

Chemistry 5.12 Spring 2003
Lectures #1 & 2, 2/5,7/03

Outline

- Discuss General Class Information (Professor Imperiali)
- General Introduction to Organic Chemistry
- I. Review of Lewis Bonding Theory (**Read Chapter 1**)
 - A. Ionic Bonding (**1-3A,6,8**)
 - B. Covalent Bonding (**1-3B,4**)
 - 1. Multiple Bonding (**1-5**)
 - 2. Formal Charge (**1-7**)
 - C. Short-Hand for Chemists
 - 1. Line-Angle Formulas: Simplified Structures (**1-10**)
 - 2. Dashes and Wedges: Molecules in 3-D (**2-5**)
 - 3. Curved Arrow Formalism: Electrons in Motion (**1-14**)
- II. Resonance (**1-9**)
 - A. Rules for Drawing Resonance Structures
 - B. Relative Energy of Resonance Structures
 - C. Structure and Reactivity from Resonance

Suggested Problems: 1-25,36,39,41

Problem Set #1 Posted: Due Monday 2/10 by 4pm

Organic Chemistry 5.12 Spring 2003

Prof. Barbara Imperiali

Dr. Sarah Tabacco

Text: Organic Chemistry, L.G. Wade, Jr., 5th Ed.

Recitations: Twice a week, beginning second week. Section changes should be made through the 5.12 website. **All changes must be made by Friday 2/14.**

Problem Sets: Turn in to TA's box in Chem. Ed. office by 4pm on the due date. Lowest grade will be dropped. **No late work accepted.**

Midterms: During class period. Lowest grade will be dropped. **No make-up exams.**

Exam #1 Friday, 2/21
Exam #2 Friday 3/14
Exam #3 Monday, 4/14
Exam #4 Monday, 5/5

Grading: Upon request, exams can be regraded within one week.
Problem sets will not be regraded.

Problem Sets: 10%
Midterm Exams: 50%
Final Exam: 40%

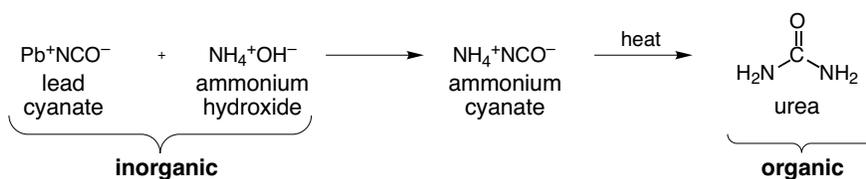
Organic Chemistry: What is it?

1780: Organic compounds very complex and only obtained from living sources (vitalism)

Vitalism: Belief that a "magic" vital force, present in plants and animals, is necessary for the synthesis of organic compounds

1789: Antoine Laurent Lavoisier observed that organic compounds are composed primarily of carbon and hydrogen

1828: Friedrich Wohler synthesized an organic compound (urea) from inorganic compounds (lead cyanate and ammonium hydroxide).



Modern organic chemistry is the chemistry of carbon compounds.

"The Age of Organic Chemistry"

- > 95% of All Known Compounds Composed of Carbon
- **Organic Chemistry Crucial to Our Way of Life:**
Clothing, Materials (Polymers), Petroleum, Medicine, OUR BODIES
- > 50% of Chemists Are Organic

STRUCTURE

Determining the Way in Which Atoms Are Put Together in Space to Form Complex Molecules

MECHANISM

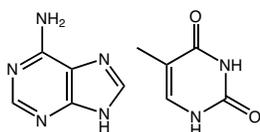
Understanding the Reactivity of Molecules: How and Why Chemical Reactions Take Place

SYNTHESIS

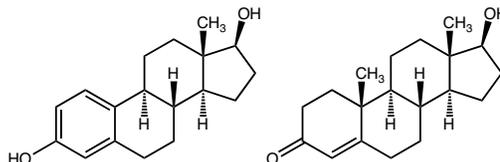
Building Complex Molecules From Simple Molecules Using Chemical Reactions

Why Carbon?

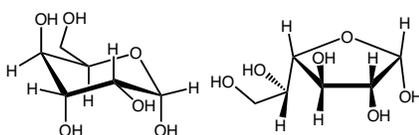
- Carbon forms a variety of strong covalent bonds to itself and other atoms.
- This allows organic compounds to be structurally diverse.



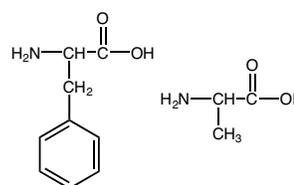
DNA Bases



Hormones



Carbohydrates



Amino Acids

Why Does Carbon Bond in This Way?

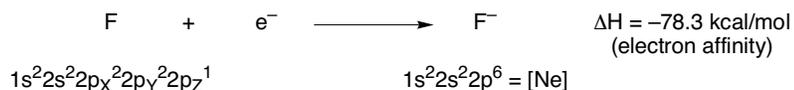
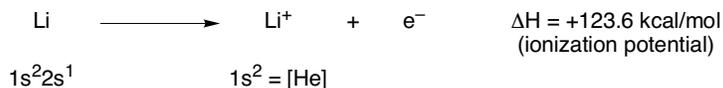
I. Review of Lewis Bonding Theory (READ CH 1)

- Atoms **transfer** or **share** electrons to gain a filled valence shell of electrons.

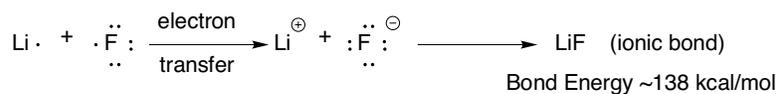
A. Ionic Bonding

- Between atoms of widely different electronegativity ($\Delta EN > 2$); usually a metal and a non-metal; atoms held together by electrostatic attraction, **not electron sharing**

e.g. LiF is ionic (EN: Li = 1.0. F = 4.0)



- Using Lewis Dot Structures:

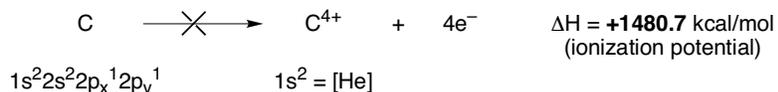


B. Covalent Bonding (Electron Sharing)

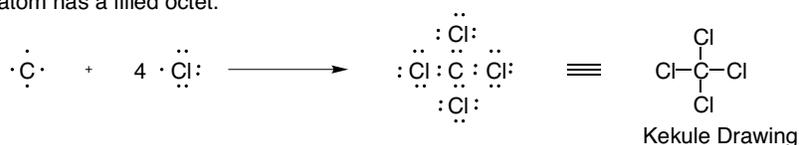
- Very important in organic molecules!
- Between atoms of similar electronegativity; usually non-metallic

e.g. CCl₄ is covalent . . . Why?

- Large thermodynamic penalty for ionization of carbon to C⁴⁺



- Instead, each chlorine atom shares one valence electron with carbon so that every atom has a filled octet.



- Each chlorine atom still has three unshared pairs of electrons (lone pairs).

lone pair: unshared electron pair; non-bonding pair of electrons

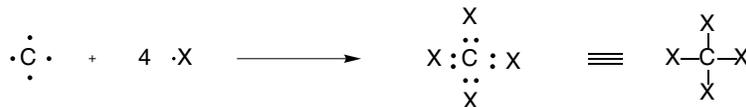
How can you tell how many bonds and how many lone pairs an atom will have?

Count the Valence Electrons!

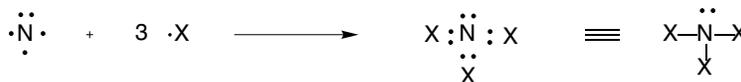
	neutral atom	# valence e ⁻ s	# bonds	# lone pairs
	H	1	1	0
2nd row	C	4	4	0
	N	5	3	1
	O	6	2	2
	F	7	1	3

- Second row elements want to be surrounded by eight valence electrons (an octet).

e.g. Carbon wants four more electrons (4 bonds).



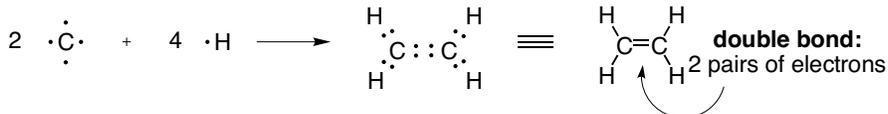
e.g. Nitrogen wants three more electrons (three bonds, one lone pair).



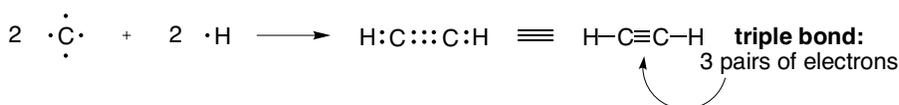
1. Multiple Bonding

- Two atoms can share more than one pair of electrons to gain a filled shell (very common in organic molecules)

e.g. Ethylene (C₂H₄)

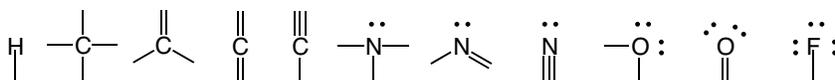


e.g. Acetylene (C₂H₂)



- Each line represents one shared electron pair.

Summary of Bonding (Neutral Atoms)

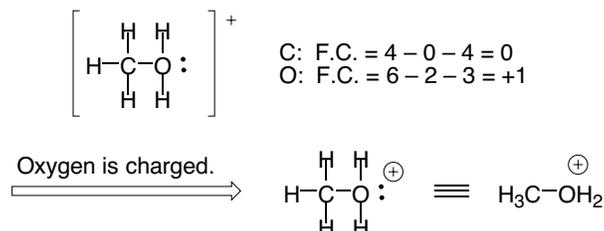


2. Formal Charge

- Not all atoms are neutral in a Lewis or Kekule structure
- Formal charges help chemists to keep track of the placement of electrons in molecules
 - Does not indicate that all of the charge is actually localized on one atom

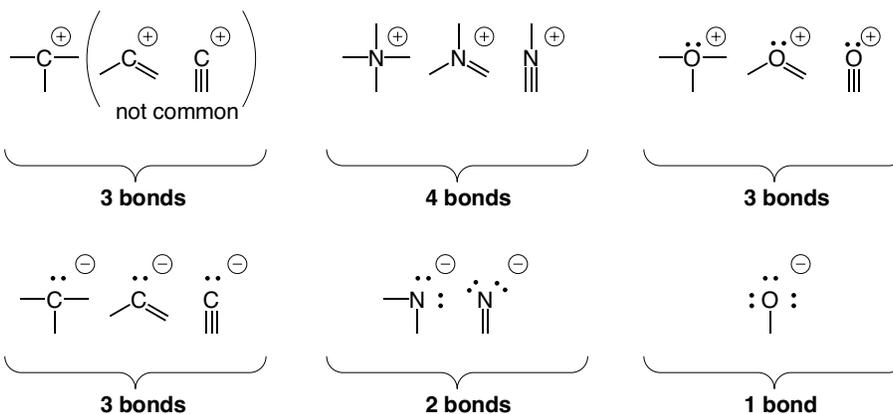
$$\text{Formal Charge} = (\text{group \#}) - (\# \text{ non-bonding } e^-s) - 1/2 (\# \text{ shared } e^-s)$$

e.g. [H₃C-OH₂]⁺ Which atom has the formal charge?



Always indicate formal charge on problem sets and exams!

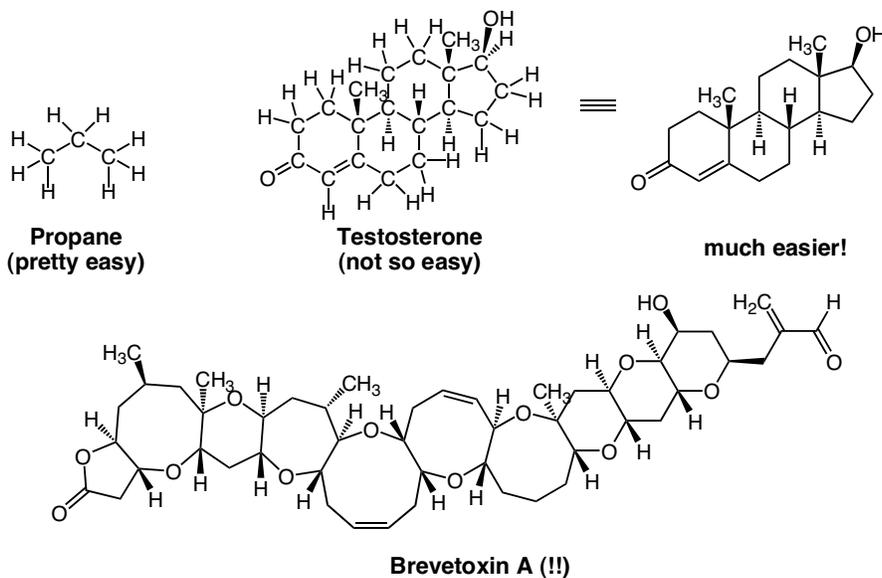
Summary of Bonding (Charged Atoms)



Be able to recognize common bonding patterns.

C. Short-Hand for Chemists: Easy Communication

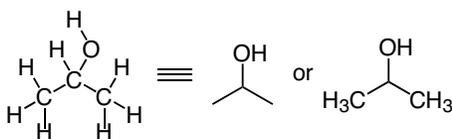
1. Line-Angle Formulas: Drawing Complex Molecules Quickly



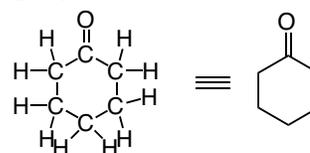
Rules for Drawing Line-Angle Formulas

- Bonds are represented by lines (one line = two shared electrons)
- Do not draw carbon or hydrogen atoms, except at termini (for aesthetics)
- Assume carbon atoms are at ends of lines and where they meet
- Assume enough C–H bonds to give each carbon atom four bonds (an octet)
- Draw heteroatoms and attached hydrogen atoms (N,O,S,P,F,Cl,Br,I, etc.)

e.g. isopropanol: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

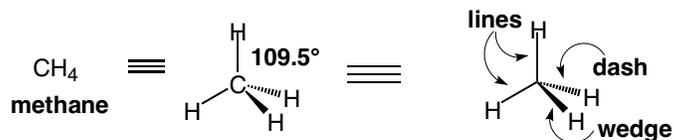


e.g. cyclohexanone



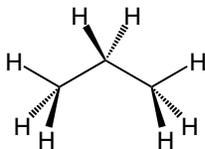
2. Using Dashes and Wedges: Molecules Are Not Flat!

- Tetra-Substituted Carbon Is Tetrahedral (more on this later).

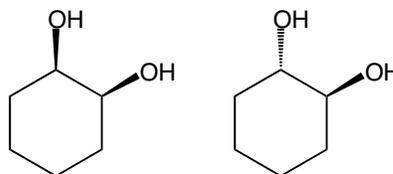


lines: in the plane of the paper
dashes: going back into the paper (away from you)
wedges: coming out of the paper (toward you)

e.g. Propane



e.g. Isomers of 1,2-Cyclohexanediol



Representing Molecules

Lewis/Kekule Structures: Represent atoms sharing electrons to form bonds

Line-Angle Structures: Simplify the drawing of complex molecular structures

Dashes and Wedges: Allow chemists to draw molecules in 3-D

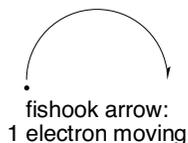
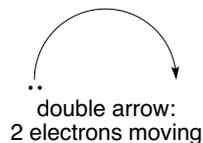
BUT! These simplified structures do not accurately represent the electronic nature or reactivity of organic molecules!

It helps to think about electrons in motion . . .

BUT HOW DO WE REPRESENT ELECTRONS IN MOTION?

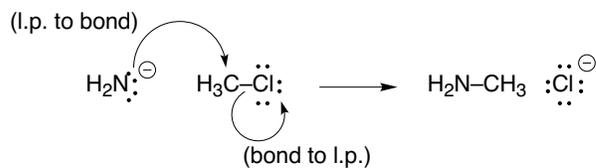
3. Curved Arrow Formalism (Arrow Pushing)

- Chemists use arrows to represent the motion of electrons within and between molecules.



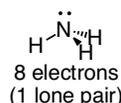
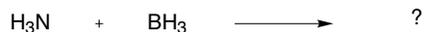
- The tail starts at the electrons that are moving (lone pair or bond).
- The head shows where the electrons end up (lone pair or bond).

e.g. electron motion in a substitution reaction (much more detail later)



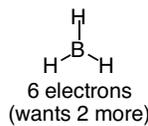
Sample Problem: Using What You Know

- Use what you know about Lewis bonding to predict the product of the following reaction. Remember to indicate formal charge. Use curved arrows to show the mechanism (movement of electrons).



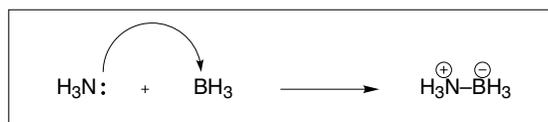
- Nitrogen atom is **nucleophilic** (nuclei-loving).

nucleophile: electron-rich atom, often negatively charged, with a free lone pair to donate to another atom



- Boron atom is **electrophilic** (electron-loving).

electrophile: electron-poor atom with a low-lying vacant or easily vacated orbital; wants to accept electrons from a nucleophile



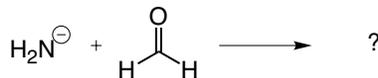
Formal Charge: N: $5 - 0 - 4 = +1$
B: $3 - 0 - 4 = -1$

- Chemical reactions generally involve the movement of electrons between two or more molecules, **but electrons also move within a molecule.**

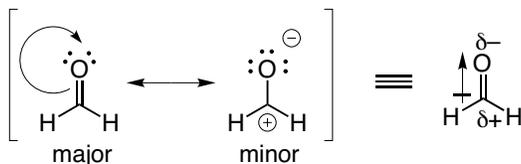
II. Resonance: Electronic Motion Within a Molecule

- The reactivity of a molecule is not always explained by one Lewis structure.
- Molecules can be thought of as **hybrids** or **weighted averages** of two or more Lewis structures, each with a different placement of electrons.
- These structures, called **resonance structures**, are not real or detectable, but they are a useful conceptual tool for understanding the reactivity of molecules.

e.g. How can you predict where a nucleophile (such as H_2N^-) will react with formaldehyde (CH_2O)?



- Use resonance to better understand the electronic nature of formaldehyde . . .



- The minor resonance structure suggests that the carbon atom is electron-deficient (electrophilic).

The nucleophile will react with the electrophilic carbon atom.



A. Rules for Drawing Resonance Structures

1. **Only electrons move!** Nuclei and the sigma- (single bond-) framework are unchanged (Resonance occurs in the pi-system: conjugated lone pairs and pi-bonds).
2. Every resonance structure must be a **valid Lewis structure**.
3. Keep track of **lone pairs** and **formal charges**.
4. Use **arrow-pushing formalism** to interconvert and identify possible resonance structures.
5. Always use **double-headed arrow** (\longleftrightarrow) in between resonance structures.
6. **Lower energy** resonance structures **contribute most** to the overall structure of the molecule.

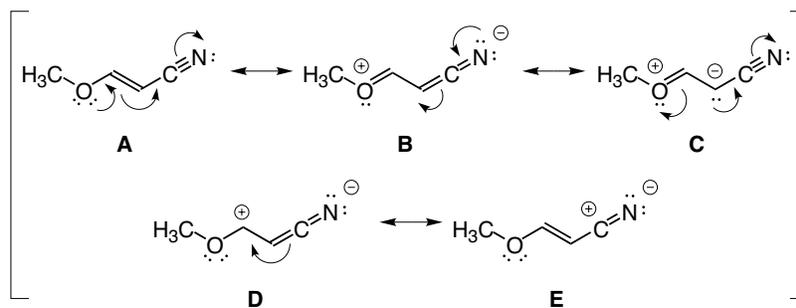
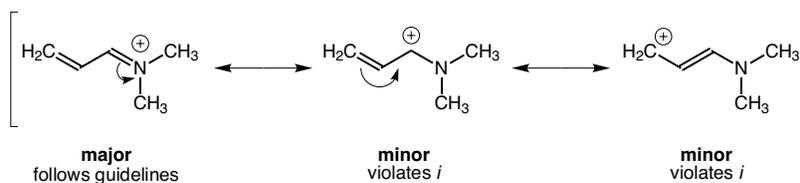
How do you predict the relative energies of resonance structures?

B. Guidelines for Predicting Energies of Resonance Structures (In Order of Importance)

i) Filled Octets: Second row elements (C, N, O, F) want an octet (filled valence shell of electrons). Because C is the least electronegative, structures in which C has 6 electrons, 3 bonds and a positive charge are possible (not possible with N, O, F).

ii) Negative charges on most **electronegative atoms**.

iii) Minimize charge separation.



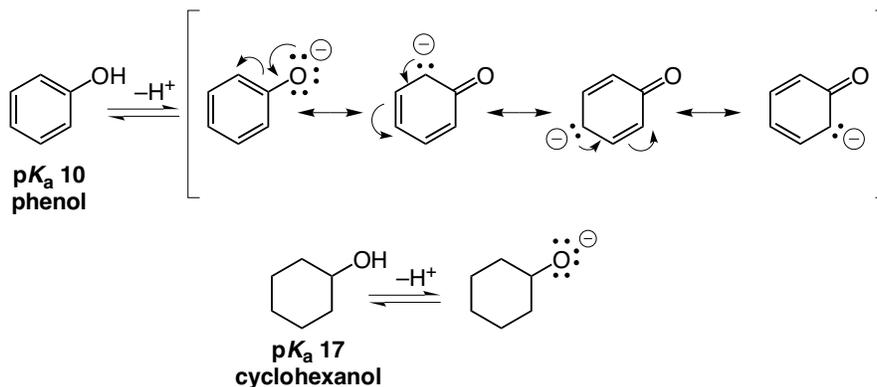
- A:** follows guidelines
B: violates *iii*: 2 formal charges
C: violates *ii & iii*: negative charge on C; 2 formal charges
D: violates *i & iii*: 6 electrons on C; 2 formal charges
E: violates *i & iii*: 6 electrons on C; 2 formal charges

Relative Energy: $A \ll B < C \ll D \sim E$

Relative Importance: A (major) $> \underbrace{B > C > D \sim E}_{\text{minor}}$

Delocalization of Charge = Stabilization

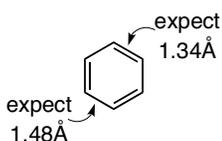
- The conjugate base of phenol (phenoxide) is stabilized by resonance.
- Because phenoxide ion is stabilized, phenol is more acidic than cyclohexanol.



- In general, the more resonance structures there are, the greater the stabilization.
- Equivalent resonance structures provide more stabilization than inequivalent ones.

C. Structure and Reactivity Info from Resonance Structures

e.g. Benzene



- Drawn this way, benzene appears to have two types of carbon-carbon bonds (single and double).
- Experimental data indicates that all of the carbon-carbon bonds in benzene are equivalent and rather unreactive.
- Benzene is approximately 35 kcal/mol more stable than would be expected because the electrons are delocalized around the ring.

