyzer is turned 90º to the plane of initial polarization, all the light will be blocked from reaching the detector.

Chemists use polarimeters to investigate the influence of compounds (in the sample cell) on plane polarized light. Samples composed only of achiral molecules (e.g. water or hexane), have no effect on the polarized light beam. However, if a single enantiomer is examined (all sample molecules being right-handed, or all being left-handed), the plane of polarization is rotated in either a clockwise (positive) or counter-clockwise (negative) direction, and the analyzer must be turned an appropriate matching angle, **α**, if full light intensity is to reach the detector. In the above illustration, the sample has rotated the polarization plane clockwise by +90º, and the analyzer has been turned this amount to permit maximum light transmission.

The observed rotations ($\alpha$) of enantiomers are opposite in direction. One enantiomer will rotate polarized light in a clockwise direction, termed **dextrorotatory** or (+), and its mirror-image partner in a counter-clockwise manner, termed **levorotatory** or (–). The prefixes dextro and levo come from the Latin *dexter*, meaning right, and *laevus*, for left, and are abbreviated *d* and *l* respectively. If equal quantities of each enantiomer are examined , using the same sample cell, then the magnitude of the rotations will be the same, with one being positive and the other negative. To be absolutely certain whether an observed rotation is positive or negative it is often necessary to make a second measurement using a different amount or concentration of the sample. In the above illustration, for example, α might be –90º or +270º rather than +90º. If the sample concentration is reduced by 10%, then the

positive rotation would change to +81º (or +243º) while the negative rotation would change to –81º, and the correct α would be identified unambiguously.

Since it is not always possible to obtain or use samples of exactly the same size, the observed rotation is usually corrected to compensate for variations in sample quantity and cell length. Thus it is common practice to convert the observed rotation, α, to a **specific rotation**, by the following formula:

$$[\alpha]_D = \frac{\alpha}{lc} \tag{5.3.1}$$

where

- $[\alpha]_D$ is the specific rotation
- $l$ is the cell length in dm
- $c$ is the concentration in g/ml
- $D$ designates that the light used is the 589 line from a sodium lamp

Compounds that rotate the plane of polarized light are termed **optically active**. Each enantiomer of a stereoisomeric pair is optically active and has an equal but opposite-in-sign specific rotation. Specific rotations are useful in that they are experimentally determined constants that characterize and identify pure enantiomers. For example, the lactic acid and carvone enantiomers discussed earlier have the following specific rotations.

| | |
|---|---|
| Carvone from caraway: $[\alpha]_D$ = +62.5º | this isomer may be referred to as (+)-carvone or *d*-carvone |
| Carvone from spearmint: $[\alpha]_D$ = –62.5º | this isomer may be referred to as (–)-carvone or *l*-carvone |
| Lactic acid from muscle tissue: $[\alpha]_D$ = +2.5º | this isomer may be referred to as (+)-lactic acid or *d*-lactic acid |
| Lactic acid from sour milk: $[\alpha]_D$ = –2.5º | this isomer may be referred to as (–)-lactic acid or *l*-lactic acid |

A 50:50 mixture of enantiomers has no observable optical activity. Such mixtures are called **racemic mixtures**, and are designated (±). When chiral compounds are created from achiral compounds, the products are racemic unless a single enantiomer of a chiral co-reactant or catalyst is involved in the reaction. The addition of HBr to either cis- or trans-2-butene is an example of racemic product formation (the chiral center is colored red in the following equation).

| | | |
|---|---|---|
| $CH_3CH{=}CHCH_3$ + HBr | ⟶ | (±) $CH_3CH_2CHBrCH_3$ |

Chiral organic compounds isolated from living organisms are usually optically active, indicating that one of the enantiomers predominates (often it is the only isomer present). This is a result of the action of chiral catalysts we call enzymes, and reflects the inherently chiral nature of life itself. Chiral synthetic compounds, on the other hand, are commonly racemates, unless they have been prepared from enantiomerically pure starting materials.

There are two ways in which the condition of a chiral substance may be changed:
**1.** A racemate may be separated into its component enantiomers. This process is called **resolution**.
**2.** A pure enantiomer may be transformed into a racemic mixture. This process is called **racemization**.

## Contributors and Attributions

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# 5.4: Sequence Rules for Specifying Configuration

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- absolute configuration
- *R* configuration
- *S* configuration

**Study Notes**

When designating a structure as *R* or *S*, you must ensure that the atom or group with the lowest priority is pointing away from you, the observer. The easiest way to show this is to use the wedge-and-broken-line representation. You can then immediately determine whether you are observing an *R* configuration or an *S* configuration.

To name the enantiomers of a compound unambiguously, their names must include the "handedness" of the molecule. The method for this is formally known as R/S nomenclature.

## Introduction

The method of unambiguously assigning the handedness of molecules was originated by three chemists: R.S. Cahn, C. Ingold, and V. Prelog and, as such, is also often called the Cahn-Ingold-Prelog rules. In addition to the Cahn-Ingold system, there are two ways of experimentally determining the absolute configuration of an enantiomer:

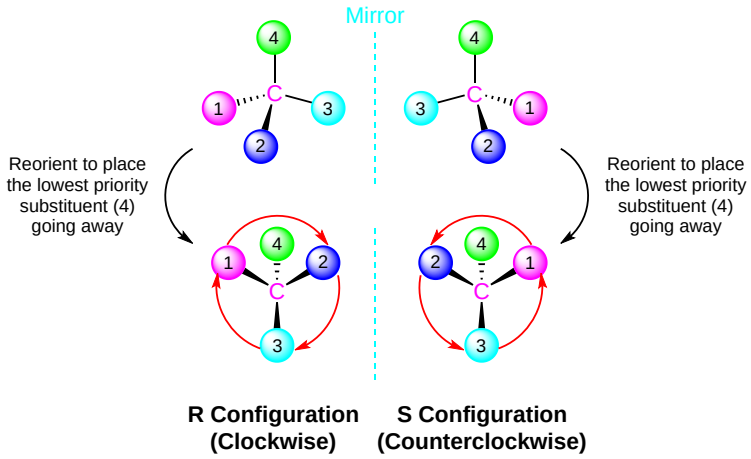
1. X-ray diffraction analysis. Note that there is no correlation between the sign of rotation and the structure of a particular enantiomer.
2. Chemical correlation with a molecule whose structure has already been determined via X-ray diffraction.

However, for non-laboratory purposes, it is beneficial to focus on the R/S system. The sign of optical rotation, although different for the two enantiomers of a chiral molecule,at the same temperature, **cannot** be used to establish the absolute configuration of an enantiomer; this is because the sign of optical rotation for a particular enantiomer may change when the temperature changes.

## Stereocenters are labeled R or S

The "right hand" and "left hand" nomenclature is used to name the enantiomers of a chiral compound. The stereocenters are labeled as R or S.

The **Cahn-Ingold-Prelog** rules of assign priorities the groups directly bonded to the chiral carbon. Having ranked the four groups attached to a chiral carbon, we describe the stereochemical configuration around the carbon by orienting the molecule so that the group with the lowest ranking (4) is given a dash bond to indicate it points directly away from us. We then look at the three remaining substituents, which now appear to radiate toward us which is shown by using wedge bonds. If a curved arrow drawn from the highest to second-highest to third-highest ranked substituent is clockwise, we say that the chirality center has the *R* configuration (Latin *rectus*, meaning “right”). If an arrow from is counterclockwise, the chirality center has the *S* configuration (Latin *sinister*, meaning “left”). To remember these assignments, think of a car’s steering wheel when making a *R*ight (clockwise) turn. Note, the ***R*** *or* ***S*** configurations represent the two enantiomers of a chiral molecule. The **R** or **S** configuration is often added as a prefix, in parenthesis, to a chiral molecule's name to indicate which enantiomer is being discussed. **Ex:** (*R*)-2-Bromobutane. If more than chiral carbon is present in a chiral molecule, each carbon's number is included before the **R** or **S** configuration. **Ex:** (2R,4S,6R)-2-bromo-6-chloro-4-methylheptane.




## Sequence Rules to Assign Priorities to Substituents

Before applying the R and S nomenclature to a stereocenter, the substituents must be prioritized according to the following rules:

### Rule 1

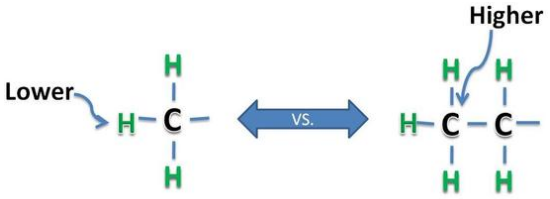
First, examine at the atoms directly attached to the stereocenter of the compound. A atom with a higher atomic number takes precedence over a atom with a lower atomic number. Hydrogen is the lowest possible priority atom, because it has the lowest atomic number.

1. The atom with higher atomic number has higher priority (I > Br > Cl > S > P > F > O > N > C > H).
2. When comparing isotopes, the atom with the higher mass number has higher priority [$^{18}O > {}^{16}O$ or $^{15}N > {}^{14}N$ or $^{13}C > {}^{12}C$ or T ($^{3}H$) > D ($^{2}H$) > H].

### Rule 2

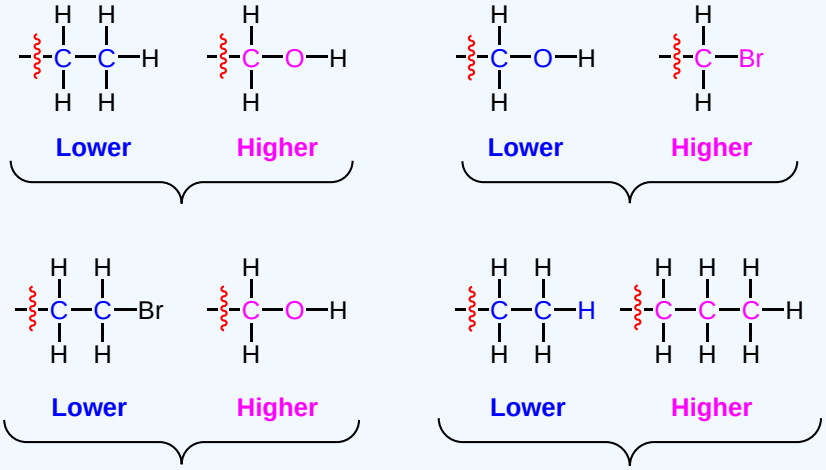
If there are two or more substituents which have the same element directly attached to chiral carbon, proceed along the substituent chains until a point of difference is found. Determine which of the chains has the first connection to an atom with the highest priority (the highest atomic number). That chain has the higher priority.

**For example**: an ethyl substituent takes priority over a methyl substituent. At the connectivity of the stereocenter, both have a carbon atom, which are equal in rank. Going down the chains, a methyl has only has hydrogen atoms attached to it, whereas the ethyl has two hydrogen atoms and a carbon atom. The carbon atom on the ethyl is the first point of difference and has a higher atomic number than hydrogen; therefore the ethyl takes priority over the methyl.



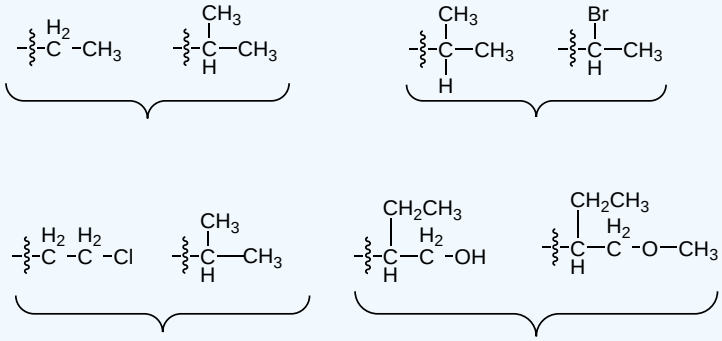

**The "H-" (left) ranks lower than the "C-" (right) based on the first point of difference and their relative molecular weights**

✔ Example 5.4.1



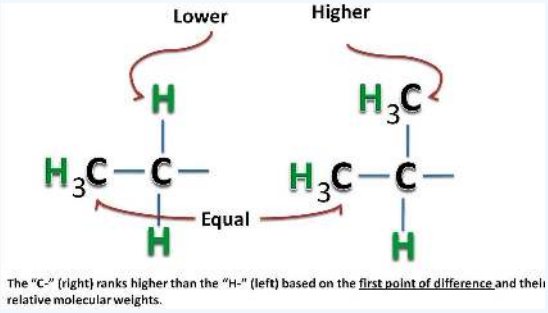

## Worked Exercise 5.4.1

For the following pairs of substituents, determine which would have the higher and lower priority based on the **Cahn-Ingold-Prelog** rules. Explain your answer.

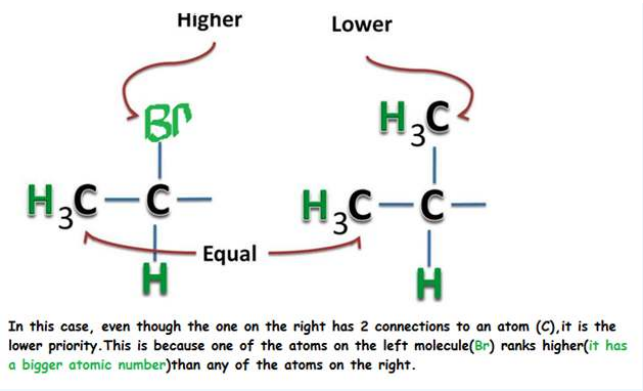


**Answer**

A 1-methylethyl substituent takes precedence over an ethyl substituent. Connected to the first carbon atom, ethyl only has one other carbon, whereas the 1-methylethyl has two carbon atoms attached to the first; this is the first point of difference. Therefore, 1-methylethyl ranks higher in priority than ethyl, as shown below:



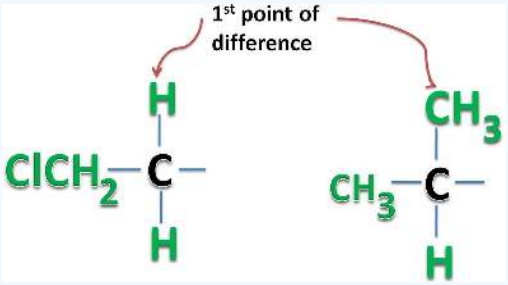

**However:**



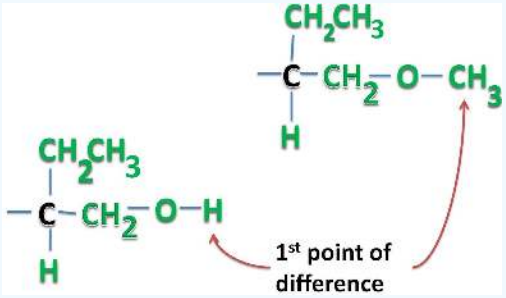

In this case, even though the one on the right has 2 connections to an atom (C), it is the lower priority. This is because one of the atoms on the left molecule(Br) ranks higher(it has a bigger atomic number)than any of the atoms on the right.

**Caution!!**

Keep in mind that priority is determined by the **first** point of difference along the two similar substituent chains. After the first point of difference, the rest of the chain is irrelevant.

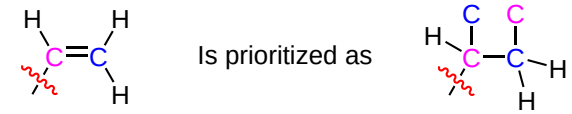



When looking for the first point of difference on similar substituent chains, one may encounter branching. If there is branching, choose the branch that is higher in priority. If the two substituents have similar branches, rank the elements within the branches until a point of difference.

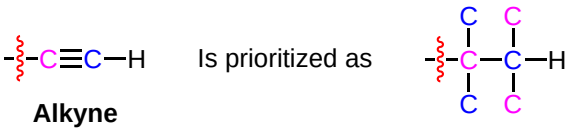



## Rule 3

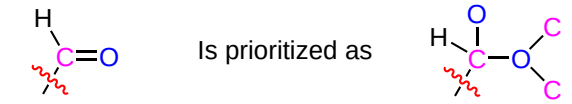
For assigning priority, multiple bonds are treated as if each bond of the multiple bond is bonded to a unique atom. For example, an alkene substituent ($CH_2$=CH-) has higher priority than an ethyl substituent ($CH_3CH_2$-). The alkene carbon priority is "two" bonds to carbon atoms and one bond to a hydrogen atom compared with the ethyl carbon that has only one bond to a carbon atom and two bonds to two hydrogen atoms. Similarly, alkyne substituent (HCC-) would have an even higher priority because the alkyne carbon is treated as if it is bonded to three carbons. This method remains the same with compounds containing a carbonyl (C=O) group. The carbon of an aldehyde substituent (O=CH-) is treated as if it is bonded to a hydrogen and two oxygen atoms.




**Alkene**



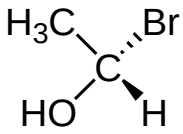

**Alkyne**




**Aldehyde**

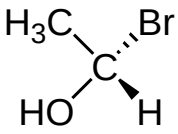
## Determining R or S Configuration Using a Molecular Model

In order to demonstrate how to determine the R/S configuration of the chiral carbon in the following molecule using molecular models, first construct a model of the bromoethanol structure:

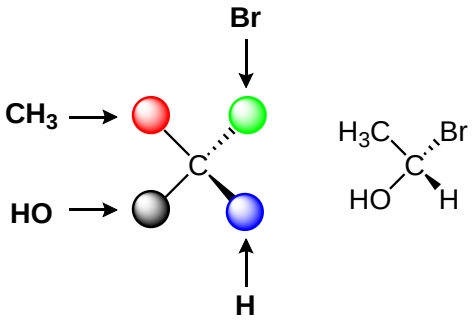


First make a molecular model of a tetrahedral carbon with four different substituents. In many cases, this will appear as a carbon with four bonds with a different colored ball attached to each bond.

For the molecule in question, determine the location of the chiral carbon and assign CIP priorities to the substituents. In this case, Br gets the highest priority because it has the highest atomic number. The O in the OH substituent gets priority 2 and the C in $CH_3$ gets priority 3. Lastly, H gets the lowest priority, 4, because it has the smallest atomic number.



Now take your molecular model and orientate it to match the molecule in question. Remember in the dash/wedge representation, two regular bonds are in the plane of the page. The wedge bond is coming toward you and the dashed bond is going away from you. If you were to hold a piece of paper directly in front of you, the substituents with the regular bond should both be touching the piece of paper. The dashed bond should be pointing behind the piece of paper and the wedge bond should be pointing in front.

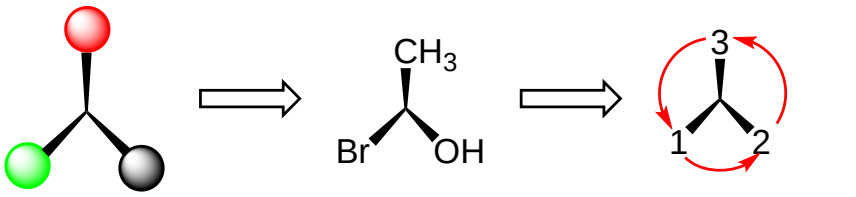



**In this structure, the bromine is going away from you, the hydrogen is coming toward you and the**

**hydroxide and methyl groups are in the plane of the page.**

Then based on the position, assign each substituent on the chiral carbon a colored ball on your molecular model. In this case, bromine is going away so it is assigned the green ball. The hydrogen is coming toward you so it is assigned the blue ball. The last two substituents are in the plane of the page, however, the $CH_3$ is positioned higher so it is assigned the red ball which leaves OH being assigned the black ball.

Lastly, grab onto the ball for the lowest priority substitutent, in this case the blue one, and point the other three substituents towards you. The three bonds should be angled towards you as if they all have wedge bonds. Assign the original substituents and their corresponding CIP priorities to the three colored balls. The green ball was assigned to Bromine which was given priority one. The OH was assigned to the black ball and given prioirty two. The $CH_3$ was assigned to the red ball and given priority three. In this case the priorities are going counter clockwise so the chiral carbon has an **S** configuration.

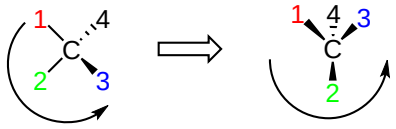



**S Configuration**

## Determining R or S Configuration Without a Molecular Model

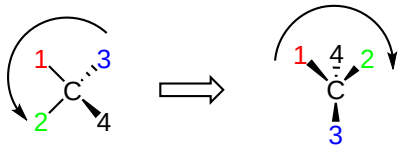
If a molecular model cannot be used there are a couple of simple methods which can be applied if the dash/wedge bond system is being used.

After assigning CIP priorities, if the lowest priority substituent (4) is on the dash bond the configuration of substituents 1-3 can be assigned directly. As shown in the figure below, the configuration of substituents 1-3 does not change when moving to sight down the bond of substituent 4. In both cases, substituents 1-3 are ordered in a counterclockwise fashion which gives the chiral carbon an S configuration.




**Counterclockwise (S Configuration)** **Counterclockwise (S Configuration)**

The opposite is true if the lowest priority substituent (4) is on the wedge bond. As shown in the figure below, the configuration of substituents 1-3 is inverted when moving to sight down the bond of substituent 4. When the lowest priority substituent is on the wedge bond, the configuration of substituents 1-3 can be assigned directly only if the direction is inverted. i.e. clockwise = S and counterclockwise = R.

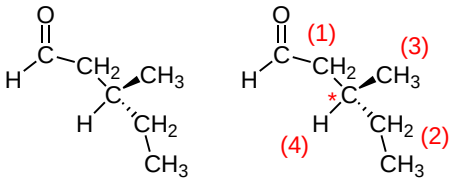



**Counterclockwise** **Clockwise (R Configuration)**

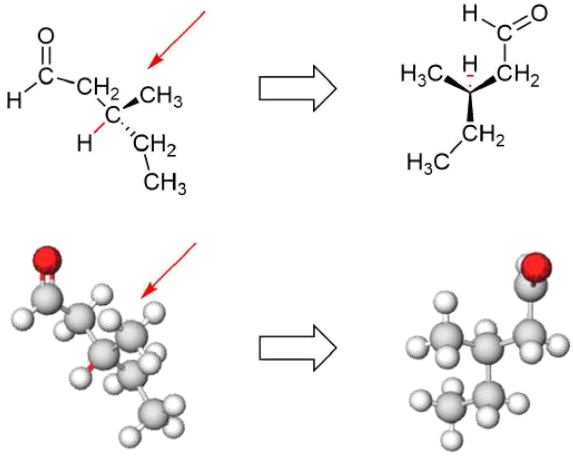
**With the lowest priority group in front, drawing an arc from 1 to 2 to 3 gives the reverse of the configuration.**

However, if the lowest priority substituent is on one of the regular bonds when the dash/wedge system is being used then configurations are best assigned by changing perspectives. This method can also be used if the three-demensional configuration of the chiral carbon is represented. First, locate the chiral carbon and assign CIP priorities to its substituents. Then while perceiving

the drawn molecule as a three-dimensional image, mentally change your perspective such that you are looking down the bond between the chiral carbon and the lowest CIP ranked substituent (#4). If done correctly, the bonds for substituents 1-3 should be coming towards you as wedge bonds. You can then follow the direction of the CIP priority numbers to determine the R/S configuration of the chiral carbon.

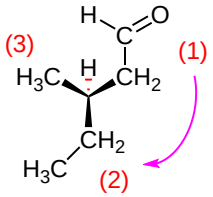



**Locate the chiral carbon and assign CIP priorities to its substituents.**



**Mentally sight down the bond between the chiral carbon and the lowest CIP ranked substituent.**

**This bond is shown in Red.**



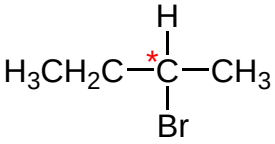

**Clockwise**
**(R Configuration)**

**Follow the direction of the CIP priority numbers to determine the R/S configuration.**

## Drawing the Structure of a Chiral Molecule from its Name

Draw the structure of (S)-2-Bromobutane:

1) Draw the basic structure of the molecule and determine the location of the chiral carbon.



2) Determine the chiral carbon's substituents and assign them a CIP priority.

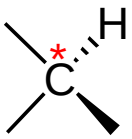
**-H** (Priority 4)

**-$CH_3$** (Priority 3)

**-$CH_2CH_3$** (Priority 2)

**-Br** (Priority 1)

3) Draw the chiral carbon in a dash/wedge form and add the lowest priority substituent to the wedge bond. In this case, the lowest priority substituent is -H.




4) Add the remaining substituents in a clockwise fashion for R and a counterclockwise fashion for S.

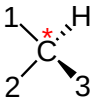



**Clockwise (R Configuration)**

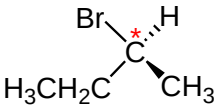



**Counterclockwise (S Configuration)**

The molecule posed in this question has an S configuration so the remaining substituents are added in a counterclockwise fashion.




**Counterclockwise (S Configuration)**




**(S)-2-Bromobutane**

## ? Exercise 5.4.1

1) Orient the following so that the least priority (4) atom is paced behind, then assign stereochemistry (*R* or *S*).

2) Draw (R)-2-bromobutan-2-ol.

3) Assign *R/S* to the following molecule.

4) Which in the following pairs would have a higher CIP priority?

a) -H or -Cl

b) -Br or -I

c) $-CH_2OH$ or $-OCH_3$

d) $-CH_2CH_3$ or $-CH=CH_2$

e) $-NH_2$ or -OH

5) Rank the following substituents in order of their CIP priority:

a) -H, $-OCH_3$, $-CH_2OH$, -OH

b) -OH, $-CO_2H$, -CH=O, $-CH_2OH$

c) -CN, $-NH_2$, -CH=O, $-NHCH_3$

d) -SH, $-SCH_3$, -OH, $-OOCH_3$

6) Determine if the chiral carbon in the following molecules have an R or S configuration. Red = Oxygen & Blue = Nitrogen.

a)

b)

**Answer**

1) A is S and B is R.



2)



3) The stereocenter is *R*.

4)

a) -Cl

b) -I

c) $-OCH_3$

d) $-CH=CH_2$

e) -OH

5) Rank the following substituents in order of their CIP priority:

a) $-OCH_3$, -OH, $-CH_2OH$, -H,

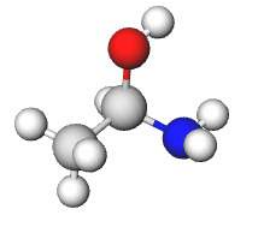
b) -OH, $-CO_2H$, -CH=O, $-CH_2OH$

c) $-NHCH_3$, $-NH_2$, -CH=O, -CN

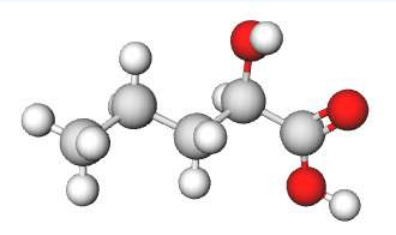
d) $-SCH_3$, -SH, $-OOCH_3$, -OH

6)

a) The chiral carbon is R. The four substituents of the chiral carbon are -OH (1), $-NH_2$ (2), $-CH_3$ (3), and -H (4). Then looking down the lowest priority bond, you should roughly see what appears in the picture below. The substituents with priorities 1-3 are ordered in a clockwise fashion so the chiral carbon is R.



b) The chiral carbon is S. The four substituents of the chiral carbon are -$CO_2H$ (1), -OH (2), -$CH_2CH_2CH_3$ (3), and -H (4). Then looking down the lowest priority bond, you should roughly see what appears in the picture below. The substituents with priorities 1-3 are ordered in a counterclockwise fashion so the chiral carbon is S.



**Exercise 5.4.2**

Identify which substituent in the following sets has a higher ranking.

a) -H or -$CH_3$

b) -$CH_2CH_2CH_3$ or $CH_2CH_3$

c) -$CH_2Cl$ or $CH_2OH$

**Answer**

a) **-$CH_3$**

b) **-$CH_2CH_2CH_3$**

c) **-$CH_2Cl$**

**Exercise 5.4.3**

Identify which substituent in the following sets has a higher ranking.

a) -$NH_2$ or -N=NH

b) -$CH_2CH_2OH$ or -$CH_2OH$

c) -$CH=CH_2$ or -$CH_2CH_3$

**Answer**

a) **-N=NH**

b) **-$CH_2OH$**

c) **-$CH=CH_2$**

## Exercise 5.4.4

Place the following sets of substituents in each group in order of lowest priority (1st) to highest priority (4th)

a) $-NH_2$, -F, -Br, $-CH_3$

b) -SH, $-NH_2$, -F, -H

**Answer**

a) $-CH_3 < -NH_2 <$ -F, < -Br

b) -H < $-NH_2 <$ -F, < -SH

## Exercise 5.4.5

Place the following sets of substituents in each group in order of lowest priority (1st) to highest priority (4th)

a) $-CH_2CH_3$, -CN, $-CH_2CH_2OH$, $-CH_2CH_2CH_2OH$

b) $-CH_2NH_2$, $-CH_2SH$, $-C(CH_3)_3$, -CN

**Answer**

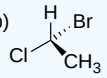
a) $-CH_2CH_3 < -CH_2CH_2OH < -CH_2CH_2CH_2OH$, < -CN

b) $-C(CH_3)_3 < -CH_2NH_2 <$ -CN < $-CH_2SH$

## Exercise 5.4.6

Assign the following chiral centers as R or S.

a) 


b) 


c) 


**Answer**

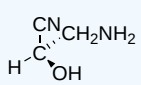
a) **S**: I > Br > F > H. The lowest priority substituent is going backwards so following the highest priority, it goes left (counterclockwise).

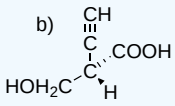
b) **R**: Br > Cl > $CH_3$ > H. Using a model kit, you need to rotate the H to the back position where the Br is. This causes the priority to go to the left (clockwise) when looking at it with the H in the back position. Alternatively, if you do not have a model kit, you can imagine the structure 3-dimensionally and since the lowest priority (H) is facing up (as drawn), if you look at it from below, starting with Br (1st priority) and moving towards Cl (2nd priority), you are moving right (clockwise) which represents R stereochemistry.

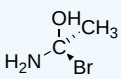
c) **Neither R or S**: Since there are two identical substituents (H's) the molecule is achiral and cannot be assigned R or S.

## Exercise 5.4.7

Assign the following chiral centers as R or S.

a) 


b) 


c) 


**Answer**

a) **R**: OH > CN (C triple bonded to N) > $CH_2NH_2$ > H. The H needs to be moved to the back position which causes the priority to go to the right (clockwise) which indicates R.

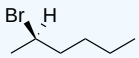
b) **S**: COOH > $CH_2OH$ > C  CH > H. Since the H is coming forward, you can assign the priority and it goes to the right (clockwise which would be R) but since the lowest priority is forward, you have to switch it to S. Alternatively, you can rotate the molecule to put the lowest priority to the back and you'll see that it rotates left (or counterclockwise) for S.

c) **S**: Br > OH > $NH_2$ > $CH_3$. Since the lowest priority is going back, you can follow the priority and see that it is going left (counterclockwise) and therefore S.

**? Exercise 5.4.8**

Draw the structure of (*R*)-2-bromohexane.

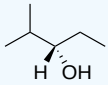
**Answer**




**? Exercise 5.4.9**

Draw the structure of (*S*)-2-methyl-3-pentanol.

**Answer**




## Outside links

- http://www.youtube.com/watch?v=EphUiPiQiCo
- http://en.Wikipedia.org/wiki/Absolute_configuration

## References

1. Schore and Vollhardt. *Organic Chemistry Structure and Function.* New York:W.H. Freeman and Company, 2007.
2. McMurry, John and Simanek, Eric. *Fundamentals of Organic Chemistry*. 6th Ed. Brooks Cole, 2006.

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# 5.5: Diastereomers

**Key Terms**

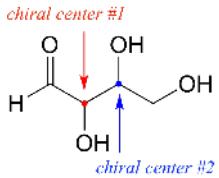
Make certain that you can define, and use in context, the key term below.

- diastereomer

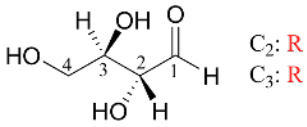
Diastereomers are two molecules which are stereoisomers (same molecular formula, same connectivity, different arrangement of atoms in space) but are *not* enantiomers. Unlike enatiomers which **are mirror images** of each other and **non-sumperimposable**, diastereomers are **not mirror images** of each other and **non-superimposable**. Diastereomers can have different physical properties and reactivity. They have different melting points and boiling points and different densities. In order for diastereomer stereoisomers to occur, a compound must have **two or more** stereocenters.

## Introduction

So far, we have been analyzing compounds with a single chiral center. Next, we turn our attention to those which have multiple chiral centers. We'll start with some stereoisomeric four-carbon sugars with two chiral centers.



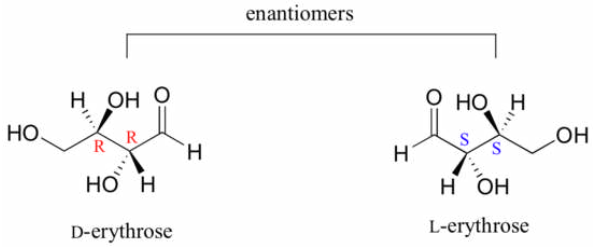

We will start with a common four-carbon sugar called D-erythrose.




D-erythrose

A note on sugar nomenclature: biochemists use a special system to refer to the stereochemistry of sugar molecules, employing names of historical origin in addition to the designators '*D*' and '*L*'. You will learn about this system if you take a biochemistry class. We will use the *D/L* designations here to refer to different sugars, but we won't worry about learning the system.

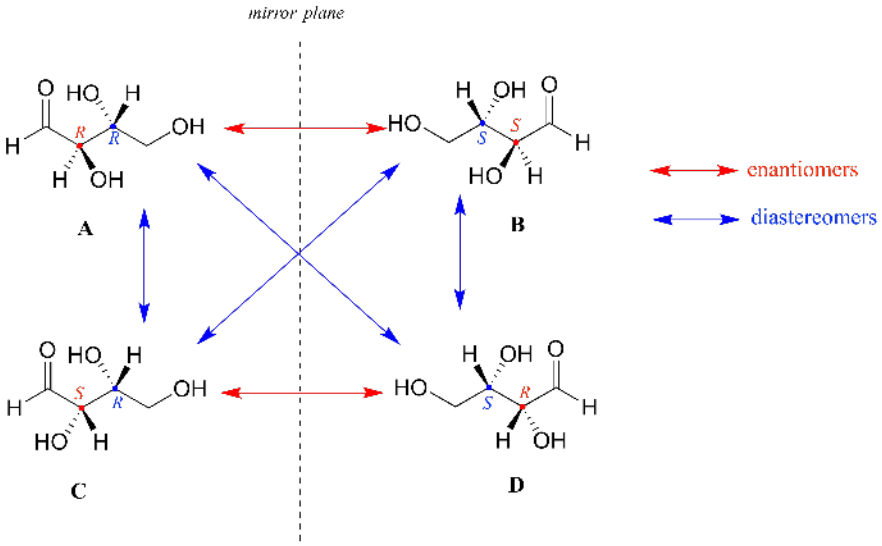
As you can see, *D*-erythrose is a chiral molecule: $C_2$ and $C_3$ are stereocenters, both of which have the *R* configuration. In addition, you should make a model to convince yourself that it is impossible to find a plane of symmetry through the molecule, regardless of the conformation. Does D-erythrose have an enantiomer? Of course it does – if it is a chiral molecule, it must. The enantiomer of erythrose is its mirror image, and is named L-erythrose (once again, you should use models to convince yourself that these mirror images of erythrose are not superimposable).




Notice that both chiral centers in L-erythrose both have the *S* configuration. To avoid confusion, we will simply refer to the different stereoisomers by capital letters.

Now let's consider all the possible stereoisomers

Look first at compound A below. Both chiral centers in have the *R* configuration (you should confirm this for yourself!). The mirror image of Compound A is compound B, which has the *S* configuration at both chiral centers. If we were to pick up compound A, flip it over and put it next to compound B, we would see that they are *not* superimposable (again, confirm this for yourself with your models!). A and B are nonsuperimposable mirror images: in other words, enantiomers.




Now, look at compound C, in which the configuration is *S* at chiral center 1 and *R* at chiral center 2. Compounds A and C are stereoisomers: they have the same molecular formula and the same bond connectivity, but a different arrangement of atoms in space (recall that this is the definition of the term 'stereoisomer). However, they are *not* mirror images of each other (confirm this with your models!), and so they are *not* enantiomers. By definition, they are **diastereomers** of each other.

Notice that compounds C and B also have a diastereomeric relationship, by the same definition.

So, compounds A and B are a pair of enantiomers, and compound C is a diastereomer of both of them. Does compound C have its own enantiomer? Compound D is the mirror image of compound C, and the two are not superimposable. Therefore, C and D are a pair of enantiomers. Compound D is also a diastereomer of compounds A and B.

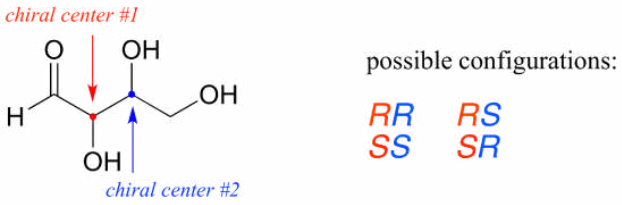
This can also seem very confusing at first, but there some simple shortcuts to analyzing stereoisomers:

## Stereoisomer Shortcuts

If ***all*** of the chiral centers are of opposite R/S configuration between two stereoisomers, they are enantiomers.

If ***at least one, but not all*** of the chiral centers are opposite between two stereoisomers, they are diastereomers.

Here's another way of looking at the four stereoisomers, where one chiral center is associated with red and the other blue. Pairs of enantiomers are stacked together.

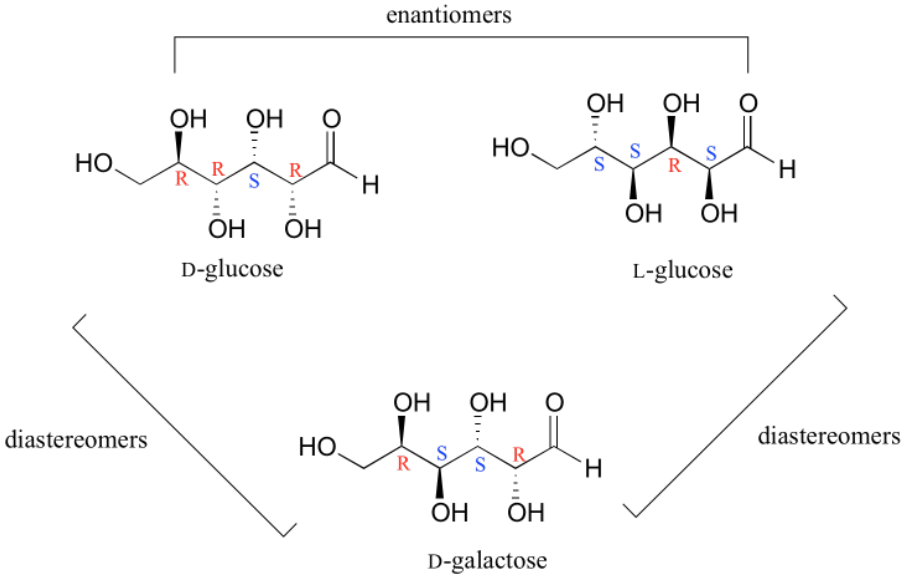



We know, using the shortcut above, that the enantiomer of RR must be SS - both chiral centers are different. We also know that RS and SR are diastereomers of RR, because in each case one - but not both - chiral centers are different.

## Determining the Maximum Number of Stereoisomers for a Compound

In general, a structure with *n* stereocenters will have a maximum of $2^n$ different stereoisomers. (We are not considering, for the time being, the stereochemistry of double bonds – that will come later). For example, let's consider the glucose molecule in its open-chain form (recall that many sugar molecules can exist in either an open-chain or a cyclic form). There are two enantiomers of

glucose, called D-glucose and L-glucose. The D-enantiomer is the common sugar that our bodies use for energy. It has $n$ = 4 stereocenters, so therefore there are $2^n = 2^4 = 16$ possible stereoisomers (including D-glucose itself).



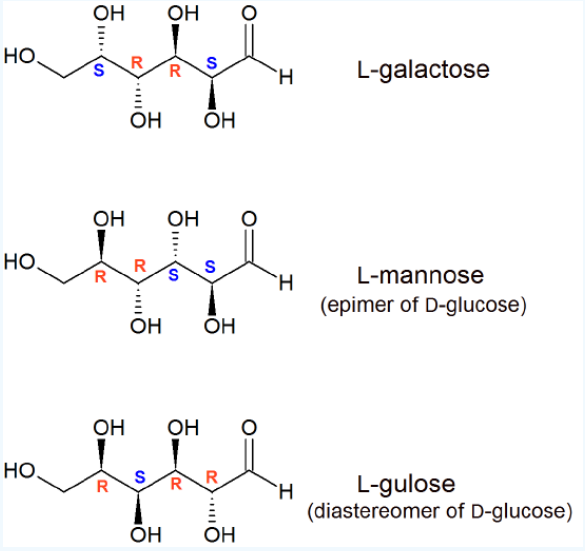

In L-glucose, all of the stereocenters are inverted relative to *D*-glucose. That leaves 14 diastereomers of D-glucose: these are molecules in which at least one, but not all, of the stereocenters are inverted relative to D-glucose. One of these 14 diastereomers, a sugar called *D*-galactose, is shown above: in D-galactose, one of four stereocenters is inverted relative to D-glucose. Diastereomers which differ in only one stereocenter (out of two or more) are called **epimers**. D-glucose and D-galactose can therefore be refered to as epimers as well as diastereomers.

### Example 5.5.1

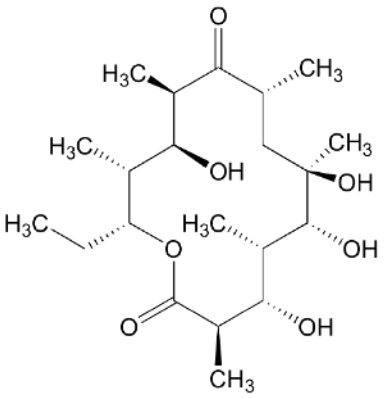
Draw the structure of L-galactose, the enantiomer of D-galactose.

Draw the structure of two more diastereomers of D-glucose. One should be an epimer.

**Answer**




Erythronolide B, a precursor to the 'macrocyclic' antibiotic erythromycin, has 10 stereocenters. It's enantiomer is that molecule in which all 10 stereocenters are inverted.



erythronolide B

In total, there are $2^{10}$ = 1024 stereoisomers in the erythronolide B family: 1022 of these are diastereomers of the structure above, one is the enantiomer of the structure above, and the last ***is*** the structure above.

We know that enantiomers have identical physical properties and equal but opposite degrees of specific rotation. Diastereomers, in theory at least, have different physical properties – we stipulate 'in theory' because sometimes the physical properties of two or more diastereomers are so similar that it is very difficult to separate them. In addition, the specific rotations of diastereomers are unrelated – they could be the same sign or opposite signs, and similar in magnitude or very dissimilar.

**? Exercise 5.5.1**

Determine the number of stereoisomers a molecule can have with…

a) 3 chiral centers

b) 1 chiral center

c) 6 chiral centers

**Answer**

Since a molecule with n chiral centers can have $2^n$ stereoisomers…

a) $2^3$ = 8 possible stereoisomers

b) $2^1$ = 2 possible stereoisomers

c) $2^6$ = 64 possible stereoisomers

**? Exercise 5.5.2*a***

a) What is the relationship between enantiomers?

**Answer**

a) They are mirror images of each other and when 2 or more chiral centers are present, every stereocenter is the opposite in its enantiomer.

**? Exercise 5.5.2*b***

b) How does the stereochemistry in diastereomers differ from each other?

**Answer**

b) In diastereomers, one or more of the chiral centers is the opposite but they all can't be the opposite or else they'd be enantiomers.

## Exercise 5.5.2c

c) What are epimers?

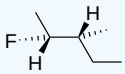
**Answer**

c) Epimers are when **only one** chiral center is the opposite (in molecules with 2 or more chiral centers) in its diastereomer.

## Exercise 5.5.3a

a) Draw the structure of (2R,3R) 2-fluoro-3-methylhexane.

**Answer**

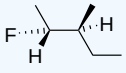



2R,3R

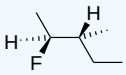
## Exercise 5.5.3b

b) Draw both diastereomers of (2R,3R) 2-fluoro-3-methylhexane.

**Answer**




2R,3S

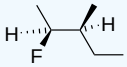



2S,3R

## Exercise 5.5.3c

c) Draw the enantiomer of (2R,3R) 2-fluoro-3-methylhexane.

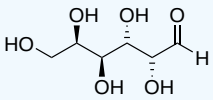
**Answer**




2S,3S

## Exercise 5.5.4a

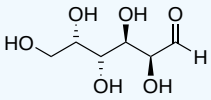
a) Draw the structure of L-galactose, the enantiomer of D-galactose.




*S, R, R, S*

D-galactose

**Answer**



*S, R, R, S*

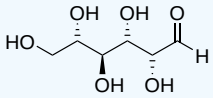
L-galactose

**? Exercise 5.5.4b**

b) Draw a diastereomer of D-galactose that is an epimer.

**Answer**

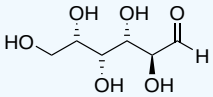
You can draw an epimer by drawing D-galactose with 1 (and only 1) of its chiral centers reversed. Here's an example when you switch only the first chiral center (in red). (There are 3 other epimers that could be drawn as long as you only swap a single chiral center in the diastereomer that you use.)



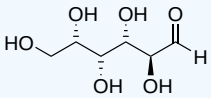
*R, R, R, S*

**? Exercise 5.5.4c**

c) Identify if the following diastereomer of galactose is an epimer of D- galactose or L- galactose.



**Answer**

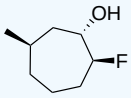


*S, R, S, S*

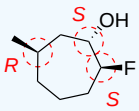
Since the diastereomer above only varies from L-galactose by 1 chiral center, the above is an epimer in relationship to L-galactose. Since it varies from D-galactose by 3 chiral centers, it is not an epimer but a diastereomer. Since not all of the chiral centers are swapped, it is not an enantiomer!

**? Exercise 5.5.5a**

a) For the compound shown below, label each chiral center as R or S.



**Answer**



## Exercise 5.5.5b

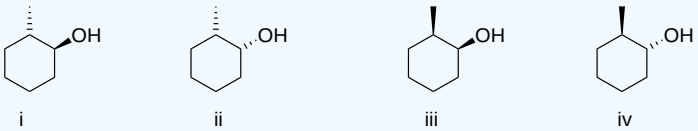
b) How many stereoisomers are possible for the compound in part a)?

**Answer**

Since there are 3 chiral centers, $2^3 = 8$ possible stereoisomers.

## Exercise 5.5.6

Consider the stereoisomers below.




i ii iii iv

a) Which is/are an enantiomer of i?

b) Which is/are a diastereomer of ii?

b) Which is/are an epimer of i?

**Answer**

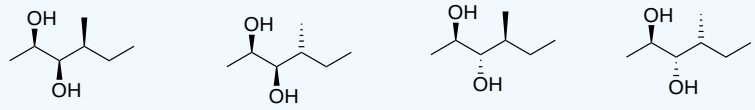
a) iv is an enantiomer of i since both chiral centers are switched and they are non superimposable mirror images.

b) i & iv are diastereomers of ii since they are stereoisomers that are not mirror images.

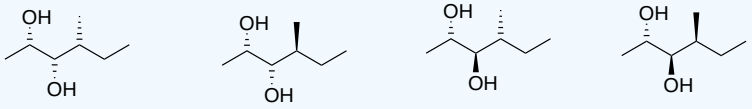
c) ii and iii are epimers of i since they are diastereomers with only 1 chiral center switched and the other one the same.

## Exercise 5.5.7

Consider the 8 stereoisomers below.




i ii iii iv




v vi vii viii

a) Which is/are an enantiomer of i?

b) Which is/are a diastereomer of i?

b) Which is/are an epimer of i?

**Answer**

a) v is an enantiomer since all three chiral centers are switched and they are non superimposable mirror images.

b) ii, iii, iv, vi, vii & viii are diastereomers of i since they are stereoisomers that are not mirror images.

c) ii,iii & viii are epimers of i since they are diastereomers with only 1 chiral center switched and the other chiral centers the same.

## Contributors and Attributions

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- Dr. Zachary Sharrett (Sonoma State University
- Prof. Steven Farmer (Sonoma State University)

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# 5.6: Meso Compounds

**Key Terms**

Make certain that you can define, and use in context, the key term below.

- meso compound

**Study Notes**

You may be confused by the two sets of structures showing “rotations.” Of course in each case the two structures shown are identical, they represent the same molecule looked at from two different perspectives. In the first case, there is a 120° rotation around the single carbon-carbon bond. In the second, the whole molecule is rotated 180° top to bottom.

## Introduction

A meso compound is an achiral compound that has chiral centers. A meso compound contains an internal plane of symmetry which makes it superimposable on its mirror image and is optically **inactive** although it contains two or more stereocenters. Remember, an internal plane of symmetry was shown to make a molecule achiral in **Section 5.2**.

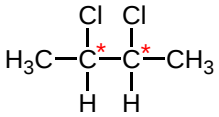
In general, a meso compound should contain two or more identical substituted stereocenters. Also, it has an internal symmetry plane that divides the compound in half. These two halves reflect each other by the internal mirror. The stereochemistry of reflected stereocenters should "cancel out". What it means here is that when we have an internal plane that splits the compound into two symmetrical sides, the stereochemistry of both left and right side should be opposite to each other, and therefore, resulting the molecule being **optically inactive**.

## Identification

A meso compound must have:

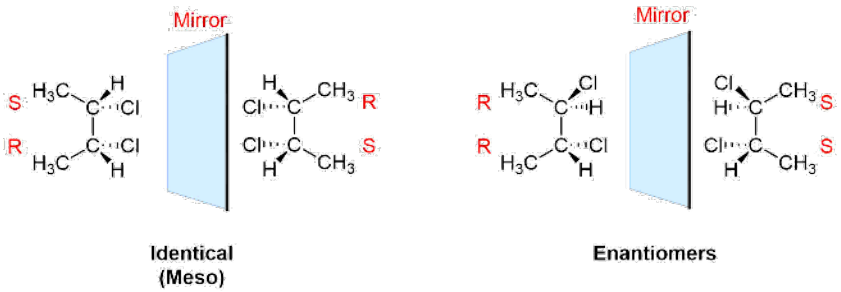
1. Two or more stereocenters.
2. An internal plane of symmetry, or internal mirror, that lies in the compound.
3. Stereochemistry that cancels out. This means reflected stereocenter should have the same substituents and be inverted. For instance, in a meso compound with two stereocenters one should be R and the other S.

The compounds 2,3-dichlorobutane contains two chiral carbons and therefore would be expected to provide $2^2 = 4$ different stereoisomers. These stereoisomers should be made up of two pairs of enantiomers.

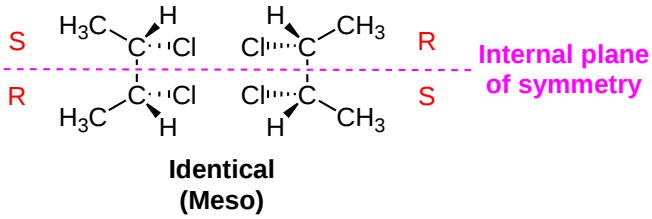



**2,3-Dichlorobutane**

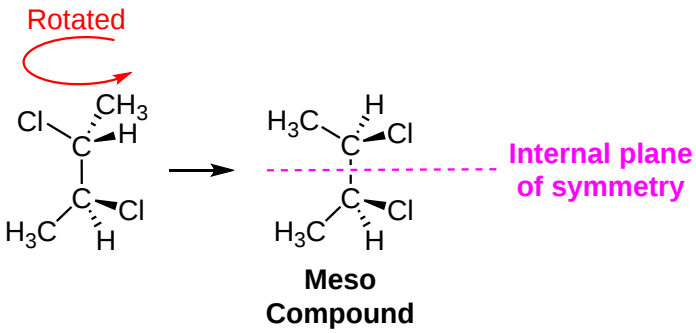
After drawing out all the possible stereoisomers of 2,3-dichlorobutane, the pair on the right in the figure below are mirror images. Also, they are non-superimposable because they have distinctly different conformation (R,R & S,S). This makes the pair enantiomers of each other. However, the pair on the left represent a meso compound, they both are identical despite being mirror images.




Upon further investigation, the meso compound has an internal plane of symmetry which is not present in the pair of enantiomers. The plane of symmetry in the meso compound comes about because there are two chiral carbons present, both chiral carbons are identically substituted (Cl, H, $CH_3$), and one chiral carbon is R and the other is S. Despite being represented as mirror images, both structures represent the same compound. This is best proven by making molecular models of both representations and then superimposing them. Overall, 2,3-dichlorobutane only has three possible stereosiomers, the pair of enantiomers and the meso compound.

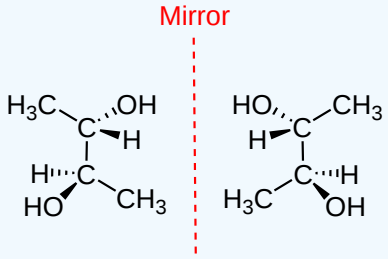



When looking for an internal plane of symmetry, it is important to remember that sigma bonds (single bonds) can rotate. Just because the immediate representation of a molecule does not have a plane of symmetry does not mean that one cannot be obtained through rotation. Often the substituents attached to a stereocenter need to be rotated to recognize the internal plane of symmetry. As the stereocenter is rotated, its configuration does not change. Building a molecular model when considering a possible meso compound is an invaluable tool because it allows for easy rotation of chiral carbons. An example of how rotation of a chiral carbon can reveal an internal plane of symmetry is shown below.




**Example 5.6.1**

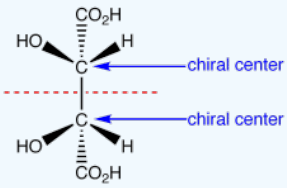
Below are the two mirror images of (meso)-2,3-Butanediol. Because it is a meso compound, the two structures are identical. Show that both mirror images can be obtained by simply rotating the three-dimensional structure provided belwo.




**(meso)-2,3-Butanediol**

GLmol

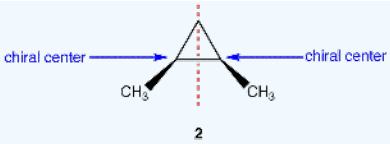
## Example 5.6.2




1

1 has a plane of symmetry (the horizontal plane going through the red broken line) and, therefore, is achiral; 1 has chiral centers. Thus, 1 is a meso compound.

## Example 5.6.3

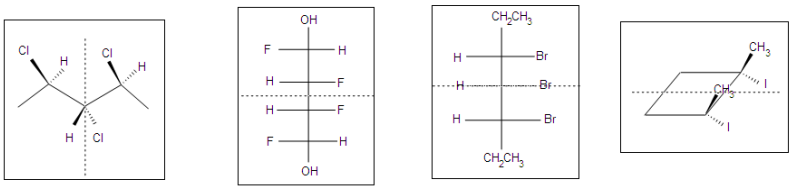



2

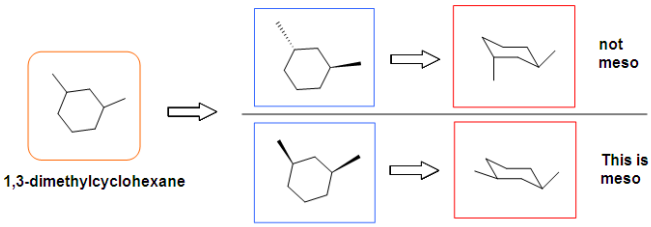
This molecules has a plane of symmetry (the vertical plane going through the red broken line perpendicular to the plane of the ring) and, therefore, is achiral, but has has two chiral centers. Thus, its is a meso compound.

## Other Examples of Meso Compounds

Meso compounds can exist in many different forms such as pentane, butane, heptane, and even cycloalkanes. Although two chiral carbons must be present, meso compounds can have many more. Notice that in every case a plane of symmetry is present.

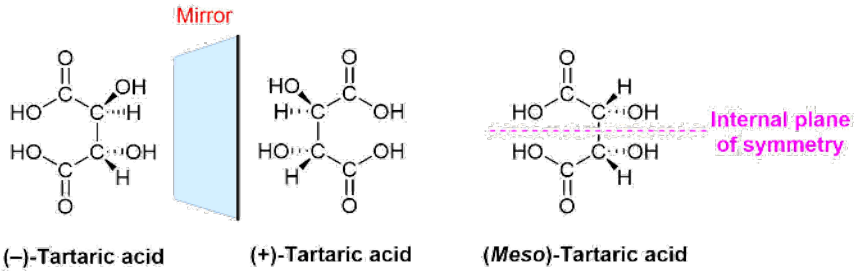


In general, a disubstituted cycloalkane is meso if the two substituents are the same and they are in a *cis* conformation. *Trans* disubstituted cycloalkanes are not meso regardless if the two substituents are the same.




## Optical Activity Analysis of a Meso Compound

When the optical activity of a meso compound is attempted to be determined with a polarimeter, the indicator will not show (+) or (-). It simply means there is no certain direction of rotation of the polarized light, neither levorotatory (-) and dexorotatory (+) because a meso compound is achiral (optically inactive). Investigations of isomeric tartaric acid (2,3-dihydroxybutanedioic acid), carried out by Louis Pasteur in the mid 19th century, were instrumental in elucidating some of the subtleties of stereochemistry. Tartaric acid, has two chiral but only three stereoisomers. Two of these stereoisomers are enantiomers and the third is an achiral a **meso** compound. Some physical properties of these stereoisomers of tartaric acid are given in the table below. Notice that the enantiomers have the same amount of optical rotation but in different directons. Meso-tartaric acid produces no optical rotation because it is achiral and not optically active. Meso-tartaric acid is actually a diastereomer of both (-) and (+)-tartaric acid, which gives it a distinctly different melting point.

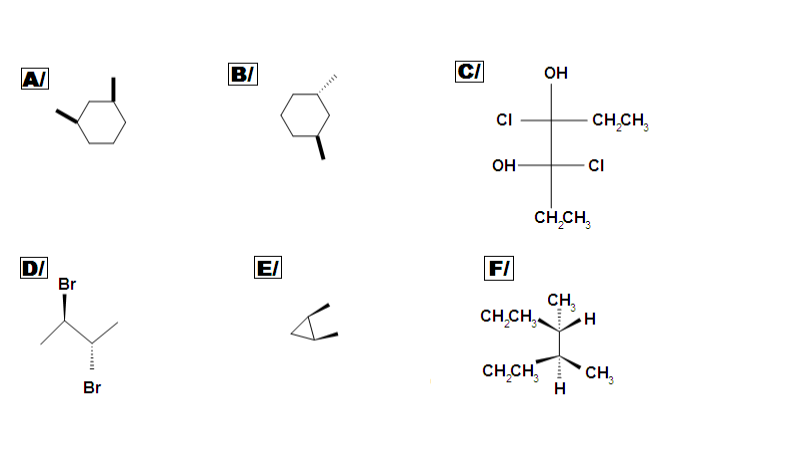



| | | |
|---|---|---|
| (+)-tartaric acid: | $[\alpha]_D$ = +13º | m.p. 172 ºC |
| (–)-tartaric acid: | $[\alpha]_D$ = –13º | m.p. 172 ºC |

| | | |
|---|---|---|
| *meso*-tartaric acid: | $[\alpha]_D = 0^o$ | m.p. 140 ºC |

## Exercise 5.6.1

1) Determine which of the following molecules are meso.




2) Explain why 2,3-dibromobutane has the possibility of being a meso compound while 2,3-dibromopentane does not.

3) Observe the following compound and determine if it is a meso compound. If so indicate the plane of symmetry. Red = oxygen. Remember sigma bonds are able to rotate.

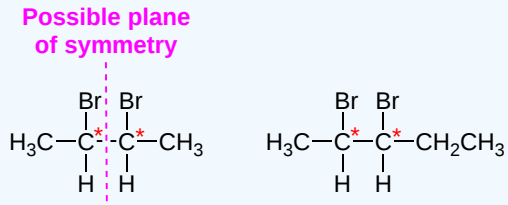
GLmol

**Answer**

1) A C, D, E are meso compounds.

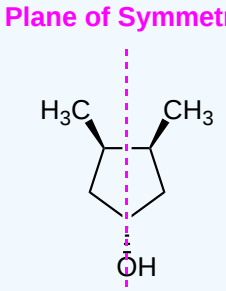
2) One of the requirements of a meso compound is that the reflected chiral carbons have the same substituents. The compound 2,3-dibromobutane, fulfills this requirement (Br, H, $CH_3$) and can possibly be a meso compound if the two

chiral carbons have the appropriate configuration (R & S). The substituents of the two chiral carbons in 2,3-dibromopentane do not have the same substituents (Br, H, $CH_3$ vs. Br, H, $CH_2CH_3$). This 2,3-dibromopentane cannot form a meso compound regardless of the configurations of its chiral carbons.



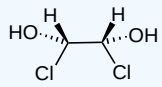

**2,3-Dibromobutane** **2,3-Dibromopentane**

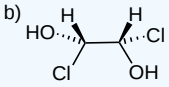
3) The compound is meso.

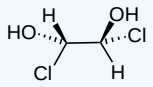



## Exercise 5.6.1

Which of the following are meso compounds?

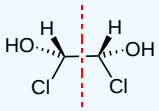
a) 


b) 


c) 

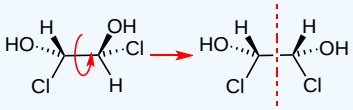

**Answer**

a) This is a meso compound. There is an internal plane of symmetry (dashed line shown in red) between the C's (and it has stereochemistry of *S* & *R*).



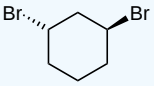
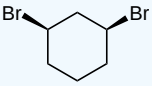
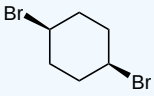

b) This is not a meso compound. No matter how you rotate the C-C bond, you do not see a plane of symmetry (and its stereochemistry is *S* & *S*)

c) This is a meso compound. There is an internal plane of symmetry (dashed line shown in red) that can be seen when you rotate the C-C bond (and it has stereochemistry of *S* & *R*).



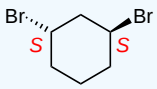

## ? Exercise 5.6.2

Which of the following are meso compounds?

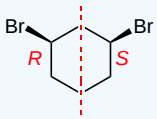
a)  b)  c) 

**Answer**

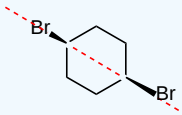
a) This is not a meso compound. There is no plane of symmetry and has stereochemistry of *S* & *S*.



b) This is a meso compound. There is an internal plane of symmetry (dashed line shown in red) and it has stereochemistry of *R* & *S*.

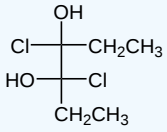
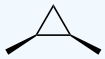
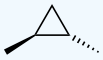


c) This is not a meso compound (even though it has planes of symmetry). The plane of symmetry shown in red makes it so that both chiral centers have symmetrical groups (the ring) and thus the compound is not chiral (so it can't be a meso compound).



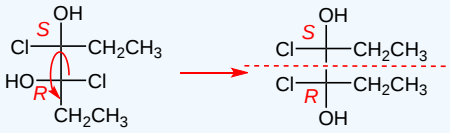
## ? Exercise 5.6.3

Which of the following are meso compounds?

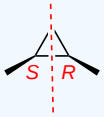
a)  b)  c) 

**Answer**

a) This is a meso compound. If you rotate between the C-C bond, you can see that it has a mirror plane between the C's (shown in red on the structure to the right). Notice how rotating a C-C bond doesn't change the stereochemistry of the molecule (*S* & *R*).



b) This is a meso compound. You can see the plane of symmetry in red and the compound has stereochemistry of *S* & *R*.



c) This is not a meso compound. There is no plane of symmetry and it has stereochemistry of *S* & *S*.

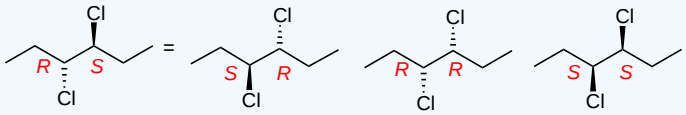


## Exercise 5.6.4

Determine (and draw) if any of the forms of 3,4-dichlorohexane are a meso compound.

**Answer**

Looking at the 4 different possibilities below, i & ii are equivalent structures (with R & S stereochemistry) so it is a meso compound. iii & iv are not meso compounds but are enantiomers to each other.




i ii iii iv

## Contributors and Attributions

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- Prof. Steven Farmer (Sonoma State University)
- Dr. Zachary Sharrett (Sonoma State University)

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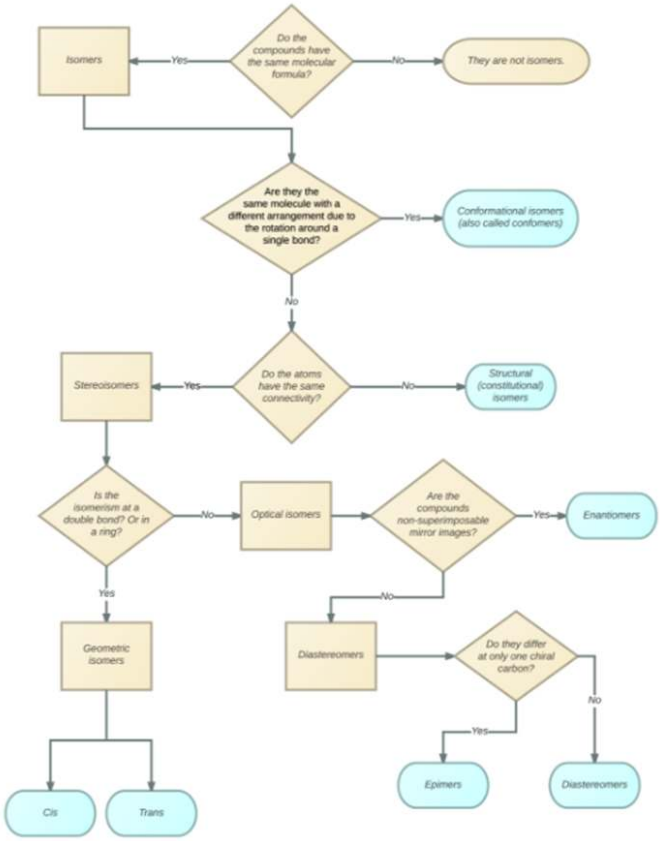
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# 5.7: A Review of Isomerism

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- constitutional
- (structural) isomers
- stereoisomers




*Different types of isomers (Vladsinger)*

## Conformational Isomers

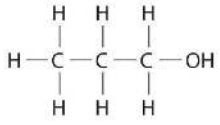
The C–C single bonds in ethane, propane, and other alkanes are formed by the overlap of an $sp^3$ hybrid orbital on one carbon atom with an $sp^3$ hybrid orbital on another carbon atom, forming a σ bond. Each $sp^3$ hybrid orbital is cylindrically symmetrical (all cross-sections are circles), resulting in a carbon–carbon single bond that is also cylindrically symmetrical about the C–C axis. Because rotation about the carbon–carbon single bond can occur without changing the overlap of the $sp^3$ hybrid orbitals, there is no significant electronic energy barrier to rotation. Consequently, many different arrangements of the atoms are possible, each corresponding to different degrees of rotation. Differences in three-dimensional structure resulting from rotation about a σ bond are called differences in conformation, and each different arrangement is called a conformational isomer (or conformer).



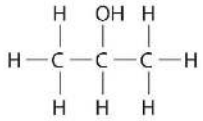
**Conformational Isomers of Pentane**

## Structural Isomers

Unlike conformational isomers, which do not differ in connectivity, structural isomers differ in connectivity, as illustrated here for 1-propanol and 2-propanol. Although these two alcohols have the same molecular formula ($C_3H_8O$), the position of the –OH group differs, which leads to differences in their physical and chemical properties.

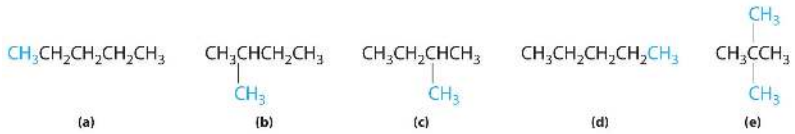


1-Propanol (*n*-propanol)



2-Propanol (isopropanol)

In the conversion of one structural isomer to another, at least one bond must be broken and reformed at a different position in the molecule. Consider, for example, the following five structures represented by the formula $C_5H_{12}$:



(a) (b) (c) (d) (e)

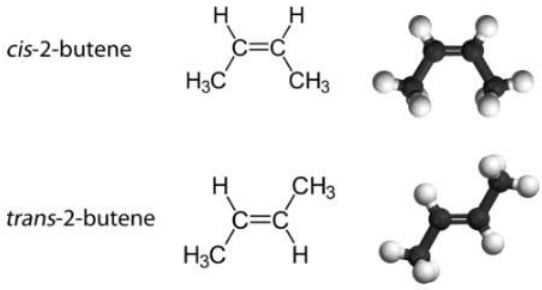
Of these structures, (a) and (d) represent the same compound, as do (b) and (c). No bonds have been broken and reformed; the molecules are simply rotated about a 180° vertical axis. Only three—n-pentane (a) and (d), 2-methylbutane (b) and (c), and 2,2-dimethylpropane (e)—are structural isomers. Because no bonds are broken in going from (a) to (d) or from (b) to (c), these alternative representations are not structural isomers. The three structural isomers—either (a) or (d), either (b) or (c), and (e)—have distinct physical and chemical properties.

## Stereoisomers

**Stereoisomers** have the same connectivity in their atoms but a different arrangement in three-dimensional space. There are different classifications of stereoisomers depending on how the arrangements differ from one another. Notice that in the structural isomers, there was some difference in the connection of atoms. For example, 1-butene has a double bond followed by two single bonds while 2-butene has a single bond, then a double bond, then a single bond. A stereoisomer will have the same connectivity among all atoms in the molecule.

## Geometric Isomers

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. **Geometric isomers** are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the bond. Therefore, there are two different ways to construct the 2-butene molecule (see figure below). The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.

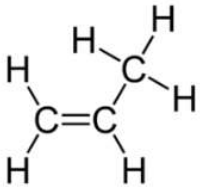


*cis*-2-butene

*trans*-2-butene

## Geometric Isomers of 2-Butene

The *cis* isomer has the two single hydrogen atoms on the same side of the molecule, while the *trans* isomer has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. This occurs with a double bond or a ring. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene (see figure below) has no geometric isomers because one of the carbon atoms (the one on the far left) involved in the double bond has two single hydrogens bonded to it.

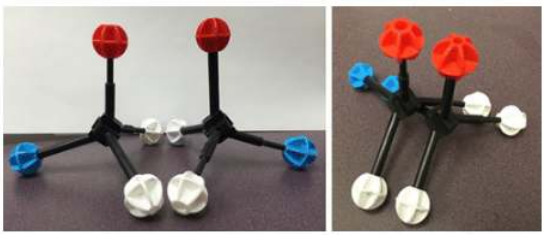



Physical and chemical properties of geometric isomers are generally different. As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

### Optical Isomers

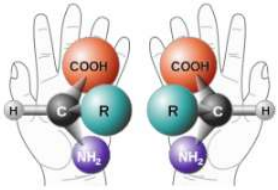
Stereoisomers that are not geometric isomers are known as optical isomers. Optical isomers differ in the placement of substituted groups around one or more atoms of the molecule. They were given their name because of their interactions with plane-polarized light. Optical isomers are labeled enantiomers or diastereomers.

**Enantiomers** are non-superimposable mirror images. A common example of a pair of enantiomers is your hands. Your hands are mirror images of one another but no matter how you turn, twist, or rotate your hands, they are not superimposable.



**Two models that are mirror images and superimposable.**

**Since they are superimposable, they are the same molecule and are not isomers.**

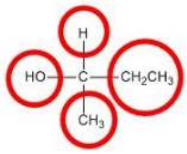



**Your hands and some molecules are mirror images but are not superimposable.**

**These pairs of molecules are called enantiomers.**

:

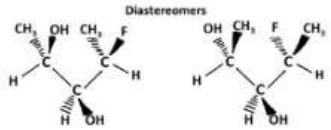
Objects that have non-superimposable mirror images are called **chiral**. When examining a molecule, carbon atoms with four unique groups attached are considered chiral. Look at the figure below to see an example of a chiral molecule. Note that we have to look beyond the first atom attached to the central carbon atom. The four circles indicate the four unique groups attached to the central carbon atom, which is chiral.




## A chiral carbon has four unique groups attached to it

:

Another type of optical isomer are **diastereomers**, which are non-mirror image optical isomers. Diastereomers have a different arrangement around one or more atoms while some of the atoms have the same arrangement. As shown in the figure below, note that the orientation of groups on the first and third carbons are different but the second one remains the same so they are not the same molecule. The solid wedge indicates a group coming out of the page/screen towards you and the dashed line indicates that a group is going away from you "behind" the page/screen.



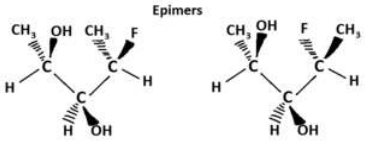

## Diastereomers differ at one or more atom. These molecules are not mirror images and they are not superimposable.

## They are optical isomers because they have the same connectivity between atoms but a different arrangement of substituent

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**Epimers** are a sub-group of diastereomers that differ at only one location. All epimers are diastereomers but not all diastereomers are epimers.




Epimers have a different arrangement around one atom, while arrangements around the other atoms are the same5.1.9" id="MathJax-Element-9-Frame" role="presentation" style="position:relative;" tabindex="0">

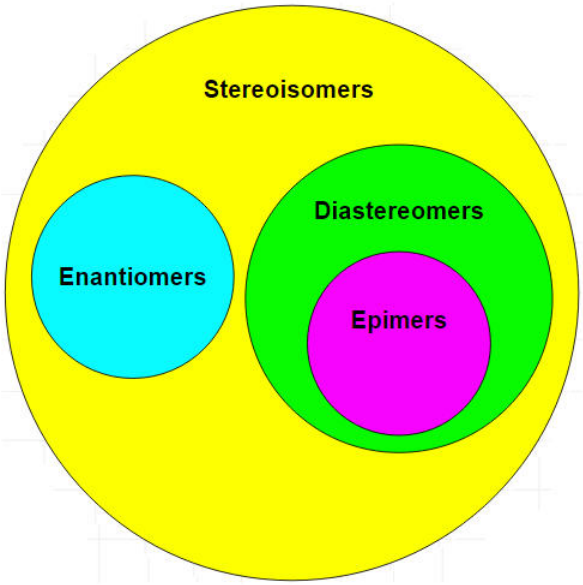
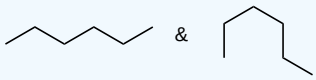



**Diagram showing the division of stereoisomers (also known as optical isomers)**

## Exercise 5.7.1

What kind of isomers are the following pairs?

a) 

b) 

c) 

**Answer**

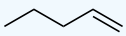
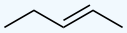
a) Since both structures have the same formula ($C_6H_{12}$) and they have the same connectivity, but are in a different arrangement of the atoms in space, they are conformational isomers.

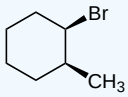
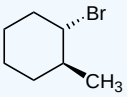
b) Since both structures have the same formula ($C_2H_6O$) but different connectivity, they are structural isomers.

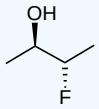
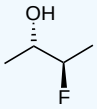
c) Since both structures have the same formula ($C_3H_9Br$) and the same connectivity but the structure on the left has *R* stereochemistry and the structure on the right has *S* stereochemistry, they are stereoisomers called enantiomers.

## Exercise 5.7.2

What kind of isomers are the following pairs?

a)  & 

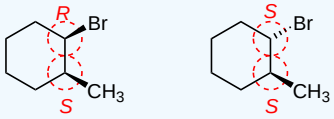
b)  & 

c)  & 

**Answer**

a) Since both structures have the same formula ($C_2H_6O$) but different connectivity of where the double bond is, they are structural isomers.

b) Both structures have the same formula and the same connectivity but the structure on the left has (*R*,*S*) stereochemistry and the structure on the right has (S,S) stereochemistry, they are stereoisomers that are diastereomers.

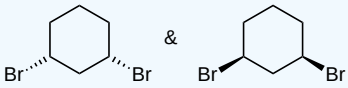


c) Both structures and have the same connectivity but their stereochemistry differs so they are stereoisomers. Since the one on the left is (R,S) and the one on the right is (S,R), they are non-super imposable mirror images of each other and enantiomers.



## ? Exercise 5.7.3

What is the relationship between the following pairs?

a) 

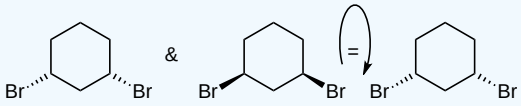
b) 

c) (*R*) – 2 chlorohexane & 1-chlorohexane

d) (2*R*, 3*R*) dichlorohexane & (2*S*, 3*R*) dichlorohexane

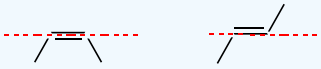
**Answer**

a) Both structures have the same connectivity and same chemical formula and when you rotate the structure on the right you can see that these are the same compound both with (R,S) stereochemistry.

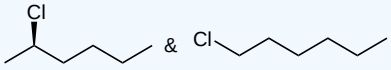


b) ) Since both structures have the same formula ($C_4H_8$) and the same connectivity they are stereoisomers since they differ in what is known as cis/trans isomerism (covered more in Ch 7).Due to the pi bond between carbons 2 & 3, there is not free

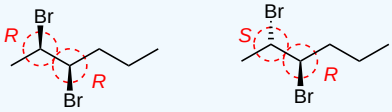
rotation between the C2-C3 bond so the structure on the left has the carbon chains on the same side of the double bond (cis) and the structure on the right has the carbon chains on opposite sides of the double bond (trans).



c) Looking at the structures below, you can see that they have the same formula ($C_6H_{13}Cl$) and different connectivity, so they are structural isomers.




d) Looking at the structures below, you can see that they have the same formula ($C_6H_{12}Br_2$) and the same connectivity, but the structure on the left is (*R*,*R*) and the structure on the right is (*S*,*R*) so since they differ by only one stereocenter, they are stereoisomers that are diastereomers (& epimers in this case).




## Contributors and Attributions

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# CHAPTER OVERVIEW

## 6: Substitutions


6.1: The SN2 Reaction
6.2: Characteristics of the SN2 Reaction
6.3: The SN1 Reaction
6.4: Characteristics of the SN1 Reaction
6.5: Carbocation Structure and Stability


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# 6.1: The SN2 Reaction

## Objectives

After completing this section, you should be able to

1. write an expression relating reaction rate to the concentration of reagents for a second-order reaction.
2. determine the order of a chemical reaction from experimentally obtained rate data.
3. describe the essential features of the $S_N2$ mechanism, and draw a generalized **transition state** for such a reaction.

## Key Terms

Make certain that you can define, and use in context, the key terms below.

- bimolecular
- kinetics
- rate coefficient
- rate equation
- reaction rate
- second-order reaction
- $S_N2$

## Study Notes

Most of the key terms introduced in this section should already be familiar to you from your previous general chemistry course.

Reaction rate refers to the change in concentration of a reactant or product per unit of time. Using strict SI units, reaction rates are expressed in mol · $L^{-1}$ · $s^{-1}$, but in some textbooks you will find this value written as M/s. In general, the reaction rate of a given reaction changes with time, as it is dependent on the concentration of one or more of the reactants.

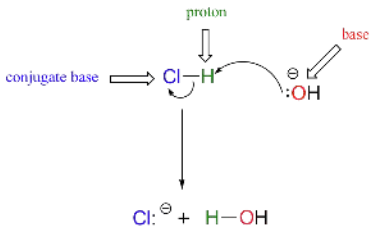
An equation which shows the relationship between the reaction rate and the concentrations of the reactants is known as the rate equation. All rate equations contain a proportionality constant, usually given the symbol *k*, which is known as the rate coefficient. Some textbooks refer to this value as the "rate constant," but this name is a little misleading as it is not a true constant. The rate coefficient of a given reaction depends on such factors as temperature and the nature of the solvent.

$S_N2$ is short for "bimolecular nucleophilic substitution." You will encounter abbreviations for other types of reactions later in this chapter.

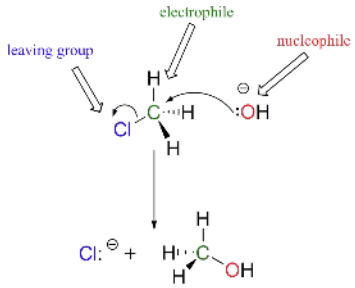
If you are unclear on the point about the inversion of configuration during an $S_N2$ reaction, construct a molecular model of a chiral alkyl halide, the **transition state** formed when this substance reacts with a nucleophile in an $S_N2$ process, and the product obtained from this reaction.

### Brønsted-Lowry acid-base reactions

In many ways, the proton transfer process in a Brønsted-Lowry acid-base reaction can be thought of as simply a special kind of nucleophilic substitution reaction, one in which the electrophile is a hydrogen rather than a carbon.



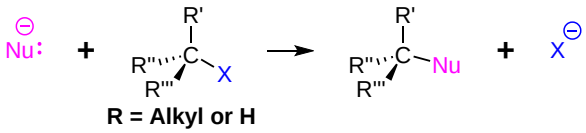

acid-base reaction




nucleophilic substitution

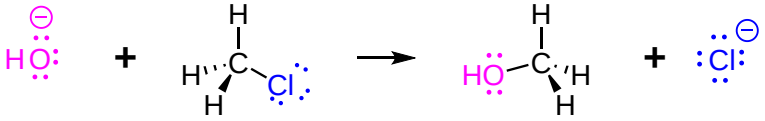
In both reaction types, we are looking at very similar players: an electron-rich species (the nucleophile/base) attacks an electron-poor species (the electrophile/proton), driving off the leaving group/conjugate base. Instead of showing a specific nucleophile like hydroxide, we will simply refer to the nucleophilic reactant as 'Nu'. In a similar fashion, we will call the leaving group 'X'. We will see as we study actual reactions that leaving groups are sometimes negatively charged, sometimes neutral, and sometimes positively charged. We will also see some examples of nucleophiles that are negatively charged and some that are neutral. Therefore, in this general picture we will not include a charge designation on the 'X' or 'Nu' species. We will generalize the three other groups bonded on the electrophilic central carbon as $R_1$, $R_2$, and $R_3$: these symbols could represent hydrogens as well as alkyl groups. Here, then, is the generalized picture of a concerted (single-step) nucleophilic substitution reaction.

## General $S_N2$ Reaction



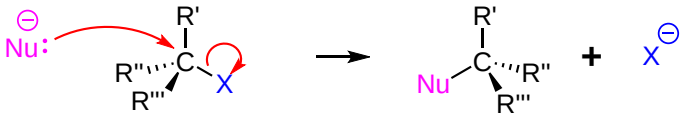

**R = Alkyl or H**

## Example



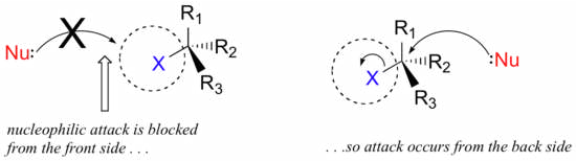

## The $S_N2$ Mechanism

Bimolecular nucleophilic substitution ($S_N2$) reactions are **concerted**, meaning they are a **one step process**. This means that the process whereby the nucleophile attacks and the leaving group leaves is simultaneous. Hence, the bond-making between the nucleophile and the electrophilic carbon occurs at the same time as the bond-breaking between the electrophilic carbon and the halogen. This is called an '**$S_N2$**' mechanism. In the term $S_N2$, S stands for 'substitution', the subscript N stands for 'nucleophilic', and the number 2 refers to the fact that this is a **bimolecular reaction**: the overall rate depends on a step in which two separate molecules (the nucleophile and the electrophile) collide. The mechanism starts when lone pair electrons from the nucleophile attacks the electrophilic carbon of the alkyl halide to form a C-Nu sigma bond. Simultaneously, X-C bond is broken when the electrons are pushed onto the leaving group. Overall during this mechanism, a set of lone pair electrons are transferred from the nucleophile to the leaving groups.



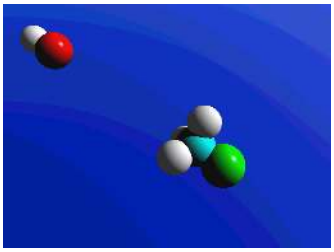

If you look carefully at the progress of the $S_N2$ reaction, you will realize something very important about the outcome. The nucleophile, being an electron-rich species, must attack the electrophilic carbon from the *back side* relative to the location of the

leaving group. Approach from the front side simply doesn't work: the leaving group - which is also an electron-rich group - blocks the way.

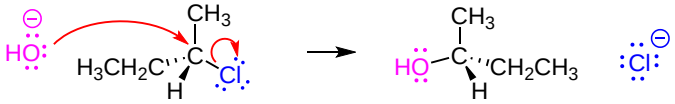



The result of this backside attack is that the stereochemical configuration at the central carbon *inverts* as the reaction proceeds. In a sense, the molecule is turned inside out. $S_N2$ reactions that begin with the R enantiomer as the substrate will form the S enantiomer as the product. Those that begin with the S enantiomer as the substrate will form the R enantiomer as the product. This concept also applies to substrates that are *cis* and substrates that are *trans*. If the *cis* configuration is the substrate, the resulting product will be *trans*. Conversely, if the *trans* configuration is the substrate, the resulting product will be *cis*.

What this means is that $S_N2$ reactions are inherently stereoselective: when the substitution takes place at a stereocenter, we can confidently predict the stereochemical configuration of the product. Below is an animation illustrating the principles we have just learned, showing the $S_N2$ reaction between hydroxide ion and methyl iodide. Notice how backside attack by the hydroxide nucleophile results in inversion at the tetrahedral carbon electrophile.



## Example




**(S)-2-Chlorobutane** **(R)-2-Butanol**

## Bimolecular Nucleophilic Substitution Reactions and Kinetics

In the term $S_N2$, (as previously stated) the number two stands for bimolecular, meaning there are two molecules involved in the rate determining step. The rate of bimolecular nucleophilic substitution reactions depends on the concentration of both the haloalkane and the nucleophile. To understand how the rate depends on the concentrations of both the haloalkane and the nucleophile, let us look at the following example. The hydroxide ion is the nucleophile and methyl iodide is the haloalkane.

$$HO^- + CH_3-I \longrightarrow CH_3OH + I^-$$

$$\text{Rate} = k[CH_3-I][HO^-]$$

If we were to double the concentration of either the haloalkane or the nucleophile, we can see that the rate of the reaction would proceed twice as fast as the initial rate.

$$\text{Rate}_1 = k[CH_3-I][HO^-]$$
$$\text{Rate}_2 = 2k[CH_3-I][HO^-]$$
$$\text{Rate}_2 = 2\,\text{Rate}_1$$

If we were to double the concentration of both the haloalkane and the nucleophile, we can see that the rate of the reaction would proceed four times as fast as the initial rate.

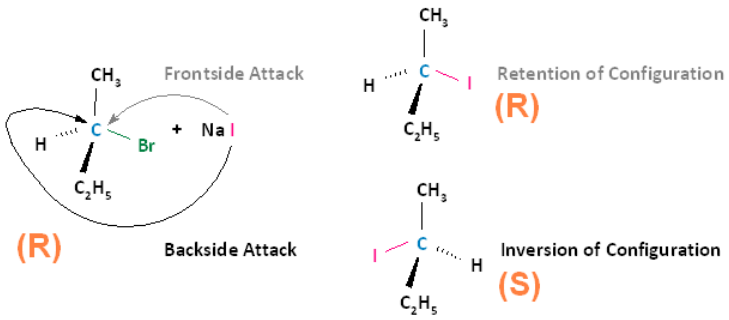
$$\text{Rate}_1 = k[CH_3-I][HO^-]$$
$$\text{Rate}_2 = 4k[CH_3-I][HO^-]$$
$$\text{Rate}_2 = 4\,\text{Rate}_1$$

The bimolecular nucleophilic substitution reaction follows second-order kinetics; that is, the rate of the reaction depends on the concentration of two first-order reactants. In the case of bimolecular nucleophilic substitution, these two reactants are the haloalkane and the nucleophile. For further clarification on reaction kinetics, the following links may facilitate your understanding of rate laws, rate constants, and second-order kinetics:

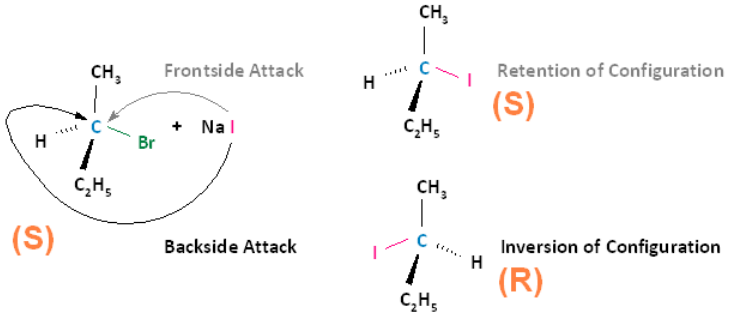
- Definition of a Reaction Rate
- Rate Laws and Rate Constants
- The Determination of the Rate Law
- Second-Order Reactions

## $S_N2$ Reactions Are Stereospecific

The $S_N2$ reaction is stereospecific. A stereospecific reaction is one in which different stereoisomers react to give different stereoisomers of the product. For example, if the substrate is an R enantiomer, a frontside nucleophilic attack results in retention of configuration, and the formation of the R enantiomer. A backside nucleophilic attack results in inversion of configuration, and the formation of the S enantiomer.




Conversely, if the substrate is an S enantiomer, a frontside nucleophilic attack results in retention of configuration, and the formation of the S enantiomer. A backside nucleophilic attack results in inversion of configuration, and the formation of the R enantiomer.




In conclusion, $S_N2$ reactions that begin with the R enantiomer as the substrate will form the S enantiomer as the product. Those that begin with the S enantiomer as the substrate will form the R enantiomer as the product. This concept also applies to substrates that are *cis* and substrates that are *trans*. If the *cis* configuration is the substrate, the resulting product will be *trans*. Conversely, if the *trans* configuration is the substrate, the resulting product will be *cis*.

### ? Exercise 6.1.1

1) The reaction below follows the $S_N2$ mechanism.

$$CH_3Cl + NaOH \longrightarrow CH_3OH + NaCl$$

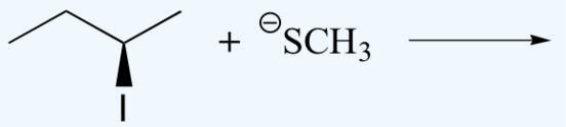
a) Write the rate law for this reaction.

b) Determine the value of the rate coefficient, k, if the initial concentrations are 0.01 M $CH_3Cl$, 0.01 M NaOH, and the initial reaction rate is 6 x $10^{-10}$ M/s.

c) Calculate the initial reaction rate if the initial reactant concentrations are changed to 0.02 M $CH_3Cl$ and 0.0005 M NaOH.

2) Predict the product of a nucleophilic substitution of (S)-2-bromopentane reacting with $CH_3CO_2^-$, Show stereochemistry.

3) Predict the structure of the product in this $S_N2$ reaction. Be sure to specify stereochemistry.




**4)** Since everything is relative in chemistry, one reaction's nucleophile can be another reaction's leaving group. Some functional groups can only react as a nucleophile or electrophile, while other functional groups can react as either a nucleophile or electrophile depending on the reaction conditions. Classify the following compounds as nucleophile, electrophile, or leaving groups. More than one answer may be possible.

a) bromoethane

b) hydroxide

c) water

d) chlorocyclohexane

e) ethanol

f) bromide

**Answer**

1) a) rate = k [$CH_3Cl$] [$OH^-$]

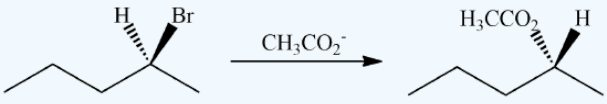
b) substitute the data into the rate expression above and apply algebra to solve for k

k = 6 x $10^{-6}$ $Lmol^{-1}s^{-1}$

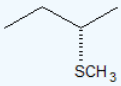
c) Using the rate law above, substitute the value for k from the previous question along with the new concentrations to determine the new initial rate.

rate = 6 x $10^{-10}$ M/s

2)




3)




4)

a) electrophile (Alkyl halides are always electrophiles - one reason they are an o-chem student's best friend.)

b) strong nucleophile

c) weak nucleophile and good leaving group

d) electrophile (Alkyl halides are always electrophiles - one reason they are an o-chem student's best friend.)

e) weak nucleophile, a poor electrophile without clever chemistry (stay tuned for future chapters), good leaving group

f) good nucleophile and a good leaving group

---

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# 6.2: Characteristics of the SN2 Reaction

## Objectives

After completing this section, you should be able to

1. discuss the role of steric effects in $S_N2$ reactions.
2. arrange a given series of alkyl halides in order of increasing or decreasing reactivity towards nucleophilic substitution through the $S_N2$ mechanism.
3. suggest a reason why vinyl halides and aryl halides do not undergo $S_N2$ reactions.
4. discuss how the nature of the nucleophile affects the rate of an $S_N2$ reaction.
5. arrange a given series of common nucleophiles (e.g., $CN^-$, $I^-$, $Br^-$ $Cl^-$, $H_2O$) in order of increasing or decreasing nucleophilicity.
6. discuss how the nature of the leaving group affects the rate of an $S_N2$ reaction.
7. arrange a given series of leaving groups in order of increasing or decreasing ability to leave during an $S_N2$ reaction.

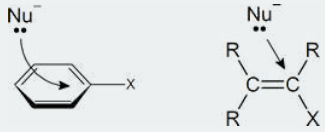
## Key Terms

Make certain that you can define, and use in context, the key terms below.

- leaving group

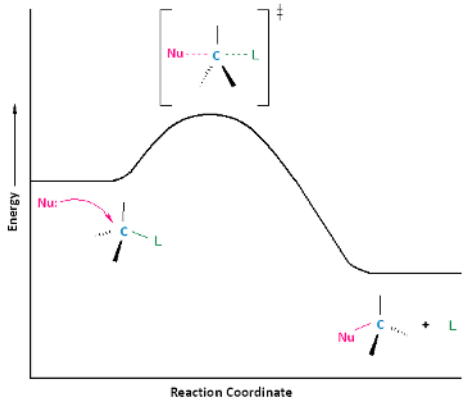
## Study Notes

Both aryl and vinylic halides are relatively unreactive in $S_N2$ displacement mechanisms, mostly because during the backside attack of the molecule the incoming nucleophile is sterically hindered by both substituents and electron density from any double bonds present. Also, leaving groups on $sp^2$-hybridized carbons tend to be held tighter than $sp^3$-hybridized carbons.



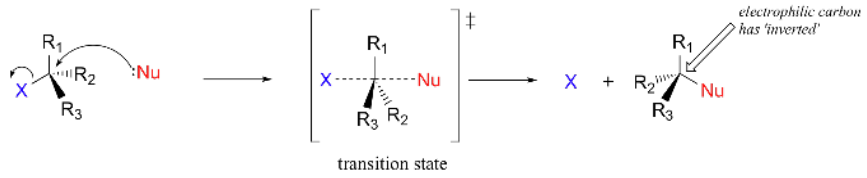

### Potential Energy Diagram for an $S_N2$ Reaction

The potential energy diagram for an $S_N2$ reaction is shown below. This is a single-step, concerted process so a single transition state is formed. A transition state, unlike a reaction intermediate, is a very short-lived species that cannot be isolated or directly observed. For an $S_N2$ reaction the transition state directly determines the energy of activation which must be overcome for the reaction to occur. Factors which affect the stability of the transition state affect the rate of the $S_N2$ reaction.

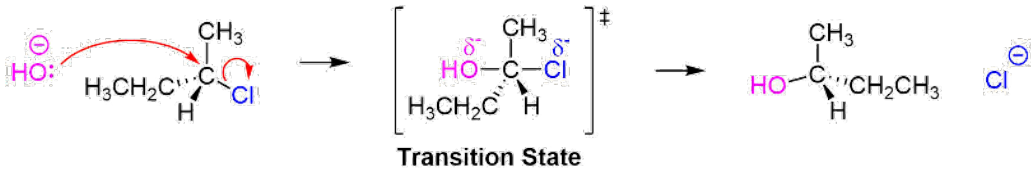



For an $S_N2$ reaction, the transition state represents the half way point of the reaction. The C-Nu bond is in the process of forming and is represented by a dashed bond. The X-C bond is in the process of breaking and is also represented by a dash bond. The negative charge of the nucleophile is in the process of being transfered to the leaving groups. This is represented by both the

nucleophile and the leaving group having a partial negative charge. The electrophilic carbon and the three 'R' substituents all lie on the same plane. Brackets and a double-dagger are placed around the structure to represent that it is a transition state.

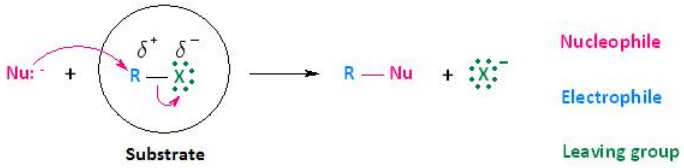



## Example

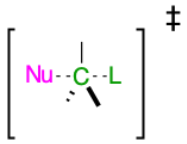



## Sterically Hindered Substrates Will Reduce the $S_N2$ Reaction Rate

Steric hindrance about the electrophilic carbon, is one of the most important factors Determining the rate of $S_N2$ reactions. Although the substrate, in the case of nucleophilic substitution of haloalkanes, is considered to be the entire molecule circled below we are most interested in the electrophilic carbon that bears the leaving group.



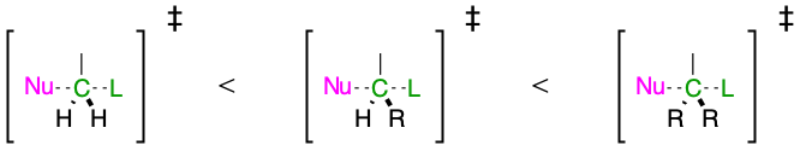

The $S_N2$ **transition state** is very crowded. Recall that there are a total of five groups around the electrophilic center, the nucleophile, the leaving group, and three substituents.



$S_N2$ Transition State

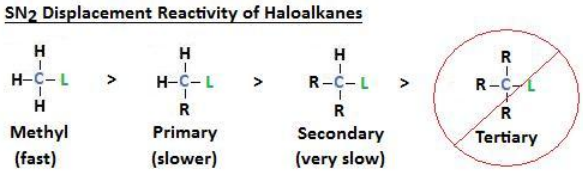
If each of the three substituents were hydrogen atoms, as illustrated in the first example below, there would be little steric repulsion created in the planar portion of the transition state thereby increasing the ease at which the nucleophilic substitution reaction occurs. If one of the hydrogens, however, were replaced with an R group, such as a methyl or ethyl group, there would be an increase in steric repulsion created in the planar portion of the transition state. If two of the hydrogens were replaced by R groups, there would be an even greater increase in steric repulsion in the transition state.

Steric repulsion of $S_N2$ Transition States

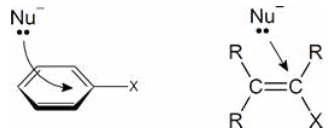


How does steric hindrance affect the rate at which an $S_N2$ reaction will occur? As each hydrogen is replaced by an R group, the rate of reaction is significantly diminished. The increases steric hindrance destabilizes the transition state causing it to become higher in energy. This in turn increases the energy of activation and decreases the reaction rate.

The diagram below illustrates this concept, showing that electrophilic carbons attached to three hydrogen atoms results in faster nucleophilic substitution reactions, in comparison to primary and secondary haloalkanes, which result in nucleophilic substitution reactions that occur at slower or much slower rates, respectively. Notice that a tertiary haloalkane, that which has three R groups attached, does not undergo nucleophilic substitution reactions at all. The addition of a third R group to this molecule creates a carbon that is entirely blocked.




Vinyl and aryl halides are unreactive toward $S_N2$ displacement due to extreme steric factors. To perform an $S_N2$ reaction, the incoming nucleophile would have to enter the plane of the C-C double bond and move through the molecule to achieve the backside displacement required.



In addition to alkyl groups being added to the electrophilic carbon, it turns out that the addition of substitutes on neighboring carbons will slow nucleophilic substitution reactions as well.

In the example below, 2-methyl-1-bromopropane differs from 1-bromopropane in that it has a methyl group attached to the carbon that neighbors the electrophilic carbon. The addition of this methyl group results in a significant decrease in the rate of a nucleophilic substitution reaction.




If R groups were added to carbons farther away from the electrophilic carbon, we would still see a decrease in the reaction rate. However, branching at carbons farther away from the electrophilic carbon would have a much smaller effect.

## The Nucleophile

Nucleophilic functional groups are those which have electron-rich atoms able to donate a pair of electrons to form a new covalent bond. In both laboratory and biological organic chemistry, the most relevant nucleophilic atoms are oxygen, nitrogen, and sulfur, and the most common nucleophilic functional groups are water, alcohols, phenols, amines, thiols, and occasionally carboxylates.

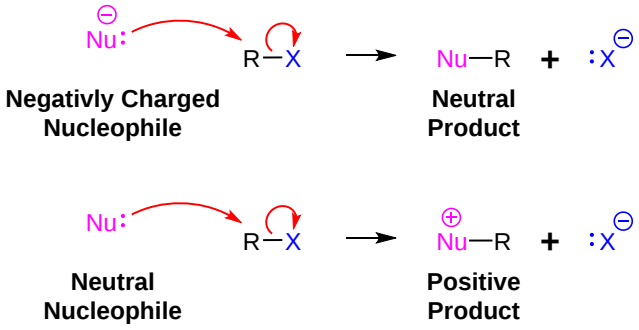
When thinking about nucleophiles, the first thing to recognize is that, for the most part, the same quality of 'electron-richness' that makes a something nucleophilic also makes it basic: *nucleophiles can be bases, and bases can be nucleophiles*. It should not be surprising, then, that most of the trends in basicity that we have already discussed also apply to nucleophilicity.

Some confusion in distinguishing basicity (base strength) and nucleophilicity (nucleophile strength) is inevitable. Since basicity is a less troublesome concept; it is convenient to start with it. Basicity refers to the ability of a base to accept a proton. Basicity may be related to the $pK_a$ of the corresponding conjugate acid, as shown below. The strongest bases have the weakest conjugate acids and vice versa. The range of basicities included in the following table is remarkable, covering over fifty powers of ten! In general, as the pKa of the conjugate acid increases the base becomes a stronger nuclophile. This, however, is not always the case.

| Base | $I^{(-)}$ | $Cl^{(-)}$ | $H_2O$ | $CH_3CO_2^{(-)}$ | $RS^{(-)}$ | $CN^{(-)}$ | $RO^{(-)}$ | $NH_2^{(-)}$ | $CH_3^{(-)}$ |
|---|---|---|---|---|---|---|---|---|---|
| Conj. Acid | HI | HCl | $H_3O^{(+)}$ | $CH_3CO_2H$ | RSH | HCN | ROH | $NH_3$ | $CH_4$ |
| $pK_a$ | -9 | -7 | 0.0 | 4.8 | 8 | 9.1 | 16 | 33 | 48 |

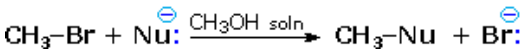
Increasing base strength

**Nucleophilicity** is a more complex property. Any compound, neutral or charged, which has lone pair electrons can act a neuclophile. After a $S_N2$ reaction neutral nucleophiles make a positively charges products and negatively charged nucleophiles make neutral products. In general, negatively charges compound tend to make better nucleophilies.




Specifically, nucleophilicity refers to the rate of substitution reactions at the halogen-bearing **carbon atom** of a reference alkyl halide, such as $CH_3$-Br. The nucleophilicity of the $Nu:^{(-)}$ reactant in the following substitution reaction varies as shown in the chart below:

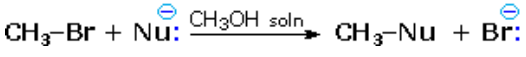
**Nucleophilicity** is a more complex property. It commonly refers to the rate of substitution reactions at the halogen-bearing **carbon atom** of a reference alkyl halide, such as $CH_3$-Br. Thus the nucleophilicity of the $Nu:^{(-)}$ reactant in the following substitution reaction varies as shown in the chart below:




Nucleophilicity: $H_2O < CH_3CO_2^{(-)} < NH_3 < Cl^{(-)} < Br^{(-)} < HO^{(-)} < CH_3O^{(-)} < I^{(-)} < CN^{(-)} < CH_3S^{(-)}$

Increasing nucleophile strength

The versatility of the $S_N2$ reaction is shown by the wide variety of functional groups which can be formed.

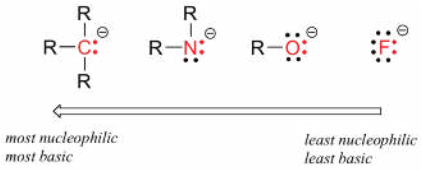



| Nucleophile | | Products | | |
|---|---|---|---|---|
| **Formula** | **Name** | **Formula** | **Name** | **Functional Group** |
| **$CH_3S^{(-)}$** | Methanethiolate | **$CH_3SCH_3$** | Dimethylsulfide | Sulfide |
| **$CN^{(-)}$** | Cyanide | **$CH_3CN$** | Acetonitrile | Nitrile |
| **$I^{(-)}$** | Iodide | **$CH_3I$** | Iodomethane | Alkyl Halide |
| **$CH_3O^{(-)}$** | Methoxide | **$CH_3OCH_3$** | Diethylether | Ether |
| **$HO^{(-)}$** | Hydroxide | **$CH_3OH$** | Methanol | Alcohol |
| **$Br^{(-)}$** | Bromide | **$CH_3Br$** | Bromomethane | Alkyl Halide |
| **$Cl^{(-)}$** | Chloride | **$CH_3Cl$** | Chloromethane | Alkyl Halide |

| | | | | |
|---|---|---|---|---|
| $NH_3$ | Ammonia | $CH_3NH_3^{(+)}$ | Methylammonium ion | Ammonium |
| $CH_3CO_2^{(-)}$ | Acetate | $CH_3O_2CH_3$ | Methyl acetate | Ester |
| $H_2O$ | Water | $CH_3OH_2^{(+)}$ | Methylhydronium ion | Protonated Alcohol |

## Periodic Trends in Nucleophilicity

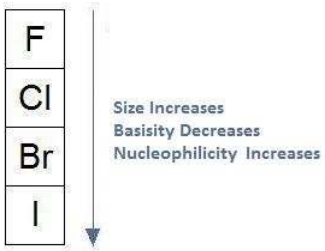
There are predictable periodic trends in nucleophilicity. Moving horizontally across the second row of the table, the trend in nucleophilicity parallels the trend in basicity:




The reasoning behind the horizontal nucleophilicity trend is the same as the reasoning behind the basicity trend: more electronegative elements hold their electrons more tightly, and are less able to donate them to form a new bond. This horizontal trend also tells us that amines are more nucleophilic than alcohols, although both groups commonly act as nucleophiles in both laboratory and biochemical reactions.

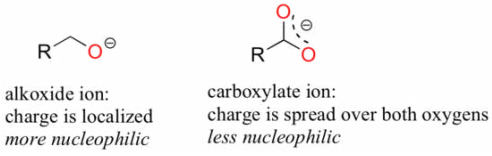
Recall that the basicity of atoms decreases as we move vertically down a column on the periodic table: thiolate ions are less basic than alkoxide ions, for example, and bromide ion is less basic than chloride ion, which in turn is less basic than fluoride ion. Recall also that this trend can be explained by considering the increasing size of the 'electron cloud' around the larger ions: the electron density inherent in the negative charge is spread around a larger area, which tends to increase stability (and thus reduce basicity).

**As Size Increases, Basicity Decreases:** In general, if we move from the top of the periodic table to the bottom of the periodic table as shown in the diagram below, the size of an atom will increase. As size increases, basicity will decrease, meaning a species will be less likely to act as a base; that is, the species will be less likely to share its electrons and act as a nucleophile.

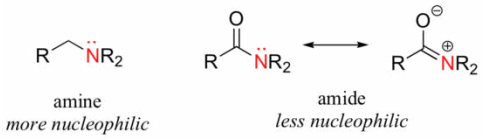



## Resonance Effects on Nucleophilicity

Resonance effects also come into play when comparing the inherent nucleophilicity of different molecules. The reasoning involved is the same as that which we used to understand resonance effects on basicity. If the electron lone pair on a heteroatom is delocalized by resonance, it is inherently less reactive - meaning less nucleophilic, and also less basic. An alkoxide ion, for example, is more nucleophilic and more basic than a carboxylate group, even though in both cases the nucleophilic atom is a negatively charged oxygen. In the alkoxide, the negative charge is localized on a single oxygen, while in the carboxylate the charge is delocalized over two oxygen atoms by resonance.



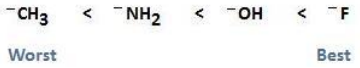

The nitrogen atom on an amide is less nucleophilic than the nitrogen of an amine, due to the resonance stabilization of the nitrogen lone pair provided by the amide carbonyl group.




## The Leaving Group

**As Electronegativity Increases, The Ability of the Leaving Group to Leave Increases**

As mentioned previously, if we move from left to right on the periodic table, electronegativity increases. With an increase in electronegativity, basicity decreases, and the ability of the leaving group to leave increases. This is because an increase in electronegativity results in a species that wants to hold onto its electrons rather than donate them. The following diagram illustrates this concept, showing $^{-}CH_3$ to be the worst leaving group and $F^{-}$ to be the best leaving group. This particular example should only be used to facilitate your understanding of this concept. In real reaction mechanisms, these groups are not good leaving groups at all. For example, fluoride is such a poor leaving group that $S_N2$ reactions of fluoroalkanes are rarely observed.




**As Size Increases, The Ability of the Leaving Group to Leave Increases:** Here we revisit the effect size has on basicity. If we move down the periodic table, size increases. With an increase in size, basicity decreases, and the ability of the leaving group to leave increases. The relationship among the following halogens, unlike the previous example, is true to what we will see in upcoming reaction mechanisms.




It turns out there is also the potential for the solvent to effect the rate of an $S_N2$ reaction. For the purposes of our course, we won't go into the details on the solvent effects.

## Summary of Factors in Affecting $S_N2$ Reactions

There are four main factors which affect $S_N2$ reaction:

1) The structure of the alkyl portion of the substrate: $S_N2$ reactions are affected by steric hindrance around the electrophilic carbon. As steric hindrance increases the rate of $S_N2$ reactions decrease. Methyl and primary substrates work well for $S_N2$ reactions, secondary substrates react slowly, and teritary substrates do not undergo $S_N2$ reactions at all.

2) The reactivity of the nucleophile: The rate of $S_N2$ reaction is increased when strong nucleophiles are used. Strong nucleophiles tend to be negatively charged and good bases. Also, being of an increases size tends to increase the nucleopihlicity of an atom.

3) The nature of the leaving group: The rate of $S_N2$ reaction is increased when leaving groups are used in the substrate. Good leaving groups tend to stabilize the electrons gained during an $S_N2$ reaction. High electronegativity, resonance, and an increases size all can stabilize electrons.

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# 6.3: The SN1 Reaction

**Objectives**

After completing this section, you should be able to

1. write an expression relating reaction rate and reactant concentration for a first-order reaction.
2. compare the kinetics of $S_N1$ and $S_N2$ reactions.
3. identify the rate-limiting step for a reaction, given the reaction energy diagram.
4. sketch a reaction energy diagram for a reaction, given the mechanism and sufficient information to identify the rate-limiting step.
5. write the mechanism of a typical $S_N1$ reaction, and discuss the important features of the mechanism.
6. discuss the stereochemistry of an $S_N1$ reaction, and explain why a racemic mixture is expected when substitution takes place at the chiral carbon atom of an optically pure substrate.
7. compare the stereochemical consequences of the $S_N1$ mechanism with those of the $S_N2$ mechanism.

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- first-order reaction
- rate-limiting step
- $S_N1$

**Study Notes**

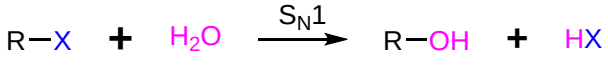
You should recognize that certain compounds (notably tertiary alkyl halides) which react very slowly by the $S_N2$ mechanism can undergo rapid nucleophilic substitution by an alternative mechanism.

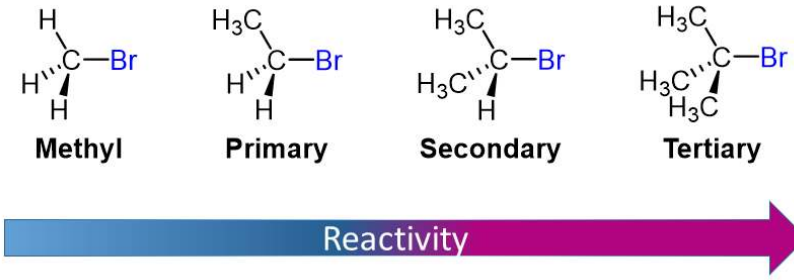
The abbreviation $S_N1$ refers to "unimolecular nucleophilic substitution." In a *first-order reaction*, the rate of the reaction depends on the concentration of only one of the reactants. Thus, when an alkyl halide reacts by an $S_N1$ mechanism, the rate of reaction is dependent on the concentration of the alkyl halide, but is independent of the concentration of the attacking nucleophile.

**Note:** In many textbooks the "rate-limiting step" is called the "rate-determining step."

## General $S_N1$ Reaction

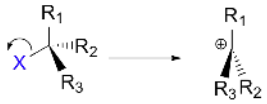
When looking at the following substitution reaction it would be expected to be extremely slow. The reaction represents a worst case scenario based off the rules of an $S_N2$ reaction. The substrate is sterically hindered, the nucleophile is relatively weak, and the solvent is polar protic. However, the reaction proceeds quickly and prefers tertiary substrates over methyl, which is opposite to the trend seen in $S_N2$ reactions. It makes sense that this substitution reaction occurs using a different mechanism than $S_N2$.



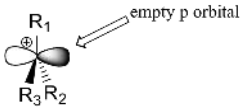



## The $S_N1$ mechanism

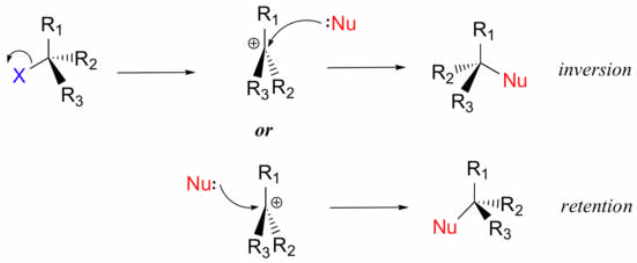
A second model for a nucleophilic substitution reaction is called the '**dissociative**', or '**$S_N1$**' mechanism. In the $S_N1$ reaction, the bond between the substrate and the leaving group is broken when the leaving group departs with the pair of electrons that formerly composed the bond.



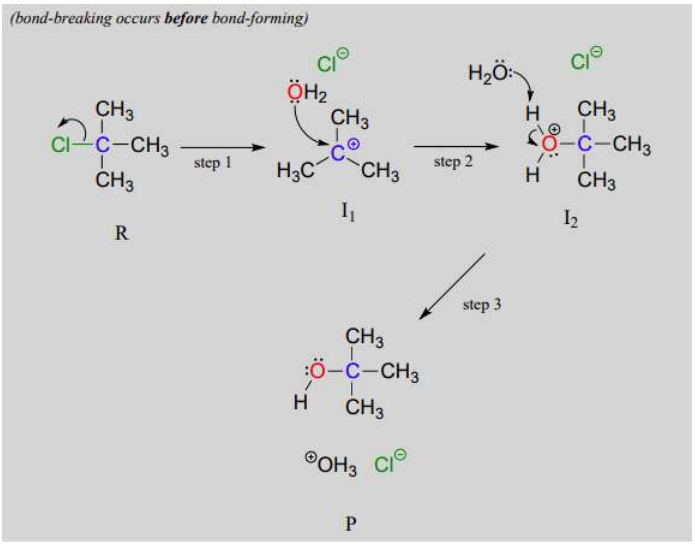

This results in the formation of a **carbocation** (from "carbon" and "cation") the word for a positively charged carbon atom. Because the carbocation has only three bonds, it bears a formal charge of +1. Recall that a carbocation is $sp^2$ hybridized, with trigonal planar geometry. The positive charge is contained in an empty, unhybridized *p* orbital perpendicular to the plane formed by the three sigma bonds. The formation of a carbocation is not energetically favored, so this step in the reaction is the slowest step and determines the overall rate of the reaction. The step which controls the overall rate of a reaction is called the **rate-determining step**.




In the second step of this two-step reaction, the nucleophile attacks the empty, 'electron hungry' *p* orbital of the carbocation to form a new bond and return the carbon to tetrahedral geometry. Since the nucleophile attacks the carbocation only after the leaving group has departed, there is no need for back-side attack. The carbocation and its substituents are all in the same plane, meaning that the nucleophile can attack from either side. As a result, both enantiomers are formed in an the $S_N1$ reaction, leading to a **racemic mixture** of both enantiomers.

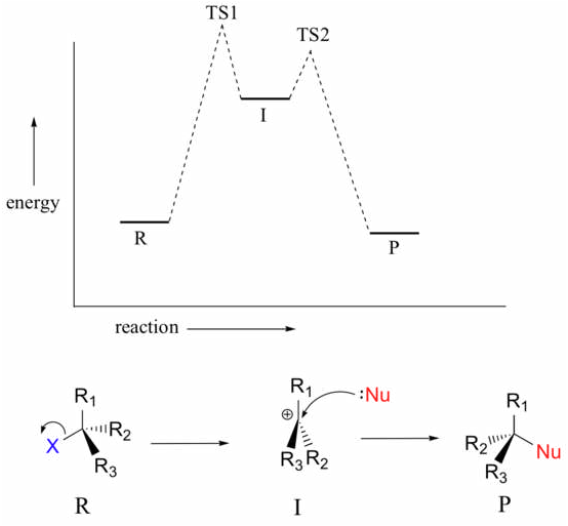



Because $S_N1$ reactions almost exclusively involve neutral nucleophile the product of this second step of the mechanism is often positively charged. The neutral substitution product is usually formed after a third, deprotonation step.



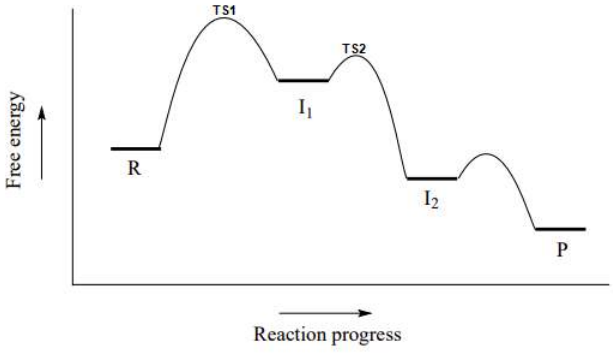
## Reaction Coordinate Diagrams and $S_N1$ Mechanism

During the $S_N1$ reaction we see an example of a reaction intermediate, a very important concept in the study of organic reaction mechanisms that was introduced earlier in the module on organic reactivity Recall that many important organic reactions do not occur in a single step; rather, they are the sum of two or more discreet bond-forming / bond-breaking steps, and involve transient intermediate species that go on to react very quickly. In the $S_N1$ reaction, the carbocation species is a reaction intermediate. A potential energy diagram for an $S_N1$ reaction shows that the carbocation intermediate can be visualized as a kind of valley in the path of the reaction, higher in energy than both the reactant and product but lower in energy than the two transition states. The following reaction coordinate diagram shows an example of a an $S_N1$ reaction with a negatively charged nucleophile.



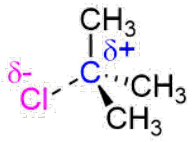

There are several important consequences to the **unimolecular** nature of the rate-determining step in the the $S_N1$ reaction. The first step (dissociation) is the rate determining step, so the rate is controlled only by the loss of the leaving group and does not involve any participation of the nucleophile. Therefore, the rate of the reaction is dependent only on the concentration of the substrate, not on the concentration of the nucleophile.

This can also be shown for the reactions with a neutral nucleophile which includes an extra step of deprotonation. A potential energy diagram for this mechanism shows that each of the two positively-charged intermediates ($I_1$ and $I_2$) can be visualized as a valley in the path of the reaction, higher in energy than both the reactant and product but lower in energy than the transition states. The first, bond-breaking step is the slowest, rate-determining step - notice it has the highest activation energy and leads to the highest-energy species, $I_1$, the carbocation intermediate. Step 2 is rapid: a new covalent bond forms between a carbocation and a water nucleophile, and no covalent bonds are broken. The third step represents a Bronsted-Lowry proton transfer which is rapid, with low activation energy.




Because the first step of the mechanism is the rate determining step, the first transition state will be the most important. During the first step, a carbon-leaving group bond in a neutral substrate is broken to form a carbocation intermediate and a leaving group

anion. The breaking bond is represented as a dashed-partial bond in the transition state. A partial positive charge is shown on the carbon to represent the formation of a carbocation and a partial negative charge is shown on the leaving group to represent the formation of an anion.




**Transition State 1**
**(TS1)**

## $S_N1$ Reaction Kinetics

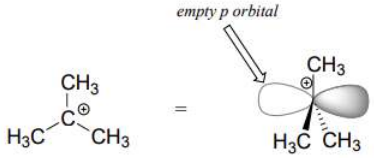
In the first step of an $S_N1$ mechanism, two charged species are formed from a neutral molecule. This step is much the slower of the three steps, and is therefore rate-determining. In the reaction energy diagram, the activation energy for the first step is higher than that for the second step indicating that the $S_N1$ reaction has *first order*, *unimolecular* kinetics because the rate determining step involves one molecule splitting apart, not two molecules colliding. It is important to remember that first order refers to the rate law expression where the generic term substrate is used to describe the alkyl halide.

$$\text{rate} = k\,[\text{substrate}]$$

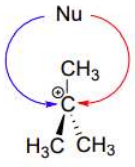
Because an $S_N1$ reaction is first order overall the concentration of the nucleophile does not affect the rate. Since the nucleophile is not involved in the rate-limiting first step, the nature of the nucleophile does not affect the rate of an $S_N1$ reaction.

## Stereochemical Considerations

We saw that $S_N2$ reactions result in inversion of stereochemical configuration at the carbon center. The difference in mechanisms means the stereochemical outcome of $S_N1$ can be different than $S_N2$. Recall that a carbocation intermediate produced during an $S_N1$ reaction is $sp^2$-hybridized, with an empty p orbital perpendicular to the plane formed by the three sigma bonds:




Because the nucleophile is free to attack from either side of the carbocation electrophile, the reaction leads to a 50:50 mixture of two stereoisomeric products. In other words: the $S_N1$ reaction occurs with both retention or inversion of configuration at the electrophilic carbon, leading to racemization if the carbon is chiral after the substitution.




However, often chemical reactions are more complicated than the mechanisms that represent limiting cases like $S_N1$ and $S_N2$. Experimental data has shown that the inversion product is favored over racemization due to the formation of **ion pairs**, in which one face of the carbocation is "blocked" by the departing anion. However, while we are still learning about these substition reactions, it is easiest to stick with the limiting cases like $S_N1$ and $S_N2$ for the time being. In future courses, you may encounter the idea that like $S_N1$ reactions don't always produce complete mixtures at the reacting center.

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# 6.4: Characteristics of the SN1 Reaction

**Objectives**

After completing this section, you should be able to

1. discuss how the structure of the substrate affects the rate of a reaction occurring by the $S_N1$ mechanism.
2. arrange a given list of carbocations (including benzyl and allyl) in order of increasing or decreasing stability.
3. explain the high stability of the allyl and benzyl carbocations.
4. arrange a given series of compounds in order of increasing or decreasing reactivity in $S_N1$ reactions, and discuss this order in terms of the Hammond postulate.
5. discuss how the nature of the leaving group affects the rate of an $S_N1$ reaction, and in particular, explain why $S_N1$ reactions involving alcohols are carried out under acidic conditions.
6. explain why the nature of the nucleophile does not affect the rate of an $S_N1$ reaction.
7. determine which of two $S_N1$ reactions will occur faster, by taking into account factors such as the structure of the substrate and the polarity of the solvent.
8. determine whether a given reaction is most likely to occur by an $S_N1$ or $S_N2$ mechanism, based on factors such as the structure of the substrate, the solvent used, etc.

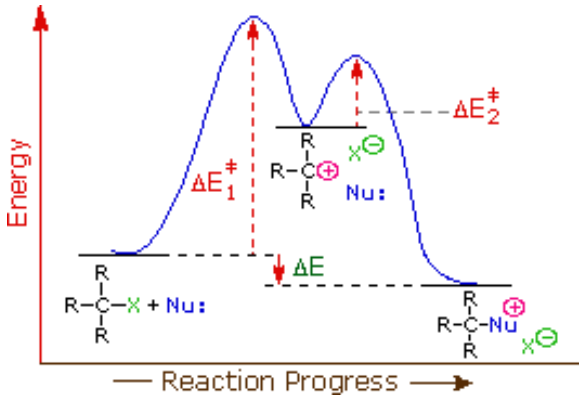
**Key Terms**

Make certain that you can define, and use in context, the key terms below.

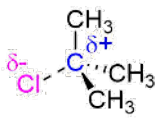
- benzylic

## The Substrate in $S_N1$Reactions

As discussed in the previous section $S_N1$ reactions follow first order kinetics due to a multi-step mechanism in which the rate-determining step consists of the ionization of the alkyl halide to form a carbocation.

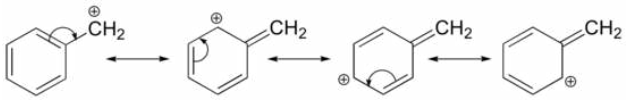



The transition state for the rate determining step shows the transition of an alkyl halide to a carbocation. Because the rate determining step is endothermic, the Hammond postulate says that the transition state more closely resembles the carbocation intermediate. Factors which stabilize this intermediate will lower the energy of activation for the rate determining step and cause the rate of reaction to increase. In general, a more stable carbocation intermediate formed during the reaction allows for a faster the $S_N1$ reaction rate.

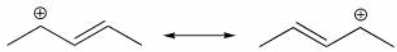



**Transition State 1 (TS1)**

The stability of alky carbocations has been shown to be 3º > 2º > 1º > methyl. Two special cases of resonance-stabilized carbocations, allyl and benzyl, must be considered and added to the list. The delocalization of the positive charge over an extended p orbital system allows for allyl and benzyl carbocations to be exceptionally stable. The resonance hybrid of an allyic cation is made up of two resonance forms while the resonance hybrid of the benzylic carbocation is made up of five.

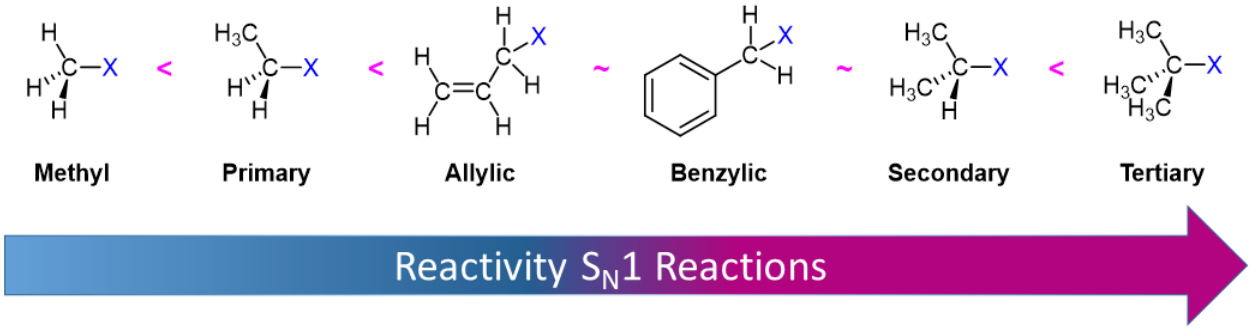


**Benzyl Carbocation**



an allylic carbocation

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Carbocation Stability | $CH_3^{(+)}$ | < | $CH_3CH_2^{(+)}$ | < | $(CH_3)_2CH^{(+)}$ | ≈ | $CH_2{=}CH\text{-}CH_2^{(+)}$ | ≈ | $C_6H_5CH_2^{(+)}$ | ≈ | $(CH_3)_3C^{(+)}$ |



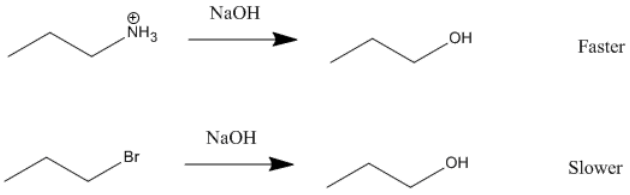

## Effects of Leaving Group

Since leaving group removal is involved in the rate-determining step of the $S_N1$ mechanism, reaction rates increase with a good leaving group. A good leaving group can stabilize the electron pair it obtains after the breaking of the C-Leaving Group bond faster. Once the bond breaks, the carbocation is formed and the faster the carbocation is formed, the faster the nucleophile can come in and the faster the reaction will be completed.

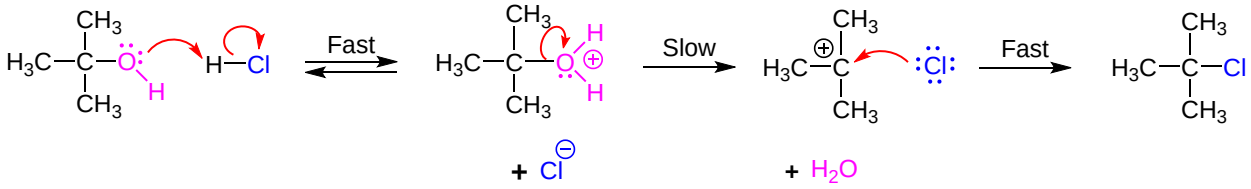
Because weak bases tend to strongly hold onto their electrons, they are lower energy molecules and they tend to make good leaving groups. Strong bases, on the other hand, donate electrons readily because they are high energy, reactive molecules. Therefore, they are not typically good leaving groups. As you go from left to right on the periodic table, electron donating ability decreases and thus ability to be a good leaving group increases. Halides are an example of a good leaving group whose leaving-group ability increases as you go down the halogen column of the periodic table.




The two reactions below only vary by the different leaving groups in each reaction. The reaction with a more stable leaving group is significantly faster than the other. This is because the better leaving group leaves faster and thus the reaction can proceed faster.

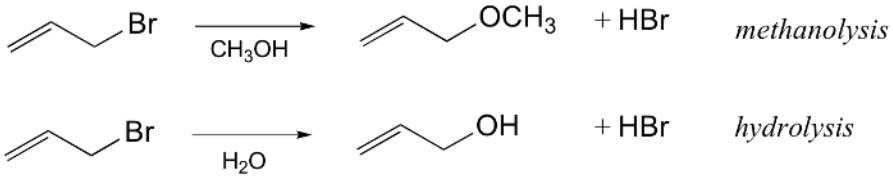



Under acidic conditions, the -OH group of an alcohol can be converted into a neutral water leaving group through protonation. As discussed in **Section 10-5**, this occurs during the conversion of a tertiary alcohol to an alkyl halide through reaction with HCl or HBr. Because the -OH group itself is a poor nucleophile, the mechanism starts with protonation to form a hydronium ion. Neutral water is then lost as a leaving group to create the carbocation intermediate which then reacts with the halide ion nucleophile to provide the alkyl halide product. This reaction works best when a tertiary alcohol is used because it produces a stable carbocation intermediate.

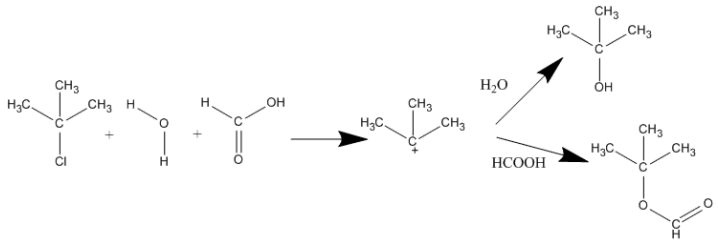



## The Nucleophile

Since nucleophiles only participate in the fast second step, their relative molar concentrations rather than their nucleophilicities should be the primary product-determining factor. If a nucleophilic solvent such as water is used, its high concentration will assure that alcohols are the major product. While recombination of the halide anion with the carbocation intermediate can occur, it simply reforms the starting compound. Also this is less likely since there are less molecules of the leaving group in solution than there are of the solvent. Note that $S_N1$ reactions in which the nucleophile is also the solvent are commonly called **solvolysis** reactions. The $S_N1$ reaction of allyl bromide in methanol is an example of what we would call **methanolysis**, while if water is the solvent the reaction would be called **hydrolysis**:




The strength of the nucleophile does not affect the reaction rate of $S_N1$ because, as described previously, the nucleophile is not involved in the rate-determining step. However, if you have more than one nucleophile competing to bond to the carbocation, the strengths and concentrations of those nucleophiles affects the distribution of products that you will get. For example, if you have $(CH_3)_3CCl$ reacting in water and formic acid where the water and formic acid are competing nucleophiles, you will get two different products: $(CH_3)_3COH$ and $(CH_3)_3COCOH$. The relative yields of these products depend on the concentrations and relative reactivities of the nucleophiles.




## Predicting $S_N1$ vs. $S_N2$ mechanisms

When considering whether a nucleophilic substitution is likely to occur via an $S_N1$ or $S_N2$ mechanism, we really need to consider two factors:

1) **The electrophile:** when the leaving group is attached to a methyl group or a primary carbon, an $S_N2$ mechanism is favored (here the electrophile is unhindered by surrounded groups, and any carbocation intermediate would be high-energy and thus unlikely). When the leaving group is attached to a tertiary, allylic, or benzylic carbon, a carbocation intermediate will be relatively stable and thus an $S_N1$ mechanism is favored.

2) **The nucleophile**: powerful nucleophiles, especially those with negative charges, favor the $S_N2$ mechanism. Weaker nucleophiles such as water or alcohols favor the $S_N1$ mechanism.

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# 6.5: Carbocation Structure and Stability

**Objectives**

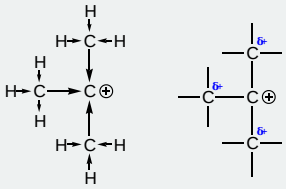
After completing this section, you should be able to

- describe the geometry of a given carbocation.
- arrange a given series of carbocations in order of increasing or decreasing stability.
- explain the relative stability of methyl, primary, secondary and tertiary carbocations in terms of hyperconjugation and inductive effects.

**Study Notes**

Although hyperconjugation can be used to explain the relative stabilities of carbocations, this explanation is certainly not the only one, and is by no means universally accepted. A more common explanation, involving the concept of an inductive effect, is given below.

It is a general principle in chemistry that the more a charge is dispersed, the more stable is the species carrying the charge. Put simply, a species in which a positive charge is shared between two atoms would be more stable than a similar species in which the charge is borne wholly by a single atom. In a tertiary carbocation, the positively charged carbon atom attracts the bonding electrons in the three carbon-carbon sigma ($\sigma$) bonds, and thus creates slight positive charges on the carbon atoms of the three surrounding alkyl groups (and, indeed, on the hydrogen atoms attached to them). Chemists sometimes use an arrow to represent this inductive release:



**Note:** These diagrams do not reflect the geometry of the carbocation. The overall charge on the carbocation remains unchanged, but some of the charge is now carried by the alkyl groups attached to the central carbon atom; that is, the charge has been dispersed.

In the tertiary carbocation shown above, the three alkyl groups help to stabilize the positive charge. In a secondary carbocation, only two alkyl groups would be available for this purpose, while a primary carbocation has only one alkyl group available. Thus the observed order of stability for carbocations is as follows:

tertiary > secondary > primary > methyl.

## Stability of carbocation intermediates

The next step in understanding why Markovnikov's rule is often followed in electrophilic additions, involves understanding the structure and stability of the carboncation intermediate formed during the mechanism.

### Carbocation Structure

Carbocations typically have three substituents which makes the carbon $sp^2$ hybridized and gives the overall molecule a trigonal planar geometry (Figure 6.5.1). The carbocation's substituents are all in the same plane and have a bond angle of 120º between them. The carbon atom in the carbocation is electron deficient; it only has six valence electrons which are used to form three sigma covalent bonds with the substituents. The carbocation carbon has an unoccupied p orbital which is perpendicular to the plane created by the substituents. The p orbital can easily accept electron pairs during reactions making carbocations excellent Lewis acids.

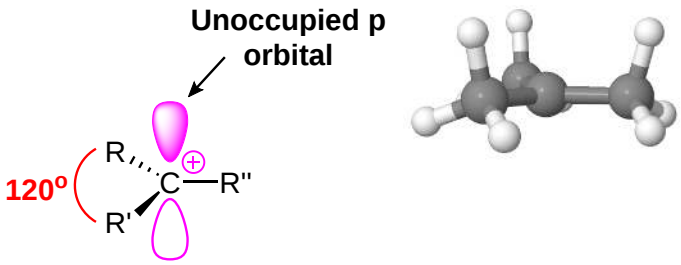
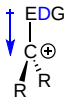



Figure 6.5.1: (1) Hybridization of a generic carbocation and (2) the structure of the tert-butyl cation ($C_4H_9^+$).

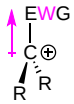
## Stability of Carbocation Intermediates

By being a reactive intermediate of the electrophilic addition mechanism, the stability of a carbocation has a direct effect on the reaction. The critical question now becomes, *what stabilizes a carbocation?*

A positively charged species such as a carbocation is very electron-poor, and thus anything which donates electron density will help to stabilize it. Conversely, a carbocation will be *destabilized* by an electron withdrawing group.



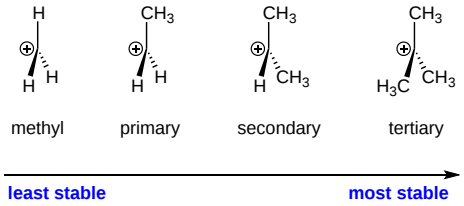

electron donating group *stabilizes* a carbocation




electron withdrawing group *destabilizes* a carbocation

Extensive experimental evidence has shown that a carbocation becomes more stable as the number of alkyl substituents increases. Carbocations can be given a designation based on the number of alkyl groups attached to the carbocation carbon. Three alkyl groups is called a tertiary (3º) carbocation, 2 alkyl groups is called secondary (2º), and 1 alkyl group is called primary (1º). No alkyl groups are attached (3 hydrogen substituents) is called a methyl carbocation.

The overall order of stability is as follows:

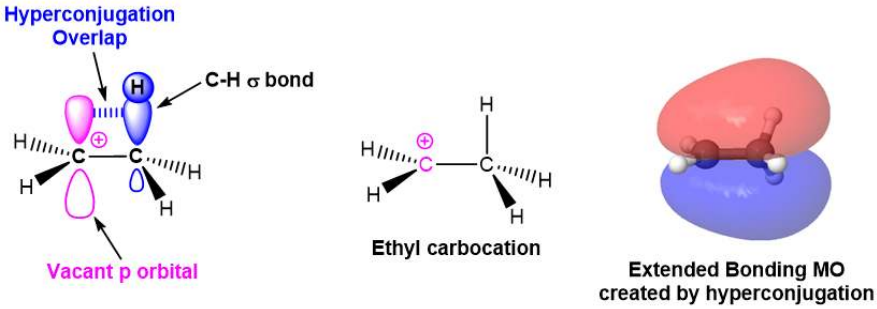



Alkyl groups stabilized carbocations for two reasons. The first is through inductive effects. As discussed in **Section 2-1**, inductive effects occur when the electrons in covalent bonds are shifted towards an nearby atom with a higher electronegativity. In this case, the positively charged carbocation draws in electron density from the surrounding substituents thereby gaining stabilization by slightly reducing its positive charge. Alkyl groups are more effective at inductively donating electron density than a hydrogen because they are larger, more polarizable, and contain more bonding electrons. As more alkyl groups are attached to the carbocation more inductive electron donation occurs and the carbocation becomes more stable.

The second reason alkyl groups stabilize carbocations is through hyperconjugation. As previously discussed in **Section 7.6**, hyperconjugation is an electron donation that occurs from the parallel overlap of p orbitals with adjacent hybridized orbitals participating in sigma bonds. This electron donation serves to stabilize the carbocation. As the number of alkyl substituents increases, the number of sigma bonds available for hyperconjugation increases, and the carbocation tends to become more stabilized.

In the example of ethyl carbocation shown below, the p orbital from a $sp^2$ hybridized carbocation carbon involved interacts with a $sp^3$ hybridized orbital participating in an adjacent C-H sigma bond. Electron density from the C-H sigma bond is donated into carbocation's p orbital providing stabilization.

The molecular orbital of the ethyl carbocation shows the interaction of electrons in methyl group's C-H sigma bonds with the adjacent empty p orbital from the carbocation. The interaction creates a bonding molecular orbital which extends over the three atom chain (C-C-H) involved in hyperconjugation. The expanded molecular orbital helps to stabilize the carbocation.




It is not accurate to say, however, that carbocations with higher substitution are *always* more stable than those with less substitution. Just as electron-donating groups can stabilize a carbocation, electron-withdrawing groups act to destabilize carbocations. Carbonyl groups are electron-withdrawing by inductive effects, due to the polarity of the C=O double bond. It is possible to demonstrate in the laboratory that carbocation A below is more stable than carbocation B, even though A is a primary carbocation and B is secondary.



**A**: more stable **B**: less stable

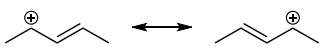
The difference in stability can be explained by considering the electron-withdrawing inductive effect of the ester carbonyl. Recall that inductive effects - whether electron-withdrawing or donating - are relayed through covalent bonds and that the strength of the effect decreases rapidly as the number of intermediary bonds increases. In other words, the effect decreases with distance. In species B the positive charge is closer to the carbonyl group, thus the destabilizing electron-withdrawing effect is stronger than it is in species A.

> In the next chapter we will see how the carbocation-destabilizing effect of electron-withdrawing fluorine substituents can be used in experiments designed to address the question of whether a biochemical nucleophilic substitution reaction is $S_N1$ or $S_N2$.

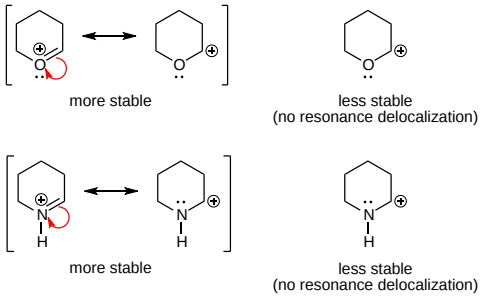
Stabilization of a carbocation can also occur through resonance effects, and as we have already discussed in the acid-base chapter, resonance effects as a rule are more powerful than inductive effects. Consider the simple case of a **benzylic** carbocation:



This carbocation is comparatively stable. In this case, electron donation is a resonance effect. Three additional resonance structures can be drawn for this carbocation in which the positive charge is located on one of three aromatic carbons. The positive charge is not isolated on the benzylic carbon, rather it is delocalized around the aromatic structure: this delocalization of charge results in significant stabilization. As a result, benzylic and **allylic** carbocations (where the positively charged carbon is conjugated to one or more non-aromatic double bonds) are significantly more stable than even tertiary alkyl carbocations.



Because heteroatoms such as oxygen and nitrogen are more electronegative than carbon, you might expect that they would by definition be electron withdrawing groups that destabilize carbocations. In fact, the opposite is often true: if the oxygen or nitrogen atom is in the correct position, the overall effect is carbocation stabilization. This is due to the fact that although these heteroatoms are electron *withdrawing* groups by induction, they are electron *donating* groups by resonance, and it is this resonance effect which is more powerful. (We previously encountered this same idea when considering the relative acidity and basicity of phenols and aromatic amines in section 7.4). Consider the two pairs of carbocation species below:




In the more stable carbocations, the heteroatom acts as an electron donating group by resonance: in effect, the lone pair on the heteroatom is available to delocalize the positive charge. In the less stable carbocations the positively-charged carbon is more than one bond away from the heteroatom, and thus no resonance effects are possible. In fact, in these carbocation species the heteroatoms actually *destabilize* the positive charge, because they are electron withdrawing by induction.

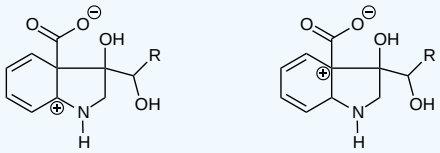
Finally, **vinylic** carbocations, in which the positive charge resides on a double-bonded carbon, are very unstable and thus unlikely to form as intermediates in any reaction.



a vinylic carbocation (very unstable)

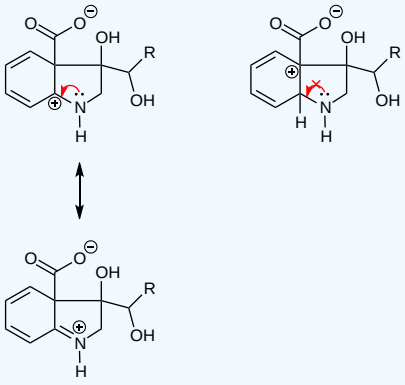
### Example 6.5.1

In which of the structures below is the carbocation expected to be more stable? Explain.



**Answer**

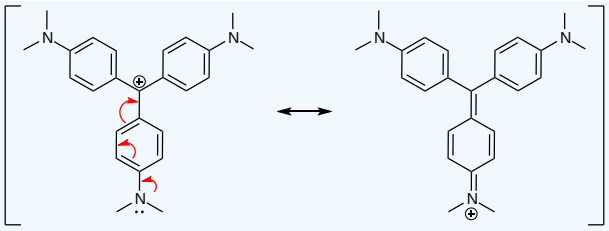
In the carbocation on the left, the positive charge is located in a position relative to the nitrogen such that the lone pair of electrons on the nitrogen can be donated to fill the empty orbital. This is not possible for the carbocation species on the right.



### Example 6.5.2

Draw a resonance structure of the crystal violet cation in which the positive charge is delocalized to one of the nitrogen atoms.

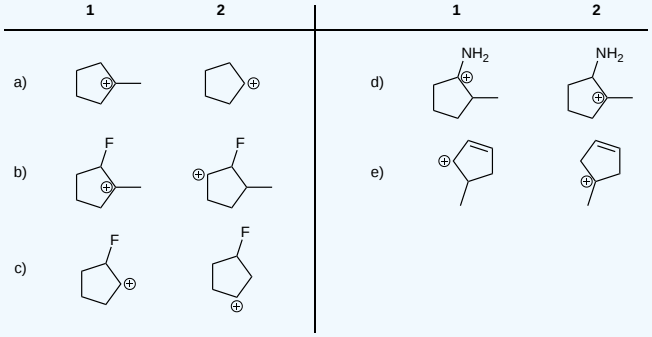
**Answer**



When considering the possibility that a nucleophilic substitution reaction proceeds *via* an $S_N1$ pathway, it is critical to evaluate the stability of the hypothetical carbocation intermediate. If this intermediate is not sufficiently stable, an $S_N1$ mechanism must be considered unlikely, and the reaction probably proceeds by an $S_N2$ mechanism. In the next chapter we will see several examples of biologically important $S_N1$ reactions in which the positively charged intermediate is stabilized by inductive and resonance effects inherent in its own molecular structure.

### Example 6.5.3

State which carbocation in each pair below is more stable, or if they are expected to be approximately equal. Explain your reasoning.




**Answer**

a. 1 (tertiary vs. secondary carbocation)
b. 1 (tertiary vs. secondary carbocation)
c. 2 (positive charge is further from electron-withdrawing fluorine)
d. 1 (lone pair on nitrogen can donate electrons by resonance)
e. 1 (allylic carbocation – positive charge can be delocalized to a second carbon)

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# CHAPTER OVERVIEW

## 7: Eliminations


7.1: An Overview of Elimination Reactions
7.2: Elimination Reactions- Zaitsev's Rule
7.3: Sequence Rules - The E,Z Designation
7.4: Leaving Groups
7.5: The E2 Reaction and the Deuterium Isotope Effect
7.6: The E2 Reaction and Cyclohexane Conformation
7.7: The E1 and E1cB Reactions

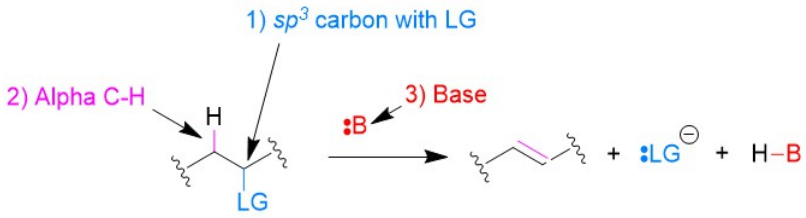

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# 7.1: An Overview of Elimination Reactions

Eliminations are one of the four basic reaction types in organic chemistry (along with additions, substitutions and rearrangements). The simple eliminations that will be examined in this section all occur on $sp^3$-hybrid carbon atoms with the following structural features:

1. An $sp^3$-hybrid carbon bearing a potential *Leaving Group* (abbreviated as C-LG).
2. A C-H bond on an $sp^3$-hybrid carbon alpha to the carbon bearing the leaving group. Recall that an "alpha" carbon means the carbon next to the functional group in question (an alkyl halide, for example).
3. A Base (abbreviated as B).




The products of these types of eliminations are the conjugate acid of the base, the leaving group and, most importantly for an organic chemist, an alkene.

These eliminations to form alkenes will also help illustrate a number of important mechanistic ideas for polar reaction mechanisms, including:

1. Acid/base chemistry,
2. Reactions between nucleophiles and electrophiles, and most importantly
3. The use of electron movement arrows to show the flow of electrons during the bond making and breaking process

Note that during the course of the reaction, the following bond making and bond breaking events must occur:

1. The alpha C-H bond is broken (and a new bond is formed between this proton and the base).
2. The carbon-leaving group bond is broken (and becomes a new lone pair on the leaving group).
3. A new pi bond is formed between the two carbon atoms using the electrons formerly part of the alpha C-H bond.

Because the pi bond cannot form without both of the other two steps occurring, it turns out there are three possible mechanistic ways of thinking about the order of breaking both the C-H and C-LG bonds:

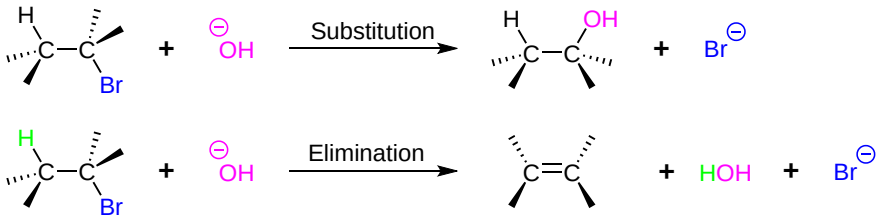
1. Break the C-H bond **at the same time** as the C-LG bond. This is known as an $E_2$ reaction mechanism.
2. Break the C-H bond **before** breaking the C-LG bond. This is known as an $E_{1CB}$ (CB stands for Conjugate Base) reaction mechanism.
3. Break the C-H bond **after** breaking the C-LG bond. This is known as an $E_1$ reaction mechanism.

Each of these three possibilities leads to a different reaction mechanism that will be examined in more depth in the following sections.

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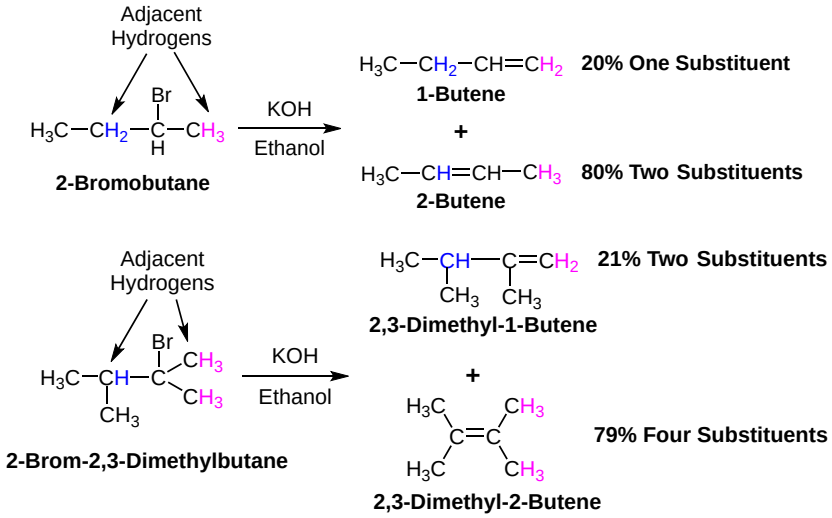
# 7.2: Elimination Reactions- Zaitsev's Rule

When an alkyl halide is reacted with a nucleophile/Lewis base two major types of reaction can occur. In a later section substitution reactions where a nucleophile displaces a leaving group at the electrophilic carbon of a substrate will be discussed. Herein, we will take a look at the case in which the nucleophile acts as a Lewis base and causes an elimination reaction by removing a hydrogen adjacent to the leaving group. These reaction are similar and are often in competition with each other.



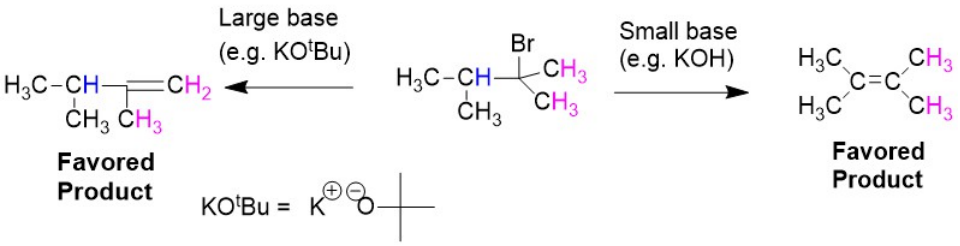

## Introduction

The prefix "regio" indicates the interaction of reactants during bond making and/or bond breaking occurs preferentially by one orientation. If two or more structurally distinct groups of adjacent hydrogens are present in a given reactant, then multiple constitutionally isomeric alkenes may be formed by an elimination. **Zaitsev's rule** is an empirical rule used to predict the major products of elimination reactions. It states that in an elimination reaction the major product is the more stable alkene with the more highly substituted double bond. This situation is illustrated by the 2-bromobutane and 2-bromo-2,3-dimethylbutane elimination examples given below.




By using the strong base hydroxide, we direct these reactions toward elimination (rather than substitution). In both cases there are two different sets of adjacent hydrogens available to the elimination reaction (these are colored red and magenta and the alpha carbon is blue). If the rate of each possible elimination was the same, we might expect the amounts of the isomeric elimination products to reflect the number of hydrogens that could participate in that reaction. For example, since there are three 1º-hydrogens (red) and two 2º-hydrogens (magenta) on beta-carbons in 2-bromobutane, statistics would suggest a 3:2 ratio of 1-butene and 2-butene in the products. This is not observed, and the latter predominates by 4:1. This departure from statistical expectation is even more pronounced in the second example, where there are six adjacent 1º hydrogens compared with one 3º-hydrogen. These results point to a strong favoring the more highly substituted product double bond predicted by **Zaitsev's Rule**.

It is also possible to produce the less substituted elimination product, called the Hofmann product. In that case, the use of a sterically large base (potassium *tert*-butoxide, $KO^tBu$, is commonly used) favors formation of the less substituted product. This difference in regioselectivity occurs because the sterically large base prefers to react with the less substituted C-H atoms.

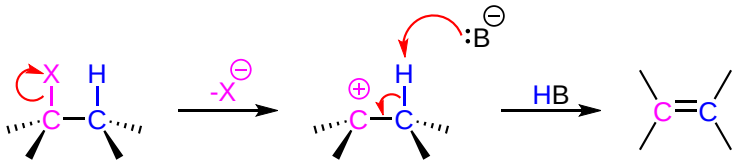



## The E1, E2, and E1cB Reactions

Elimination reaction take place by three common mechanism, E1, E2, and E1cB, all of which break the H-C and X-C bonds at different points of their mechanism. In addition, the different mechanisms will have subtle effects on the reaction products which will be discussed later in this chapter.

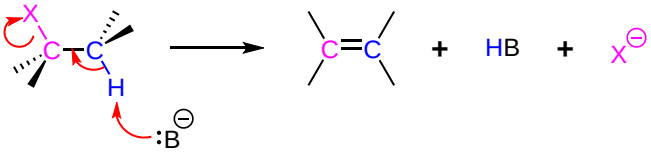
### E1 Mechanism

This mechanism starts the breaking of the C-X to provide a carbocation intermediate. A base removes a hydrogen adjacent to the original electrophilic carbon. The electrons from the broken H-C bond move to form the pi bond of the alkene. In much the same fashion as the $S_N1$ mechanism, the first step of the mechanism is slow making it the rate determining step. This means that the reaction kinetics are unimolecular and first-order with respect to the substrate.



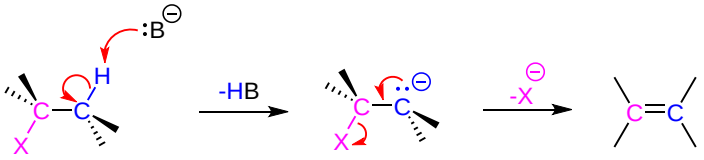

### E2 Mechanism

The E2 mechanism takes place in a single concerted step. The rate at which this mechanism occurs follows second order kinetics, and depends on the concentration of both the base and alkyl halide. The base removes a hydrogen from a carbon adjacent to the leaving group. The electrons of the broken H-C move to form the pi bond of the alkene. In doing this the C-X bond is broken causing the removal of the leaving group.




### E1cB Mechanism

The E1cB mechanism starts with the base deprotonating a hydrogen adjacent to the leaving to form a carbanion. In the second step of the mechanism the lone pair electrons of the carbanion move to become the pi bond of the alkene. This causes the C-X bond to break and the leaving group to be removed.



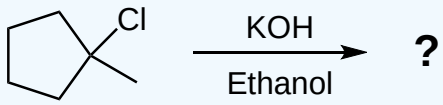

## Predicting the Products of an Elimination Reaction

For most elimination reactions, the formation of the product involves the breaking of a C-X bond from the electrophilic carbon, the breaking of a C-H bond from a carbon adjacent to the electrophilic carbon, and the formation of a pi bond between these two carbons. Which elimination mechanism is being followed has little effect on these steps. The limitations of each elimination mechanism will be discussed later in this chapter.

To determining the possible products, it is vital to first identify the electrophilic carbon in the substrate. Next identify all hydrogens on carbons directly adjacent to the electrophilic carbon. Each unique adjacent hydrogen has the possibility of forming a unique elimination product. Break a C-H bond from each unique group of adjacent hydrogens then break the C-X bond. Finally connect the adjacent carbon and the electrophilic carbon with a double bond. Repeat this process for each unique group of adjacent hydrogens. Finally, compare all of the possible elimination products. The product whose double bond has the most alkyl substituents will most likely be the preferred product.

## Worked Example 7.2.1

What would be the expected products of the following reaction? Which would be expected to be the major product?



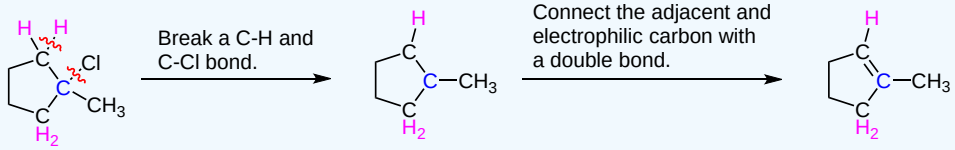

**Solution**

To solve this problem, first find the electrophilic carbon in the starting compound. This carbon is directly attached to the chlorine leaving groups and is shown in blue in the structure below. Next, identify all unique groups of hydrogens on carbons directly adjacent to the electrophilic carbon. In the starting compound, there are two distinct groups of hygrogens which can create a unique elimination product if removed. They are shown as red and green in the structure below.

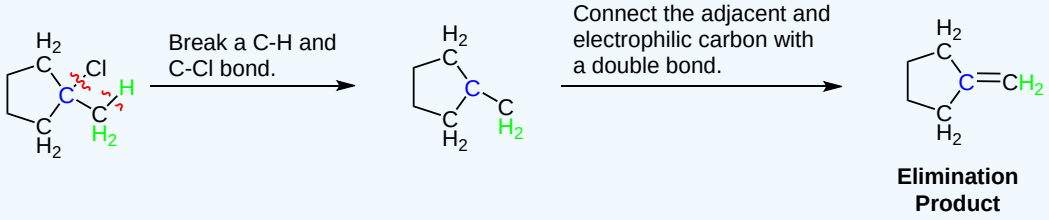



Create the possible elimination product by breaking a C-H bond from each unique group of adjacent hydrogens then breaking the C-Cl bond. Then connect the adjacent carbon and the electrophilic carbon with a double bond to create an alkene elimiation product. Repeat this process for each unique group of adjacent hydrogens. Because the starting compound in this example has two unique groups of adjacent hydrogens, two elimination products can possibly be made.

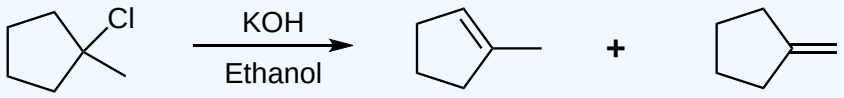
Product 1




Product 2



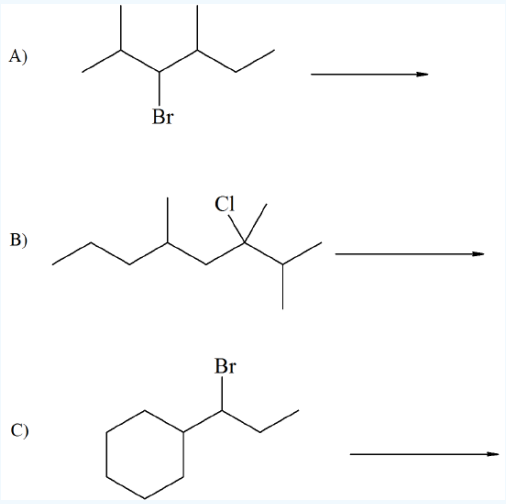

Finally, compare the possible elimination products to determine which has the most alkyl substituents. This product will most likely be the preferred. For this example product 1 has three alkyl substituents and product 2 has only two. This means product 1 will likely be the preferred product of the reaction.



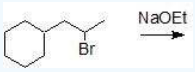

**Major Product (3 Alkyl Substituents)** **Minor Product (2 Alkyl Substituents)**

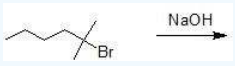
## Exercise 7.2.1

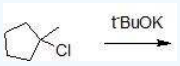
1) Ignoring the alkene stereochemistry show the elimination product(s) of the following compounds:




2) Predict the major products of the following reactions.

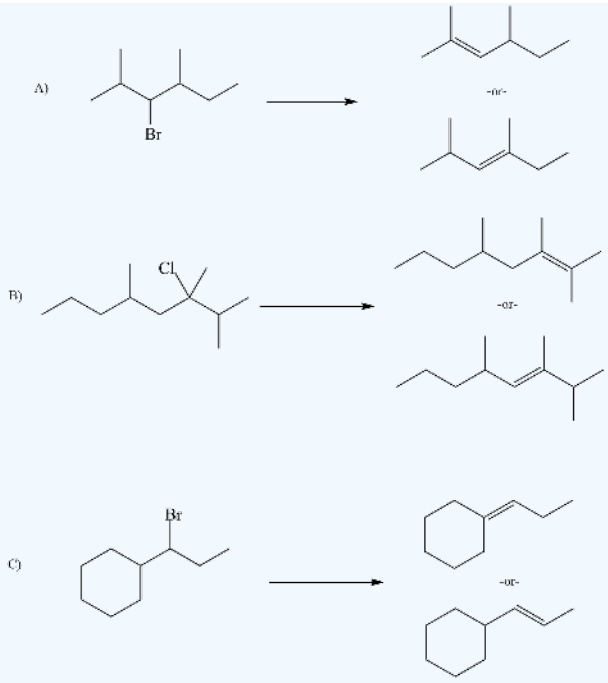
a) 


b) 

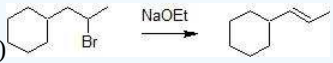

c) 

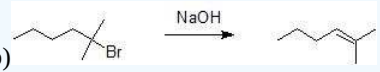

**Answer**

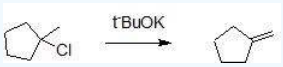
a)




2)

a) 


b) 


c) 


## Contributors and Attributions

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- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Layne Morsch (University of Illinois Springfield)

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# 7.3: Sequence Rules - The E,Z Designation

## Key Terms

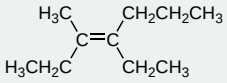
Make certain that you can define, and use in context, the key term below.

- sequence rules (Cahn-Ingold-Prelog rules)

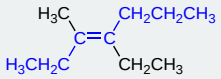
## Study Notes

The limitations of the *cis/trans* system are illustrated in the examples given below.

1. From your study of the IUPAC system, you should be able to identify this compound as 4-ethyl-3-methyl-3-heptene, but is it *cis* or *trans*?



   At first you might say *cis*, because it appears that two ethyl groups appear on the same side of the double bond. However, the correct answer is *trans*. The rule is that the designation *cis* or *trans* must correspond to the configuration of the *longest* carbon chain. Tracing out the seven-carbon chain in the compound shown above, you change sides as you pass through the double bond:

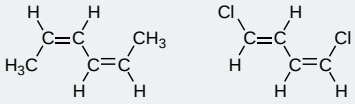


   So, the full name for this compound is *trans*-4-ethyl-3methyl-3-heptene.

2. The *cis*/*trans* system breaks down completely in a compound such as that shown below. The *E*/*Z* system, which is the subject of this section, is designed to accommodate such situations.



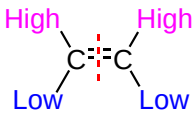
   In cases where two or more double bonds are present, you must be prepared to assign an *E* or *Z* designation to each of the double bonds. For example:



   Another use for these sequence rules will be part of the discussion of optical isomerism in Section 9.5.

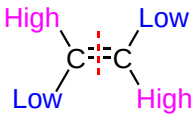
## E/*Z* nomenclature

When each carbon in a double bond is attached to a hydrogen and and a non-hydrogen substituent, the geometric isomers can be identified by using the *cis-trans* nomenclature discussed in the previous section. However, when a double bond is attached to three or four non-hydrogen substituents there are some examples where *cis-trans* nomenclature is ineffective in describing the substituents orientation in geometric isomers. In these situations the rigorous IUPAC system for naming alkene isomers, called the E/Z system, is used. The E/Z system analyzes the two substituents attached to each carbon in the double bond and assigns each either a high or low priority. If the higher priority group on both carbons in the double bond the **same** side the alkene is said to have a **Z isomer** (from German zusammen = together). You could think of Z as Zame Zide to help memorize it. If the higher priority group on **opposite** sides the alkene has an **E isomer** (from German entgegen = opposite).




**Z Configuration**

High priority substituents are on the same side of the double bond




**E Configuration**

High priority substituents are on opposide sides of the double bond

Note, if both substituents an a double bond carbon are exactly the same there is no E/Z isomerizem is possible. Also, if E/Z isomerism is possible, interchanging the substituents attached on double-bond carbon converts one isomer to the other.

Substituent priority for the E,Z system is assigned using the Cahn–Ingold–Prelog (CIP) sequence rules. These are the same rules used to assign R/S configurations to chiral centers in **Section 5.5**. A brief overview of using CIP rules to determine alkene configuration is given here but CIP rules are discussed in greater detail in **Section 5.5**.

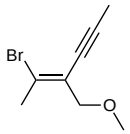
Note

The priority rules are often called the Cahn-Ingold-Prelog (CIP) rules, after the chemists who developed the system

### Rule 1) The "first point of difference" rule

First, determine the two stubstitents on each double-bond carbon separately. Rank these substituents based on **the atom** which directly attached to the double-bond carbon. The substituent whose atom has a higher atomic number takes precedence over the substituent whose atom has a lower atomic number.

Which is higher priority, by the CIP rules: a C with an O and 2 H attached to it or a C with three C? The first C has one atom of high priority but also two atoms of low priority. How do these "balance out"? Answering this requires a clear understanding of how the ranking is done. The simple answer is that the first point of difference is what matters; the O wins.




To illustrate this, consider the molecule at the left. Is the double bond here *E* or *Z*? At the left end of the double bond, Br > C. But the right end of the double bond requires a careful analysis.

At the right hand end, the first atom attached to the double bond is a C at each position. A tie, so we look at what is attached to this first C. For the upper C, it is CCC (since the triple bond counts three times). For the lower C, it is OHH -- listed in order from high priority atom to low. OHH is higher priority than CCC, because of the first atom in the list. That is, the O of the lower group beats the C of the upper group. In other words, the O is the highest priority atom of any in this comparison; thus the O "wins".

Therefore, the high priority groups are "up" on the left end (the -Br) and "down" on the right end (the -$CH_2$-O-$CH_3$). This means that the isomer shown is opposite = entgegen = *E*. And what is the name? The "name" feature of ChemSketch says it is (2*E*)-2-(1-bromoethylidene)pent-3-ynyl methyl ether.

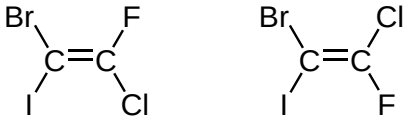
### Rule 2)

If the first atom on both substituents are the identical, then proceed along both substituent chains until the first point of difference is determined.

### Rule 3)

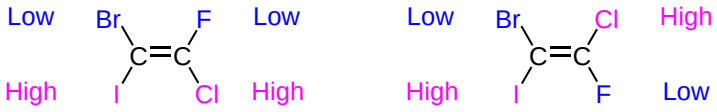
Remember that atoms involved in multiple bonds are considered with a specific set of rules. These atoms are treated as if they have the same number of single-bond atoms as they have attached to multiply bonded atoms.

An easy example which shows the necessity of the E/Z system is the alkene, 1-bromo-2-chloro-2-fluoro-1-iodoethene, which has four different substituents attached to the double bond. The figure below shows that there are two distinctly different geometric isomers for this molecule neither of which can be named using the *cis-trans* system.



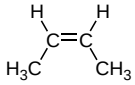
Consider the left hand structure. On the double bond carbon on the left, the two atoms attached to the double bond are Br and I. By the CIP priority rules, I is higher priority than Br (higher atomic number). Now look at carbon on the right. The attached atoms are Cl and F, with Cl having the higher atomic number and the higher priority.

When considering the relative positions of the higher priority groups, the higher priority group is "down" on the left double bond carbon and "down" at right double bond carbon. Since the two higher priority groups are both on the **same** side of the double bond ("down", in this case), they are zusammen = together. Therefore, this is the (Z) isomer. Similarly, the right hand structure is (E).

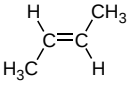



**Z Configuration** **E Configuration**

## Example 7.5.1: Butene



*cis*-2-butene
(*Z*)-2-butene



*trans*-2-butene
(*E*)-2-butene

The Figure above shows the two isomers of 2-butene. You should recognize them as *cis* and *trans*. Let's analyze them to see whether they are *E* or *Z*. Start with the left hand structure (the cis isomer). On C2 (the left end of the double bond), the two atoms attached to the double bond are C and H. By the CIP priority rules, C is higher priority than H (higher atomic number). Now look at C3 (the right end of the double bond). Similarly, the atoms are C and H, with C being higher priority. We see that the higher priority group is "down" at C2 and "down" at C3. Since the two priority groups are both on the **same** side of the double bond ("down", in this case), they are zusammen = together. Therefore, this is (*Z*)-2-butene.

Now look at the right hand structure (the *trans* isomer). In this case, the priority group is "down" on the left end of the double bond and "up" on the right end of the double bond. Since the two priority groups are on **opposite** sides of the double bond, they are entgegen = opposite. Therefore, this is (*E*)-2-butene.

## E/*Z* will work – even when *cis*/*trans* fails

In simple cases, such as 2-butene, *Z* corresponds to *cis* and *E* to *trans*. However, that is **not** a rule. This section and the following one illustrate some idiosyncrasies that happen when you try to compare the two systems. The real advantage of the *E*/*Z* system is that it will always work. In contrast, the *cis*/*trans* system breaks down with many ambiguous cases.

## Example 7.5.2

The following figure shows two isomers of an alkene with four different groups on the double bond, 1-bromo-2-chloro-2-fluoro-1-iodoethene.



(*Z*)-1-bromo-2-chloro-2-fluoro-1-iodoethene

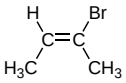


(*E*)-1-bromo-2-chloro-2-fluoro-1-iodoethene

It should be apparent that the two structures shown are distinct chemicals. However, it is impossible to name them as *cis* or *trans*. On the other hand, the *E*/*Z* system works fine... Consider the left hand structure. On C1 (the left end of the double bond), the two atoms attached to the double bond are Br and I. By the CIP priority rules, I is higher priority than Br (higher atomic number). Now look at C2. The atoms are Cl and F, with Cl being higher priority. We see that the higher priority group is "down" at C1 and "down" at C2. Since the two priority groups are both on the **same** side of the double bond ("down", in this case), they are zusammen = together. Therefore, this is the (*Z*) isomer. Similarly, the right hand structure is (*E*).

## E/*Z* will work, but may not agree with *cis*/*trans*

Consider the molecule shown at the left.




This is 2-bromo-2-butene -- ignoring the geometric isomerism for now. *Cis* or *trans*? This molecule is clearly *cis*. The two methyl groups are on the same side. More rigorously, the "parent chain" is *cis*.

*E* or *Z*? There is a methyl at each end of the double bond. On the left, the methyl is the high priority group -- because the other group is -H. On the right, the methyl is the low priority group -- because the other group is -Br. That is, the high priority groups are $-CH_3$ (left) and -Br (right). Thus the two priority groups are on opposite sides = entgegen = *E*.

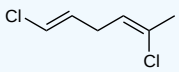
**Note**

This example should convince you that *cis* and *Z* are not synonyms. *Cis*/*trans* and *E*/*Z* are determined by distinct criteria. There may seem to be a simple correspondence, but it is not a rule. Be sure to determine *cis*/*trans* or *E*/*Z* separately, as needed.

## Multiple double bonds

If the compound contains more than one double bond, then each one is analyzed and declared to be *E* or *Z*.

**Example 7.5.3**

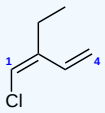



The configuration at the left hand double bond is *E*; at the right hand double bond it is *Z*. Thus this compound is (1*E*,4*Z*)-1,5-dichloro-1,4-hexadiene.

## The double-bond rule in determining priorities

**Example 7.5.4**

Consider the compound below

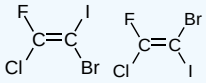



This is 1-chloro-2-ethyl-1,3-butadiene -- ignoring, for the moment, the geometric isomerism. There is no geometric isomerism at the second double bond, at 3-4, because it has 2 H at its far end.

What about the first double bond, at 1-2? On the left hand end, there is H and Cl; Cl is higher priority (by atomic number). On the right hand end, there is $-CH_2-CH_3$ (an ethyl group) and $-CH=CH_2$ (a vinyl or ethenyl group). Both of these groups have C as the first atom, so we have a tie so far and must look further. What is attached to this first C? For the ethyl group, the first C is attached to C, H, and H. For the ethenyl group, the first C is attached to a C twice, so we count it twice; therefore that C is attached to C, C, H. CCH is higher than CHH; therefore, the ethenyl group is higher priority. Since the priority groups, Cl and ethenyl, are on the same side of the double bond, this is the *Z*-isomer; the compound is (*Z*)-1-chloro-2-ethyl-1,3-butadiene.

## Example 7.5.5

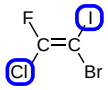
The configuration about double bonds is undoubtedly best specified by the *cis*/*trans* notation when there is no ambiguity involved. Unfortunately, many compounds cannot be described adequately by the *cis*/*trans* system. Consider, for example, configurational isomers of 1-fluoro-1-chloro-2-bromo-2-iodo-ethene, 9 and 10. There is no obvious way in which the *cis*/*trans* system can be used:



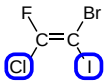
**9** **10**

A system that is easy to use and which is based on the sequence rules already described for the *R*,*S* system works as follows:

1. An order of precedence is established for the two atoms or groups attached to each end of the double bond according to the sequence rules of Section 19-6. When these rules are applied to 1-fluoro- 1-chloro-2-bromo-2- iodoethene, the priority sequence is:
    - at carbon atom 1, C1 > F
    - at carbon atom 2, I > Br
2. Examination of the two configurations shows that the two priority groups- one on each end- are either on the same side of the double bond or on opposite sides:

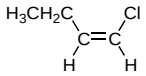


priority groups on opposite sides
(*E*) configuration

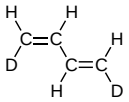


priority groups on same side
(*Z*) configuration

The *Z* isomer is designated as the isomer in which the top priority groups are on the same side (*Z* is taken from the German word zusammen- together). The *E* isomer has these groups on opposite sides (*E*, German for entgegen across). Two further examples show how the nomenclature is used:



(*Z*)-1-chloro-1-butene



(1*Z*,3*E*)-1,3-butadiene-1,4-*d*2

## Exercises

## Contributors and Attributions

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- John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."
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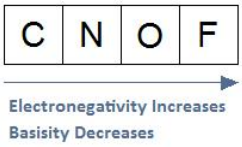
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# 7.4: Leaving Groups

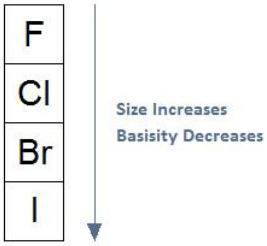
## The Nature of the Leaving Group

In order to understand the nature of the leaving group, it is important to first discuss factors that help determine whether a species will be a strong base or weak base. If you remember from general chemistry, a Lewis base is defined as a species that donates a pair of electrons to form a covalent bond. The factors that will determine whether a species wants to share its electrons or not include electronegativity, size, and resonance.

**As Electronegativity Increases, Basicity Decreases**: In general, if we move from the left of the periodic table to the right of the periodic table as shown in the diagram below, electronegativity increases. As electronegativity increases, basicity will decrease, meaning a species will be less likely to act as base; that is, the species will be less likely to share its electrons.




**As Size Increases, Basicity Decreases:** In general, if we move from the top of the periodic table to the bottom of the periodic table as shown in the diagram below, the size of an atom will increase. As size increases, basicity will decrease, meaning a species will be less likely to act as a base; that is, the species will be less likely to share its electrons. As well, when considering the leaving group ability of the atom when it is attached to carbon, the larger the orbital in the valence shell of the potential leaving group, then the weaker the bond to carbon (owing to poorer orbital overlap).



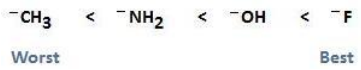

**Resonance Decreases Basicity:** The third factor to consider in determining whether or not a species will be a strong or weak base is resonance. As you may remember from general chemistry, the formation of a resonance stabilized structure results in a species that is less willing to share its electrons. Since strong bases, by definition, want to share their electrons, resonance stabilized structures are weak bases.

## Weak Bases are the Best Leaving Groups

Now that we understand how electronegativity, size, and resonance affect basicity, we can combine these concepts with the fact that weak bases make the best leaving groups. Think about why this might be true. In order for a leaving group to leave, it must be able to accept electrons. A strong bases wants to donate electrons; therefore, the leaving group must be a weak base. We will now revisit electronegativity, size, and resonance, moving our focus to the leaving group, as well providing actual examples.

> **Note**
>
> As Electronegativity Increases, The Ability of the Leaving Group to Leave Increases.

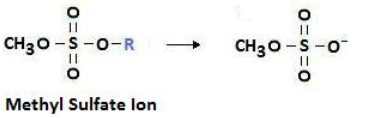
As mentioned previously, if we move from left to right on the periodic table, electronegativity increases. With an increase in electronegativity, basisity decreases, and the ability of the leaving group to leave increases. This is because an increase in electronegativity results in a species that wants to hold onto its electrons rather than donate them. The following diagram illustrates this concept, showing $^{-}CH_3$ to be the worst leaving group and $F^-$ to be the best leaving group. This particular example should only be used to facilitate your understanding of this concept. In real reaction mechanisms, these groups are not good leaving groups at all. For example, fluoride is such a poor leaving group that $S_N2$ reactions of fluoroalkanes are rarely observed.

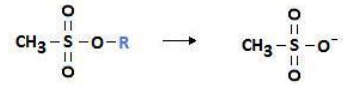



**As Size Increases, The Ability of the Leaving Group to Leave Increases:** Here we revisit the effect size has on basicity. If we move down the periodic table, size increases. With an increase in size, basicity decreases, and the ability of the leaving group to leave increases. The relationship among the following halogens, unlike the previous example, is true to what we will see in upcoming reaction mechanisms.

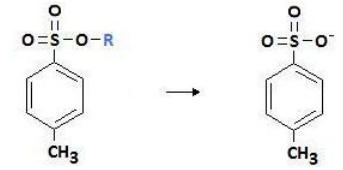



**Resonance Increases the Ability of the Leaving Group to Leave:** As we learned previously, resonance stabilized structures are weak bases. Therefore, leaving groups that form resonance structures upon leaving are considered to be excellent leaving groups. The following diagram shows sulfur derivatives of the type $ROSO_3^-$ and $RSO_3^-$. Alkyl sulfates and sulfonates like the ones shown make excellent leaving groups. This is due to the formation of a resonance stabilized structure upon leaving.


Methyl Sulfate Ion


Methanesulfonate Ion (Mesylate)


Trifluoromethanesulfonate Ion (Triflate Ion)


4-Methylbenzenesulfonate Ion (Tosylate)

Note the following common shorthands you will frequently encounter in organic chemistry:

Methanesulfonate (Mesylate) = **-OMs**

Trifluoromethanesulfone (Triflate) = **-OTf**

4-Methylbenzenesulfone (Tosylate) = **-OTs**

## Contributors and Attributions

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# 7.5: The E2 Reaction and the Deuterium Isotope Effect

## Key Terms

Make certain that you can define, and use in context, the key terms below.

- anti periplanar
- deuterium isotope effect
- E2 reaction
- periplanar
- syn periplanar

## Study Notes

An *E2 reaction* is a bimolecular elimination reaction; thus, two molecules are involved in the rate-limiting step. In this section, we are concerned with E2 reactions involving an alkyl halide and a base.

Use molecular models to assist you to understand the difference between syn periplanar and anti periplanar, and to appreciate why E2 eliminations are stereospecific.

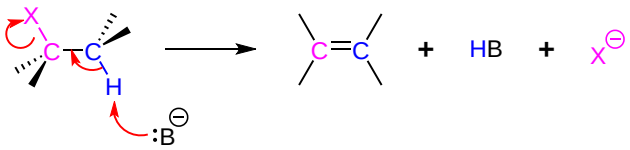
Note that when deuterium is used the kinetic isotope effect (KIE) is referred to as the deuterium isotope effect. A C–H bond is about 5 kJ/mol weaker than a C–D bond. So if the rate-limiting step involves a breaking of this bond as it does at the E2 transition state there will be a substantial difference in reaction rates when comparing deuterated and non-deuterated analogues. Indeed, the reaction of 2-bromopropane with sodium ethoxide (NaOEt) is 6.7 times faster than its deuterated counterpart, providing evidence consistent with an E2 mechanism.

## Introduction

E2, bimolecular elimination, was proposed in the 1920s by British chemist Christopher Kelk Ingold. E2 reactions are typically seen with secondary and tertiary alkyl halides, in the presence of a base (OH-, RO-, $R_2N$-). For a primary halide to undergo an E2 reaction a strong sterically hindered base is usually required. The products of an E2 reaction follow Zaitsev's rule, the most substituted alkene is usually the major product.

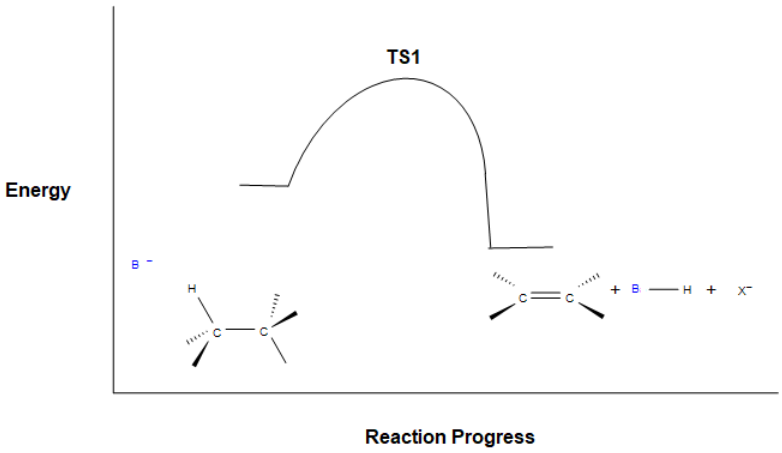
## E2 Mechanism

The E2 mechanism takes place in a single concerted step. The rate at which this mechanism occurs follows second order kinetics, and depends on the concentration of both the base and alkyl halide. The base removes a hydrogen from a carbon adjacent to the carbon with the leaving group. The electrons of the broken H-C bond move to form the pi bond of the neutral product alkene. In doing this, the C-X bond is broken causing the removal of the leaving group. Overall during this reaction an electron pair is transferred from the base to the leaving group.

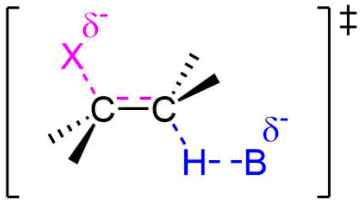



## E2 Reaction Transition State

Because the E2 reaction is predicted to follow a concerted mechanism only one transition state is expected in its energy coordinate diagram.



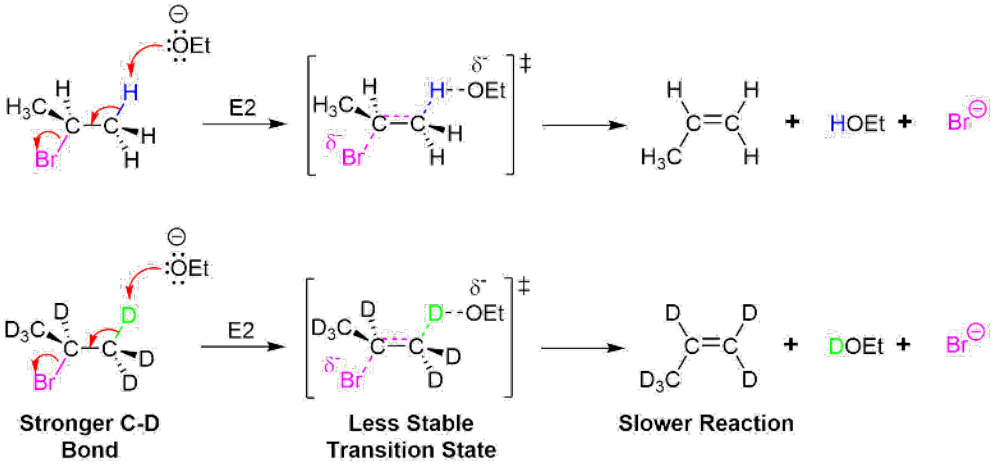

As the base begins to remove a hydrogen adjacent to the leaving group an H-B is starting to form and an H-C bond is in the process of breaking. Simultaneously, a C=C pi bond forms and the C-X bond breaks. During this reaction a set of electrons and a negative charge are transferred from the base to the leaving group. This is represented by a partial negative charge being present on both the base and the leaving group in the transition state.



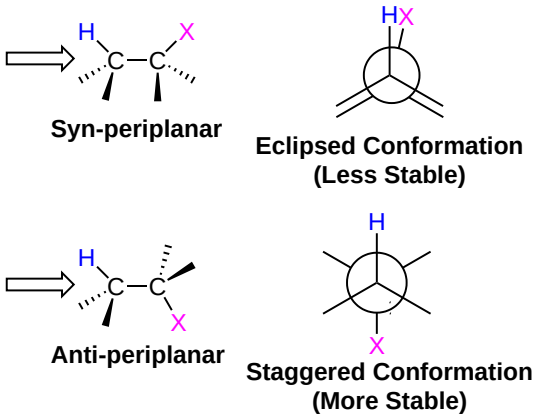
## Evidence for the E2 Mechanism and Transition State

Kinetic studies of E2 reactions show that they are second order overall and follow the rate law: rate = k[RX][Base]. This data is consistent with the predicted bimolecular E2 mechanism that includes both the alkyl halide and the base participating in the mechanism's rate-determining step.

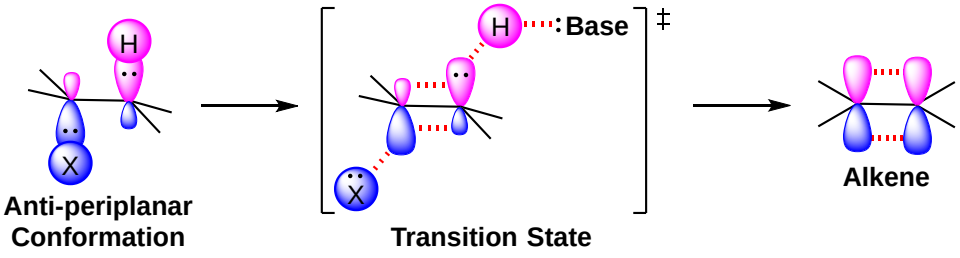
Further evidence for the predicted mechanism for the E2 reaction was provided by experiments involving the **deuterium isotope effect** (DIE). The **deuterium isotope effect** (DIE) is a phenomenon associated with molecules which have had hydrogen (H) atoms isotopically substituted with deuterium (D) atoms, exhibiting different reaction rates. The bond dissociation energy for C-D bonds is about 5 kJ/mol stronger than the bond dissociation energy of C-H bonds. This difference in energy results in a reduction in the rate of reaction, if the deuterium replacement occurs at a site of bond breaking in the rate determining step of a reaction. So if the rate-limiting step involves a breaking of this bond, as it does at the E2 transition state, there will be a substantial decrease in reaction rates when comparing deuterated and non-deuterated analogues. Indeed, the reaction of 2-bromopropane with sodium ethoxide (NaOEt) is 6.7 times faster than its deuterated counterpart, providing evidence that the C-H bond is broken during the rate determining step of the E2 mechanism. This is consistent with the predicted mechanism of the E2 reaction consisting of a single concerted step. If the rate-determining step was the leaving group bond breaking first (as in an E1 reaction) the deuterium substitution would not have caused an observable change in reaction rate.



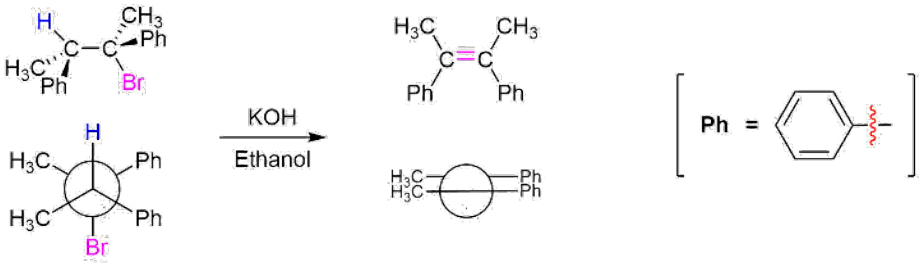

Yet another piece of evidence which supports the E2 mechanism comes when considering the stereochemistry of the elimination products. In the transition state of the E2 mechanism there are two carbons rehybridization from $sp^3$ to $sp^2$ while forming a π-bond. For good orbital overlap to occur during this change all the atoms involved in the reaction, the two carbons, the hydrogen, and the leaving group need to all lie in the same plane or **periplanar**. There are two possible ways this geometry can be achieved: **syn-periplanar** where the hydrogen and the leaving group are on the same side of the C-C bond and **anti-periplanar** where the hydrogen and the leaving group are on opposite sides of the C-C bond. To obtain a syn-periplanar geometry the substituents attached to the C-C bond must adopt an energetically unfavorable eclipsed conformation. The energy barrier to syn-orientation is such that syn-elimination is rarely observed in E2 reactions. E2 eliminations typically take place from the anti-periplanar conformation, as this is the most stable conformation due to the substituents attached to the C-C bond being staggered.




When viewing the transition state of the E2 mechanism when in the anti-periplanar conformation, the two $sp^3$ hybridized orbitals making up the C-H and C-X sigma bonds are in the same plane. When these two carbons rehybridization from $sp^3$ to $sp^2$, the p orbitals forming the π-bond will also have good overlap.

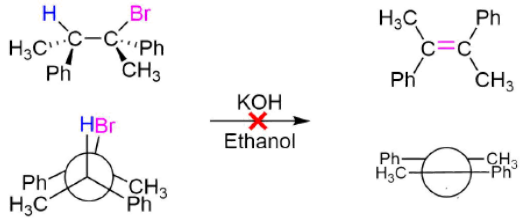



The stereochemical consequences of reactant molecules obtaining anti-periplanar geometry prior to E2 reactions has been observed in numerous experiments and provides further evidence of the proposed mechanism. For example, (2S, 3R)-2-bromo-2,3-diphenylbutane only forms (Z)-2,3-diphenyl-2-butene as a product of E2 elimination. To form the Z alkene isomer, the starting material must obtain the anti-periplanar geometry preferred for E2 reactions.




**2-Bromo-2,3-diphenylbutane (Anti-periplanar geometry)** **(Z)-2,3-Diphenyl-2-butene**

No isomeric E alkene product is formed because the starting materials would need to obtain a staggard, syn-periplanar geometry. The syn-periplanar geometry would be transferred to the transition state making it higher in energy and harder to form. The fact that only the Z alkene isomer forms provides further evidence that the E2 mechanism takes place by a single bimolecular step.

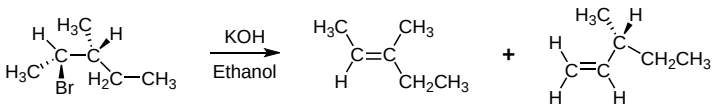



**2-Bromo-2,3-diphenylbutane (Syn-periplanar geometry)** **(E)-2,3-Diphenyl-2-butene (Not Formed!)**

## Predicting the Stereochemical Product of E2 Reactions

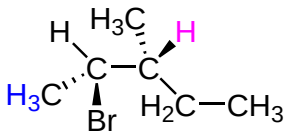
E2 reactions have the requirements of a leaving group and a hydrogen on a carbon adjacent to the leaving group carbon. For non-ringed compounds, the C-C can usually undergo free rotation to place the C-X and C-H bonds anti-periplaner to each other. Stereochemical considerations usually come into play when both of the carbons in the C-C bond are chiral. When these carbons are achiral but contain the other requirements for an E2 reaction, products lacking stereochemistry are usually produced.

When both of the carbons in the C-C bond are chiral, one carbon will have a leaving group and the other carbon will have a single hydrogen. To consider the stereochemistry of an E2 product, start by creating a Newman projection looking down the C-C bond. Then rotate the C-C bond until the C-X and C-H bonds are in the anti position. The Newman projection now shows the relative positioning of the substituents on the C-C bond as they will appear in the double bond formed. It should be noted that if syn elimination was possible, a positional isomer of the double bond will be created. Consider the elimination products for (2R, 3R)-2-bromo-3-methylpentane.

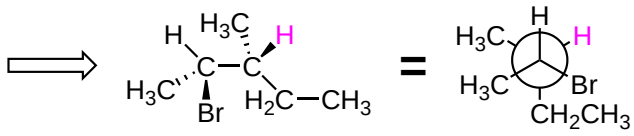



**Major** **Minor**

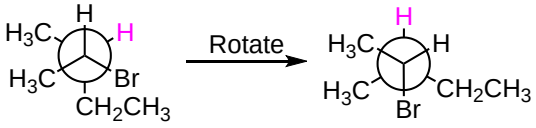
First, locate hydrogens on carbons adjacent to the leaving group. The compound used in this example has two unique sets of hydrogens.



Because the adjacent hydrogen colored fuchsia is attached to a chiral carbon it require special consideration. Convert the structure into a Newman projection along the C-C bond that will for the alkene elimination product. The C-C bond can be view down either direction and still product the correct product.

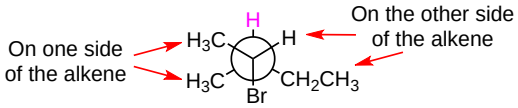


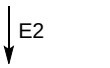
Then rotate such the the adjacent H and the leaving group are in the anti position.

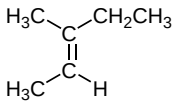



**Anti Position**

This Newman projection shows the relative positioning of the substituents on the double bond formed. Note, none of the Z isomer is formed because it would require syn orientation of the H and Br.

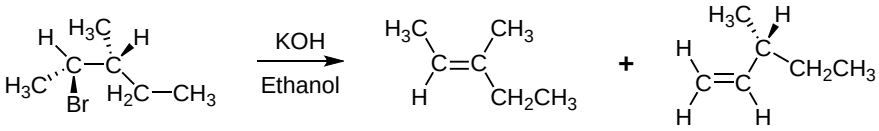


**(E)-3-Methyl-2-pentene**

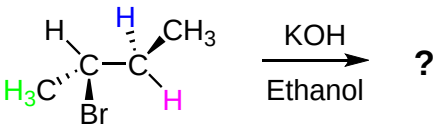
Lastly, consider the products made by other adjacent hydrogens and apply Zaitsev's rule to predict the preferred product.




**Major** **Minor**

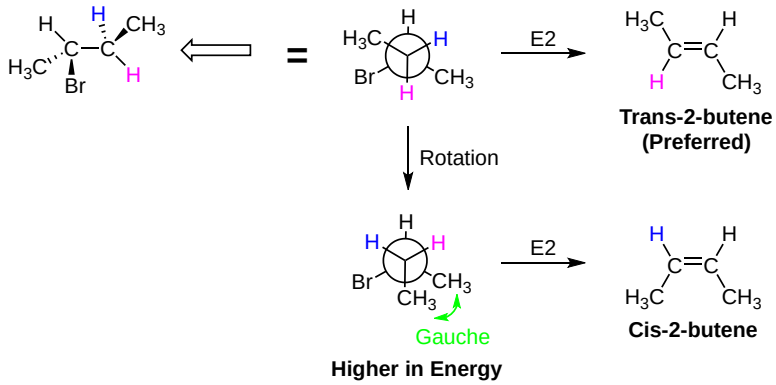
## Determining *Cis* and *Trans* Products in Elimination Reaction

Understanding that E2 reactions require an anti-periplanar geometry can explain cis and trans alkene isomers can form as products. This occurs as an important exception to the rule that stereoisomers only form as elimination products when both of the carbons in the C-C bond forming the alkene are chiral. When considering the E2 reaction products of (R)-2-butane, there are two groups of hydrogens on carbons adjacent to the leaving group a $CH_3$ and a $CH_2$.

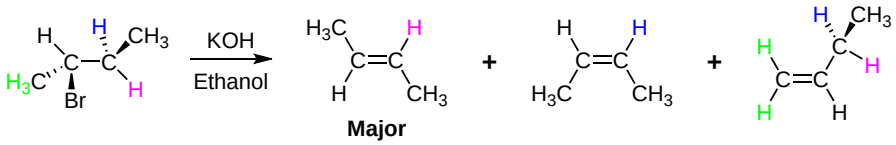



The carbon in the $CH_2$ group is achiral so both the H's appear to be equivalent. However, when the anti-periplanar geometry requirement is applied each hydrogen will produce its own unique product. Once the reactant is converted into a Newman projection it can be seen that the Br leaving group and the hydrogen colored blue are in the anti orientation and are ready to be eliminated. It should also be noted that the two $CH_3$ groups are also in the anti position which gives them the least amount of steric interaction possible. Because the $CH_3$ groups are on opposite sides of the Newman projection the $CH_3$ groups will be on opposite sides of the alkene thus creating the product *trans*-2-butene. When the Newman projection is rotated such that the fuchsia colored hydrogen is anti to the Br leaving group, the two $CH_3$ groups are now on the same. This orientation creates the isomer *cis*-2-butene. However, to obtain this orientation the two $CH_3$ groups must overcome the steric strain associated with a gauche conformation. This makes the transition state leading the cis isomer higher in energy and more difficult to form. Because of this, the trans isomer

will be the major product. It is clear that the two hydrogens of the $CH_2$ group are not equivalent despite their not being attached to a chiral carbon.

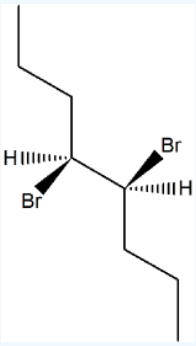



After considering all the products made during this E2 reaction the preferred product can be determined. The *cis* and *trans* isomer both have two alkene substituents while the third product only has one. Of the *cis* and *trans* isomer, the *trans* isomer is expected to be easier to form. Zaitsev's rule says that trans-2-butene will be the major product of this reaction.



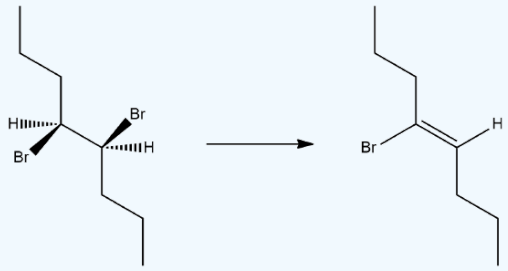

## Exercise 7.5.1

1) What is the product of the following molecule in an E2 reaction? What is the stereochemistry?



**Answer**

The stereochemistry is (*Z*) for the reaction.



## Contributors and Attributions

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- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
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# 7.6: The E2 Reaction and Cyclohexane Conformation

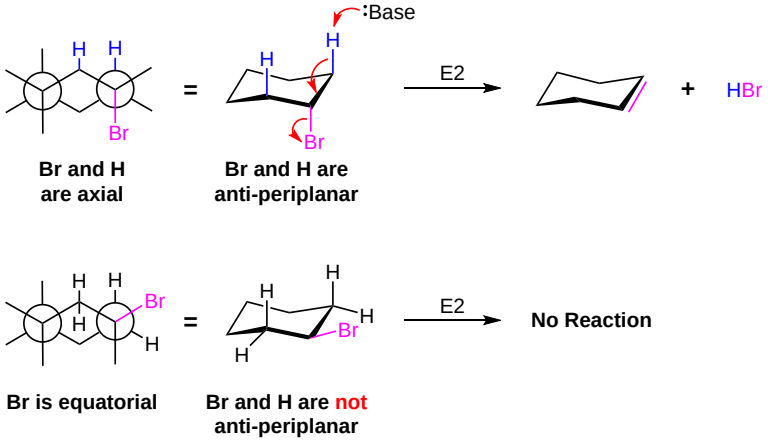
**Objectives**

After completing this section, you should be able to

1. identify anti periplanar arrangements of atoms in substituted cyclohexanes.
2. determine which cyclohexane conformation will generate a specific anti periplanar arrangement.

## Stereochemical Requirements of the E2 Reaction

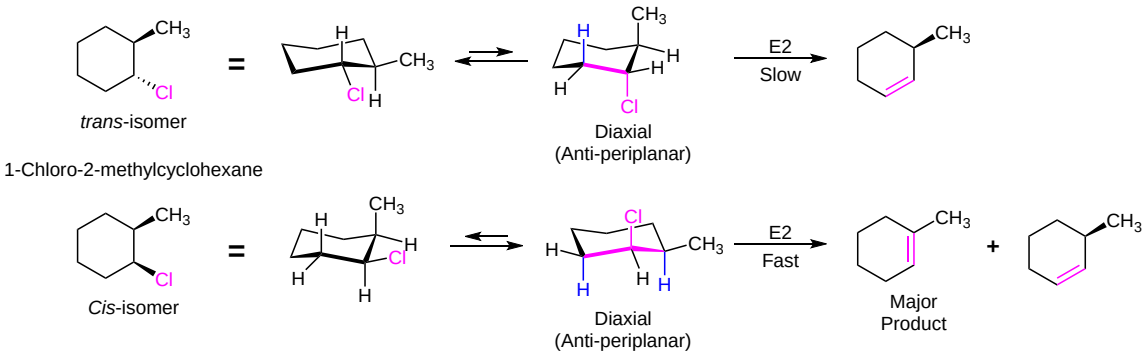
E2 elimination reactions of certain isomeric cycloalkyl halides show unusual rates and regioselectivity which can provide important supporting evidence that anti-periplanar is the preferred orientation of reactant species in the E2 transition state. Unlike open chain structures, cyclic compounds generally restrict the spatial orientation of ring substituents to relatively few arrangements. The compounds used here all have six-membered rings, so to achieve the anti-periplanar orientation required for the E2 reaction both the halogen and the adjacent hydrogen much assume an axial conformation.




For the compound, 2-methyl-1-chlorocyclohexane, the *cis* to the *trans* isomers have distinctly different reaction rates and form different preferred products. For example, *trans*-2-methyl-1-chlorocyclohexane reacts with alcoholic KOH at a much slower rate than does its *cis*-isomer. For trans-methyl-1-chlorocyclohexane, to obtains a chair conformation which places the chlorine substituent in the axial orientation required for E2 elimination, the methyl substituents is also forced into an axial position. Having both substituents in the axial position makes this chair conformer of the *trans*-isomer much less stable and presents an energy barrier that must be overcome for an E2 reaction to occur. When *cis*-2-methyl-1-chlorocyclohexane obtains a chair conformation which places its chlorine substituent in an axial orientation, the methyl substituent is forced into an equatorial orientation. Having one substituent axial and one equatorial makes this chair conformation of the cis-isomer lower in energy and thus easier to form. Consequently, the E2 reaction rates with the *trans*-isomer are slower than with the *cis*-isomer.

Furthermore, the product from E2 elimination of the *trans*-isomer is 3-methylcyclohexene (not predicted by Zaitsev's rule), whereas the *cis*-isomer gives the 1-methylcyclohexene as the preferred product (as predicted by Zaitsev's rule). The trans-isomer only has one adjacent hydrogen which can obtain an axial orientation along with the chlorine. The adjacent hydrogen which would lead to a 1-methylcyclohexene product cannot obtain the diaxial, anti-periplanar orientation with chlorine so an E2 reaction cannot occur. This makes 3-methylcyclohexene the preferred E2 elimination product of the *trans*-isomer showing that the anti-periplanar orientation requirement of E2 reactions is more important in determining products for this reaction than Zaitsev's rule.

In the *cis*-isomer the smaller chlorine atom assumes an axial position in the more stable chair conformation, and here there are two adjacent axial hydrogens. Removing one hydrogen forms the product, 3-methylcyclohexene, while removing the other hydrogen forms 1-methylcyclohexene. Here Zaitsev's rule determines that the more substituted alkene, 1-methylcyclohexene, is the preferred product.

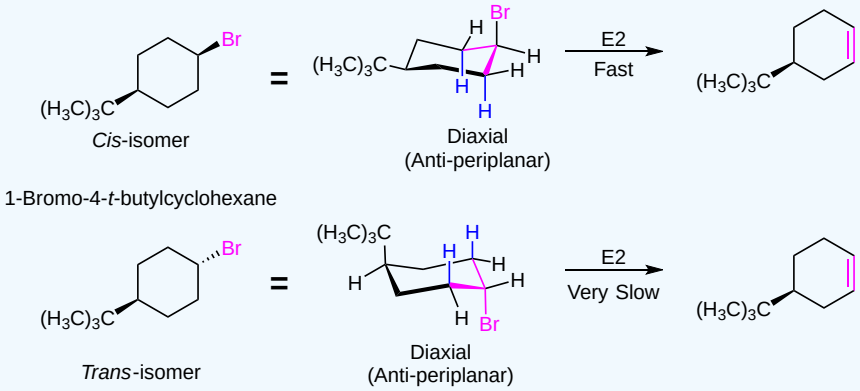



## Worked Exercise 7.6.1

Which isomer would be expected to undergo E2 elimination quicker cis or trans-1-bromo-4-tert-butylcyclohexane? Explain your answer.

**Answer**

In the case of the 1-bromo-4-tert-butylcyclohexane isomers, the tert-butyl group is so large that it will always assume an equatorial orientation, leaving the bromine to be axial in the *cis*-isomer and equatorial in the *trans*-isomer. Because of symmetry, the two axial adjacent hydrogens in the *cis*-isomer react equally with base, resulting in rapid elimination to the same alkene (actually a racemic mixture). This reflects the fixed anti orientation of these hydrogens to the bromine atom. To assume a conformation having an axial bromine, the *trans*-isomer must tolerate serious crowding distortions. Such conformers are therefore present in extremely low concentration, and the rate of elimination is very slow. Indeed, substitution by hydroxide anion predominates in this situation.

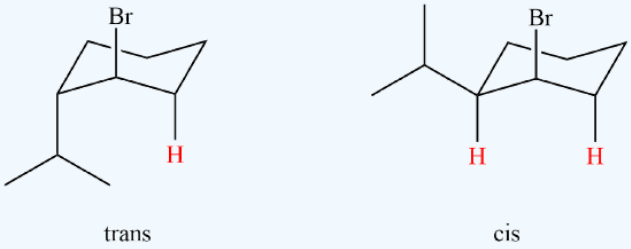



## Exercise 7.6.1

Which of the following compounds will react faster in an E2 reaction; *trans*-1-bromo-2-isopropylcyclohexane or *cis*-1-bromo-2-isopropylcyclohexane?

**Answer**

The *cis* isomer will react faster than the *trans*. The *cis* isomer has two possible perpendicular hydrogen in which it can eliminate from.




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# 7.7: The E1 and E1cB Reactions

**Key Terms**

Make certain that you can define, and use in context, the key terms below.

- E1 reaction
- E1cB reaction

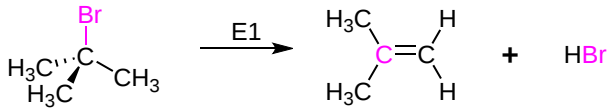
**Study Notes**

The abbreviation E1 stands for “unimolecular elimination”; that is, an E1 reaction is an elimination reaction in which only one species is involved in the rate-limiting step.

Unimolecular Elimination (E1) is a reaction in which the removal of an HX substituent results in the formation of a double bond. It is similar to a unimolecular nucleophilic substitution reaction ($S_N1$) in various ways. One being the formation of a carbocation intermediate. Also, the only rate determining (slow) step is the dissociation of the leaving group to form a carbocation, hence the name unimolecular. Thus, since these two reactions behave similarly, they compete against each other. Many times, both these reactions will occur simultaneously to form different products from a single reaction. However, one can be favored over another through thermodynamic control. Although Elimination entails two types of reactions, E1 and E2, we will focus mainly on E1 reactions with some reference to E2.

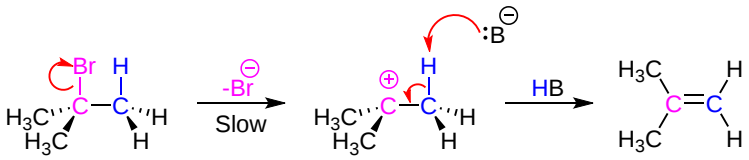
## General E1 Reaction

An E1 reaction involves the removal of the halogen leaving group followed by the deprotonation of an adjacent hydrogen to produce an alkene product. In order to accomplish this, a Lewis base is required.




## Mechanism

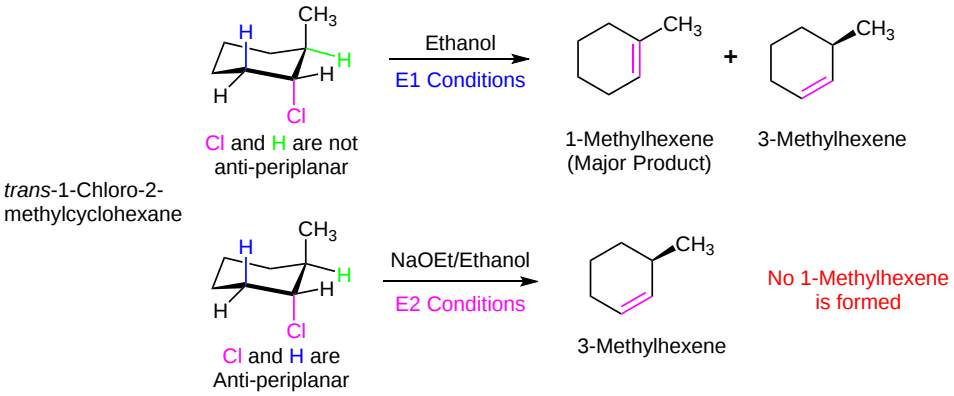
This mechanism starts with the spontaneous removal of the leaving group. The leaving group also removes the electrons from the C-Br bond, making the attached carbon a carbocation. In much the same fashion as the $S_N1$ mechanism, the first step of the E1 mechanism is slow thus making it the rate determining step. This makes E1 reaction kinetics unimolecular and first-order with respect to the substrate. Next, a Lewis Base ($B^-$) deprotonates an adjacent hydrogen from the carbocation. The electrons of the C-H bond are donated to the adjacent C-C bond, forming a double bond. Unlike E2 reactions, which require the adjacent proton to be *anti* to the leaving group, E1 reactions only require a neighboring hydrogen. This is due to the fact that the leaving group has left the molecule to form an achiral, trigonal planar carbocation.




## Evidence for the E1 Mechanism

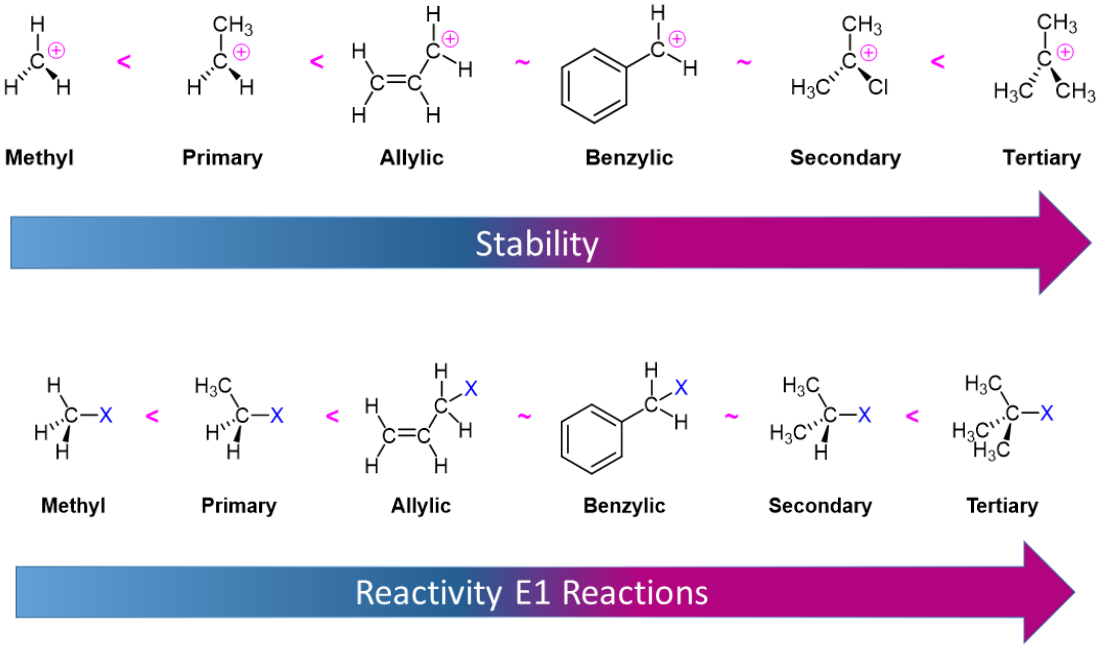
The primary evidence in support of the E1 mechanism is the fact that E1 reaction follow first-order kinetics which is consistent with the reaction mechanism containing a unimolecular dissociation as the rate determining step. Another piece of evidence is seen in the fact that E1 reactions show no deuterium isotope effect. Experiments have shown that there is no difference in reaction rate when deuterated and nondeuterated substrates are used. This is consistent with the E1 mechanism because a C-H bond is not broken in the rate determining step.

Lastly, because the halogen and hydrogen are removed in different steps, the mechanism of E1 reactions predicts that they will not require the anti-periplanar geometry required for E2 reactions. E1 reactions do not have the geometric constraints of E2 reactions discussed in **Sections 11-8** and **11-9**. In Section 11-9 an example showed that trans-1-Chloro-2-methylcyclohexane was capable of only forming the product 3-methylhexene during an E2 reaction due to the anti-periplanar constraints. When the same substrate is reacted under E1 conditions two elimination products (1-methylhexene and 3-methylhexene) are produced. In the substrate, the hydrogen marked as green cannot obtain anti-periplanar geometry with the Cl leaving group. Under E2 conditions this hydrogen and the Cl cannot be eliminated to form an elimination product. However, under E1 conditions the hydrogen and the Cl eliminate, despite the lack of anti-periplanar geometry, to form 1-methylhexene.




## Alkyl Halide Reactivity in E1 Reactions

Due to the fact that E1 reactions create a carbocation intermediate, reactivity of alkyl halides toward E1 reaction mirror those present in $S_N1$ reactions.

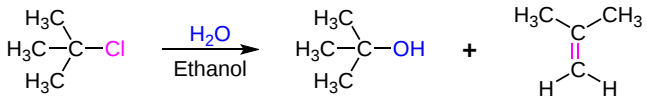



As expected, tertiary carbocations are favored over secondary, primary and methyl carbocations. This is due to the phenomena of hyperconjugation, which essentially allows a nearby C-C or C-H bond to interact with the p orbital of the carbon to bring the electrons down to a lower energy state. Thus, this has a stabilizing effect on the molecule as a whole. In general, primary and methyl carbocations do not proceed through the E1 pathway for this reason, unless there is a means of carbocation rearrangement to move the positive charge to a nearby carbon that is more stable. Secondary and Tertiary carbons form more stable carbocations, thus E1 reactions occur quite rapidly at these atoms.

Secondary carbocations can be subject to the E2 reaction pathway, but this generally occurs in the presence of a good/strong base. Adding a weak base to the reaction disfavors E2, essentially pushing towards the E1 pathway. In many instances, solvolysis occurs rather than using a base to deprotonate. This means heat is added to the solution, and the solvent itself deprotonates a hydrogen. The medium can effect the pathway of the reaction as well. Polar protic solvents may be used to hinder nucleophiles, thus disfavoring E2/$S_N2$ from occurring.

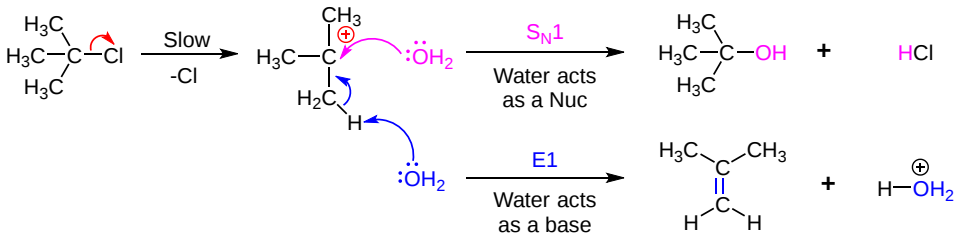
## The Connection Between $S_N1$ and E1 Reactions

The E1 and $S_N1$ mechanisms both begin with the rate-determing step, the unimolecular removal of a leaving group to form a carbocation intermediate. Sharing the rate-determining step causes alkyl halides to produce both $S_N1$ substitution and E1 elimination products whenever they are reacted with nonbasic nucleophiles in a protic solvent. For example, the hydrolysis of *tert*-butyl chloride in a solution of water and ethanol gives a mixture of 2-methyl-2-propanol (60%) and 2-methylpropene (40%) at a rate independent of the water concentration.




**2-Chloro-2-methylpropane** **2-Methyl-2-propanol (60%)** **2-Methylpropene (40%)**

To produce the alcohol product, water attacks the carbocation as a nucleophile as part of an $S_N1$ reaction. To produce the alkene product, water acts as a base and deprotonates an adjacent hydrogen as part of an E1 reaction. As expected, the mechanism of the two reactions have similar characteristics. They both show first order kinetics; neither is much influenced by a change in the nucleophile/base; and both are relatively non-stereospecific.




To summarize, when carbocation intermediates are formed one can expect them to react further by one or more of the following modes:

1. The cation may bond to a nucleophile to give a substitution product.
2. The cation may transfer a adjacent proton to a base, giving an alkene product.
3. The cation may rearrange to a more stable carbocation, and then react by mode #1 or #2.

## Comparing E1 and E2 Mechanisms

When considering whether an elimination reaction is likely to occur via an E1 or E2 mechanism, we really need to consider three factors:

1) **The base:** strong bases favor the E2 mechanism, whereas, E1 mechanisms only require a weak base.

2) **The alkyl halide:** primary alkyl halides have the only structure useful in distinguishing between the E2 and E1 pathways. Since primary carbocations do not form, only the E2 mechanism is possible.

**Ultimately, whether the elimination mechanism is E1 or E2 is not very important, since the product is the same alkene. We need to remember, however, that Zeitzev´s rule always determines the most likely alkene to be formed.**

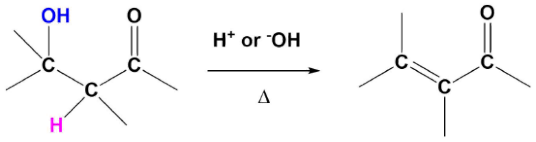
| Reaction Parameter | E2 | E1 |
|---|---|---|
| alkyl halide structure | tertiary > secondary > primary | tertiary > secondary >>>> primary |
| nucleophile | high concentration of a strong base | weak base |

| mechanism | 1-step | 2-step |
|---|---|---|
| rate limiting step | bimolecular transition state | carbocation formation |
| rate law | rate = k[R-X][Base] | rate = k[R-X] |

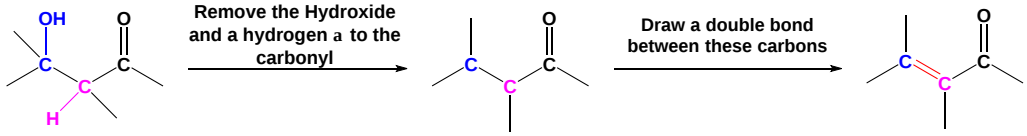
## The E1cB Reaction

Although E1 reactions typically involve a carbocation intermediate, the E1cB reaction utilizes a carbanion intermediate. A proton adjacent to a carbonyl group is removed using a strong base. This proton is acidic because the resulting conjugate base anion is stabilized by delocalization on to the carbonyl group. This anion causes the expulsion of an adjacent leaving group to create an alkene which is conjugated with the carbonyl which is called an enone. This reaction is generally utilized when a poor leaving group, such as a hydroxide, is involved. This poor leaving group makes the direct E1 or E2 reactions difficult. This reaction is used later in a reaction called an aldol condensation which will be discussed in **Section 23-3**.

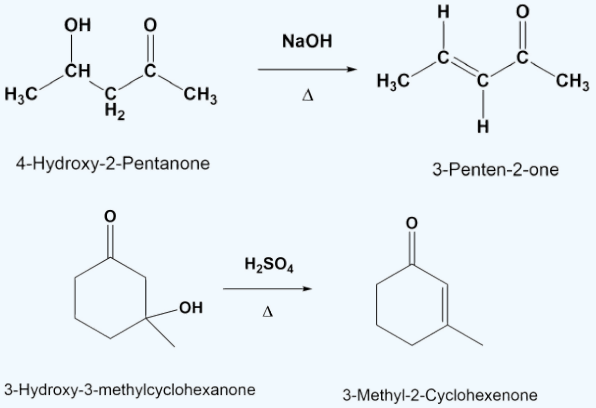
### General Reaction




### Predicting the Product of an E1cB Reaction



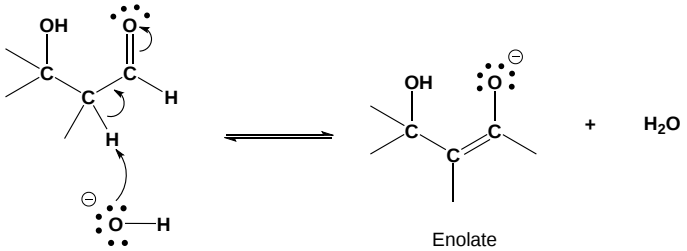

**Example 11.10.1**




## E1cB Mechanism

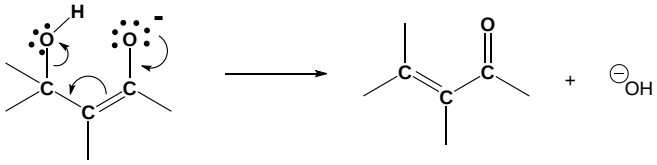
The mechanism starts with the base removing a hydrogen to form an alkoxide anion. The alkoxide reforms the carbonyl C=O bond promoting the elimination of alcohol OH as a leaving group which also reforms the base catalyst. Although the base catalyzed elimination of alcohols is rare, it happens in this case in part due to the stability of the conjugated enone product.

**1) Deprotonation to form the anion**




Enolate

**2) Leaving Group Removal**



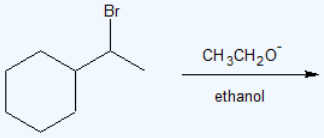

Enone

Note! The double bond always forms in conjugation with the carbonyl.

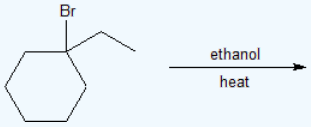
## Exercise 7.7.1

1. Predict the dominant elimination mechanism (E1 or E2) for each reaction below. Explain your reasoning.

a)

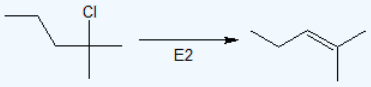



b)

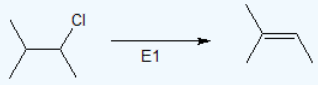



2) Specify the reaction conditions to favor the indicated elimination mechanism.

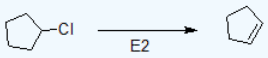
a)




b)

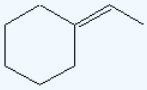


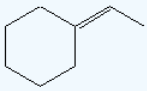

c)




**Answer**

1)

a)  E2 reaction b/c secondary alkyl halide with a strong base.

b)  E1 reaction b/c tertiary alkyl halide with a weak base.

2)

a) strong base, such as hydroxide, an alkoxide, or equivalent

b) water or alcohol or equivalent weak base with heat

c) strong base, such as hydroxide, an alkoxide, or equivalent

## Contributors and Attributions

- Dr. Dietmar Kennepohl FCIC (Professor of Chemistry, Athabasca University)
- Prof. Steven Farmer (Sonoma State University)
- William Reusch, Professor Emeritus (Michigan State U.), Virtual Textbook of Organic Chemistry
- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Layne A. Morsch (University of Illinois Springfield)

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# CHAPTER OVERVIEW

## 8: Additions


8.1: Electrophilic Addition Reactions (EARs)
8.2: Addition of Hydrogen Halides to Symmetrical Alkenes
8.3: Alkene Asymmetry and Markovnikov's Rule
8.4: Hydration- Acid Catalyzed Addition of Water
8.5: Addition of Halogens
8.6: Formation of Halohydrins
8.7: Stability of Alkenes
8.8: Reduction of Alkynes
8.9: Hydration of Alkenes - Addition of $H_2O$ by Hydroboration

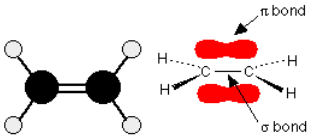

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# 8.1: Electrophilic Addition Reactions (EARs)

## Introduction

We are going to start by looking at ethene, because it is the simplest molecule containing a carbon-carbon double bond. What is true of C=C in ethene will be equally true of C=C in more complicated alkenes.



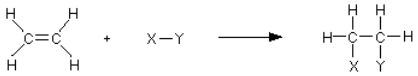

Ethene , $C_2H_4$, is often modeled as shown above. The double bond between the carbon atoms is, of course, two pairs of shared electrons. What the diagram doesn't show is that the two pairs aren't the same as each other. One of the pairs of electrons is held on the line between the two carbon nuclei as you would expect, but the other is held in a molecular orbital above and below the plane of the molecule. A molecular orbital is a region of space within the molecule where there is a high probability of finding a particular pair of electrons.

In this diagram, the line between the two carbon atoms represents a normal sigma bond - the pair of shared electrons lies in a molecular orbital on the line between the two nuclei where you would expect them to be. The other pair of electrons is found somewhere in the shaded part above and below the plane of the molecule. This bond is called a pi bond. The electrons in the pi bond are free to move around anywhere in this shaded region and can move freely from one half to the other. The pi electrons are not as fully under the control of the carbon nuclei as the electrons in the sigma bond. Because the pi bond electrons lie exposed above and below the rest of the molecule, they are relatively open to reaction with other compounds.

### Electrophilic Addition Reactions (EARs)

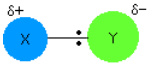
In a sense, the pi bond is an unnecessary bond. The structure would hold together perfectly well with a single bond rather than a double bond. The pi bond often breaks and the electrons in it are used to join other atoms (or groups of atoms) onto the alkene molecule. To continue with our example, ethene undergoes addition reactions. An addition reaction is a reaction in which two molecules join together to make a bigger one. Nothing is lost in the process. All the atoms in the original molecules are found in the bigger one. The pi bond is electron rich and takes the role of the nucleophile seeking out an electrophile with its full or partial positive charge.

Using a general molecule X-Y as the electrophile reacting with ethene, the atoms 'X' and 'Y' are added to the carbon chain across the vinylic carbons as shown below.

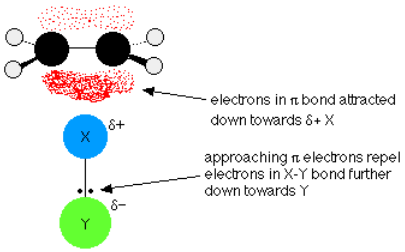



### Understanding the Electrophilic Addition Mechanism

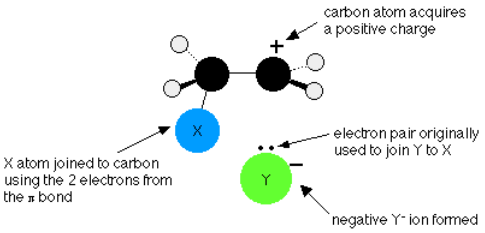
The mechanism for the reaction between ethene and a molecule X-Y begins by recognizing the electrophilic nature of X-Y. Trends in relative electronegativity help identify bonds to create partial positives within polar compounds. As shown below, we are going to assume that Y is more electronegative than X, so that the pair of electrons is pulled slightly towards the Y end of the bond. This polarity means that the X atom carries a slight positive charge (partial positive).



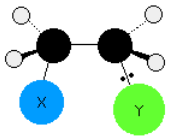

The slightly positive X atom is an electrophile and attracts the exposed pi electrons in the ethene. Now imagine what happens as they approach each other. The electrons in the half of the pi bond nearest the XY are attracted to the partial positive charge as shown below.




The two electrons in the pi bond move closer towards the X until a covalent bond is made. Simultaneously, the electrons in the X-Y bond are pushed entirely onto the Y to form the anion $Y^-$ ion and a carbocation as shown below.

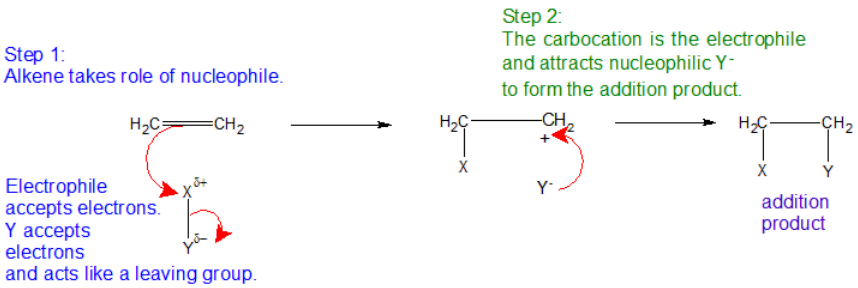



In the final step, the lone pair on $Y^-$ is attracted to the positively charged carbocation and they react to form a second covalent bond and the product below.




## EAR Mechanism

The movements of the electrons for the EAR mechanism are shown with curved arrows.




## Regiochemistry and Regioselective Reactions

Regiochemistry is the orientation of the electrophile relative to the pi bond of the alkene. Electrophilic addition reactions of alkenes can be regioselective depending on the symmetry and structure of the alkene. The details will be discussed in a later sections of this chapter.

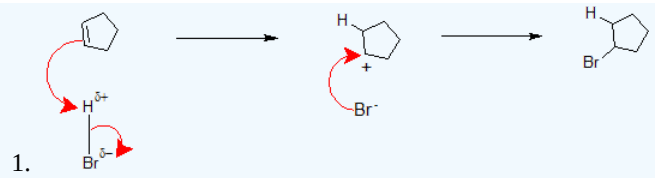
### Stereoselective Reactions

Different stereoisomeric reactants produce different stereoisomeric products. Electrophilic addition reactions of alkenes can be stereoselective depending on the symmetry and structure of the alkene. The details will be discussed in a later sections of this chapter.

**? Exercise 8.1.1**

1. In the next section, we will apply the Electrophilic Addition mechanism to actual compounds. Draw the complete mechanism when hydrogen bromide gas is bubbled through a solution of cyclopentene.

**Answer**

1. 


## Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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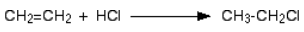
# 8.2: Addition of Hydrogen Halides to Symmetrical Alkenes

This section looks at the reaction of symmetrical alkenes (like ethene, but-2-ene or cyclohexene) with hydrogen halides such as hydrogen chloride and hydrogen bromide. Since these alkenes have identical groups attached to each end of the carbon-carbon double bond, regioselectivity does not apply.

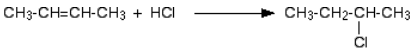
## Addition to symmetrical alkenes

All alkenes undergo addition reactions with the hydrogen halides. A hydrogen atom joins to one of the carbon atoms originally in the double bond, and a halogen atom to the other.

For example, with ethene and hydrogen chloride, you get chloroethane:




With but-2-ene you get 2-chlorobutane:

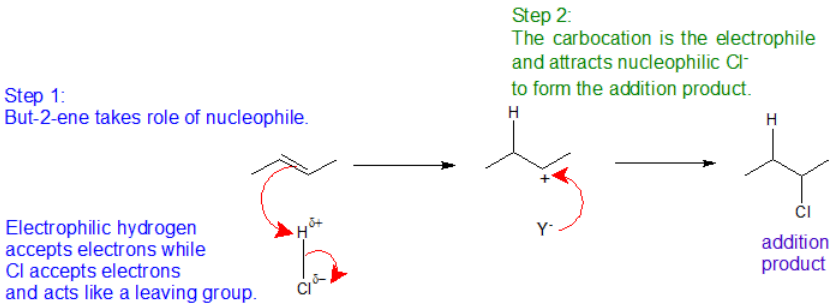



What happens if you add the hydrogen to the carbon atom at the right-hand end of the double bond, and the chlorine to the left-hand end? You would still have the same product. The chlorine would be on a carbon atom next to the end of the chain - you would simply have drawn the molecule flipped over in space. That would be different of the alkene was unsymmetrical - that's why we have to look at them separately.

## Mechanism

The addition of hydrogen halides is one of the easiest electrophilic addition reactions because it uses the simplest electrophile: the proton. Hydrogen halides provide both a electrophile (proton) and a nucleophile (halide). First, the electrophile will attack the double bond and take up a set of electrons, attaching it to the molecule (1). This is basically the reverse of the last step in the E1 reaction (deprotonation step). The resulting molecule will have a single carbon- carbon bond with a positive charge on one of them (carbocation). The next step is when the nucleophile (halide) bonds to the carbocation, producing a new molecule with both the original hydrogen and halide attached to the organic reactant (2). The second step will only occur if a good nucleophile is used.

*Mechanism of Electrophilic Addition of Hydrogen Chloride to But-2-ene*




All of the halides (HBr, HCl, HI, HF) can participate in this reaction and add on in the same manner. Although different halides do have different rates of reaction, due to the H-X bond getting weaker as X gets larger (poor overlap of orbitals)s.

## Reaction rates

**Variation of rates when you change the halogen**

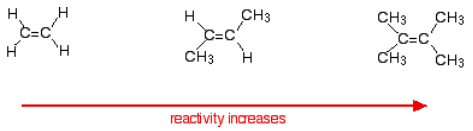
Reaction rates increase in the order HF < HCl < HBr < HI. Hydrogen fluoride reacts much more slowly than the other three, and is normally ignored in talking about these reactions.

When the hydrogen halides react with alkenes, the hydrogen-halogen bond has to be broken. The bond strength falls as you go from HF to HI, and the hydrogen-fluorine bond is particularly strong. Because it is difficult to break the bond between the hydrogen and the fluorine, the addition of HF is bound to be slow.

**Variation of rates when you change the alkene**

This applies to unsymmetrical alkenes as well as to symmetrical ones. For simplicity the examples given below are all symmetrical ones- but they don't have to be.

Reaction rates increase as the alkene gets more complicated - in the sense of the number of alkyl groups (such as methyl groups) attached to the carbon atoms at either end of the double bond. For example:



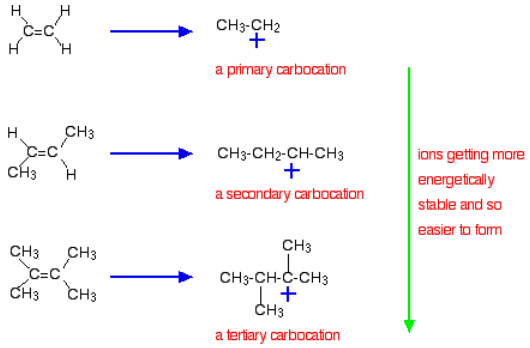

There are two ways of looking at the reasons for this - both of which need you to know about the mechanism for the reactions.

Alkenes react because the electrons in the pi bond attract things with any degree of positive charge. Anything which increases the electron density around the double bond will help this.

Alkyl groups have a tendency to "push" electrons away from themselves towards the double bond. The more alkyl groups you have, the more negative the area around the double bonds becomes.

The more negatively charged that region becomes, the more it will attract molecules like hydrogen chloride.

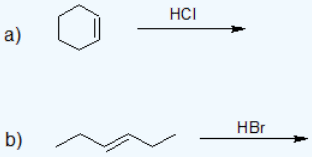
The more important reason, though, lies in the stability of the intermediate ion formed during the reaction. The three examples given above produce these carbocations (carbonium ions) at the half-way stage of the reaction:




The stability of the intermediate ions governs the activation energy for the reaction. As you go towards the more complicated alkenes, the activation energy for the reaction falls. That means that the reactions become faster.

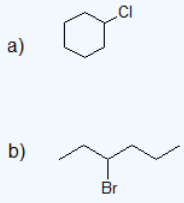
## Exercise

1. Draw the bond-line structures for the products of the following reactions.




**Answer**

1.



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- Jim Clark (Chemguide.co.uk)
- John D. Robert and Marjorie C. Caserio (1977) *Basic Principles of Organic Chemistry, second edition.* W. A. Benjamin, Inc. , Menlo Park, CA. ISBN 0-8053-8329-8. This content is copyrighted under the following conditions, "You are granted permission for individual, educational, research and non-commercial reproduction, distribution, display and performance of this work in any format."

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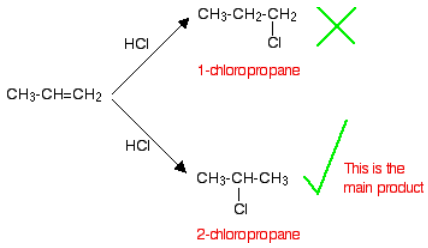
# 8.3: Alkene Asymmetry and Markovnikov's Rule

## Addition to unsymmetrical alkenes

In terms of reaction conditions and the factors affecting the rates of the reaction, there is no difference whatsoever between these alkenes and the symmetrical ones described above. The problem comes with the orientation of the addition of the hydrogen and the halogen across the double bond.

### Markovnikov's Rule

If HCl adds to an unsymmetrical alkene like propene, there are two possible ways it could add. However, in practice, there is only one major product according to Markovnikov's Rule.



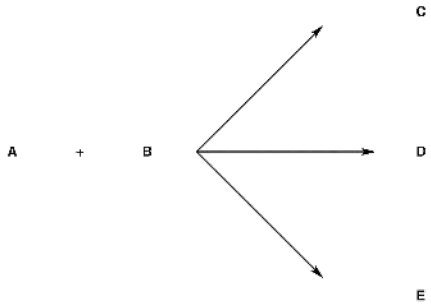

> Markovnikov's Rule: When HX is added to an unsymmetrical alkene, the hydrogen becomes attached to the carbon with the most hydrogens attached to it already.

Applying Markovnikov's Rule to the reaction above, the hydrogen bonds with the $CH_2$ group, because the $CH_2$ group has more hydrogens than the CH group. Notice that only the hydrogens directly attached to the carbon atoms at either end of the double bond count.

## Regioselectivity - a closer look

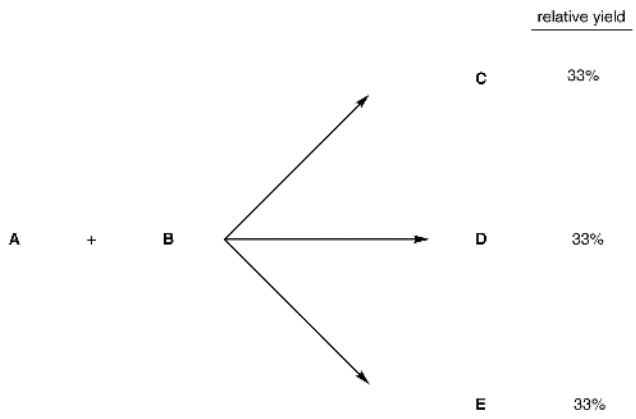
If more than one reaction could occur between a set of reactants under the same conditions giving products that are constitutional isomers and if one product forms in greater amounts than the others, the overall reaction is said to be regioselective.

Say three reactions could occur between the hypothetical reactants **A** and **B** under the same conditions giving the constitutionally isomeric products **C**, **D**, and **E**.



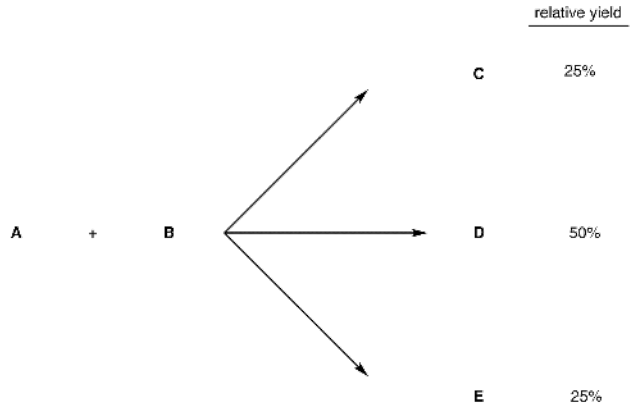

There are two possibilities:

1. The three products form in equal amounts, i.e., of the total product 33% is **C**, another 33% **D**, the remaining 33% **E**. (These percentages are called relative yields of the products.)



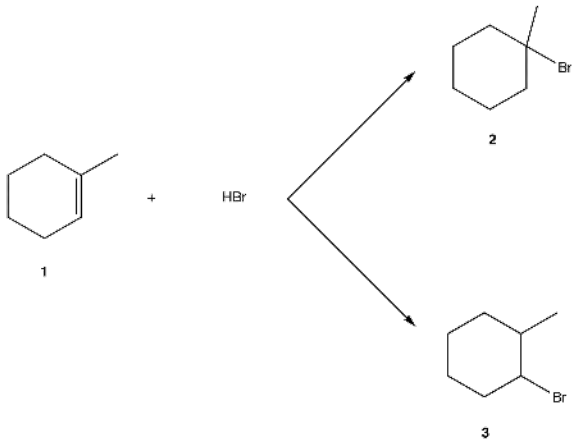

If this is what is observed, the overall reaction between **A** and **B** is not regioselective.

2. One product forms in greater amounts than the others. Say, for example, the relative yields of **C**, **D**, and **E** are 25%, 50%, and 25%, respectively.




If this is what is observed, the overall reaction between **A** and **B** is regioselective.

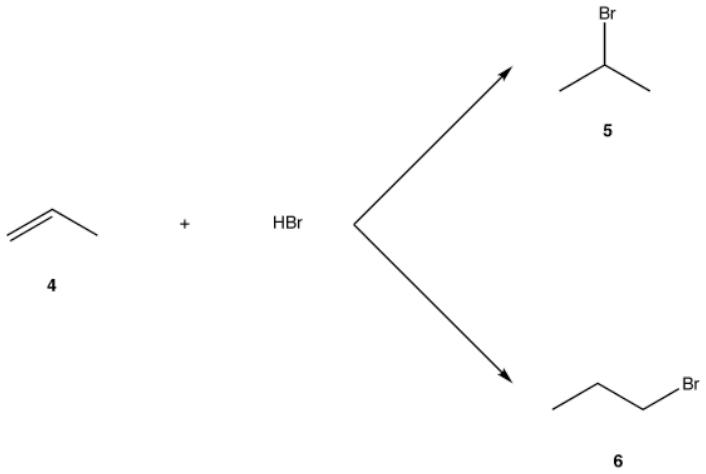
eg:




Experimentally, **2** is the major product; **3** is the minor product. Thus, the overall reaction between **1** and HBr is regioselective toward **2**.

If more than one reaction could occur between a set of reactants under the same conditions giving products that are constitutional isomers and if only one product is observed, the overall reaction is said to be 100% regioselective or regiospecific.

eg:

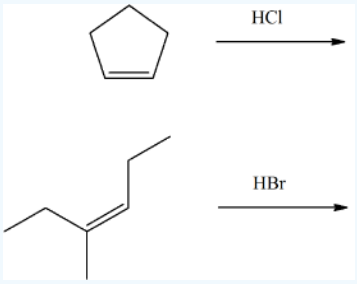



The only observed product is **5**. (Relative yields of **5** and **6** are 100% and 0%, respectively.) Thus the overall reaction between **4** and HBr is regiospecific toward **5**.

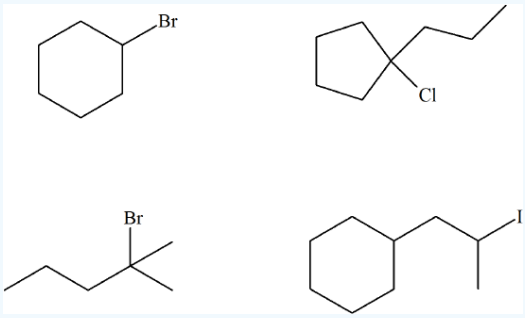
Regiospecificity is merely the limiting case of regioselectivity. All regiospecific reactions are regioselective, but not all regioselective reactions are regiospecific.

## ? Exercises

**1.** Predict the product(s) for the following reactions:

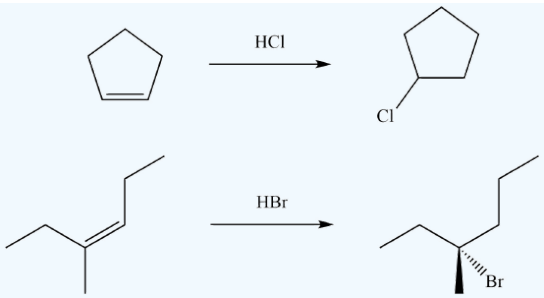



**2.** In each case, suggest an alkene that would give the product shown.

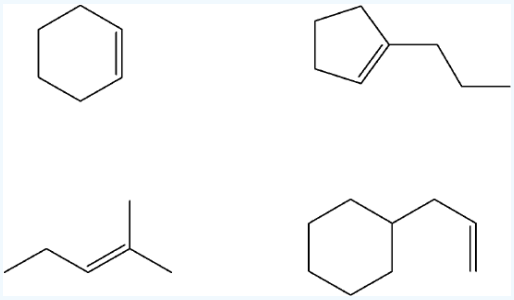



**Answers**

**1.**




**2.**



## Contributors and Attributions

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- Prof. Steven Farmer (Sonoma State University)
- Jim Clark (Chemguide.co.uk)
- Gamini Gunawardena from the OChemPal site (Utah Valley University)

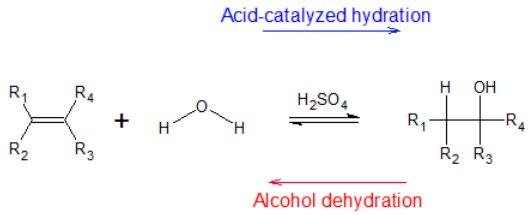
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# 8.4: Hydration- Acid Catalyzed Addition of Water

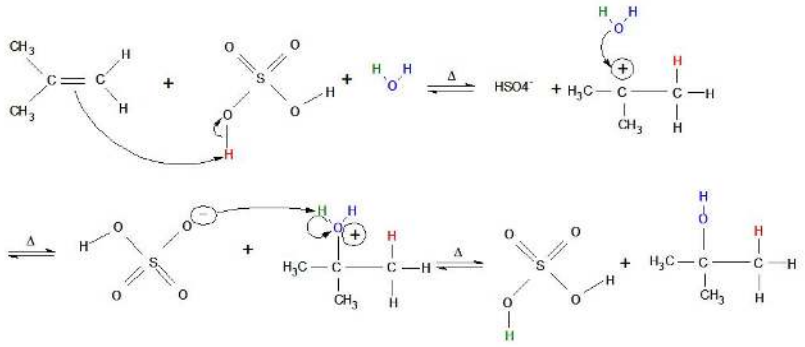
## What Is Electrophilic Hydration?

Electrophilic hydration is the addition of hydrogen and a hydroxyl group across the two carbons of a double bond. Electrophilic hydration is the reverse of dehydration of alcohols and so begins the circular nature of organic chemistry. Alcohols can be dehydrated to form alkenes and alkenes can undergo electrophilic addition reactions to form alcohols. Electrophilic hydrogen is essentially a proton: a hydrogen atom stripped of its electrons. Electrophilic hydrogen is commonly used to help break double bonds or restore catalysts.

Electrophilic hydration of alkenes has practical applications in making alcohols for fuels and reagents for other reactions. The basic reaction under certain temperatures (given below) is the following:




## Mechanism for Acid-catalyzed Hydration of Alkenes



### But...Why Does Electrophilic Hydration Work?

- An alkene placed in an aqueous non-nucleophilic strong acid immediately "reaches out" with its double bond and attacks one of the acid's hydrogen atoms (meanwhile, the bond between oxygen and hydrogen performs heterolytic cleavage toward the oxygen—in other words, both electrons from the oxygen/hydrogen single bond move onto the oxygen atom).
- A carbocation is formed on the original alkene (now alkane) in the more-substituted position, where the oxygen end of water attacks with its 4 non-bonded valence electrons (oxygen has 6 total valence electrons because it is found in Group 6 on the periodic table and the second row down: two electrons in a 2s-orbital and four in 2p-orbitals. Oxygen donates one valence electron to each bond it forms, leaving four 4 non-bonded valence electrons).
- After the blue oxygen atom forms its third bond with the more-substituted carbon, it develops a positive charge (3 bonds and 2 valence electrons give the blue oxygen atom a formal charge of +1).
- The bond between the green hydrogen and the blue oxygen undergoes heterolytic cleavage, and both the electrons from the bond move onto the blue oxygen. The now negatively-charged strong acid picks up the green electrophilic hydrogen.
- Now that the reaction is complete, the non-nucleophilic strong acid is regenerated as a catalyst and an alcohol forms on the most substituted carbon of the current alkane. At lower temperatures, more alcohol product can be formed.

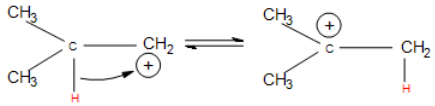
### What is Regiochemistry and How Does It Apply?

Regiochemistry deals with where the substituent bonds on the product. **Zaitsev**'s and **Markovnikov**'s rules address regiochemistry, but Zaitsev's rule applies when synthesizing an alkene while Markovnikov's rule describes where the substituent bonds onto the product. In the case of electrophilic hydration, Markovnikov's rule is the only rule that *directly* applies. See the following for an in-depth explanation of regiochemistry Markovnikov explanation: Radical Additions--Anti-Markovnikov Product Formation

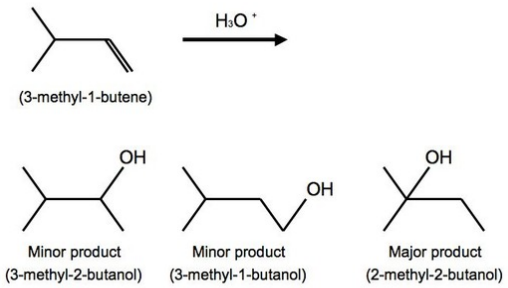
In the mechanism for a 3º alcohol shown above, the red H is added to the least-substituted carbon connected to the nucleophilic double bonds (it has less carbons attached to it). This means that the carbocation forms on the 3º carbon, causing it to be highly stabilized by *hyperconjugation*—electrons in nearby sigma (single) bonds help fill the empty p-orbital of the carbocation, which lessens the positive charge. More substitution on a carbon means more sigma bonds are available to "help out" (by using overlap) with the positive charge, which creates greater *carbocation stability*. In other words, **carbocations form on the most substituted carbon** connected to the double bond. Carbocations are also stabilized by resonance, but resonance is not a large factor in this case because any carbon-carbon double bonds are used to initiate the reaction, and other double bonded molecules can cause a completely different reaction. If the carbocation does originally form on the less substituted part of the alkene, carbocation rearrangements occur to form more substituted products.

## Carbocation Rearrangements - a review

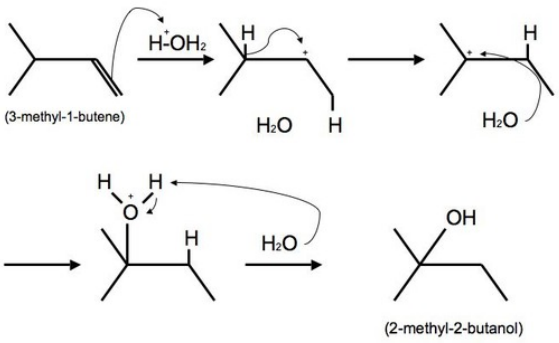
- **Hydride shifts:** a hydrogen atom bonded to a carbon atom next to the carbocation leaves that carbon to bond with the carbocation (after the hydrogen has taken both electrons from the single bond, it is known as a hydride). This changes the once neighboring carbon to a carbocation, and the former carbocation becomes a neighboring carbon atom.



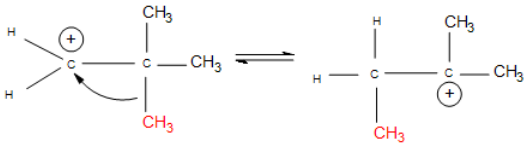

In a more complex case, when alkenes undergo hydration, we also observe hydride shift. Below is the reaction of 3-methyl-1-butene with $H_3O^+$ that furnishes to make 2-methyl-2-butanol:




Once again, we see multiple products. In this case, however, we see two minor products and one major product. We observe the major product because the -OH substitutent is attached to the more substituted carbon. When the reactant undergoes hydration, the proton attaches to carbon #2. The carbocation is therefore on carbon #2. Hydride shift now occurs when the hydrogen on the adjacent carbon formally switch places with the carbocation. The carbocation is now ready to be attacked by $H_2O$ to furnish an alkyloxonium ion because of stability and hyperconjugation. The final step can be observed by another water molecule attacking the proton on the alkyloxonium ion to furnish an alcohol. We see this mechanism below:




- **Alkyl shifts:** if no hydrogen atoms are available for a hydride shift, an entire methyl group performs the same shift.

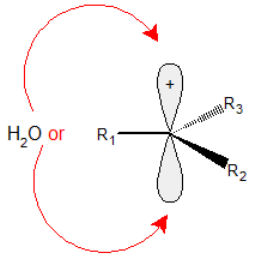


The nucleophile attacks the positive charge formed on the most substituted carbon connected to the double bond, because the nucleophile is seeking that positive charge. In the mechanism for a 3º alcohol shown above, water is the nucleophile. When the green H is removed from the water molecule, the alcohol attached to the most substituted carbon. Hence, **electrophilic hydration follows Markovnikov's rule.**

## Stereochemistry of Acid-catalyzed Hydration

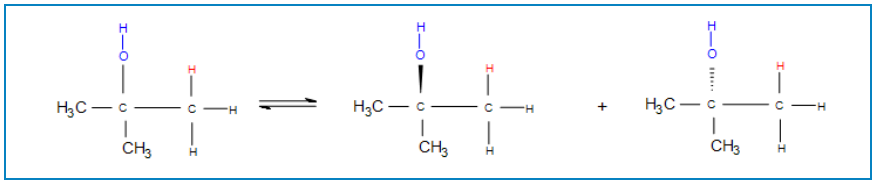
**Stereochemistry deals with how the substituent bonds on the product directionally**. Dashes and wedges denote stereochemistry by showing whether the molecule or atom is going into or out of the plane of the board. Whenever the bond is a simple single straight line, the molecule that is bonded is equally likely to be found going into the plane of the board as it is out of the plane of the board. This indicates that **the product is a racemic mixture**.

There is no stereochemical control in acid-catalyzed hydration reactions. The carbocation intermediate has the trigonal planar geometry of $sp^2$ hybridization which allows the subsequent reaction with water from either orientation.




There is no stereochemical control with a carbocation intermedate.

Electrophilic hydration adopts a stereochemistry wherein the substituent is equally likely to bond pointing into the plane of the board as it is pointing out of the plane of the board. The 3º alcohol product could look like either of the following products:



Note: Whenever a straight line is used along with dashes and wedges on the same molecule, it could be denoting that the straight line bond is in the same plane as the board. Practice with a molecular model kit and attempting the practice problems at the end can help eliminate any ambiguity.

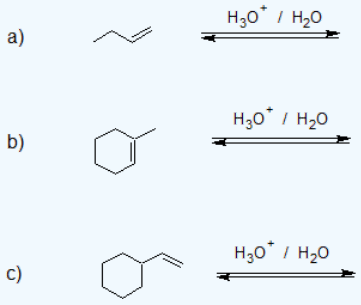
### Is this a Reversible Synthesis?

Electrophilic hydration is reversible because an alkene in water is in equilibrium with the alcohol product. To sway the equilibrium one way or another, the temperature or the concentration of the non-nucleophilic strong acid can be changed. For example:

- Less sulfuric or phosphoric acid and an excess of water help synthesize more alcohol product.
- Lower temperatures help synthesize more alcohol product.

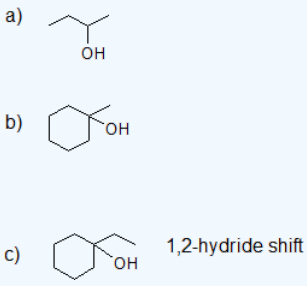
**? Exercise**

1. Draw the bond-line structure for the major product of each reaction.




**Answer**

1.




## Contributors and Attributions

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- Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)
- Jim Clark (Chemguide.co.uk)
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# 8.5: Addition of Halogens

**Learning Objective**

- predict the products/specify the reagents for halogenation of alkenes

## Introduction

As the halogen molecule, for example $Br_2$, approaches the double bond of an alkene, electrons in the double bond repel electrons in the bromine molecule causing polarization of the halogen bond. This interaction induces a dipole moment in the halogen molecule bond allowing one of the halogens to gain a partial positive charge and take the role of electrophile. The nucleophilic pi electrons form a bond to the electrophilic halogen while the halogen molecular bond heterolytically breaks to release bromide as a leaving group. The halogen addition is not regioselective but stereoselective. Stereochemistry of this addition is analogous to the oxymercuration mechanism. In this reaction, a bromonium (halogenium) ion froms as the intermediate. The bromonium ion formation stabilizes the positive charge and prevents carbocation rearrangement. In the second step, the bromide released from the first step takes the role of thenucleophile and reacts with the cyclic bromonium ion with back side orientation. Therefore, the stereochemistry of the product is a **vicinial dihalides** through **anti-addition**.

$$R_2C{=}CR_2 + X_2 \rightarrow R_2CX{-}CR_2X \tag{8.5.1}$$

Halogens that are commonly used in this type of the reaction are: $Br_2$ and $Cl_2$. In thermodynamical terms $I_2$ is too slow for this reaction because of the size of its atom, and $F_2$ is too vigorous and explosive. Solvents that are used for this type of electrophilic halogenation are inert (e.g., $CCl_4$) can be used in this reaction.

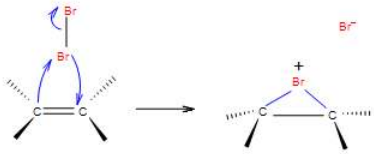
Because halogen with negative charge can attack any carbon from the opposite side of the cycle it creates a mixture of steric products.Optically inactive starting material produce optically inactive achiral products (meso) or a racemic mixture.

### Electrophilic addition mechanism consists of two steps.

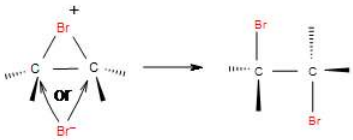
Before constructing the mechanism let us summarize conditions for this reaction. We will use $Br_2$ in our example for halogenation of ethylene. Halogens can act as electrophiles due to polarizability of their covalent bond. Addition of halogens is stereospecific and produces vicinial dihalides with anti-addition. Cis starting materials will give a mixture of enantiomers and trans starting materials produce a meso compound.

| | |
|---|---|
| Nucleophile | pi electrons of alkene double bond |
| Electrophile | halogen ($Cl_2$ or $Br_2$) |
| Regiochemistry | none |
| Stereochemistry | anti-additon |

Step 1: The addition the Br-Br bond polarizes, heterolytic cleavage occurs and Br with the positive charge forms a intermediate cycle with the double bond.

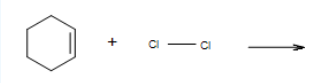



Step 2: The bromide anion reacts with either carbon of the bridged bromonium ion from the back side of the ring. The ring opens up and the two halogens are in the **anti-position** relative to each other.



Exercise

1. What is the mechanism of adding $Cl_2$ to the cyclohexene?

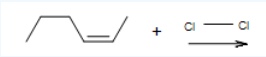


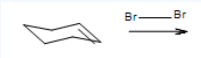
2. A reaction of $Br_2$ molecule in an inert solvent with alkene follows?

a) syn addition

b) anti addition

c) Morkovnikov rule

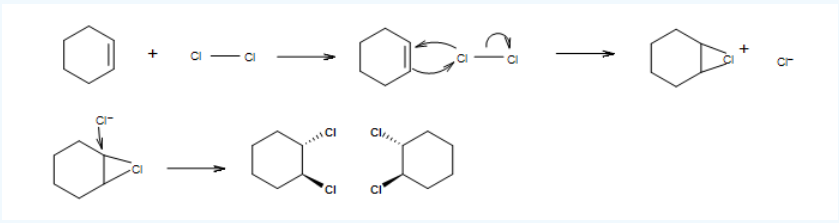
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4. 

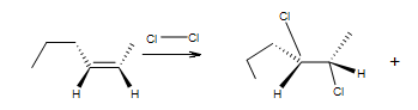
**5.** Predict the product of the product of 1,2-dimethylcyclopentene reacting with $Br_2$ with proper stereochemistry.

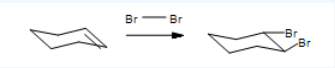
**6.** Predict the products for 1,2-dimethylcyclpentene reacting with HCl, give the proper stereochemistry. What is the relationship between the two products?

**Answer**

1. 

2. b

3.  enantiomer

4. 

**5.**



**6.**



> These compounds are enantiomers.

## References


1. Vollhard,K.Peter C., and Neil E.Schore.Organic Chemistry:Structure and Function.New Yourk: W.H.Freeman and Company 2007
2. Chemestry-A Europian Journal 9 (2003) :1036-1044


## Contributors and Attributions

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- Jim Clark (Chemguide.co.uk)

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# 8.6: Formation of Halohydrins

**Learning Objective**

- predict the products/specify the reagents for hydrohalogenation of alkenes

## Introduction

The proton is not the only electrophilic species that initiates addition reactions to the double bond of alkenes. Lewis acids like the halogens, boron hydrides and certain transition metal ions are able to accept the alkene pi-electrons. The resulting positively charged intermediates attract nucleophiles to give addition products.The electrophilic character of the halogens is well known. Fluorine adds uncontrollably with alkenes, and the addition of iodine is unfavorable, so these are not useful preparative methods. Chlorine ($Cl_2$) and bromine ($Br_2$) react selectively with the double bond of alkenes, so we will focus on these reactions.

The addition of chlorine and bromine to alkenes, as shown below, produces vicinal dihalo-compounds. In this reaction, we can assume that the solvent was something that is not nucleophilic, such as tetrahydrofuran (THF).

$R_2C{=}CR_2 + X_2 \longrightarrow R_2CX\text{-}CR_2X$

If this same reaction is performed in a nucleophilic solvent like water or an alcohol, then the solvent becomes the nucleophile in the second step and reacts with the bromonium (or chloronium) ion to form a halohydrin as shown below.

$$R_2C{=}CR_2 + X_2 + H_2O \longrightarrow R_2COH\text{-}CR_2X$$

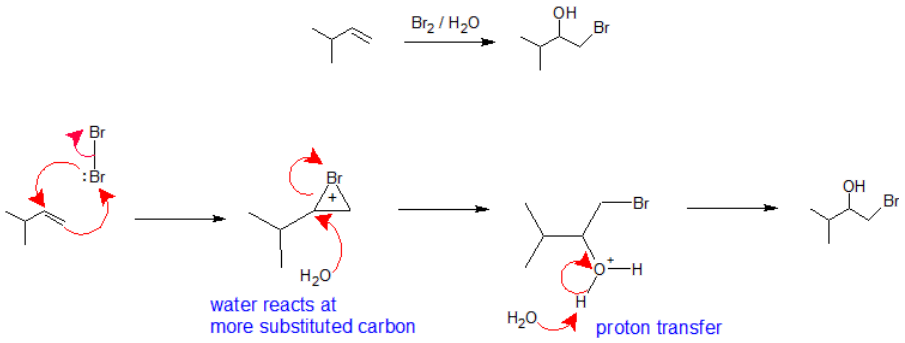
There are also other halogen-containing reagents that add to double bonds, such as hypohalous acids, HOX, and sulfenyl chlorides, RSCl. These reagents are unsymmetrical, so their addition to unsymmetrical double bonds may in principle take place in two ways. In practice, these addition reactions are regioselective, with one of the two possible constitutionally isomeric products being favored. The electrophilic moiety in both of these reagents is the halogen.

$(CH_3)_2C{=}CH_2 + HOBr \longrightarrow (CH_3)_2COH\text{-}CH_2Br$

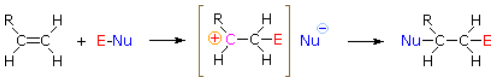
$(CH_3)_2C{=}CH_2 + C_6H_5SCl \longrightarrow (CH_3)_2CCl\text{-}CH_2SC_6H_5$

## Mechanisms explain the Regioselectivity

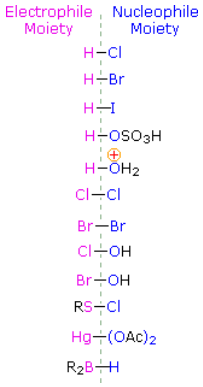
$X_2/H_2O$ or $X_2$/ROH: The regioselectivity of halohydrin formation from an alkene reaction with a halogen in a nucleophilic solvent is analogous to the oxymercuration-demercuration pathway. The halogen molecule takes the role of electrophile accepting nucleophilic pi electrons from the alkene while simultaneously forming a bond with the other vinyl carbon to create a bromonium (or chloroium) ion. The bromonium (or chloronium) ion formation stabilizes the positive charge and prevents carbocation rearrangement. The solvent takes the role of the nucleophile because it is present is a much greater percentage than the leaving group and reacts with the most substituted carbon of the cyclic bromonium (or chloronium) ion to create regiochemistry. The stereochemistry of this reaction is anti-addition because the solvent approaches the bromonium ion with back side orientation to produce the addition product. However, since the interaction of the halogen with the alkene can occur from above or below, there is no stereochemical control in this reaction and a mixture of enantiomers will be produced when applicable. The final step of this mechanism is a proton transfer to a solvent water molecule to neutralize the addition product.



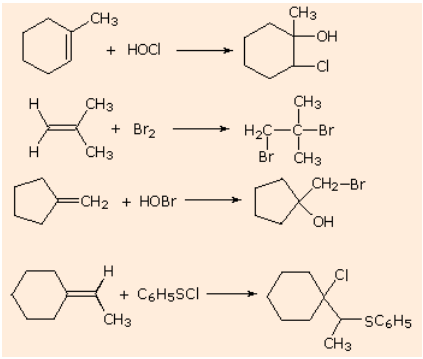
HOX or RSCl: The regioselectivity of the hypohalous acids and sulfenyl chloride reactions may be explained by the same mechanism we used to rationalize the Markovnikov rule. Bonding of an electrophilic species to the double bond of an alkene forms preferentially to produce the more stable (more highly substituted) carbocation. This intermediate should then combine rapidly with a nucleophilic species to produce the addition product.



To apply this mechanism we need to determine the electrophilic moiety in each of the reagents. By using electronegativity differences we can dissect common addition reagents into electrophilic and nucleophilic moieties, a**s shown on the right**. In the case of hypochlorous and hypobromous acids (HOX), these weak Brønsted acids (pKa's ca. 8) do not react as proton donors; and since oxygen is more electronegative than chlorine or bromine, the electrophile will be a halide cation. The nucleophilic species that bonds to the intermediate carbocation is then hydroxide ion, or more likely water (the usual solvent for these reagents), and the products are called halohydrins. Sulfenyl chlorides add in the opposite manner because the electrophile is a sulfur cation, RS(+), whereas the nucleophilic moiety is chloride anion (chlorine is more electronegative than sulfur).

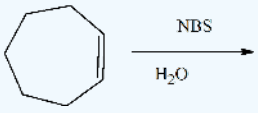



Below are some examples illustrating the addition of various electrophilic halogen reagents to alkene groups. Notice the specific regiochemistry of the products, as explained above.



## Exercise

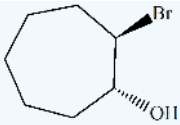
**1.** Predict the product of the following reaction:




**2.** When butene is treated with NBS in the presence of water, the product shows that the bromine is on the least substituted carbon, is this Markovnikov or anti-Markovnikov?

**Answer**

**1.**




**2.** Since the bromine is the first addition to the alkene, this addition would be an anti-Markovnikov addition.

## Contributors

- Prof. Steven Farmer (Sonoma State University)
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# 8.7: Stability of Alkenes

## Objectives

After completing this section, you should be able to

- explain why *cis* alkenes are generally less stable than their *trans* isomers.
- explain that catalytic reduction of a *cis* alkene produces the same alkane as the catalytic reduction of the *trans* isomer.
- explain how heats of hydrogenation ($\Delta H°_{hydrog}$) can be used to show that *cis* alkenes are less stable than their *trans* isomers, and discuss, briefly, the limitations of this approach.
- arrange a series of alkenes in order of increasing or decreasing stability.
- describe, briefly, two of the hypotheses proposed to explain why alkene stability increases with increased substitution. [**Note:** This problem is a typical example of those instances in science where there is probably no single "correct" explanation for an observed phenomenon.]

## Key Terms

Make certain that you can define, and use in context, the key terms below.

- catalytic hydrogenation
- heat of hydrogenation ($\Delta H°_{hydrog}$)
- hyperconjugation

## Study Notes

The two alkenes, *cis*-$CH_3CH{=}CHCH_3$ and $(CH_3)_2C{=}CH_2$ have similar heats of hydrogenation (−120 kJ/mol and −119 kJ/mol, respectively), and are therefore of similar stability. However, they are both less stable than *trans*-$CH_3CH{=}CHCH_3$ (−116 kJ/mol).

You may wonder why an $sp^2$ -$sp^3$ bond is stronger than an $sp^3$-$sp^3$ bond. Bond strength depends on the efficiency with which orbitals can overlap. In general, *s* orbitals overlap more efficiently than do *p* orbitals; therefore, the *s*-*s* bond in the hydrogen molecule is stronger than the *p*-*p* bond in fluorine. In hybrid orbitals, the greater the *s* character of the orbital, the more efficiently it can overlap: an $sp^2$ orbital, which has a 33% *s* character, can overlap more effectively than an $sp^3$ orbital, with only 25% *s* character.

## Hydrogenation

Alkene hydrogenation is the addition of hydrogen gas ($H_2$) to an alkene which saturates the bond and forms an alkane. Alkene hydrogenation reactions require a transition metal catalyst, such as Pt or Pd, to speed up the reaction. The hydrogenation reaction is used in this section to investigate the stability of alkenes, however, it will be discussed in greater detail in **Section 8.7**. Hydrogenation reactions are exothermic and the enthalpy change in this reaction is called the heat of hydrogenation ($\Delta H°_{hydrog}$). Since the double bond is breaking in this reaction, the energy released during hydrogenation is proportional to the energy in the double bond of the molecule. By comparing the heat of hydrogenations from a series of alkenes that produce the same alkane, a quantitative measure of relative alkene stabilities can be produced. These experiments will lead to an general understanding of structural features which tend to stabilize or destabilize alkenes.

## The Catalyst

A catalyst increases the reaction rate by lowering the activation energy of the reaction. Although the catalyst is not consumed in the reaction, it is required to accelerate the reaction sufficiently to be observed in a reasonable amount of time. Catalysts commonly used in alkene hydrogenation are: platinum, palladium, and nickel. The metal catalyst acts as a surface on which the reaction takes place. This increases the rate by putting the reactants in close proximity to each other, facilitating interactions between them. With this catalyst present, the sigma bond of $H_2$ breaks, and the two hydrogen atoms instead bind to the metal (see #2 in the figure below). The $\pi$ bond of the alkene weakens as it also interacts with the metal (see #3 below).

Since both the reactants are bound to the metal catalyst, the hydrogen atoms can easily add, one at a time, to the previously double-bonded carbons (see #4 and #5 below). The position of both of the reactants bound to the catalyst makes it so the hydrogen atoms are only exposed to one side of the alkene. This explains why the hydrogen atoms add to same side of the molecule, called syn-addition.

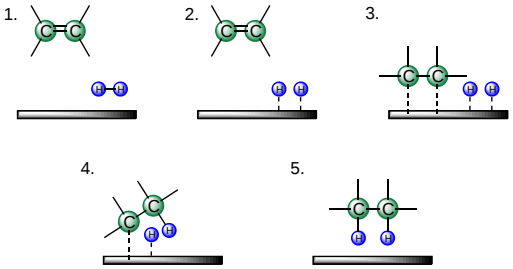


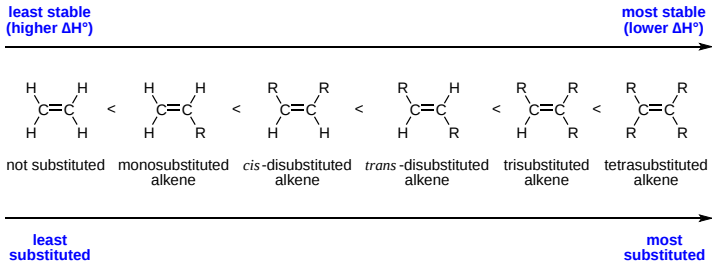

Figure 8.7.1: *Hydrogenation takes place in the presence of a metal catalyst.*

**Note**

The catalyst remains intact and unchanged throughout the reaction.

## Heats of Hydrogenation

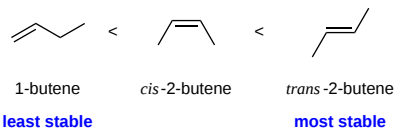
The stability of alkene can be determined by measuring the amount of energy associated with the hydrogenation of the molecule. Since the double bond is breaking in this reaction, the energy released in hydrogenation is proportional to the energy in the double bond of the molecule. This is a useful tool because heats of hydrogenation can be measured very accurately. The $\Delta H^o$ is usually around -30 kcal/mol for alkenes. Stability is simply a measure of energy. Lower energy molecules are more stable than higher energy molecules. More substituted alkenes are more stable than less substituted ones due to hyperconjugation. They have a lower heat of hydrogenation. The following illustrates stability of alkenes with various substituents:




## Cis/Trans Isomers

Between cis and trans isomers of an alkene, the cis isomer tends to be less stable due to the molecular crowding created nonbonding interaction between two alky groups on the same side of the double bond. The crowding creates steric strain which distorts bond angles creating less effective bond orbital overlap and desabilizing the molecule. Steric strain has previously been seen in gauche interactions in Newman projections (**Section 3.7**) and 1,3-diaxial interactions in substituted cyclohexanes (**Section 4.7**). Steric strain is directly related to the size of the species being crowded. The difference in energy between *cis* and *trans* 2-butene is 5 kJ/mol, however, this difference would be greater if larger group were being held in the *cis* position. Two *cis*-*tert*-butyl group can create over 40 kJ/mol of steric strain.

See the following isomers of butene:



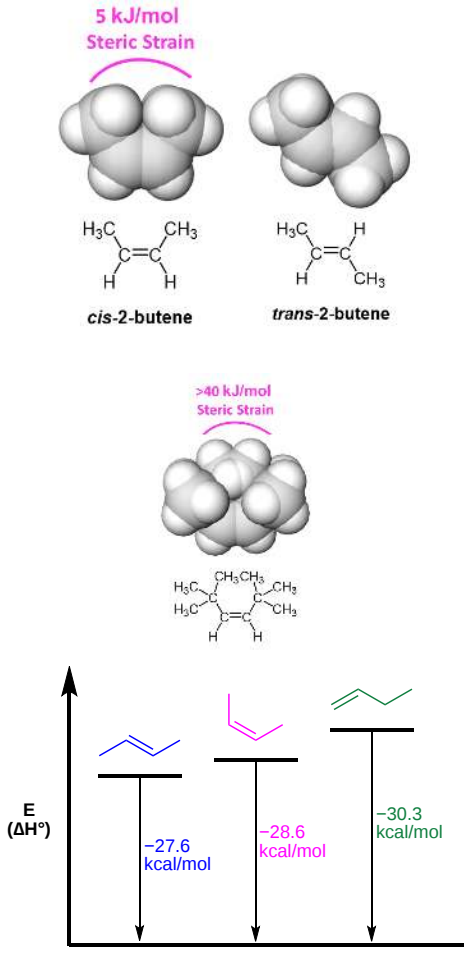


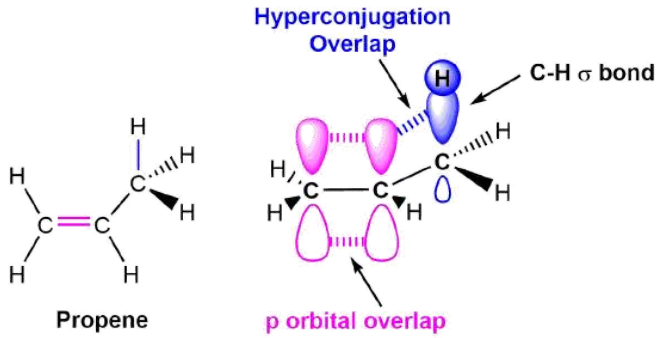

Figure 8.7.2*: Trans-2-butene is the most stable because it has the lowest heat of hydrogenation.*

## Alkene Stabilization by Alkyl Substituents

In general, the stability of an alkene increases with the number of alkyl substituents. This effect is due by the combination of two factors:

### Hyperconjugation

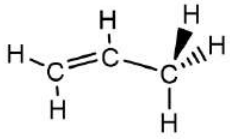
In classical valence-bond theory, electron delocalization can only occur by the parallel overlap of adjacent p orbitals. According to hyperconjugation theory, electron delocalization could also occur by the parallel overlap of p orbitals with adjacent hybridized orbitals participating in sigma bonds. This electron delocalization serves to stabilize the alkene. As the number of alkyl substituents increases, the number of sigma bonds available for hyperconjugation increases, and the alkene tends to become more stabilized. In the example of propene shown below, a p orbital from a $sp^2$ hybridized carbon involved in the double bond interacts with a $sp^3$ hybridized orbital participating in an adjacent C-H sigma bond.



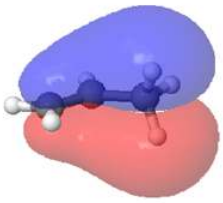


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In a molecular orbital description of hyperconjugation, the electrons in sigma molecular orbitals (C-H or C-C) of alkyl substituens, interact with adjacent unpopulated non-bonding or antibonding molecular orbitals from the double bond. The interaction creates a bonding molecular orbital which extends over the four atom chain (C=C-C-H) involved in hyperconjugation. The expanded molecular orbital helps to stabilize the double bond.



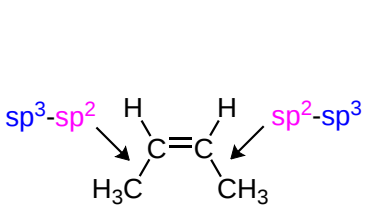
Propene



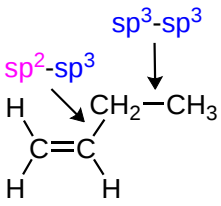
**Extended Bonding MO created by hyperconjugation**

## Bond Stability

Bond strengths play an important part in determining the overall stability of a molecule. A C-C bond between a $sp^3$ carbon and a $sp^2$ carbon is slightly stronger than a C-C bond between two $sp^3$ carbons. Increasing the number alkyl substituents of a double bond also increases the number of $sp^3$-$sp^2$ C-C bonds making the alkene more stable. This is idea can be clearly seen when comparing the isomers 1-butene and 2-butene. The molecule 1-butene is monosubstituted and contains a $sp^3$-$sp^3$ C-C and a $sp^3$-$sp^2$ C-C bond. The disubstituted, 2-butene, contains 2 $sp^3$-$sp^2$ C-C bonds which contributes to its greater stability.



**2-Butene (More Stable)**



**1-Butene (Less Stable)**

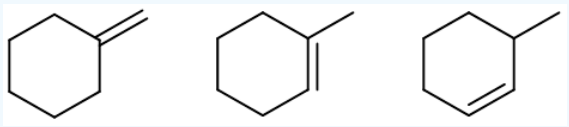
**Note**

In cycloalkenes smaller than cyclooctene, the cis isomers are more stable than the trans as a result of ring strain.

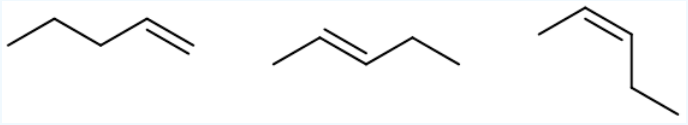
**Exercise 8.7.1**

Of the three following isomers which would be expected to be the most stable?

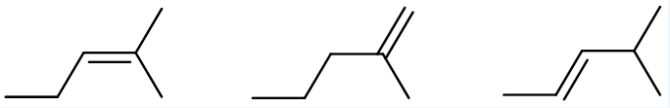
a)



b)



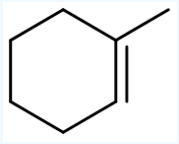
c)



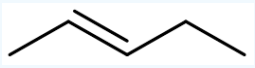
**Answer**

1)

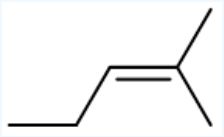
a)



b)

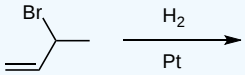


c)



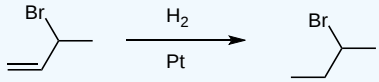
## Exercise 8.7.2

3-Bromobut-1-ene reacts with hydrogen gas in the presence of a platinum catalyst. What is the name of the product?



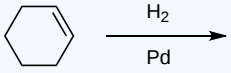

**Answer**

2-Bromobutane (numbering changes when alkene is no longer present)



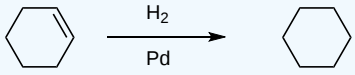

## Exercise 8.7.3

Cyclohexene reacts with hydrogen gas in the presence of a palladium catalyst. What is the name of the product?




**Answer**

Cyclohexane



**? Exercise 8.7.4**

What is the stereochemistry (syn or anti addition) of an alkene hydrogenation reaction?

**Answer**

Syn-addition

**? Exercise 8.7.5**

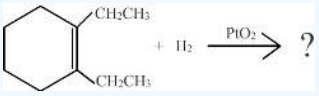
When looking at their heats of hydrogenation, is the cis or the trans isomer generally more stable?

**Answer**

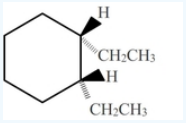
Trans

**? Exercise 8.7.6**

Show the product for the following




**Answer**




## References


1. Fox, Marye Anne, and James K. Whitesell. Organic Chemistry. 3rd ed. Sudbury, MA: Janes and Bartlett Publishers, 2004.
2. Hanson, James R. Functional Group Chemistry. Bristol, UK: The Royal Society of Chemistry, 2001.
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4. Vollhardt, Peter C., and Neil E. Schore. Organic Chemistry: Structure and Function. 5th ed. New York, NY: W.H. Freeman and Company, 2007.
5. Zlatkis, Albert, Eberhard Breitmaier, and Gunther Jung. A Concise Introduction to Organic Chemistry. New York: McGraw-Hill Book Company, 1973.



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# 8.8: Reduction of Alkynes

## Objectives

After completing this section, you should be able to

1. write equations for the catalytic hydrogenation of alkynes to alkanes and cis alkenes.
2. identify the reagent and catalyst required to produce a given alkane or cis alkene from a given alkyne.
3. identify the product formed from the reaction of a given alkyne with hydrogen and a specified catalyst.
4. identify the alkyne that must be used to produce a given alkane or cis alkene by catalytic hydrogenation.

## Key Terms

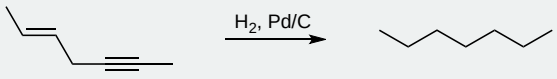
Make certain that you can define, and use in context, the key terms below.

- Lindlar catalyst

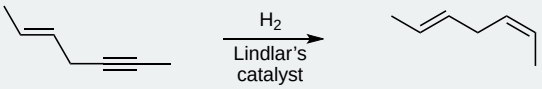
## Study Notes

The Lindlar catalyst allows a chemist to reduce a triple bond in the presence of a double bond.

Thus

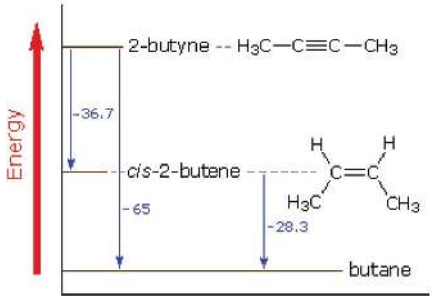



but




### Hydrogenation and the Relative Stability of Hydrocarbons

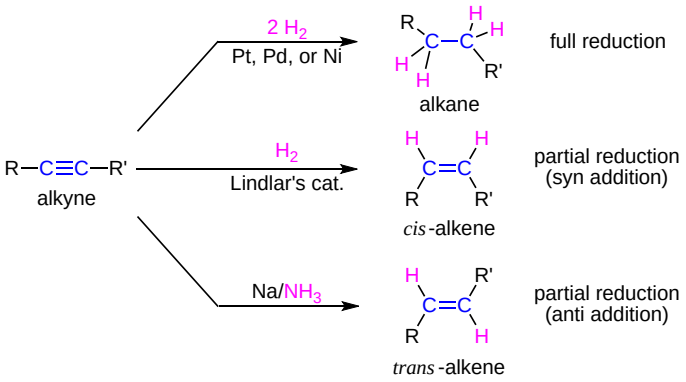
Like alkenes, alkynes readily undergo catalytic hydrogenation partially to **cis**- or *trans*- alkenes or fully to alkanes depending on the reaction employed.




The catalytic addition of hydrogen to 2-butyne provides heat of reaction data that reflect the relative thermodynamic stabilities of these hydrocarbons, as shown above. From the heats of hydrogenation, shown in blue in units of kcal/mole, it would appear that alkynes are thermodynamically less stable than alkenes to a greater degree than alkenes are less stable than alkanes. The standard bond energies for carbon-carbon bonds confirm this conclusion. Thus, a double bond is stronger than a single bond, but not twice as strong. The difference ( 63 kcal/mole ) may be regarded as the strength of the π-bond component. Similarly, a triple bond is stronger than a double bond, but not 50% stronger. Here the difference ( 54 kcal/mole ) may be taken as the strength of the second π-bond. The 9 kcal/mole weakening of this second π-bond is reflected in the heat of hydrogenation numbers ( 36.7 - 28.3 = 8.4 ).

## Overview of Reduction of Alkynes

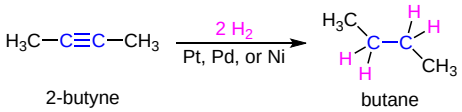
Alkynes can undergo reductive hydrogenation reactions similar to alkenes. With the presence of two pi bonds within alkynes, the reduction reactions can be partial to form an alkene or complete to form an alkane. Since partial reduction of an alkyne produces an alkene, the stereochemistry provided by the reaction's mechanism determines whether a *cis*- or *trans*- alkene is formed. The three most significant alkyne reduction reactions are summarized below:




Note that this last reaction to produce the *trans*-alkene does **NOT** involve a hetergeneous metal catalyst. For our purposes, we will note that although this reaction can be useful, it is beyond the scope of our course.

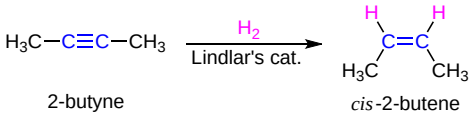
## Catalytic Hydrogenation of an Alkyne

Much like alkenes, alkynes can be fully hydrogenated into alkanes with the help of a platinum, palladium, or nickel catalyst. Because the reaction is catalyzed on the surface of the metal, it is common for these catalysts to dispersed on carbon (Pd/C) or finely dispersed as nickel (Raney-Ni). The presence of two pi bonds in the alkyne cause two equivalents of $H_2$ to be added during the reaction. During the reaction an alkene intermediate is form but not isolated.

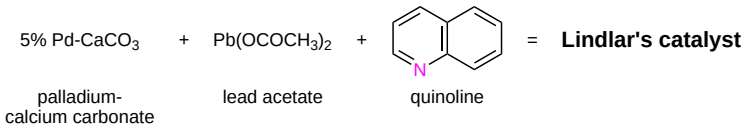



## Hydrogenation of an Alkyne to a *Cis*-Alkene

For catalytic hydrogenation, the Pt, Pd, or Ni catalysts are so effective in promoting addition of hydrogen to both double and triple carbon-carbon bonds that the alkene intermediate formed by hydrogen addition to an alkyne cannot be isolated. A less efficient catalyst, **Lindlar's catalyst** permits alkynes to be converted to alkenes without further reduction to an alkane. Lindlar's Catalyst transforms an alkyne to a *cis*-alkene because the hydrogenation reaction is occurring on the surface of the metal. Both hydrogen atoms are added to the same side of the alkyne as shown in the syn-addition mechanism for hydrogenation of alkenes in the previous chapter.




Lindlar's catalyst is prepared by deactivating (or poisoning) a conventional palladium catalyst. Lindlar's catalyst has three components: palladium-calcium carbonate, lead acetate, and quinoline. The quinoline serves to prevent complete hydrogenation of the alkyne to an alkane.

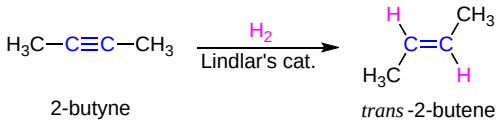




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## Hydrogenation of an Alkyne to a *Trans*-Alkene

The anti-addition of hydrogen to an alkyne pi bond occurs when reacted with sodium or lithium metal dissolved in ammonia. This reaction, also called dissolving metal reduction, involves radicals in its mechanism and produces a *trans*-alkene as it product.




2-butyne — *trans* -2-butene

---

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# 8.9: Hydration of Alkenes - Addition of $H_2O$ by Hydroboration

**Objectives**

After completing this section, you should be able to

- identify hydroboration (followed by oxidation) as a method for bringing about the (apparently) non-Markovnikov addition of water to an alkene.
- write an equation for the formation of a trialkylborane from an alkene and borane.
- write an equation for the oxidation of a trialkylborane to an alcohol.
- draw the structure of the alcohol produced by the hydroboration, and subsequent oxidation, of a given alkene.
- determine whether a given alcohol should be prepared by oxymercuration-demercuration or by hydroboration-oxidation, and identify the alkene and reagents required to carry out such a synthesis.
- write the detailed mechanism for the addition of borane to an alkene, and explain the stereochemistry and regiochemistry of the reaction.

**Key Terms**

Make certain that you can define, and use in context, the key term below.

- hydroboration

**Study Notes**

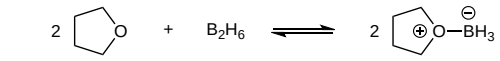
The two most important factors influencing organic reactions are polar (or electronic) effects and steric effects.

Hydroboration-oxidation is a two step pathway used to produce alcohols. The reaction proceeds in an anti-Markovnikov manner, where the hydrogen (from $BH_3$ or $BHR_2$) attaches to the more substituted carbon and the boron attaches to the least substituted carbon in the alkene double bond. Furthermore, the borane acts as a Lewis acid by accepting two electrons in its empty p orbital from an alkene that is electron rich. This process allows boron to have an electron octet. A very interesting characteristic of this process is that it does not require any activation by a catalyst. The hydroboration mechanism has the elements of both hydrogenation and electrophilic addition and it is a stereospecific (***syn addition),*** meaning that the hydroboration takes place on the same face of the double bond, this leads ***cis*** stereochemistry.

## Introduction

Hydroboration-oxidation of alkenes has been a very valuable laboratory method for the stereoselectivity and regioselectivity of alkenes. An additional feature of this reaction is that it occurs without rearrangement.

First off it is very important to understand little bit about the structure and the properties of the **borane** molecule. Borane exists naturally as a very toxic gas and it exists as dimer of the general formula $B_2H_6$ (diborane). Additionally, the dimer $B_2H_6$ ignites spontaneously in air. Borane is commercially available in ether and tetrahydrofuran (THF), in these solutions the borane can exist as a Lewis acid-base complex, which allows boron to have an electron octet.

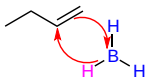



tetrahydrofuran (THF) ($BH_3$ • THF)

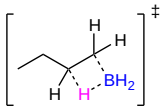
## The Mechanism

### Step 1

- Part 1: Hydroboration of the alkene. In this first step the addition of the borane to the alkene is initiated and proceeds as a concerted reaction because bond breaking and bond formation occurs at the same time. This part consists of the vacant 2p orbital of the boron electrophile pairing with the electron pair of the pi bond of the nucleophile.

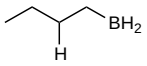


**Transition state**



*** Note that a carbocation is not formed. Therefore, no rearrangement takes place.**

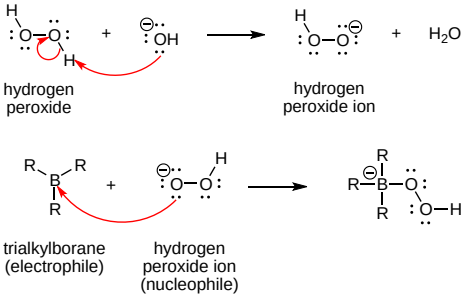
- Part 2: The Anti Markovnikov addition of Boron. The boron adds to the less substituted carbon of the alkene, which then places the hydrogen on the more substituted carbon. Both, the boron and the hydrogen add simultaneously on the same face of the double bond (syn addition).



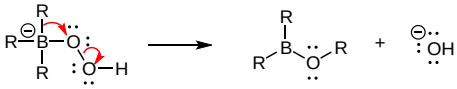
## Oxidation of the Trialkylborane by Hydrogen Peroxide

### Step 2

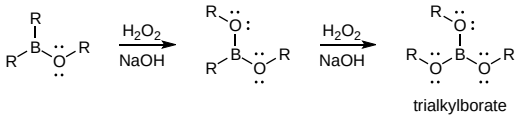
- Part 1: The first part of this mechanism deals with the donation of a pair of electrons from the hydrogen peroxide ion. the hydrogen peroxide is the nucleophile in this reaction because it is the electron donor to the newly formed trialkylborane that resulted from hydroboration.



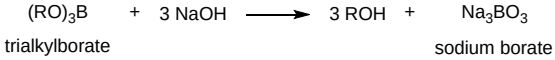

- Part 2: In this second part of the mechanism, a rearrangement of an R group with its pair of bonding electrons to an adjacent oxygen results in the removal of a hydroxide ion.



**Two more of these reactions with hydroperoxide will occur in order give a trialkylborate**



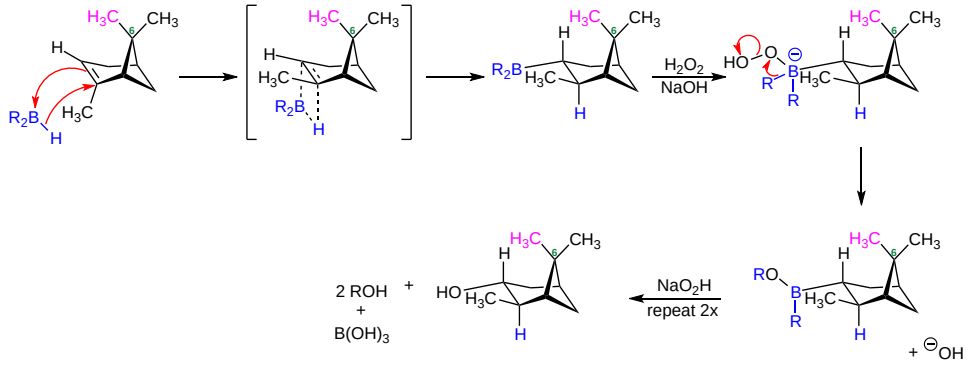

- Part 3: This is the final part of the oxidation process. In this part the trialkylborate reacts with aqueous NaOH to give the alcohol and sodium borate.




If you need additional visuals to aid you in understanding the mechanism, click on the outside links provided here that will take you to other pages and media that are very helpful as well.

## Stereochemistry of Hydroboration

The hydroboration reaction is among the few simple addition reactions that proceed cleanly in a *syn* fashion. As noted above, this is a single-step reaction. Since the bonding of the double bond carbons to boron and hydrogen is concerted, it follows that the geometry of this addition must be syn. Furthermore, rearrangements are unlikely inasmuch as a discrete carbocation intermediate is never formed. These features are illustrated for the hydroboration of α-pinene.

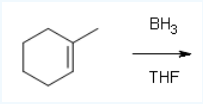



Since the hydroboration procedure is most commonly used to hydrate alkenes in an anti-Markovnikov fashion, we also need to know the stereoselectivity of the second oxidation reaction, which substitutes a hydroxyl group for the boron atom. Independent study has shown this reaction takes place with retention of configuration so the overall addition of water is also syn.

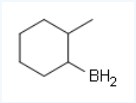
The hydroboration of α-pinene also provides a nice example of steric hindrance control in a chemical reaction. In the less complex alkenes used in earlier examples the plane of the double bond was often a plane of symmetry, and addition reagents could approach with equal ease from either side. In this case, one of the methyl groups bonded to C-6 (colored purple in the equation) covers one face of the double bond, blocking any approach from that side. All reagents that add to this double bond must therefore approach from the side opposite this methyl.

### ? Exercise 8.9.1

What are the products of this reactions?

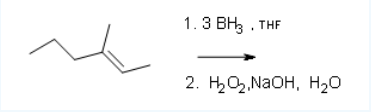



**Answer**

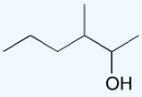



### ? Exercise 8.9.2

What are the products of this reactions?

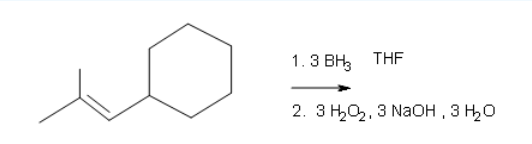



**Answer**

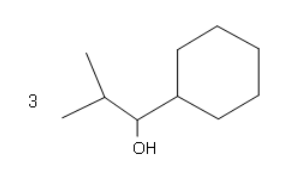


## Exercise 8.9.3

What are the products of this reactions?

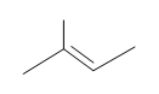



**Answer**

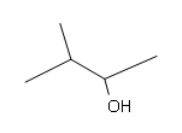



## Exercise 8.9.4

Draw the structural formulas for the alcohols that result from hydroboration-oxidation of this alkene.



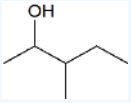
**Answer**




## Exercise 8.9.5

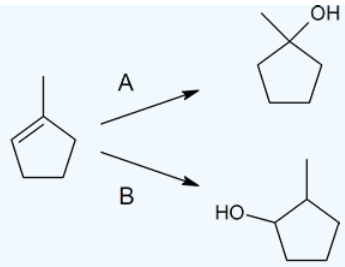
Draw the structural formulas for the alcohols that result from hydroboration-oxidation of (E)-3-methyl-2-pentene. If you need clarification or a reminder on the nomenclature of alkenes refer to the link below on naming the alkenes.

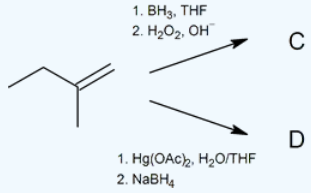
**Answer**




## Exercise 8.9.6

Write out the reagents or products (A–D) shown in the following reaction schemes.

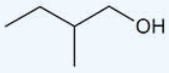


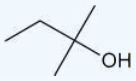




**Answer**

A: 1. $Hg(OAc)_2$, $H_2O$/THF; 2. $NaBH_4$

B: 1. $BH_3$, THF; 2. $H_2O_2$, $OH^-$

C: 


D: 


## References

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