

## Week 1

# The Basics: Bonding and Molecular Structure

### 1.1 Course Information

- 9/28:
- No labs this week.
  - Virtual lab: Watch a video and record data in your notebook; answer embedded quiz questions.
  - Collaborative Learning in Organic Chemistry (CLOC).
    - 2hr Sunday or Monday.
    - Contact Dr. Britni Ratliff (ratliff@uchicago.edu).
    - Pass/Fail grading (based on attendance).
    - You work on problems related to the lecture content under the supervision of someone who's taken the class before.
    - You can opt-in/out on a quarter-by-quarter basis.
  - Review syllabus: Download alternate textbooks, put exam dates in the calendar, add office hours to calendar.
  - Develop an understanding of how structure affects reactivity — mechanistic principles.
  - You don't have to memorize anything, but you have to remember everything.
    - Like learning a language.
      - Vocabulary, grammar (principles), apply to understand and predict.

### 1.2 Defining Organic Chemistry

- **Organic chemistry:** Traditionally, the chemistry of living organisms. Now, the chemistry of carbon compounds.
  - Carbon is of particular import because it can bond with itself, and it can form strong bonds with other elements (e.g., C, O, H, S, N, and P) as well.
  - Carbon is bound in simple molecules (such as CO<sub>2</sub> and CH<sub>4</sub>), and highly complex ones (such as proteins, DNA, and RNA).
- Carbon compounds:

- Natural: Sugars, fats, gasoline, hydrocarbons, hormones, natural drugs, peptides, rubber, silk, starch, cotton, etc.
- Synthetic: Dyes, fragrances, soaps, drugs, medicines, plastics, materials, teflon, nylon, etc.
- OChem is a central science that feeds into fields such as biochemistry, molecular biology, molecular medicine, math/theory (e.g., buckyballs), engineering, and physics.

## 1.3 Gen Chem Review

- Today:
  1. Intro (done).
  2. Atomic structure and bonding (review from Gen Chem).
  3. Chemical bonds — octet rule.
  4. Writing Lewis structures.
  5. Formal charges.
- Atomic structure and bonding.
  - Atoms  $\rightarrow$  elements  $\rightarrow$  compounds.
  - Nucleus (protons and neutrons) surrounded by electrons.
  - This year, we'll concern ourselves with the main group elements.
  - Electron configuration:
    - Aufbau principle: Electrons fill orbitals from lowest energy to highest energy.
    - Pauli exclusion principle: 2 electrons/orbital with opposite spin quantum numbers (must pair  $+\frac{1}{2}$  with  $-\frac{1}{2}$ ).
    - Hund's rule: Orbitals with equivalent energy get partially filled first before more electrons are added.
    - Example:  $1s^2 2s^2 2p^6 3s^1$  is Na.
  - Valence electrons are key in this class.
- Noble gas configurations and the octet rule.
  - Lewis noticed that there is a special stability associated with a filled outer shell.
  - Thus, we generally have 8 electrons in the filled outer shell.
    - For example,  $\text{Cl} \xrightarrow{+1e^-} \text{Cl}^-$  and  $\text{Na} \xrightarrow{-1e^-} \text{Na}^+$ .
  - Chemical bonds form because they allow the atoms to achieve a filled octet.
  - Two kinds of bonding: Ionic and covalent.
    - Ionic: Not covered much this year. Lose or gain an electron (forming cations and anions, respectively) to form a filled outer shell. Usually involves a metal and a nonmetal.
    - Covalent: Covered a lot this year. Sharing electrons to satisfy the need for an octet.
    - The atoms involved dictate whether bonding will be ionic or covalent.
  - Electronegativity: The ability of an atom to attract its valence shell electrons.
    - Defined by Pauling, who let  $\text{Li} = 1.0$  and  $\text{F} = 4.0$ .
    - This is a very important concept for understanding bonding and reactivity.
    - EN increases across and up on the periodic table: More protons and a shorter distance away from the nucleus both mean a greater pull on the electrons.
    - Mnemonic (highest to lowest electronegativity): F O Cl N Br I S C H P.

- Non-polar covalent bonds form when  $\Delta EN < 0.5$ .
- Polar covalent bonds form when  $\Delta EN \approx 0.5 - 1.9$ .
- Exceptions to the octet rule: H wants  $2e^-$ . Be wants  $4e^-$ . B and Al want  $6e^-$ . Molecule has an odd number of electrons (e.g., NO with 11 electrons is stable).
- Lewis structures.
  - General rules/procedure (there are exceptions).
    1. Determine the total number of valence electrons for the molecule. Add electrons for negative charges; remove for positive charges.
    2. Draw a skeleton and join atoms with single bonds. Put the atom that likes to make the most bonds in the center.
    3. Deduct 2 electrons from the count in step 1 for each single bond. Fill outside atoms with lone pair electrons.
    4. The remaining electrons go on the central atom.
    5. If you have too few electrons for every atom to have an octet, use lone pair electrons to convert single bonds to double bonds. We can also use triple bonds.
  - $CH_4$  and  $NH_3$  presented as worked examples.

9/30:

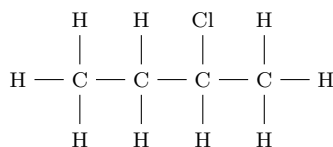
- Today:
  4. Lewis Structures.
  5. Formal charges.
  6. Isomers.
  7. Structural formulas.
  8. Resonance.
  9. Orbitals and bonding.
- Lewis structures:
  - $H_2CO$  (formaldehyde) and  $CH_3COOH$  (acetic acid) presented as worked examples.
- Formal charge determination:
  - If the number of valence electrons does not equal the total number of electrons on an atom, then you will have a formal charge.
  - Rule:

$$\begin{aligned}\text{Formal Charge} &= \text{normal valence } e^- - \text{actual } e^- \\ &= \text{valence } e^- - \left( \text{nonbonding } e^- + \frac{1}{2} \text{bonding } e^- \right) \\ &= \text{valence } e^- - (\text{dots} + \text{lines})\end{aligned}$$

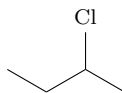
- $CH_3COO^-$  (acetate) has a formal charge of  $6 - 7 = -1$  on its singly bonded oxygen.
- $CH_3NH_3^+$  (methyl ammonium) has a formal charge of  $5 - 4 = +1$  on its nitrogen.
- Exceptions: Open shell Group III central atoms (e.g., B and Al).
  - $BF_3$  acts as a Lewis acid because it wants to grab  $2e^-$  to form an octet.
  - It often acts in acid-base coupling reactions, grabbing a lone pair from an oxygen in an adjacent molecule and bonding through it.

## 1.4 OChem Basics

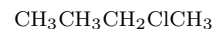
- Isomers:
  - Constitutional isomers: Same molecular formula but different bond connectivities.
  - Acetone vs. 3-propanol, yet both are  $C_3H_6O$ .
- Structural formulas:



(a) Dash structural formula.



(b) Bond line formula.



(c) Condensed formula.

Figure 1.1: Structural formulas.

- **Dash structural formula:** A Lewis structure.
- **Bond line formula:** No C–H's, show a vertex for each carbon, show heteroatoms and heteroatom H's. *Also known as line-angle structure, zig-zag structure.*
- **Condensed formula:** All atoms written out with no bonds or lone pairs.
- **3D representation:** A dash structural/bond line formula with wedges and dashes.
- **Resonance:** When a molecule or an ion can be represented by 2 or more Lewis structures, i.e., two or more structures with the same skeleton connected by different electrons.
  - Resonance structures or resonance contributors.
  - The actual molecule is somewhere between the contributors.
  - $CO_3^{2-}$  presented as a worked example.
  - Guidelines:
    1. Only lone pairs or  $\pi$  electrons move (never move single bonds).
    2. No structure with greater than  $8e^-$  on a 2nd row atom.
    3. The species with the maximum number of octets is the strongest contributor.
    4. Charge on suitable atoms (e.g., negative charge on the atom with the highest electronegativity).
  - Resonance stabilization comes from delocalization. When 2 or more resonance structures, the “real” structure is somewhere in between (the real is more stable than any contributor).
  - $CH_3COO^-$  (acetate),  $CH_2CHCH_2^+$ , and  $(CH_3)_2CO$  presented as worked examples.
  - You can also depict delocalization with a curving dashed bond and  $\delta^-$ 's.

## 1.5 Bonding and Orbital Diagrams

10/5:

- Today:
  9. Orbital theory and bonding.
  10. Methane.
  11. Ethane.
  12. Ethylene.

13. Acetylene.
  14. Comparison of  $sp^3$ ,  $sp^2$ ,  $sp$  orbitals.
  15. VSEPR Model + Molecular Symmetry.
- Orbital theory and bonding:
    - Defines **atomic orbitals**.
    - Reviews  $s$  and  $p$  orbital shapes, positive and negative regions, and nodes.
    - Energy of orbitals diagram.
    - Phosphorous and sulfur can exceed the octet rule since they have  $d$  orbitals in which to stash extra electrons.
    - Filled with the Aufbau/Pauli Exclusion principles, and Hund's Rule.
    - Goes over bonding energy diagram.
    - Mathematically, we have a Linear Combination of Atomic Orbitals (or LCAO).
      - Electrons are represented as waves; thus, they have  $+$  and  $-$  phases.
      - Opposite phases are destructive; this forms  $\sigma^*$  orbitals.
      - Same phases are constructive; this forms  $\sigma$  orbitals.
    - Goes over MO diagrams.
  - **Atomic orbital:** A space where electrons are likely to be found 95% of the time.
  - **Degenerate** (orbitals): Two orbitals with the same energy.
  - **Chemical bond:** A favorable interaction between 2 atoms, i.e., one that helps to fill the outer orbitals to achieve a noble gas configuration.
  - Bonding in methane:

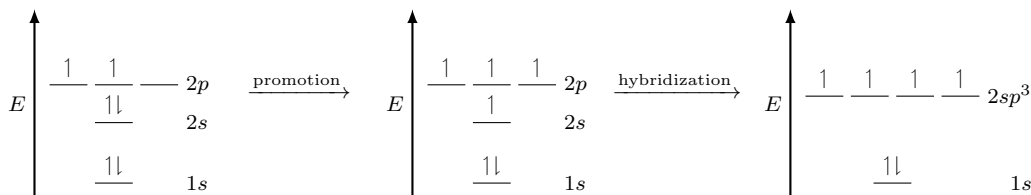


Figure 1.2: Bonding in methane.

- Draws an orbital diagram for carbon.
- Promotes an electron from  $2s \rightarrow 2p_z$ .
- Hybridizes  $2s, 2p_x, 2p_y, 2p_z$  into 4 degenerate  $sp^3$  orbitals of weighted average energy, each containing only 1 electron.
- Links each of these  $sp^3$  electrons to the 1s electron in  $H_2$ , forming  $\sigma$  orbitals.
- The new orbitals adopt a tetrahedral arrangement to be as far apart as possible.
- Bonding in ethane.
  - Two  $sp^3$  electrons combine in a  $\sigma$  orbital; no electrons go into the  $\sigma^*$  MO.
- The structure of ethylene.
  - Side by side overlap of  $p$  orbitals forms a  $\pi$  bond.
  - The angle between the hydrogens in ethylene is slightly less than  $120^\circ$ .

- The bond is slightly shorter than in ethane (greater  $s$  character plus an additional type of bond).
- Features of the C=C double bond.
  - $sp^2$ -hybridized carbons making  $3\sigma$  and  $1\pi$  bond.
  - A  $\pi$  bond is weaker than a  $\sigma$  bond, but still strong.
  - $\sigma_{sp^2-sp^2}$  is stronger than  $\sigma_{sp^3-sp^3}$ .
  - Restricted rotation (hard to twist  $C_2H_2$  by  $90^\circ$ ).
  - cis-trans isomerism as a result of restricted rotation.
  - The  $\pi$  bond acts like a Lewis base with some systems since the  $\pi$  electrons are held relatively weakly. In other words, the  $\pi$ -electrons are exposed.
- Draws an MO diagram for the carbons.
- The structure of acetylene.
  - 2  $\pi$  bonds, 1  $\sigma$  bond.
  - Even greater strength, but not quite as much greater as the  $\sigma_{sp^3-sp^3} \rightarrow \sigma_{sp^2-sp^2}$  difference.