

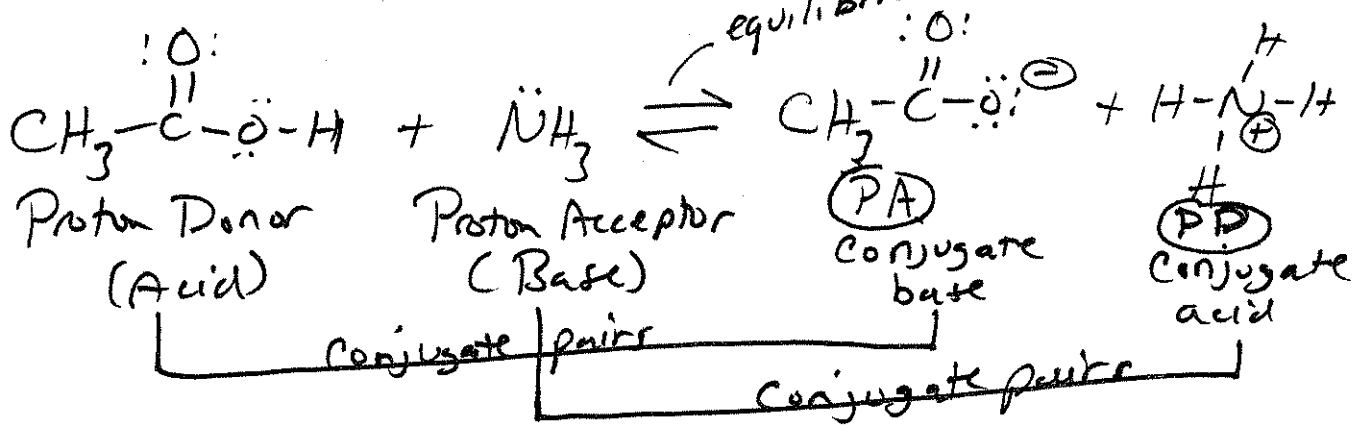
Chapter 3: Reactions of Organic Compounds as Acids + Bases

Bronsted-Lowry Theory of Acids and Bases

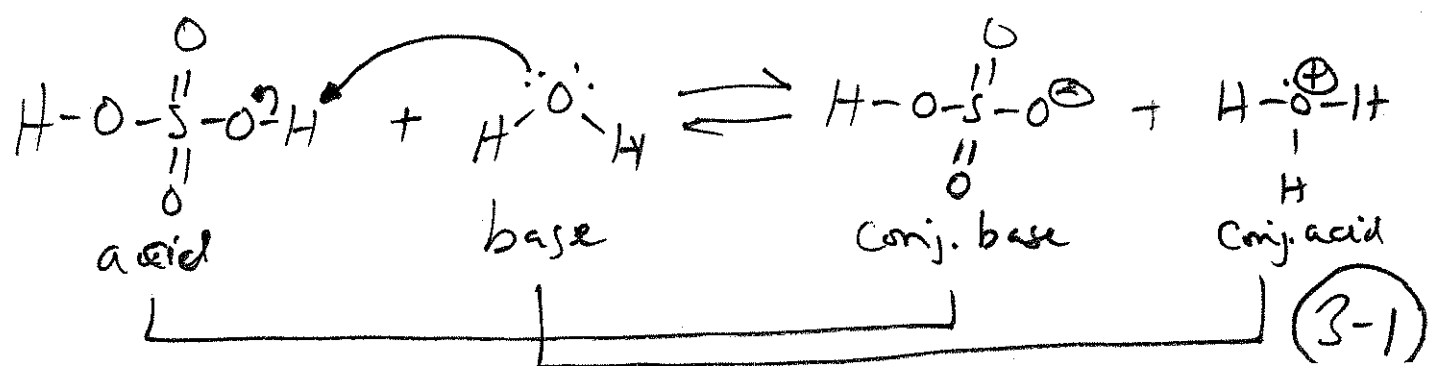
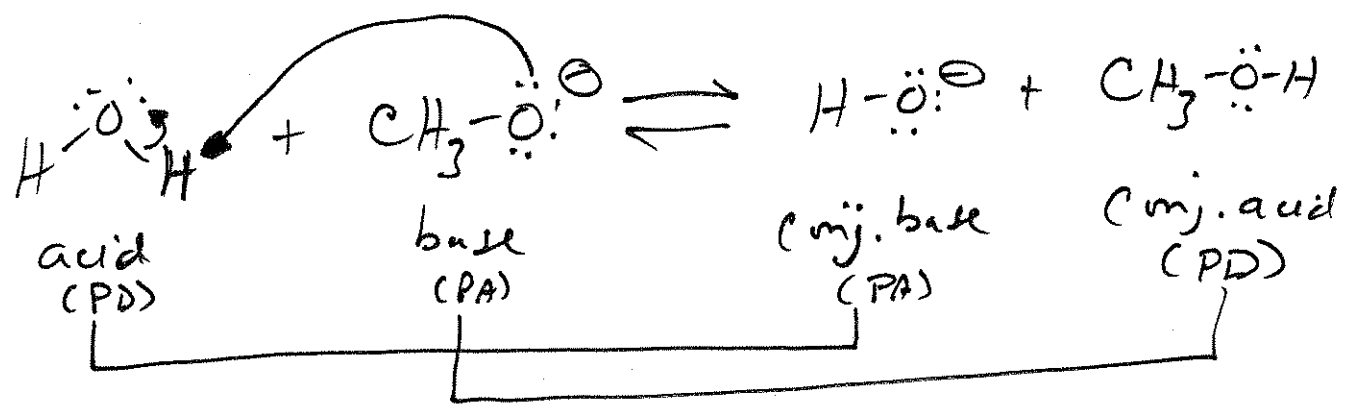
Acid = proton donor (PD)

Base = proton acceptor (PA)

ex:



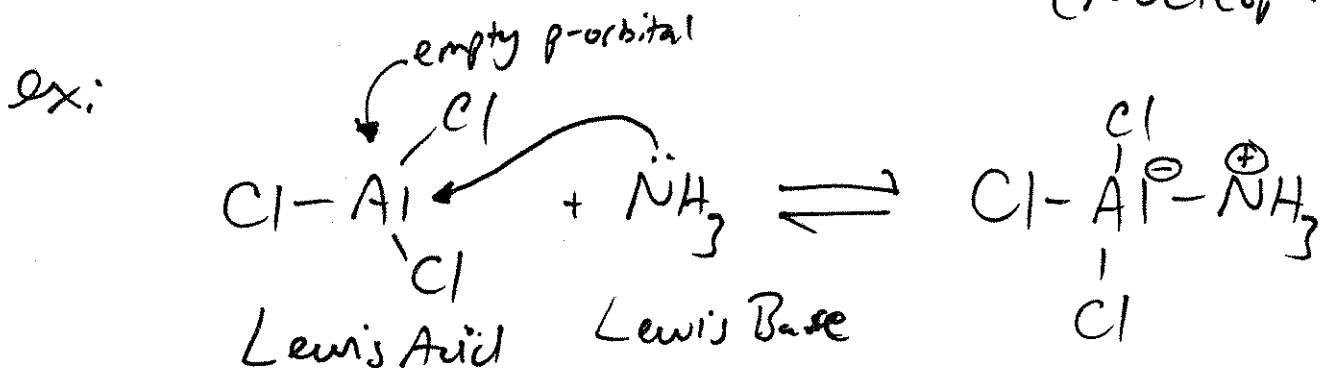
- Some species, such as water, can function as either an acid or a base



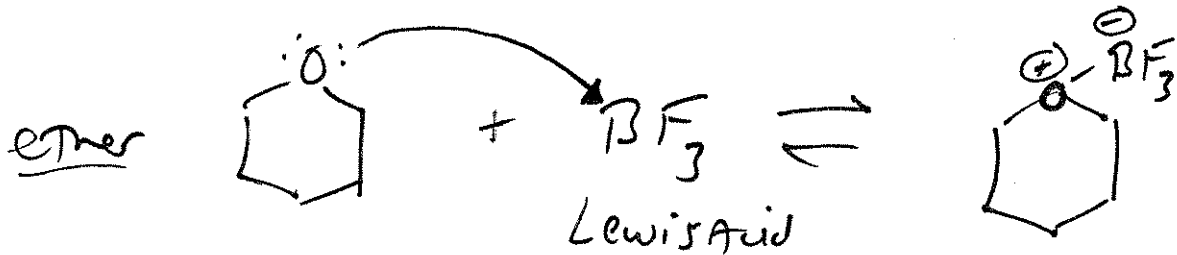
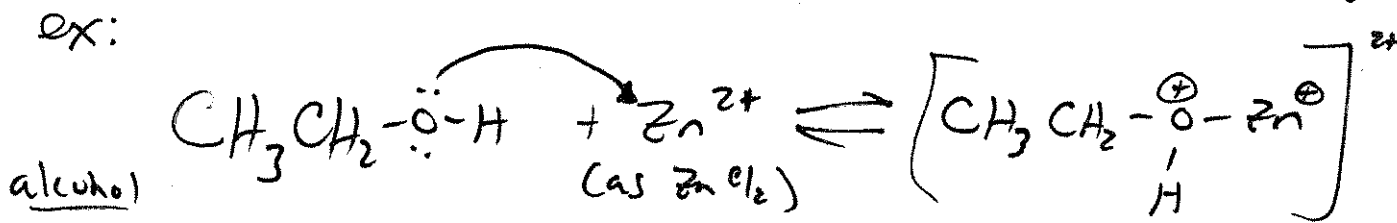
Lewis Theory of Acids and Bases

Acid = electron pair acceptor
(Electrophile)

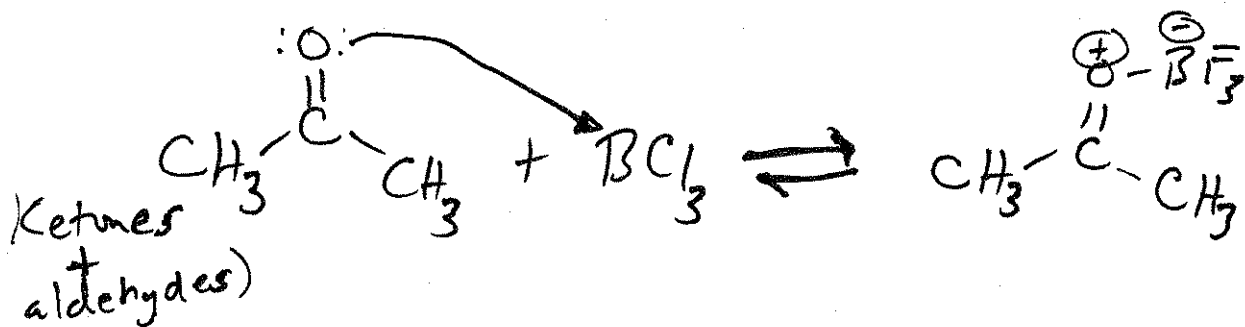
Base = electron pair donor
(Nucleophile)



- Common Lewis Acids → Compounds w/ group IIIA atoms (empty p-orbital) Al + B
also Zn²⁺ + Fe²⁺ (empty d-orbital) which can accept e⁻ density



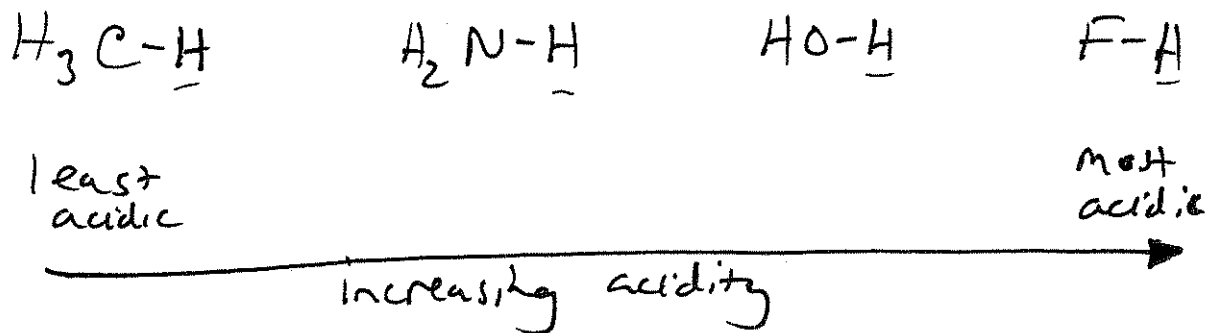
- Organic compounds with nonbonding electrons act as Lewis Bases
- Some Lewis Acids are aprotic acids - They react with Lewis Bases by accepting e⁻ pairs



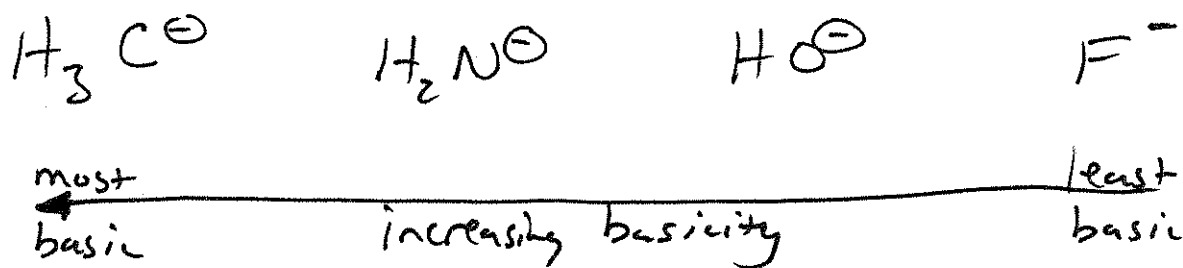
Section 3.3 in text → READ - explains use of curved arrows to show mechanisms

Relative Acidity Across A Period

- a strong acid must have a stable conj. base



- Why? A more electronegative atom bears a negative charge more easily



- H-F loses a proton most easily (is the strongest acid in the series) because its conjugate base is most stable.
- A strong acid produces a weak base

Size: Negative charge that can be spread over a larger space is more stable

ex



least acidic $\xrightarrow{\text{increasing acidity}}$ most acidic

Conj. base



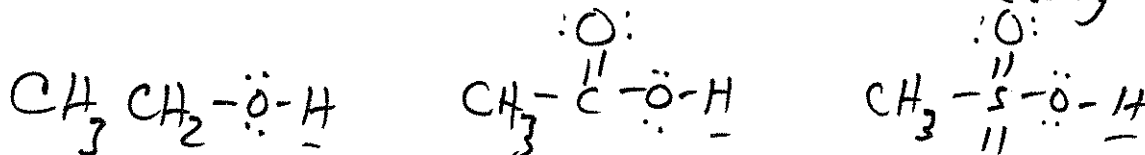
$\xrightarrow{\text{increasing atomic radius}}$

largest + therefore most stable anion therefore H-I strongest acid

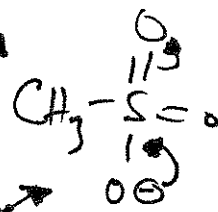
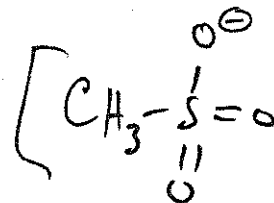
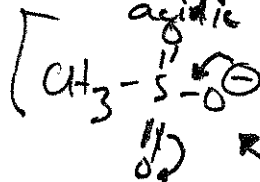
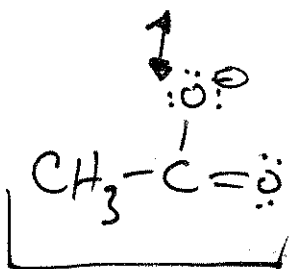
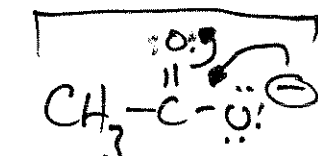
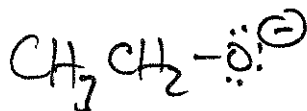
Resonance Stabilization

→ The more resonance structures possible for an anion, the more stable the anion (consequently have a stronger acid → H^+ more easily lost)

ex:



least acidic $\xrightarrow{\text{increasing acidity}}$ most acidic



(3-4)

Equilibria of Acid-Base Reactions

Acid strength: depends on the extent of ionization in H_2O



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

Note: conc. of H_2O is omitted because it's present in large excess

Stronger acid = larger K_a

- usually use pK_a for acid strength

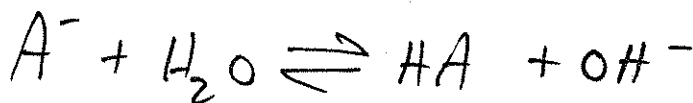
$$pK_a = -\log K_a$$

Smaller pK_a = stronger acid

✳ See Front of Textbook for pK_a Table

$pK_a = 3.4$ ← stronger acid than $pK_a = 10.2$

Base Strength



$$K_b = \frac{[HA][OH^-]}{[A^-]} \quad pK_b = -\log K_b$$

$$K_a \times K_b = 1 \times 10^{-14} \rightarrow pK_a + pK_b = 14 \text{ } \textcircled{\otimes}$$

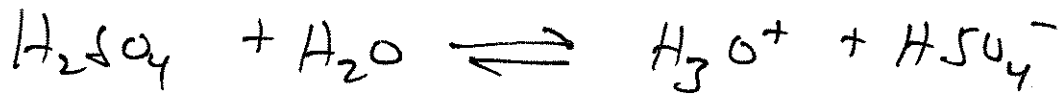
Smaller pK_b = stronger base

If you have a:

Strong acid \rightarrow weak conj. base

Strong base \rightarrow weak conj. acid

ex:



$pK_a =$

$pK_b =$

stronger
acid

stronger
base $\left(\begin{array}{c} \rightarrow \\ \leftarrow \end{array} \right)$

weaker
acid

weaker
base



$pK_a =$

$pK_b =$

weaker
acid

weaker
base $\left(\begin{array}{c} \leftarrow \\ \rightarrow \end{array} \right)$ stronger
acid

stronger
base

• Acid-Base Reactions are Equilibrium Rxns

\rightarrow Equilibrium constant = K_{eq} \rightarrow related to the

$$\Delta G^\circ = -RT \ln K_{eq}$$

change in free
energy for the
rxn, ΔG .

$$\Delta G^\circ = -2.303 RT \log K_{eq}$$

where $R =$ gas constant; $1.987 \times 10^{-3} \frac{\text{kcal}}{\text{mol}\cdot\text{K}}$

$T =$ temp. in Kelvin

$K_{eq} = 1$ $\Delta G = 0 \rightarrow$ Rxn at equilibrium

$K_{eq} > 1$ ΔG is negative $(-)$ \rightarrow Rxn will proceed to the right

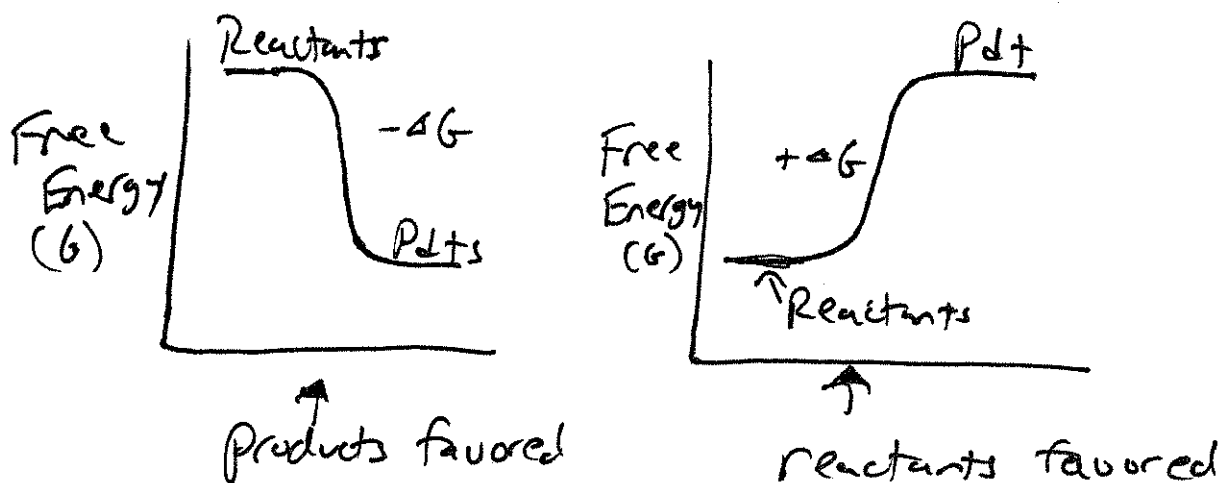
$K_{eq} < 1$ ΔG is positive \rightarrow reverse rxn (left side of rxn) is favored

* How are K_{eq} and K_a related?

$$K_{eq} = \frac{K_a \text{ of reactant acid}}{K_a \text{ of prod acid}} \quad \text{or} \quad pK_{eq} = pK_a - pK_a$$

$pK_{eq} = -\log K_{eq}$ $\begin{matrix} \uparrow & & \uparrow \\ \text{reactant} & & \text{prod} \\ \text{acid} & & \text{acid} \end{matrix}$

• Equilibrium favors lower energy state



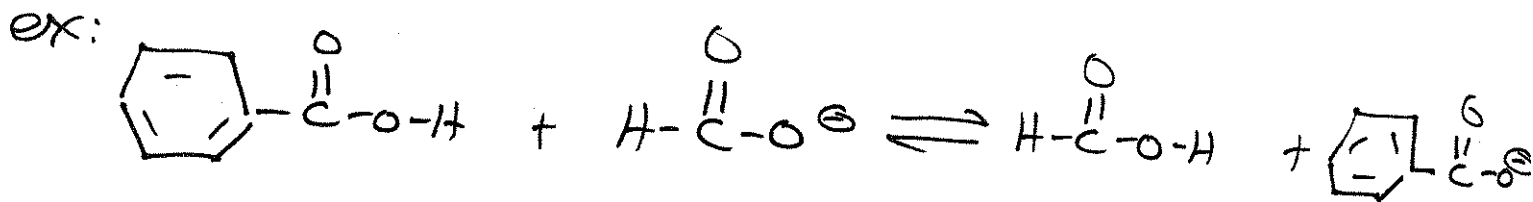
ΔG has two components; $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

ΔH° = enthalpy of rxn (heat)

ΔS° = change in entropy \rightarrow randomness of a system (disorder)

Using The pKa Values Table

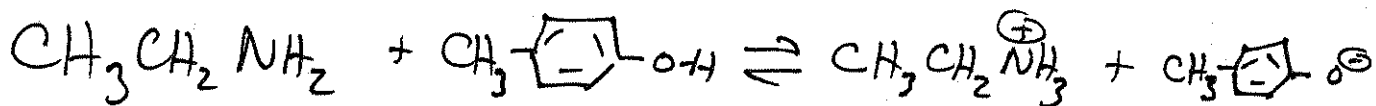
measured in H_2O
(pKa of an acid may vary w/ solvent & with temp.)



• To which side does the equilibrium lie for this acid base rxn? left \leftarrow or right \rightarrow

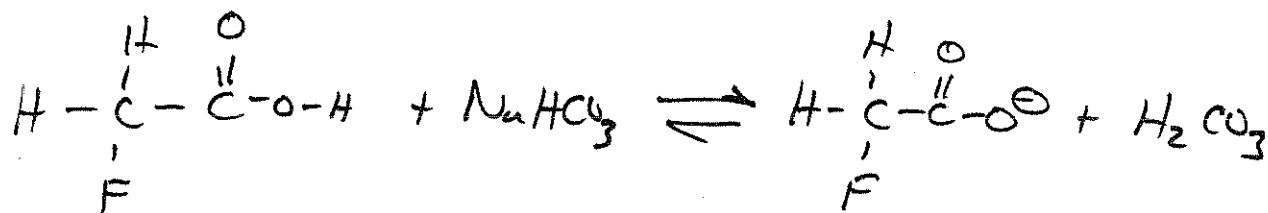
* remember: lower pKa = stronger acid
higher pKa = weaker acid

• Not all organic acid pKa's are listed in the table.



• Which side is favored in the rxn above?

→ If the acid is not listed on the table, find similar acids to predict favored side.



• Which side is favored in the above rxn? Right or Left

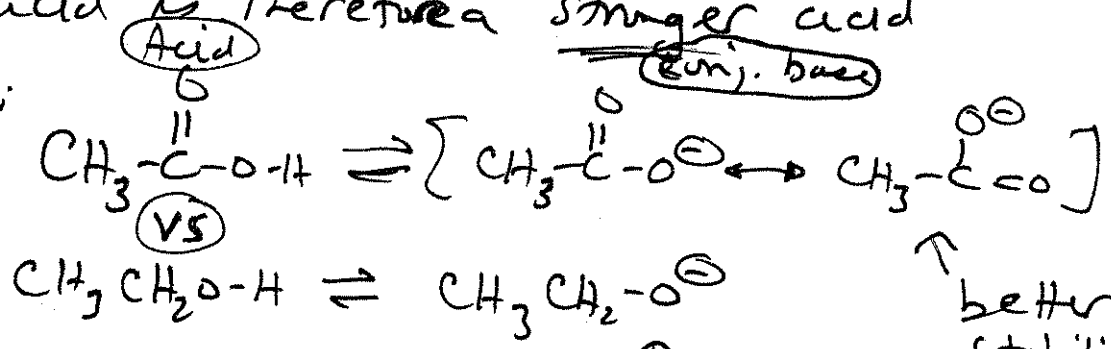
→ F more electronegative than Cl

The Effects of Structural Changes on Acidity

Resonance Effect

→ if able to delocalize a charge by resonance on a conjugate base, then it will be a weaker base + the parent acid is therefore a stronger acid

remember:



↑ better stabilized anion therefore weaker base
↓ Conj. acid is stronger

↑ can't be delocalized therefore stronger base
↓ Conj. acid is weaker

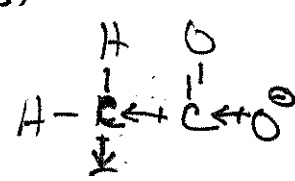
Inductive + Field Effects

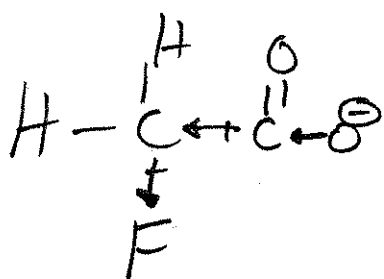
Structure	pKa
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$	4.76
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{CH}_3-\text{C}-\text{C}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$	4.87
$\begin{array}{c} \text{H} \quad \text{O} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\ \\ \text{F} \end{array}$	2.59

← weakest acid

↑ strongest acid

F → very electronegative; draws e⁻ density toward fluorine creating e⁻ deficiency on the carbon; e⁻ density also withdrawn thru σ-bonds from C=O group (3-9)



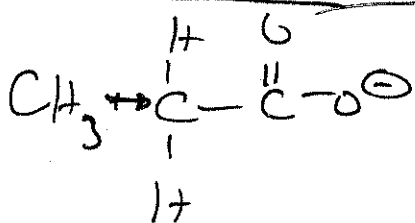


Example of The Inductive Effect

- In This case, The inductive effect helps stabilize The conjugate base by spreading out The charge.

Consequently, The parent acid is stronger compared to $\text{H}-\text{C}(\text{H})_2-\text{C}(=\text{O})-\text{OH}$.

Inductive Effect
 ↓
 Transmitted Thru
 σ-bonds

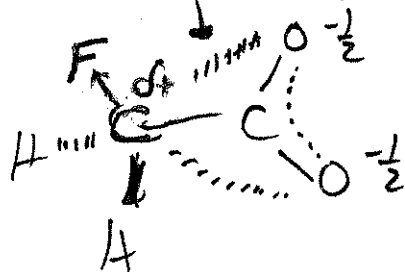


- Alkyl groups are electron donating. The inductive effect makes This Conj. base slightly less stable Than

$\text{H}-\text{C}(\text{H})_2-\text{C}(=\text{O})-\text{O}^-$. Consequently $\text{CH}_3-\text{C}(\text{H})_2-\text{C}(=\text{O})-\text{OH}$ is a slightly weaker acid.

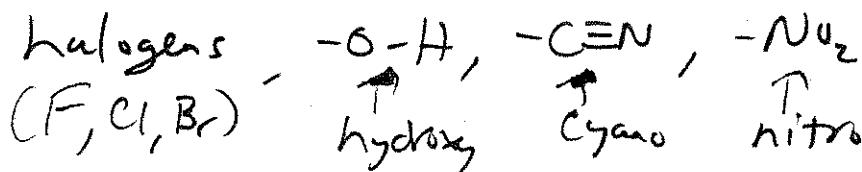
Field Effects

- Results from bond dipoles (like inductive effect) but is transmitted Thru space, not Thru bonds.

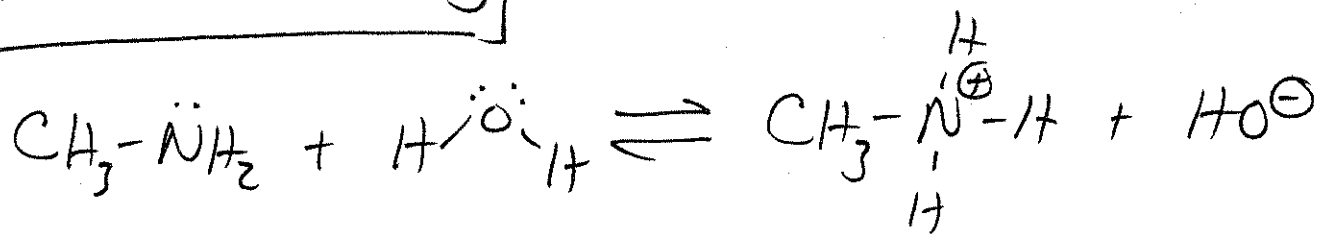


- Many times, a combination of The inductive & field effects are called The Inductive Effect

- Important electron withdrawing groups on α-Carbon of carboxylic acids That affect acidity ⇒



Amine Basicity



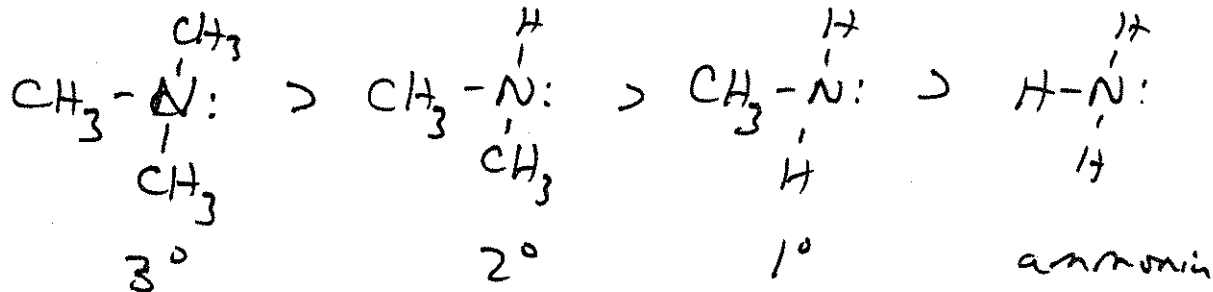
• Amine Basicity is determined by two factors:

a) availability of nitrogen lone pair to a proton donor

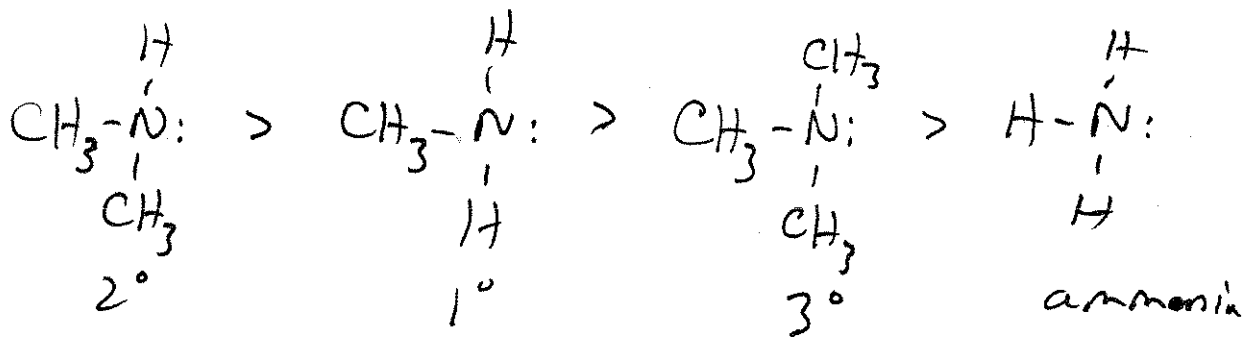
b) stabilization of positively charged N in the conjugate acid

ie more e⁻ donating substituents (alkyl groups)
more stable N[⊕] charge

• You would think that the trend would be:



but this is NOT the case. The ACTUAL TREND IS



Why? Because the conj. acid of trimethylamine can't be solvated as easily (because of CH₃'s) and alkyl groups also interfere with lone pair availability (3-11)