Acids and Bases

<u>Definitions</u>

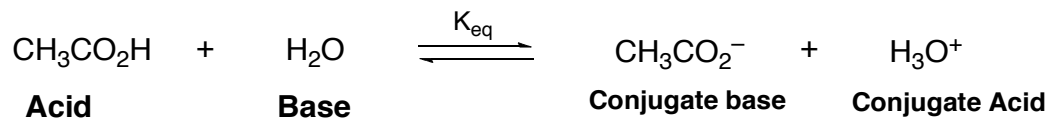1. Arrhenius:

   a)

   b)
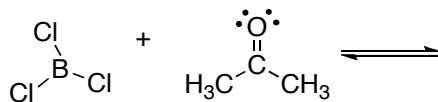
2. Bronsted-Lowry

   a)

   b)

$$CH_3CO_2H \quad + \quad H_2O \quad \overset{K_{eq}}{\rightleftharpoons} \quad CH_3CO_2^- \quad + \quad H_3O^+$$

    Acid   **Base**   **Conjugate base**   **Conjugate Acid**

3. Lewis

   a)

   b)

In this course/organic chemists:

Acid = proton donor

Lewis Acid = non-protic acids

Chemists use pKa values to discuss relative acidities of protic acids.

We will: *1) reexamine how one experimentally determines a pKa value*

                    2) determine the direction/shift of an acid/base equilibrium

                    3) examine pKa values for various protic functional groups

Determination of pKa

$$K_{eq} = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H][H_2O]}$$

$$K_a = K_{eq}[H_2O] = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H][\ 1\ ]}$$

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

$$pH = -\log[H_3O]^+$$

If you take the log of both sides of equation above, you get:

$$\log K_a = \log [H_3O^+] + \log \frac{[CH_3CO_2^-]}{[CH_3CO_2H]}$$

When the acid is 50% dissociated the acid concentration will equal the conjugate base concentration. Thus, log 1 = 0 and this leaves

$$pKa = pH @ 50\% \text{ dissociation of the acid}$$

Discussing pKa:

The stronger the acid, the smaller the pKa

Strong Acids have weak conjugate bases

Predicting Acid/base equilibria:

1. Find the most acidic proton of each acid

2. Estimate the pKa value based on "known" values

3. The direction of equilibria shifts in the direction of the weaker acid (the one with the higher pKa value)

   Note: the shift will be 99.9% complete (quantative) if Δ pKa of acid/conj acid is > 3

Examples:

$$HBr \quad + \quad H_2O \quad \rightleftharpoons \quad Br^- \quad + \quad H_3O^+$$
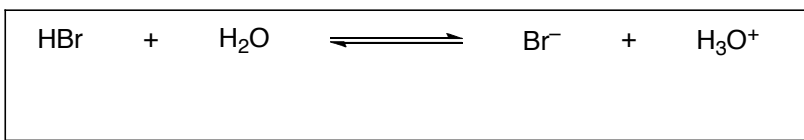
Amines: think organic base
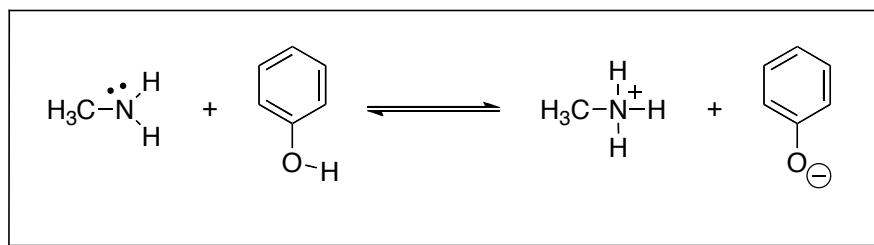
Amines can also be acids:
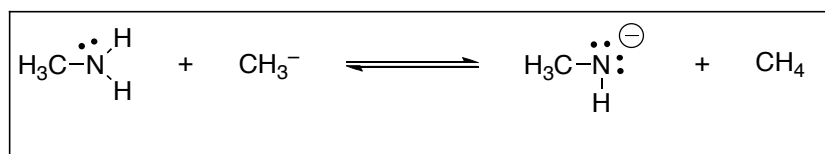
Carboxylic acids…the organic acids:
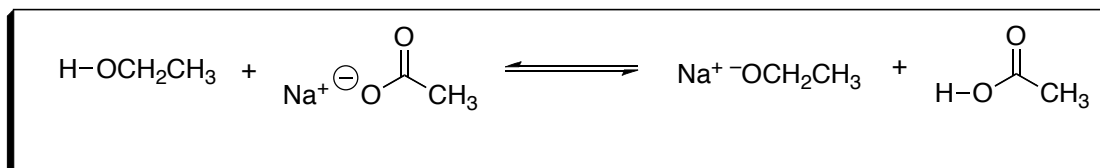
7. (40 pts) For the following reactions:

a) Circle the acids and conjugate acids.
b) Estimate the pKa values for each. The table below may be of some help.
c) Use your pKa values to determine the direction of equilibrium. Indicate whether the reaction is quantitatively to the left, mostly left, 50:50, mostly right or quantitatively to the right. Quantitaive means >100:1.
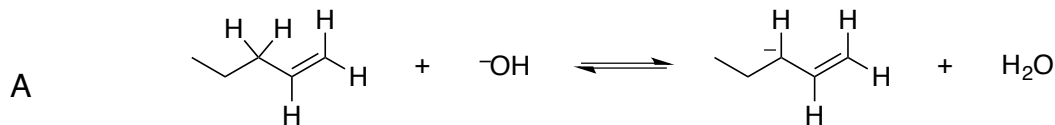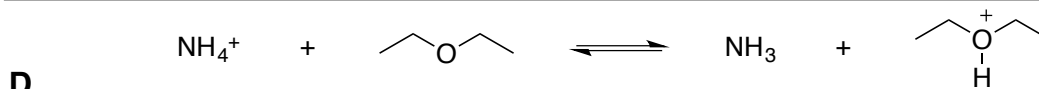
A

Circle 1:   quant. left   mostly left   50:50   mostly right   quant. right

B
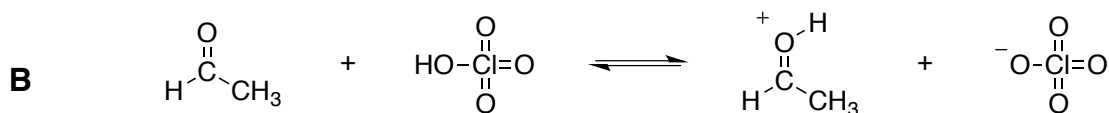
Circle 1:   quant. left   mostly left   50:50   mostly right   quant. right

C

Circle 1:   quant. left   mostly left   50:50   mostly right   quant. right

D
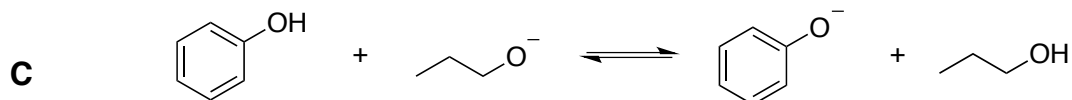
Circle 1:   quant. left   mostly left   50:50   mostly right   quant. right

Estimating/Predicting pKa Values of Compounds

(Used for comparing apples to apples)

Structural features that affect pKa:

A. Resonance
B. Electronegativity/Element Effect
C. Inductive (through bond) effects
D. Hybridization

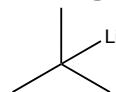## Note: A particular compound's pKa value is dependent on all the features.

Acid	Conj. Base	pKa	
H_2SO_4	HSO_4^-	–9	
HNO_3	NO_3^-	–1.3	Resonance stabilization
CH_3CO_2H	$CH_3CO_2^-$	4.76	
HCl	Cl^-	–7	
HF	F^-	3.18	
H_2O	HO^-	14 (or 15.7)	Electronegative stabilization
NH_3	NH_2^-	38	The atom effect
CH_4	CH_3^-	48	
CH_3CO_2H	$CH_3CO_2^-$	4.76	
$ClCH_2CO_2H$	$ClCH_2CO_2^-$	2.86	
FCH_2CO_2H	$FCH_2CO_2^-$	2.59	Inductive effect stabilization
F_3CCO_2H	$F_3CCO_2^-$	–0.26	

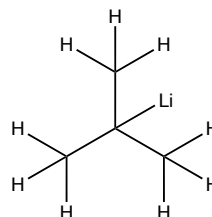## Strongest Bases that are routinely used in Organic Chemistry

C_4H_9Li
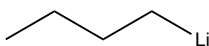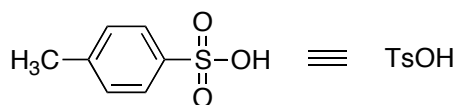

n-butyl lithium (^{n}BuLi)

tert-butyl lithium (^{t}BuLi)
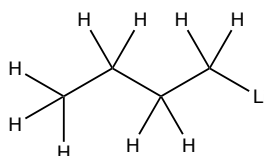
Common Bases used by Organic Chemists

Strong bases

H_3C — Li$^+$ *t*-butyllithium

Li$^+$ *n*-butyllithium

– Li$^+$ lithium diisopropylamide

– Na$^+$ sodium amide

K^+ $^-OC(CH_3)_3$ potassium *tert*-butoxide (KO^{t}Bu)

Na^+ $^-OCH_2CH_3$ sodium ethoxide

Na^+ $^-OCH_3$ sodium methoxide

Na^+ ^-OH sodium hydroxide

$(CH_3CH_2)_3N$ triethylamine (Et$_3$N)

pyridine

Weak bases
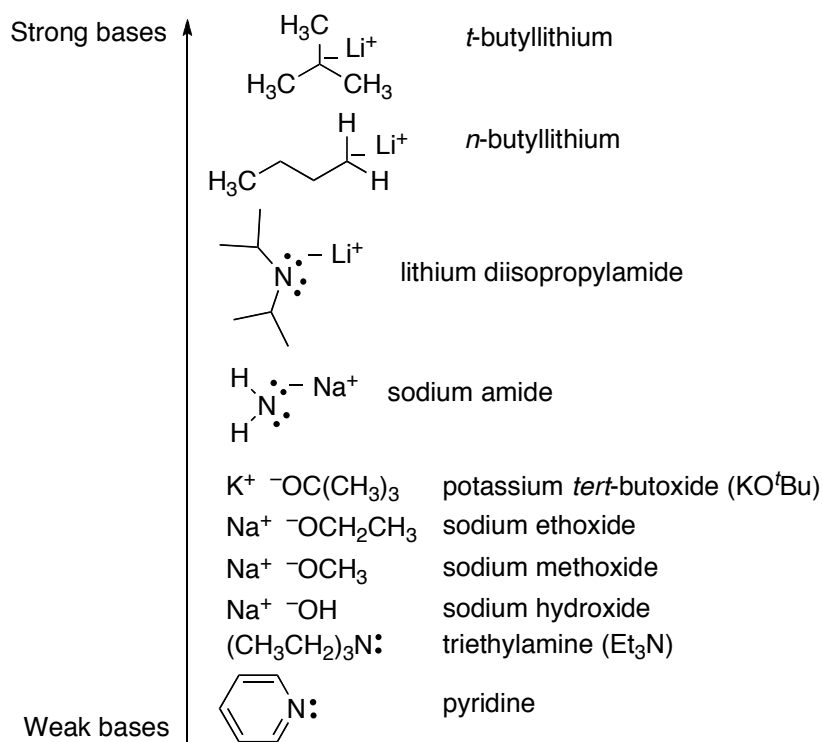
Common Acids used by Organic Chemists

- **Strong acids:**

  The mineral acids (HBr, HCl, H_2SO_4, HNO_3, etc)

  H_3C — S—OH ≡ TsOH

  para-toluenesulfonic acid

- **Weak acids:**

  Carboxylic acids and phenols

  the carboxylic acid functional group

  H_3C — C — OH

  acetic acid   —OH phenol H_3C — —OH 4-methylphenol