

## 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  $\sim 140$  Å.
  - All carbons  $sp^2$ .
  - Planar.
  - $\pi$  electrons above and below the ring.
  - Special stabilization.
- Covers drawing dipoles.
- Polar and nonpolar molecules:
  - Dipole = distance  $\times$  change between charges.
  - $\mu = r \times Q$
  - $1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$ .
  - 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 the shape, bonding, physical properties, and reactivity of organic compounds.
- Families of carbon compounds:
  - Hydrocarbons: Aliphatic, aromatic.
  - Methyl, ethyl, propyl,  $R$  = alkyl groups.

- Phenyl: Ph- or  $\phi$ -.
- Benzyl: Ph-CH<sub>2</sub>-, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>-, 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<sub>2</sub>R, NHR', NRR'R''.
- Thiols or mercaptols: 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<sub>2</sub>.
  - Acid anhydride: R-COOCO-R'.
- Nitrile: R-C≡N.
- Acrylonitrile (compound, not a group): =-C≡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<sub>2</sub>H<sub>6</sub>O, not C<sub>2</sub>H<sub>5</sub>OH or CH<sub>3</sub>CH<sub>2</sub>OH.
- 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 lot 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  $\chi$  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.
- **Dipole-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**.
  - Depends 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,  $\geq 6$  is insoluble. More soluble in organic solvents.
- Organic solvents:
  - $\text{CH}_2\text{Cl}_2$  — methylene chloride.
  - $\text{HCCl}_3$  — chloroform.
  - $\text{H}_3\text{CCOCH}_3$  — 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:

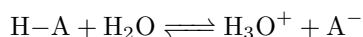
- The frequencies absorbed vary based on the type. Higher stretching frequencies for lighter atoms and stronger bonds.
- IR radiation causes transitions in vibrational modes of bonds.
- The stronger the bond and the lighter the atoms, the faster the vibration of the molecule and the higher the stretching frequency.
- The  $\Delta E$ '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  $3000\text{ cm}^{-1}$ . 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=C stretch in *trans*-but-2-ene is not IR active, but the C=C 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 $1500\text{ cm}^{-1}$ to $1600\text{ cm}^{-1}$           |
| C=C                | $\sim 1650\text{ cm}^{-1}$   |
| C=O                | $\sim 1710\text{ cm}^{-1}$ (shifts to $\sim 1735\text{ cm}^{-1}$ for esters)               |
| C $\equiv$ C       | $2100\text{ cm}^{-1}$ to $2300\text{ cm}^{-1}$   |
| C $\equiv$ N       | $2100\text{ cm}^{-1}$ to $2300\text{ cm}^{-1}$   |
| C–H (aldehyde)     | Two peaks at $2710\text{ cm}^{-1}$ and $2810\text{ cm}^{-1}$                               |
| $sp^3$ C–H         | Just to the right of $3000\text{ cm}^{-1}$   |
| $sp^2$ C–H         | Just to the left of $3000\text{ cm}^{-1}$  |
| $sp$ C–H           | $\sim 3300\text{ cm}^{-1}$   |
| N–H                | $\sim 3300\text{ cm}^{-1}$ (one peak for $-\text{NH}-$ , two peaks for $-\text{NH}_2$ )    |
| O–H (alcohol)      | $\sim 3400\text{ cm}^{-1}$ (a broad, smooth peak)  |
| O–H (acid)         | $\sim 2500\text{ cm}^{-1}$ to $3500\text{ cm}^{-1}$ (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:



- Does curved-arrow formalism for the above reaction.

- The reaction equilibrium is given by

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

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

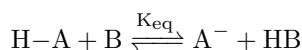
$$K_{\text{a}} = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

- Note that  $[\text{H}_2\text{O}] = 55.5 \text{ M}$ .

– Derived from the density of water:

$$\frac{1 \text{ g}}{1 \text{ mL}} = \frac{1000 \text{ g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = \frac{55.5 \text{ mol}}{1 \text{ L}}$$

- $\text{p}K_{\text{a}} = -\log K_{\text{a}}$  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,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$ .
  - Also for the weak acids  $\text{CH}_3\text{CO}_2\text{H}$ , 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:



– Let

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

– Then

$$K_{\text{eq}} = \frac{K_{\text{a}_1}}{K_{\text{a}_2}}$$

$$\log K_{\text{eq}} = \log K_{\text{a}_1} - \log K_{\text{a}_2}$$

$$= \text{p}K_{\text{a}_2} - \text{p}K_{\text{a}_1}$$

$$K_{\text{eq}} = 10^{\Delta \text{p}K_{\text{a}}}$$

so for any acid-base reaction, the position of the equilibrium can be predicted from the relative  $\text{p}K_{\text{a}}$ 's. This also makes intuitive sense: The stronger acid *should* push harder on the equilibrium, forcing it to the other side.

- 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, so the conjugate base is more stable, so acidity increases).
- 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 in the conjugate base, and thus are less easily given away in the reverse reaction.
- 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 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.

## 2.5 Acids and Bases in Nonaqueous Solutions

10/21:

- The strongest base you can have in water is  $\text{OH}^-$ .
  - This is because strong bases (e.g.,  $\text{H}_2\text{N}^-$ ) give you
$$\text{H}_2\text{N}^- + \text{H}-\text{OH} \rightleftharpoons \text{HO}^- + \text{NH}_3$$
  - Since  $\text{p}K_{\text{a}}(\text{H}_2\text{O}) = 14$  and  $\text{p}K_{\text{a}}(\text{NH}_3) = 38$ ,  $K_{\text{eq}} = 10^{38-14} = 10^{24}$ .
- We need a solvent with less acidic protons, e.g., hexane, diethyl ketone.
  - $\text{Li}(\text{CH}_2)_3\text{CH}_3$ , LDA (lithium diisopropylamide), NaH are all very strong bases.
- **Lewis acid:** Electron pair acceptor.
- **Lewis base:** Electron pair donor.
- $\text{AlCl}_3$  has an empty  $p$ -orbital with which it can accept electrons.