1. Lewis Structures.

1.1 What is Organic Chemistry? Why Study It?

Organic chemistry is the study of the chemical behavior of compounds containing the element C. C is unique among all the elements for its ability to form strong bonds to itself (catenate). Thus, by bonding to itself, C can form a multitude of chemically and thermally stable chain, ring, and branched compounds. This ability of C to catenate is what makes it possible in for millions of carbon-containing compounds to exist.

In this course we'll be studying the structure, reactivity, and synthesis of organic compounds. For example, we'll look at the following reaction.

\[
\begin{array}{c}
\text{H}_2\text{C} - \\
\text{H}_2\text{C} - \\
\text{H}_2\text{C} \\
\end{array}
\xrightarrow{\text{Br}_2}
\begin{array}{c}
\text{H}_2\text{C} - \\
\text{H}_2\text{C} - \\
\text{H}_2\text{C} \\
\end{array}
\]

We'll ask, what are the three-dimensional shapes of the starting material and the product? What parts of the starting material are likely to be transformed under given conditions? What are the unstable intermediates in this reaction, if any? How many different products can be obtained? And, what is the nature of the bonds that are broken and the bonds that are formed?

1.2 Electronic Structure of Atoms and Molecules. Valence Structures.

- every atom has a characteristic number of electrons, given by its number in the periodic table. H has 1, C has 6, N has 7, O has 8, Cl has 17 electrons. Every electron in an atom resides in a region of space called an orbital, which has its own characteristic energy. Orbitals are divided into groups called shells. It takes two electrons to fill shell 1, which has only one s orbital. It takes eight electrons to fill shell 2, which has one s and three p orbitals. The order of energy of orbitals is as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s .... (The 3d orbital needs not to be filled for shell 3 to be considered filled.)
Following the *aufbau principle*, the electrons in an atom go into these orbitals in order of increasing energy. So the following atoms have the electronic structures shown – Figure 1.12.

**The electrons with which we concern ourselves are the outer-shell, or valence, electrons.** Valence electrons are the electrons in the outermost shell. For neutral atoms the number of valence electrons can be obtained by looking at the element's column in the periodic table: H has 1, C has 4, N has 5, O and S have 6, F and the other halogens have 7. F– or Ne has no or eight valence electrons, depending on how you count it, because their outer shell is filled.

**1.3 Lewis Structures**

Atoms link together to form molecules because they "like" to achieve a filled shell configuration. They achieve this by giving up or taking electrons (ionic bonds) or by sharing electrons (covalent bonds). In organic chemistry, we can have molecules that consist of as few as two atoms (CO) or those that consist of millions of atoms (DNA). The tremendous diversity of structures is what makes life possible. **In organic compounds, most bonds are covalent and the compounds are usually written as Lewis Structures**

**Rules to construct the electronic structure of organic molecules.**

Consider amide ion NH$_2^-$, ammonium ion NH$_4^+$, methanol CH$_3$OH, hydrogen cyanide HCN, and methyl acetate, CH$_3$CO$_2$CH$_3$.

1. Count the total number of valence electrons. Add one for every negative charge and subtract one for every positive charge. So, e.g., NH$_2^-$ has 8
valence electrons \((5 + 2 \times 1 + 1)\) and \(\text{NH}_4^+\) has 8 also \((5 + 4 \times 1 - 1)\). Methanol has 14, HCN has 10, and methyl acetate has 30 valence electrons \((3 \times 4 + 6 \times 1 + 2 \times 6)\).

(2) Attach the atoms in the correct order using single bonds, being careful to give no atom more than four bonds (duet for H). Each bond uses two valence electrons.

There are often many ways of combining the same atoms (this is called isomerism), and so you must have more information than just the empirical formula to do this. This may be supplied by an extended formula or by other information that we will learn to interpret later in the course. For \(\text{NH}_2^-\) and \(\text{NH}_4^+\), there is only one way to attach the atoms to each other (Draw). These use up 4 electrons and 8 electrons, respectively, leaving 4 and 0 unused electrons, respectively. For methanol, the way the formula is written suggests that there are three H's attached to C and one attached to O. For HCN, there are two ways to arrange the atoms (H–C–N or C–N–H), but we can tell by the way the formula is written that the atoms should be attached H–C–N. We use up four electrons, leaving six. For methyl acetate, there are several ways to arrange the atoms, but we can tell by the way the formula is written that the atoms should be attached as shown. (The designation CH₃, the methyl group, indicates C bound to three H atoms and one other atom.) This uses up 20 valence electrons, leaving 10 more.

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H–C–O–H} & \quad \text{H–C–N} \\
\text{H} & \quad \text{H–C–C–O–C–H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

When you are constructing the single bond framework of an organic compound, it is useful to remember that \textbf{H and the halogen atoms are normally found on the periphery of an organic structure}, and not in the middle, because they have only one free valence. The CH₃ group has only one valence, too.

(3) Place the extra valence electrons on the \textit{heteroatoms} (atoms that are different from C and H) or \textit{between pairs of neighboring electron-deficient}
atoms, being careful to give no more than a total of 8 electrons to each atom. (Each bond to an atom counts as two electrons.) Usually C makes a total of four bonds, N three, O two, and H and the halogens one.

For NH$_4^+$, no extra electrons need to be placed. For NH$_2^-$, four electrons go on N. For methanol, the four electrons go on O. For HCN, the six electrons go on N. For methyl acetate, the five pairs of electrons can be distributed among the two O atoms to give the structure shown. (Alternatively, two pairs of electrons may be placed on each O and one pair between the electron-deficient C and upper O.)

(4) Are any atoms electron-deficient by two or more electrons? If so, take a lone pair of electrons on a next-door neighbor and turn it into a bond between the electron-poor atom and its neighbor. If you have a choice of neighbors from which to borrow a pair of electrons, choose it from the neighbor that lacks its "normal" number of bonds.

Neither NH$_2^-$, NH$_4^+$, nor CH$_3$OH have any electron-deficient atoms. In HCN, the C atom only has four electrons around it, so it needs to borrow two pairs of electrons from N. A triple bond between C and N results. In methyl acetate, the second carbon atom has only 3 bonds, giving it 6 electrons in its outer shell, so it is electron-deficient. We can amend this by borrowing a pair of electrons from the O on the top or on the right, but it is better to borrow it from the O on the top, which only has one bond so far, than the O to the right, which already has two bonds.

Note: if you have an odd total number of electrons, in the end you will end up with one atom that has only seven total electrons around it. That's OK;
such a compound is called a free radical, and its reactivity is characterized by the fact that one of its atoms is electron-deficient.

(5) Assign formal charges. The formal charge for any atom is calculated by (valence electrons – number of unshared electrons – number of bonds).

Because C, N, O, and H and the halogens require four, three, two, and one electrons to complete their valence shells, respectively, they usually make four, three, two, and one bonds to other atoms, respectively. This leads to the following table. – show Table

<table>
<thead>
<tr>
<th>Atom</th>
<th>0 bonds</th>
<th>1 bond</th>
<th>2 bonds</th>
<th>3 bonds</th>
<th>4 bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td></td>
<td>+1 (or -1)</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>-1</td>
<td>0</td>
<td>+1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O, S</td>
<td>-1</td>
<td>0</td>
<td>+1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F, Cl, Br, I</td>
<td>-1</td>
<td>0</td>
<td>+1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>+1 (or -1)</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B, Al</td>
<td></td>
<td>0</td>
<td>-1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note that C with four bonds is uncharged; likewise for N with three bonds, O with two bonds, and H and the halogens with one bond. For C with three bonds and H with no bonds, whether a formal charge of +1 or -1 is assigned depends on whether the atom bears a lone pair of electrons or not. In any case, the sum of all the formal charges in a compound must add up to the total charge on that compound. For methanol, HCN, and methyl acetate, no formal charges need to be assigned, but for NH\textsubscript{2} and for NH\textsubscript{4}\textsuperscript{+}, they must be assigned.

We need to distinguish strongly between formal charge and electron deficiency. An atom is electron-deficient when it lacks an octet (or for H, a duet). An atom has a formal charge if the total number of electrons in its bonds and lone pairs is different from its number of valence electrons.
An atom with one of these properties may or may not have the other. For example, consider NH$_3$ and NH$_4^+$. In both of these compounds, N is electron-sufficient, but in one it has a formal charge and the other it doesn't. Now consider CH$_3$ and CH$_4$. In both of these compounds, C has no formal charge, but in one it is electron-deficient and in the other it is not. One way to think about it is as follows. Formal charge is a bookkeeping mechanism that we use to keep track of the number of electrons, it is in our mind. Electron deficiency is a real property that has real consequences for the behavior of organic compounds. This is illustrated by the fact that O atoms with a formal positive charge (e.g., H$_3$O$^+$) are quite commonly seen in organic chemistry, despite O's strong electronegativity; yet an electron-deficient O atom with only six electrons around it is extremely rare.

Problems. Draw the electronic structures of the following compounds: CO, NO, H$_2$CN$_2$ (use a triangular C–N–N arrangement, with both H's on C). Also try benzene, which has six carbon atoms in a ring, each attached to one H atom.

1.4 Common Bonding Situations.
We've seen that C "normally" makes 4 bonds, N 3, O 2, and H and halogens 1. But there are a lot of ways that these valences can be fulfilled. Here are some of the most common:
- C normally makes four bonds. The four bonds can be made to four different atoms, as in CH$_4$. Or two can be to one atom and the other two to two others, as in formaldehyde or ethylene. Or three can be to one atom and the fourth to another, as in acetylene or HCN. Occasionally one sees molecules where C makes two bonds to one atom and two bonds to another, as in CO$_2$.
Sometimes, C makes only three bonds. There are three kinds of trivalent C: free radicals, carbanions, and carbocations, depending on whether the C has a total electron count of 6, 7, or 8 electrons. Compounds containing trivalent C are usually very reactive compounds that exist only fleetingly as intermediates; that is, they rapidly are converted to other species containing tetravalent C.
- O normally makes two bonds. The two bonds can be to two different atoms,
as in water, or to the same atom, as in acetone. Sometimes we see O with only one bond, and in this case it almost always has a formal minus charge, as in HO⁻, because it must have a total electron count of 8 being very electronegative. Sometimes we see O with three bonds, as in H₃O⁺, and here it must have a formal + charge and a total electron count of 8.

- N normally makes three bonds. Ammonia, pyridine, and HCN are three examples. Sometimes N is divalent, as in NH₂⁻, and here it has a formal minus charge. Sometimes N is tetravalent, as in NH₄⁺, and here it has a formal + charge. H and the halogens normally make one bond. Sometimes H is bonded to nothing else. It may have an empty outer shell, as in H⁺, or a filled outer shell, as in H⁻. A halogen bound to nothing else may be neutral, with seven electrons in its outer shell, but more often it has 8 electrons and a formal minus charge.

- Normally P and S are perfectly analogous to N and O. But sometimes they are “hypervalent”, and a lone pair can be replaced by a double bond to O. So we have phosphoric acid, DMSO, and mesyl (methanesulfonyl) chloride.

1.5 Bond Polarity.

Nonpolar bonds have \( \Delta \) (electronegativity) \( \leq 0.4 \). C has electronegativity near center of scale, so most of its bonds are covalent. Bond polarity has very important effect on reactivity. Compare C—H and C—C bonds to C—O, C—Cl, C—Mg bonds. But electronegativity is not the only thing important in reactivity!

1.6 Resonance Structures.

Sometimes, after you have assigned all the electrons to a structure and you start sharing heteroatom lone pairs with electron-deficient atoms, you find that there is more than one way to arrange the electrons. The structures that are obtained thereby are called resonance structures. Two structures are resonance structures if they differ only in the location of double and triple bonds and nonbonding electrons. They must not differ in the location of single bonds, i.e. in which atoms are bound to which other atoms. Let’s look at nitromethane, \( H_3CNO_2 \) as an example. In this compound, N is bound to two O’s and one C. After we compute the total number of valence electrons...
electrons and assign them all to the various atoms, we obtain the structure shown. We can borrow a pair of electrons from either the top O or the bottom one. Which should it be?

\[ \text{H} - \text{C} - \text{N} - \text{H} \quad \text{↔} \quad \text{H} - \text{C} - \text{N} - \text{H} \]

In fact, either one is OK. The fact that we can borrow from either O means that after assignment of formal charges, we have two possible structures. In one of them, the top O is doubly bound and neutral and the bottom O is singly bound and has a formal positive charge; in the other, the situation is reversed.

**Does this mean that the two O atoms in nitromethane are different?**

N–O bond lengths and all spectroscopic properties show that the two O atoms are exactly identical. We rationalize this by saying that the two structures are resonance structures that each contribute an equal weight toward the description of the compound. Two resonance structures are drawn with a double-headed arrow (↔) between them.

The doubleheaded arrow doesn't mean that the compound is going back and forth between the two resonance descriptions. In the case of nitromethane, the two resonance descriptions of nitromethane are two equally good descriptions of what is going on out there in the real world, but each one alone is inadequate. To really describe what is going on in the real compound, we need to transform the two resonance descriptions into mathematical equations and average the two equations. The equation we get is a better description of the real nitromethane.

**In nitromethane, the two resonance structures are equally good descriptions of the compound. This is not always true.** Sometimes, one resonance structure is sometimes a better description of the compound than the others. For example, let's take our drawing for methyl acetate and move the pair of electrons in the second bond between C and the top O back up to O. (Remember, resonance structures differ only in the placement of lone
pairs and double and triple bonds.) We use a curved arrow to show the change in location of the electrons. After we assign formal charges, we get a new resonance structure. The central C is electron-deficient now, so we can generate the old resonance structure by moving a pair of electrons from the top O to between C and O, or we can make a new resonance structure by borrowing a pair of electrons from the O on the right. Again we need to assign formal charges.

Thus, three resonance structures are possible. Which is the best description of the real methyl acetate? Use the following rules in the order shown to determine the best resonance structure.

1. Resonance structures in which any atom has more than an octet (duet for H) are not acceptable.
2. It is acceptable to draw a resonance structure in which electron-deficient atoms are present, but the fewer the electron-deficient atoms, the better the resonance structure. (Cf. structures 1 and 2 of methyl acetate above.) If there must be electron-deficient atoms, they should be relatively electropositive ones (C, B) rather than electronegative ones (N, O).
3. Structures with fewer formal charges are better than those with more formal charges, unless this violates rule #2.
4. If there must be formal charges, the negative charges should be located on atoms that are as electronegative as possible, and the positive charges should be located on atoms that are as electropositive as possible.

Using these rules, we deduce that the left-hand structure for methyl acetate is the best. This does not mean that the other resonance structures have no contribution to the electronic nature of the compound. As we shall see later, often a minor resonance structure gives us an insight into the reactivity of a compound. We will see this when we discuss the reactivity of carbonyl compounds later.
To generate resonance structures, use the following rules and techniques.

1. Any double bond $A=B$ may be broken and the two electrons in that bond given to atom $A$ or atom $B$. Both electrons may be given to one atom, or one electron may be given to each atom.

$$H_2C=CH_2 \leftrightarrow H_2^+\hat{C}-CH_2 \leftrightarrow H_2\hat{C}-\dot{C}CH_2 \leftrightarrow H_2\dot{C}-\dot{C}H_2.$$

2. The lone pair on any atom may be shared with its next-door neighbor to make a new double bond if and only if that neighbor is electron-deficient.

$$H_2\hat{N}-\dot{C}CH_2 \leftrightarrow H_2\hat{N}=CH_2.$$

3. The lone pair on an atom may be shared with an electron-saturated neighbor if and only if a double bond to that neighbor breaks at the same time, with the electrons in that bond moving to the neighbor's neighbor. $H2N$

$$H_2\hat{N}-CH=CH_2 \leftrightarrow H_2\hat{N}=CH-\dot{C}H_2 \text{, and } O=CH-\dot{C}H_2 \leftrightarrow \overset{\ddots}{C}=CH_2$$

The purpose of this rule is to prevent any atom from acquiring more than an octet.

4. A C atom bonded to four different atoms does not participate in resonance. N bound to three atoms or O bound to two atoms can donate a pair of electrons to a neighbor, but it cannot accept a pair of electrons.

5. In a ring of alternating double bonds, the double bonds can be moved around to generate a new structure that is different from the original one.

Problems. Draw the best resonance structure for each of the following compounds. Then draw a second resonance structure for each one. HONO$_2$ (N is bound to three O atoms), $H_2CN_2$ (use a linear C–N–N arrangement, with both H's on C), [(H$_3$C)$_2$CN(CH$_3$)$_2$]$^+$ (C has two CH$_3$ groups attached, as does N), $H_2CCHC(O)CH_3$ (four C's in a chain, with an O attached to the third and two, one, and three H's attached to the first, third, and fourth), HOCHCH$_2$ (a chain of O–C–C, with one, one, and two H's attached to O, the middle C, and the furthest C, respectively).

Why are resonance structures important? As we have seen, a single
Lewis structure is often not sufficient to give us a good description of a compound. Just as important, though, is the fact that *the more low-energy resonance structures can be drawn for a compound, the lower in energy that compound is.* This is especially true of structures in which one or more atoms is electron-deficient. For example, $^+\text{CH}_2\text{CH}_3$ is very high in energy but $^+\text{CH}_2\text{CH}=$CH$_2\leftrightarrow \text{CH}_2=$CHCH$_2^+$ is much lower in energy.

Another important reason for understanding resonance structures: *The lowest energy structure is the best description of a compound, but it is usually the second-best resonance structure that tells you about the reactivity of a compound.*

**1.7 Atomic and Molecular Orbitals. sp$^3$ Hybridization.**

We can use *molecular orbital (MO) theory* to describe the structure of molecules in more detail. MO theory also provides a means of predicting the shapes of molecules. In MO theory, our first hypothesis is that bonding occurs by the overlap of singly occupied atomic orbitals. So if we look at H$_2$, we see that two singly occupied s orbitals, each with a spherical shape, come together in space to form a new MO with an oblong shape (Show Figure 1.34). Electrons in this new MO have less energy than electrons in either of the two atomic orbitals with which we started. As a result, energy is released, and the molecule that is formed is more stable than the individual atoms from which it was formed. You might think that the atoms could keep coming together until they were merged, but at a certain distance the repulsion between the positively charged nuclei becomes important. The balance point is called the *bond distance.* At this point the energy of the system is at a minimum. We can draw diagrams like the ones shown in Figure 1.32.

If two He atoms come together, we can draw exactly the same picture, except that we would have to put the two extra electrons in the anti-bonding orbital. Then we would have equal amounts of loss and gain in energy. The net result would be no gain in energy for the system, and the two He atoms would be happier to fly apart than they would be to stick together.

**1.8 Bond Strengths.**
Bonds can be broken homolytically (one electron to each atom) or heterolytically (two electrons to one atom, none to the other). Bond strengths of A—B are defined as the ability to separate A—B into A· and ·B.

**Bonds differ in strength. Some are strong, some weak. How to tell?**

1) Bonds between two electronegative elements are weak. E.g., O—O (35).

2) Bonds between two elements of different size are weaker than bonds between elements of the same size. E.g., cf. C—F (116), C—Cl (79), and C—I (52).

3) Bonds between two small elements are usually strong. E.g., C—H (98), C—O (79), C—C (81), C—N (66), O—H (109).

4) Double bonds are stronger than single bonds. But the C=C bond (145) is not twice as strong as the C—C bond (81); on the other hand, the C=O bond (173) is more than twice as strong as the C—O (79) bond, and the C≡N bond (204) is just about thrice as strong as the C—N (69) bond.

**Why does size matter?** It has to do with overlap between orbitals. Overlap between two small orbitals is much better than overlap between a big orbital and a small orbital.

A strong bond is one in which the bonding MO is much lower in energy than the component AOs. This terminology is a little counterintuitive: a high-energy bond is weak, and a low-energy bond is strong. Heterolytic cleavage of bonds is typical of acids and bases, as is the reverse reaction, the formation of bonds from an acid and a base. Here, a filled orbital comes together with an empty orbital to make two new orbitals, one of which is lower in energy than either partner.