CHEM 22000 (Organic Chemistry I) Notes

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Weeks

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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_2 and CH_4), 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 → elements → 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 elections/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, $\text{Cl} \xrightarrow{1\,e^-} \text{Cl}^-$ and $\text{Na} \xrightarrow[-1\,e-]{} \text{Na}^+$.
  - 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 for 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 Li = 1.0 and 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 $\Delta\text{EN} < 0.5$.
        - Polar covalent bonds form when $\Delta\text{EN} \approx 0.5 - 1.9$.
    - Exceptions to the octet rule: H wants $2\,e^-$. Be wants $4\,e^-$. B and Al want $6\,e^-$. 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:

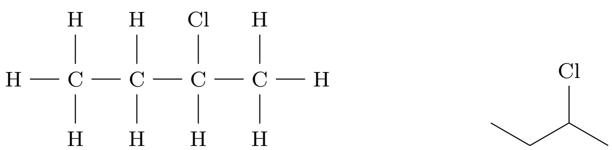
- Today:
    4. Lewis Structures.
    5. Formal charges.
    6. Isomers.
    7. Structural formulas.
    8. Resonance.
    9. Orbitals and bonding.
- Lewis structures:
    - H_2CO (formaldehyde) and CH_3COOH (acetic acid) presented as worked examples.
- Formal charge determination:
    - If the number 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 $2\,e^-$ 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-propenol, yet both are C_3H_6O.
- Structural formulas:



$CH_3CH_3CH_2ClCH_3$

(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 π electrons move (never move single bonds).
    2. No structure with greater than $8\,e^-$ 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 δ^-'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 σ^* orbitals.
    - Same phases are constructive; this forms σ 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:

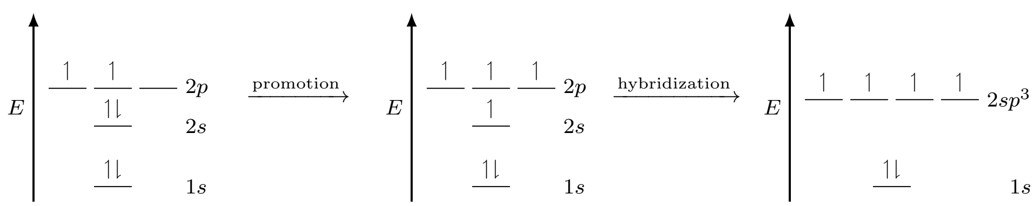


Figure 1.2: Bonding in methane.

  - Draws an orbital diagram for carbon.
  - Promotes an electron from $2s \to 2p_z$.
  - 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 σ 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 σ orbital; no electrons go into the σ^* MO.
- The structure of ethylene.
  - Side by side overlap of p orbitals forms a π bond.
  - The angle between the hydrogens in ethylene is slightly less than 120°.

    - 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 3σ and 1π bond.
        - A π bond is weaker than a σ 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°).
        - cis-trans isomerism as a result of restricted rotation.
        - The π bond acts like a Lewis base with some systems since the π electrons are held relatively weakly. In other words, the π-electrons are exposed.
    - Draws an MO diagram for the carbons.
- The structure of acetylene.
    - 2 π bonds, 1 σ bond.
    - Even greater strength, but not quite as much greater as the $\sigma_{sp^3-sp^3} \to \sigma_{sp^2-sp^2}$ difference.

1.6 VSEPR Theory

10/7:

- There's a special kind of electronegativity that relates to hybridization: An sp-hybridized carbon is more electronegative than an sp^3-hybridized carbon, for instance.
- VSEPR Model:
    - Electron pairs want to stay as far apart as possible in space.
    - Consider the bonding electrons (number of atoms bound) and nonbonding electrons.
    - Describe shape based on the position of nuclei.
- Constructs VSEPR table for linear, trigonal planar, tetrahedral, trigonal pyramidal, bent

Week 2

Families of Carbon Compounds / Acids and Bases

2.1 Families of Carbon Compounds

10/7:

- Hydrocarbons:
  - Alkanes (C_nH_{2n+2}) and cycloalkanes C_nH_{2n}.
  - Alkenes (C_nH_{2n}).
  - Alkynes (C_nH_{2n-2}).
- Aromatic:
  - Contains a benzene ring.
  - All bonds ~ 140 Å.
  - All carbons sp^2.
  - Planar.
  - π electrons above and below the ring.
  - Special stabilization.
- Covers drawing dipoles.
- Polar and nonpolar molecules:
  - Dipole = distance × change between charges.
  - $\mu = r \times Q$
  - $1\,\mathrm{D} = 3.336 \times 10^{-30}\,\mathrm{C\,m}$.
  - Analyzes molecules by drawing a Lewis structure, drawing a dipole along each bond, and drawing and labeling a net dipole, if applicable.
  - Goes through a number of examples.
  - Acetonitrile is a strong polar solvent.
- **Functional group**: A common arrangement that determines shape, bonding physical and reactivity of organic compounds.
- Families of carbon compounds:
  - Hydrocarbons: Aliphatic, aromatic.
  - Methyl, ethyl, propyl, R = alkyl groups.

- Phenyl: Ph- or ϕ-.
- Benzyl: Ph$-$CH$_2$-, $C_6H_5CH_2$-, Bn-
- Compounds with R$-$Z where Z is a heteroatom.
  - If Z is a halogen X, then the halogroup makes it an alkyl halide or haloalkane.
- Alkenyl halide: X$-$=.
- Aryl halide: Ph$-$X.
- Alcohols or phenols: R$-$OH.
- Ether: R$-$O$-$R$'$.
- Amines: NH_2R, NHRR$'$, NRR$'$R$''$.
- Thiols or mercathols: R$-$SH.
- Carbonyl group: R$-$CO$-$R$'$.
- Aldehyde: R$-$COH.
- Ketone: R$-$CO$-$R$'$.
- Carboxylic acid derivatives:
  - Acid: R$-$COOH.
  - Ester: R$-$COOR$'$.
  - Acid chloride: R$-$COCl.
  - Acid halide: R$-$COX.
  - Amide: R$-$CONH$_2$.
  - Acid anhydride: R$-$COOCO$-$R$'$.
- Nitrile: R$-$C$\equiv$N.
- Acrylonitrile: $=-$C$\equiv$N.

2.2 Discussion Section

- ACS in-text citations should be in superscripts as a list of number with no brackets or parentheses.
- Molecular formulas are C_2H_6O, not C_2H_5OH or CH_3CH_2OH.
- Make a table if you have a lot of data to put in (make it readable!).
- Distillation:
  - We need a boiling chip and stir bar inside the flask.
  - Vapor comes up from a round-bottomed flask, encounters a rubber stopper and gets diverted through a condenser instead.
  - Make use of countercurrent exchange and increase pressure by inflowing water in the gravitationally lower portion of the condenser.
  - Boiling chip is a coarse material with a lof of micropores inside.
  - The surface energy is reduced when the fluid is inside the micropores; within, it can more easily become a gas.
- As the mole fraction χ of a substance A increases...
- Raoult's law:
$$P_{\text{total}} = \frac{P_A \chi_A}{P_B \chi_B} = \frac{P_A \chi_A}{P_B (1 - \chi_A)}$$
- Dalton's law: The total pressure is equal to the sum of the partial pressures.

2.3 Intermolecular Forces and IR Spectroscopy

10/12:

- Intermolecular forces and physical properties.
- **Boiling point**: The temperature at which the vapor pressure is equal to the pressure of the atmosphere above.
  - The stronger the intermolecular forces, the higher the boiling point.
  - The higher the molecular weight, the higher the boiling point.
- **Melting point**: The temperature at which the crystalline solid and liquid are in equilibrium.
  - The stronger the intermolecular forces, the higher the melting point.
  - The more symmetrical, the higher the melting point.
- Solubility.
- Intermolecular forces.
  - All electrostatic attractions related to bond polarity.
  - 3 types: Dipole-dipole forces, hydrogen bonding, and dispersion forces.
- **Dipoloe-dipole forces**: Attraction between opposite poles (1 kcal/mol to 3 kcal/mol).
- **Hydrogen bonding**: Dipole-dipole interaction between H-atoms bonded to O, N, F (2 kcal/mol to 10 kcal/mol).
- **Dispersion forces**: Weak (< 1 kcal/mol). Momentary distortion of the electron cloud (temporary dipole). Induces dipoles in surrounding molecules. *Also known as* **London forces**.
  - Depends on **relative polarizability**.
  - Dependes on the surface area of the molecule — more surface area means more distance electrons can spread apart.
- **Relative polarizability**: How far valence electrons are from the nucleus.
- Solubility:
  - For something to be soluble, you need to have favorable forces between them.
  - Ionic compounds are soluble in water, less soluble in polar solvents, and insoluble in nonpolar solvents.
  - Organic compounds: < 3 carbons is soluble, 4-5 carbons is borderline, ≥ 6 is insoluble. More soluble in organic solvents.
- Organic solvents:
  - CH_2Cl_2 — methylene chloride.
  - $HCCl_3$ — chloroform.
  - H_3CCOCH_3 — acetone.
  - Diethyl ether.
  - THF.
  - Cyclohexane.
- In TLC, the silica gel is very polar, so polar compounds will not move far up the plate. Nonpolar solvents will drag nonpolar compounds up pretty high.
- HOMO and LUMO get closer as conjugation increases.
- IR spectroscopy:

- The frequencies absorbed vary based on the type. Higher stretching frequencies for lighter atoms and stronger bonds.
- IR radiation causes transitions in vibrational modes of bonds.
- The stronger the bond and the lighter the atoms, the faster the vibration of the molecule and the higher the stretching frequency.
- The ΔE's are inherent characteristics of the bonds and nuclei.
- Bonds absorb light of characteristic energy, frequency, and wavelength.
- We usually report IR spectra in terms of the wavenumber $\bar{\nu}$.
- The frequencies absorbed can indicate bond types and functional groups in the molecule.
- Anything above 1500 (of wavenumber less than 1500) is called the **fingerprint region** — it may not tell you what a molecule is, but it will tell you if two molecules are the same.
- Sharp peaks at high wavenumbers are characteristic of N−H interactions.
- Make a line at $3000\,\mathrm{cm}^{-1}$. Things to the right of that indicate aliphatic C−H's. Things to the left indicate sp^2 C−H groups. Things more to the left indicate sp C−H groups.
- Not all bonds are visible — stretching bands must change the dipole. Thus, for example, the C=H stretch in trans-but-2-ene is not IR active, but the C=H stretch in cis-but-2-ene is IR active.
- If you want to substitute D for H, the peak formerly associated with the R−H bond will move lower.

COMMON ABSORPTIONS	
Aromatic C−C	Two peaks usually in the range of $1500\,\mathrm{cm}^{-1}$ to $1600\,\mathrm{cm}^{-1}$
C=C	$\sim 1650\,\mathrm{cm}^{-1}$
C=O	$\sim 1710\,\mathrm{cm}^{-1}$ (shifts to $\sim 1735\,\mathrm{cm}^{-1}$ for esters)
C≡C	$2100\,\mathrm{cm}^{-1}$ to $2300\,\mathrm{cm}^{-1}$
C≡N	$2100\,\mathrm{cm}^{-1}$ to $2300\,\mathrm{cm}^{-1}$
C−H (aldehyde)	Two peaks at $2170\,\mathrm{cm}^{-1}$ and $2810\,\mathrm{cm}^{-1}$
sp^3 C−H	Just to the right of $3000\,\mathrm{cm}^{-1}$
sp^2 C−H	Just to the left of $3000\,\mathrm{cm}^{-1}$
sp C−H	$\sim 3300\,\mathrm{cm}^{-1}$
N−H	$\sim 3300\,\mathrm{cm}^{-1}$ (one peak for −NH−, two peaks for $-NH_2$)
O−H (alcohol)	$\sim 3400\,\mathrm{cm}^{-1}$ (a broad, smooth peak)
O−H (acid)	$\sim 2500\,\mathrm{cm}^{-1}$ to $3500\,\mathrm{cm}^{-1}$ (a very broad, ugly [not smooth] peak)

Table 2.1: Common IR spectroscopy absorptions.

2.4 Acids and Bases

10/14:

- **Brønsted-Lowry acid**: A proton donor.
- **Brønsted-Lowry base**: A proton acceptor.
- General reaction:

$$\mathrm{H{-}A} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{A^-}$$

  - Does curved-arrow formalism for the above reaction.

- The reaction equilibrium is given by

$$\begin{aligned} K_{\text{eq}} &= \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}][\text{H}_2\text{O}]} \\ K_{\text{eq}}[\text{H}_2\text{O}] &= \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \\ K_\text{a} &= \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \end{aligned}$$

- Note that $[H_2O] = 55.5\,\text{M}$.
- $\text{p}K_\text{a} = -\log K_\text{a}$ gives numbers that are easier to work with.
  - The larger the $\text{p}K_\text{a}$, the weaker the acid.
  - The smaller the $\text{p}K_\text{a}$, the stronger the acid.
- Gives $\text{p}K_\text{a}$'s and conjugate bases for the strong acids HI, HBr, HCl, H_2SO_4, and HNO_3.
  - Also for the weak acids CH_3CO_2H, HF,
- There is a relationship between acid strength and conjugate base strength.
  - The stronger the acid (lower $\text{p}K_\text{a}$), the weaker the conjugate base.
  - The weaker the acid (higher $\text{p}K_\text{a}$), the stronger the conjugate base.
- Almost any reaction can be thought of as an acid/base reaction using the Lewis definition.
- Acid-base reaction equilibria:

$$\text{H}{-}\text{A} + \text{B} \xrightleftharpoons{\text{K}_\text{eq}} \text{A}^- + \text{HB}$$

  - Let

$$K_{\text{a}_1} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \qquad\qquad K_{\text{a}_2} = \frac{[\text{H}_3\text{O}^+][\text{B}^-]}{[\text{HB}]}$$

  - Then

$$\begin{aligned} K_{\text{eq}} &= \frac{K_{\text{a}_1}}{K_{\text{a}_2}} \\ \log K_{\text{eq}} &= \log K_{\text{a}_1} - \log K_{\text{a}_2} \\ &= \text{p}K_{\text{a}_2} - \text{p}K_{\text{a}_1} \\ K_{\text{eq}} &= 10^{\Delta \text{p}K_\text{a}} \end{aligned}$$

    so for any acid-base reaction, the position of the equilibrium can be predicted from the relative $\text{p}K_\text{a}$'s.
- Factors influencing acidity:
  - Bond strength and size.
    - As bond strength decreases, acidity increases.
    - As size of the conjugate base increases, acidity increases (there is more area over which to delocalize the positive charge).
  - Electronegativity.
    - As electronegativity differences increase, acidity increases.
  - Hybridization.

    - *sp* orbitals are more acidic than sp^3, with sp^2 in between. This is because the electrons are held closer to the nucleus and are less easily given away.
  - Inductive effects.
    - Electronic effects transmitted through bonds.
    - Electron donating or electron withdrawing groups.
    - Stronger electron withdrawing groups create more acidic compounds (the conjugate base is more stable, and the proton more easily dissociates).
    - Falls off with distance.
    - Alkyl groups are electron donating.
  - Resonance effects.
    - Pulling a proton off of an alcohol leaves negative charge on the oxygen; pulling a proton off a carboxylic acid group leads to an anion that has resonance (and thus is more stable, so the the acid is stronger).
  - Solvation effects.
    - Charges that are more accessible (primary vs. tertiary) are more easily solvated and thus have more stable conjugate bases. Thus, an acid that has charges on its conjugate base that are more easily solvated is stronger.