

ASSIGNED READINGS:

TODAY'S CLASS:

- 1.15 Molecular dipole moments
 1.16 Review of acids & bases
 1.17 Organic acids & bases: pK_a & pH
 1.18 Effect of structure on pK_a
 1.19 Introduction to delocalized electrons & resonance
 7.2-7.5 Understanding & drawing resonance structures

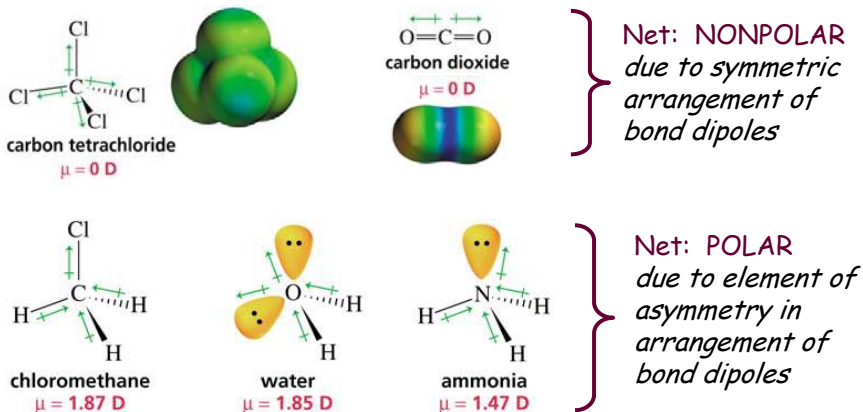
NEXT CLASS: finish Ch.1, plus 7.10

<http://artsandscience.concordia.ca/facstaff/P-R/rogers>

(1)

1.15 Review: Dipole Moment of Molecules

The vector sum of magnitude and direction of individual bond dipole determines overall dipole moment of a molecule



(2)

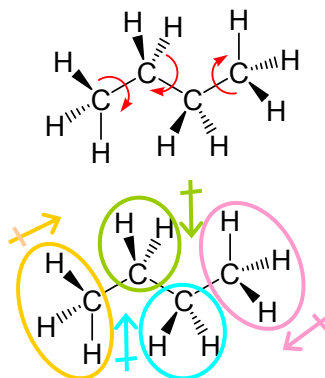
Judging polarity of organic molecules

1. Consider lone pairs as contributing δ^- character
2. Treat C-H bonds as if they were totally nonpolar (even though $\Delta\chi = 0.4$ and $D = 0.4$)

WHY?

- Molecules are flexible:
 - Free rotation occurs about single bonds
 - Exist in many different "conformations"

THUS: on average...
small regional dipoles
caused by C-H bonds
end up canceling out
over whole molecule!

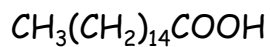
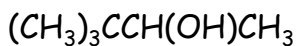


(3)

Identify the polar vs. nonpolar character of...

(label δ^-/δ^+ in net polar regions of molecules only)

Draw intuitively helpful structures, with polarity:



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1.16-1.17: Brønsted-Lowry Acids and Bases

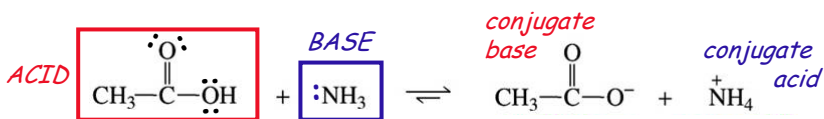
Acids donate a proton

Which is the most acidic H?

- the most δ^+ H (...in a polar bond) in the molecule

Bases accept a proton

- Use a pair of e⁻s (e.g., lone pair) to form a covalent bond to the δ^+ -H

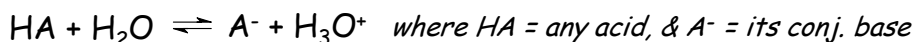


- removing ONE H⁺ from an acid produces its conjugate base
- adding ONE H⁺ to a base produces its conjugate acid

- Reactions between acids & bases are INSTANTANEOUS
 - base removes the most acidic H⁺ from the acid molecule
 - equilibrium is reached in less than a second
 - if no rxn occurs: base wasn't strong enough → eqm lies to left (i.e., acid's conjugate base was stronger!)

(5)

Measuring acid strength: K_a & pK_a



Acid

dissociation

$$\text{constant} = K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

$$pK_a = -\log(K_a)$$

IMPORTANT:

- pH** describes a **solution** (how much H₃O⁺ is present?)
- pK_a** describes a **compound** (how good at losing an H⁺ is it?)

Chemists use pK_a in two ways:

- To see inherent acidity of compound i.e., **strength**:

Lower pK_a ⇔ stronger acid (weaker conj. B)

Higher pK_a ⇔ weaker acid (stronger conj. B)

- To identify protonation state of a compound in solution, i.e., **speciation**:

A compound will exist primarily in its:

acidic form at a pH < its pK_a

basic form at a pH > its pK_a

The stronger an acid is, the weaker its conjugate base

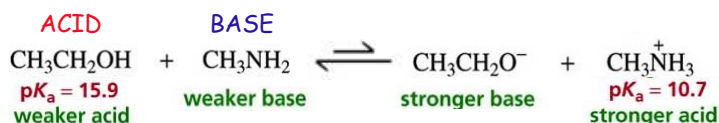
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Predicting if an acid-base rxn will occur...

To efficiently deprotonate another molecule: the attacking base (B:) must be **stronger** than the other molecule's conjugate base...

How to analyze a potential A/B reaction:

1. Identify which is more basic (**BASE**) & which is more acidic (**ACID**)
2. Identify the corresponding conjugate species
3. Compare strengths of the 2 bases: **BASE**, & **ACID**'s conj. Base
 - look up pK_a 's of the acids \Rightarrow think about conj. bases
 - the stronger base = better at accepting H^+
 - at equilibrium: stronger base preferentially carries the H^+



Convention: organic chemists use pK_a data (not pK_b)

\therefore to discuss base strength, must infer from pK_a of conj. acid

(7)

Acidity & basicity: depend on STRUCTURE

Table 1.8: Approximate pK_a values (see text's back cover for more)

STRONG ACIDS	MODERATELY STRONG...	← WEAK ACIDS →		...EXTREMELY WEAK
$pK_a < 0$	$pK_a \sim 5$	$pK_a \sim 10$	$pK_a \sim 15$	$pK_a \gg 15$
$\text{H}_3\text{O}^{\oplus}$ protonated water			H_2O water	
ROH_2^{\oplus} a protonated alcohol			ROH an alcohol	
$\begin{array}{c} \text{OH}^{\oplus} \\ \\ \text{R}-\text{C}-\text{OH} \end{array}$ a protonated carboxylic acid	$\begin{array}{c} \text{O} \\ \\ \text{R}-\text{C}-\text{OH} \end{array}$ a carboxylic acid	RNH_3^{\oplus} a protonated amine		RNH_2 an amine RCH_3 an alkane

Note: "R" is short for any unidentified carbon-based group like CH_3 , CH_3CH_2 , etc...

(8)

Acidity & basicity: depend on STRUCTURE

- The stronger the base, the weaker is its conjugate acid
(if it's so good at bonding to H⁺, then it's harder for it to let go...)
- A base deprotonates an acid by forming a covalent bond to H⁺ 1s orbital
 - BOTH e⁻s for the bond come from B:
 - Thus: a base will be *stronger* if it REALLY needs to share its e⁻s
a base will be weaker if it is quite stable carrying its e⁻s

What factors decrease basicity? (*more stable* ⇔ *less basic*)

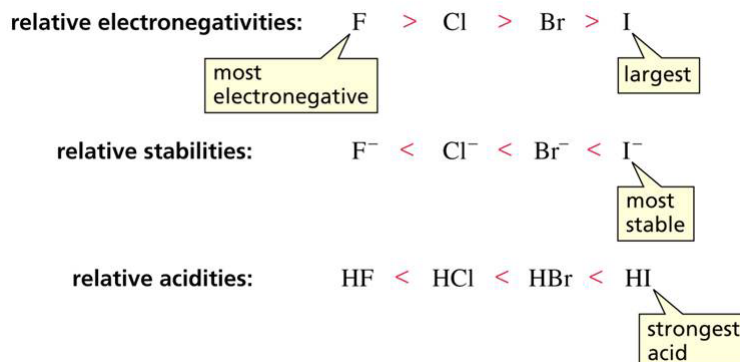
- 1.) Diminished electron density
 - lone pair on large atom → *Lone pairs on smaller atoms are more basic...*
 - due to inductive effects (e⁻-withdrawing groups)
 - due to resonance (delocalization of electrons) } *To compare lone pairs on same type of atom, consider these.*
- 2.) Diminished ability to share electrons
 - lone pair on highly electronegative atom } *Consider this when lone pairs are on atoms of similar size (same row).*

(9)

When comparing / predicting acid strengths:

- 1.) consider their conjugate bases
- 2.) compare atom carrying lone pair (= atom with bond to H in acid)
1st: consider SIZE

- When atoms are very different in size, the stronger acid will have its proton attached to the largest atom



(10)

When comparing / predicting acid strengths:

- 1.) consider their conjugate bases
- 2.) compare atom carrying lone pair (= atom with bond to H in acid)

1st: consider SIZE

2nd: if sizes similar → compare ELECTRONEGATIVITY

- When atoms are similar in size, the stronger acid will have its proton attached to the more electronegative atom

CH₃OH
methanol
pK_a = 15.5

CH₃NH₂
methylamine
pK_a = 40

(11)

When comparing / predicting acid strengths:

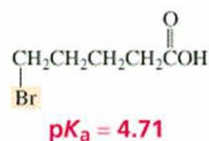
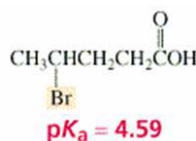
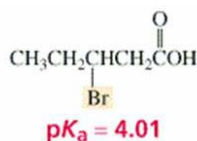
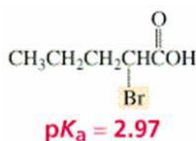
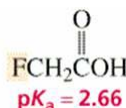
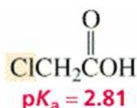
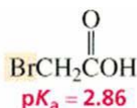
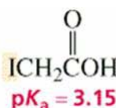
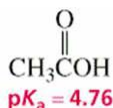
- 1.) consider their conjugate bases
- 2.) compare atom carrying lone pair (= atom with bond to H in acid)

1st: consider SIZE

2nd: if sizes similar → compare ELECTRONEGATIVITY

3rd: if same element → compare rest of molecule (EWGs)

- Inductive electron withdrawal increases the acidity of an acid
(by stabilizing the conjugate base)



(12)

When comparing / predicting acid strengths:

- 1.) consider their conjugate bases
- 2.) compare atom carrying lone pair (= atom with bond to H in acid)
 - 1st: consider SIZE
 - 2nd: if sizes similar → compare ELECTRONEGATIVITY
 - 3rd: if same element → compare rest of molecule (EWGs)
 - 4th: → compare degree of resonance stabilization

Acetic acid's conjugate base is stabilized by resonance
⇒ e⁻ pair is delocalized over many atoms

CH_3COOH
pK_a = 4.76
acetic acid

$\text{CH}_3\text{CH}_2\text{OH}$
pK_a = 15.9
ethanol

Ethanol's conjugate base is NOT...



(13)

Resonance Contributors and the Resonance Hybrid

Resonance contributors (individual resonance structures) are imaginary, but the resonance hybrid is real

What does the true structure of acetate look like?

(14)

ASSIGNED READINGS

BEFORE NEXT LECTURE:

Read: rest of Bruice Ch.1

Review: Chem206: acids & bases

- conjugate pairs
- pH, pK_a , pK_b
- reactions of acids & bases
- effect of structure on acidity