

Chapter 1. Chemical Bonding

Mastery of the following concepts discussed in Chapter 1 is essential for all aspects of understanding Organic Chemistry:

(1) ***Covalent bonds and Lewis structures.***

Lewis structures are the "words and grammar" of the language of Organic Chemistry. For most of this course the atoms of greatest interest will usually be H, C, N, O and F (and the other halogens), so that writing Lewis structures for molecules involving only these atoms will be emphasized. Lewis structures display how atoms are connected in a molecule and how valence electrons are distributed about the atoms as shared pairs and unshared pairs.

(2) ***Lewis Structures and Electronegativity.***

The ability of atoms to attract valence electrons differs. These differences are related to the electronegativity (a pure number) of each atom. The greater the electronegativity of an atom, the greater its ability to attract valence electrons. The electronegativity of the atoms of interest in organic chemistry are for the following atoms: H = 2.1, C = 2.5, N = 3.0, O = 3.5, F = 4.0. In this group, F is the most electronegative atom and H is the least electronegative atom. The bond in HF will be very polar with the electrons in the bond being pulled close to F and away from H.

(3) ***Lewis Structures and Formal Charges.***

A neutral molecule contains the same number of electrons and protons. Although the molecule as a whole may be neutral, individual atoms may be viewed in Lewis structures as acquiring a positive or negative charge. Such atoms are said to possess a "formal charge". The atoms in a Lewis structure are considered neutral if the number of assigned valence electrons is equal to the number in the neutral atom (equal to the group number or positive core charge) and "formally charged" if the assigned valence electrons are greater or lesser than the group number. Each atom in a Lewis structure may be assigned a formal charge according to the following procedure:

Valence electrons are assigned to atoms in the following manner by inspection of the Lewis structure:

- (1) Valence electrons in bonds are considered to be shared equally by each atom so that for each shared pair, the atom is assigned one electron; the number of electrons assigned to an atom is therefore equal to the number of bonds that the atom possesses in the Lewis structure.
- (2) Valence electrons which are not shared are considered to belong exclusively to the atom possessing the unshared pair.

The formal charge (FC) on atoms in a correct Lewis structure containing only H, C, N, O, X (any halogen atom) is given by the following formula (where GN is the group number of the atom in the periodic table, i.e., H = 1, C = 4, N = 5, O = 6 and F = 7):

$$\text{FC} = \text{GN} - \text{number of bonds} - \text{number of unshared electrons}$$

(4) **Lewis Structures and Resonance.**

Acceptable Lewis structures are those which best represent the actual structure of the electrons in a molecule. The best Lewis structures are those representing the lowest energy distribution of valence electrons (in bonds as shared pairs and on atoms as unshared pairs). Such structures usually possess an octet of electrons around C, N, O and F and a duet of electrons around H.

For molecules possessing multiple bonds, sometimes two or more acceptable Lewis structures can be drawn which differ only in the positions of the valence electrons, but not in the connections of the atoms. If a set of two or more Lewis structures are identical in the position of the atoms but differ in the position of the valence electrons, the set of such structures is termed *resonance structures*. Resonance structures may be termed equivalent or non-equivalent. Equivalent resonance structures are different Lewis structures with respect to the position of valence electrons, but possess exactly the same number and kinds of bonds.

Whenever a molecule can be represented by two or more Lewis structures which satisfy the octet rule, *none* of the individual resonance structures are accurate representations of the distribution of valence electrons in the actual molecules; this must be taken into account in correlating physical and chemical properties represented by resonance structures, especially equivalent resonance structures. In these cases the structure of the molecule is poorly represented by a single resonance structure and is better represented by a hybrid or "some mix" of the possible acceptable resonance structures.

Resonance structures in a set can be interconverted by redistribution of the valence electrons. A curve arrow notation is employed as "electron bookkeeping" to systematically interconvert the Lewis structures in a set of resonance structures. This arrow notation is a chemical grammar used in order to make sense of structural interconversions in organic chemistry. Assignment 1 provides practise in learning this chemical grammar.

(5) **Curved arrow convention:**

Curved arrows are employed to show the movement of electron pairs, not atoms such that:

- (a) The tail of the arrow begins at the initial position of the electron pair (which may either be a SP or an UP) and the head of the arrow indicates the final position of the electron pair. In general the SP is part of a multiple bond. In Molecular Orbital terminology the SP involved in

resonance are usually electrons. The pair represented by the arrow either goes between two atoms to form a new bond or on an atom to form an unshared pair. If the pair represented by the arrow comes from the SP of a bond onto an atom, the bond is broken. If the pair comes from the UP of an atom and goes between two atoms, a new bond is formed.

- (b) Movement of a pair to an atom or between two atoms cannot generate a resonance form in which the octet rule can be violated.
 - (c) The atom at the tail of the arrow becomes positively charged by one unit as the result of the movement of the electron pair and the atom at the head of the arrow becomes negatively charged by one unit.
 - (d) When an electron pair moves onto a atom, another pair must leave that atom in order to maintain the octet rule.
 - (e) When correctly applied, the curved arrow convention completely determines the final structure and can be reversibly applied. If reversibility cannot be achieved, one of the structures is incorrect.
 - (f) The natural polarization of a double bond with different atoms is in the direction which places more electrons about the more electronegative atom. Electron movement of curved arrow will generally proceed toward positive sites and away from negative sites.
- (6) ***Lewis Structure and Molecular Shapes.***

The VSEPR Model. Lewis structures are "chemical graphs" which show how atoms are connected in a molecule. They do not provide any information on the shape of a molecule in three dimensions. However, the 3D shape of a molecule can be determined from the Lewis structure by applying the rules of the valence shell electron pair repulsion (VSEPR) model. The model predicts the orientation of the bonded and non-bonded valence electrons of a Lewis structure in 3D. The visualization of molecules in 3D is required for an understanding of many aspects of organic chemistry.

The most effective way to become fluent in the visualization of the shapes of molecules is to use molecular models, which may be either ball and stick models or computer models. Both types will be employed in the course.

(7) ***Lewis structures, the VSEPR Model and Hybridization.***

If the shape of a molecule is known, the so-called "hybridization" of the atoms of the molecule may be deduced. Carbon atoms in stable molecules are almost always bonded to 2, 3 or 4 other atoms. When bonded to 2 other atoms, the carbon hybridization is sp and the two bonded atoms fall on a line that passes through the carbon atom. When bonded to 3 other atoms, the carbon atom is sp² hybridized and the three bonded atoms are in a plane containing the carbon atom. When bonded to 4 other atoms, the 4 bonded atoms are positioned at the corners of a tetrahedron of which the carbon atom is the center.

Since hybridization is directly related to molecular shape, the connections between Lewis structures and hybridization can be made through the VSEPR model.

Appendix

Review of Writing Lewis structures.

Lewis structures represent the distribution of valence electrons as shared pairs (SP) between atoms or unshared pairs (UP) localized on atoms.

For C, N, O, F the octet rule is always followed (exception: carbon may possess a sextet of valence electrons in certain high energy situations). For H, the duet rule is always followed.

For molecules, each atom contributes a number of valence electrons equal to its group number in the periodic table (C = 4, N = 5, O = 6, F = 7). This makes sense if we consider that each atom can be considered as a set of valence electrons and a positive core of its atomic number minus the two electrons in the 1s orbital, i.e., C = +4, N = +5, O = +6 and F = +7. Thus, the number of positive charges of the core equals the number of valence electrons.

The valence electrons, once incorporated into the molecule, belong to the molecule and may be distributed into bonds as required to satisfy the valences of the atoms and fulfill the octet rule (for C, N, O and F) and duet rule (for H)

For ions, a valence electron must be added for each negative charge on the ion and a valence electron must be removed for each positive charge on the ion.

Formal procedure for writing a Lewis structure:

- (1) Compute the total number of valence electrons by multiplying the group number of each atom in the composition by the group number of the atom and then summing the result.
- (2) An acceptable Lewis structure must account for all of the valence electrons as SP or UP.
- (3) The molecular constitution (the way the atoms are connected) must be known or unambiguously determined by the rules of valence.
- (4) Given a molecular constitution, use pairs of electrons to form bonds between each of the atoms according to the rules of valence.
- (5) Add any remaining electrons so that the octet rule is followed for C, N, O and F and the duet rule is followed for H.
- (6) The lowest energy Lewis structure possesses octets about C, N, O and F and duets about H.

Valence and Valence Electrons

Valence: The number of bonds that one atom can make with another atom. Maximum valence of C, N, O is 4 (Octet rule)
Carbon: 4 as a molecule; 3 as a cation (Sextet) and as an anion.
Nitrogen: 3 or 4 as a molecule, 2 as an anion or 4 as a cation.
Oxygen: 2 as a molecule, 1 as an anion, 3 as a cation.

Valence Electrons: The number of electrons in the outermost electron shell of an atom.

C has 4 valence electrons
N has 5 valence electrons
O has 6 valence electrons
F has 7 valence electrons

Notice the **difference** between the valence of an atom (how many other atoms it can bond to) and the number of valence electrons possessed by an atom (the number of electrons in its outermost electronic shell).

Qualitative use of resonance structures to predict molecular properties:

Resonance structures in a set of acceptable Lewis structures may be classified as (1) *equivalent isovalent*; (2) *dipolar isovalent*; or (3) *heterovalent*. Two Lewis structures are termed isovalent if they possess the same number of bonds. Two Lewis structures are termed heterovalent resonance if they differ by one or more bonds. Equivalent isovalent structures possess the same number of bonds and are neutral or possess the same charge on atoms. Dipolar isovalent structures possess the same number of bonds but different charges.

In general, the order of stability of resonance structures is: equivalent isovalent > dipolar isovalent > heterovalent. Understanding the difference between isovalent and heterovalent structures is critical for an understanding of the roles played by N and O atoms in conjugation with carbon atoms through multiple bonds.

In isovalent structures the unshared pairs on heteroatoms are delocalized (no bond to heteroatom atom broken to make resonance). In isovalent resonance the bonding bond is involved in resonance (bond to heteroatom broken to make resonance).

Rules for writing resonance structures:

The following rules are useful in deciding on the relative importance of resonance structures in contributing to the actual structure of a molecule.

- (1) All resonance structures must possess the same bond connections and position of atoms. This feature distinguishes resonance structures from constitutionally isomeric structures. Resonance structures possess the same number, type and positions of atoms, but different positions of valence electrons; isomers possess the same number and type of atoms, but differ in the way the atoms are connected.
- (2) There are no exceptions to the rule that H never exceeds a duet and that C, N, O and F never exceed the octet.
- (3) All other factors being comparable, isovalent resonance is more important than heterovalent resonance.
- (4) Structures which create separation of charge are less important than structures which do not.
- (5) Heterovalent resonance is only important when formal negative charge is placed on atoms of greater electronegativity and formal positive charge is placed on atoms of lower electron negativity.
- (6) Effective resonance between resonance structures requires the atoms involved in the resonance to be planar.

- (7) Resonance stabilization is most effective when the contributing structures are all equivalent. When the latter is the case, the resonance stabilization is most effective the greater the number of equivalent structures.

Examples of Equivalent Isovalent, Dipolar Isovalent and Heterovalent Resonance Structures

