

Acids and Bases

Definitions

1. Arrhenius:

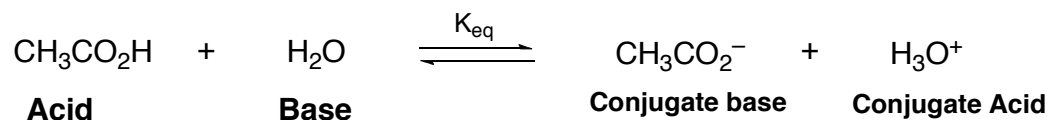
a)

b)

2. Bronsted-Lowry

a)

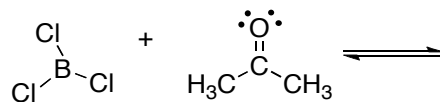
b)



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

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

$$K_a = K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{CH}_3\text{CO}_2^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{CO}_2\text{H}][1]}$$

$$\text{pKa} = -\log(K_a)$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

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

$$\log K_a = \log [\text{H}_3\text{O}^+] + \log \frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

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

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

Discussing pKa:

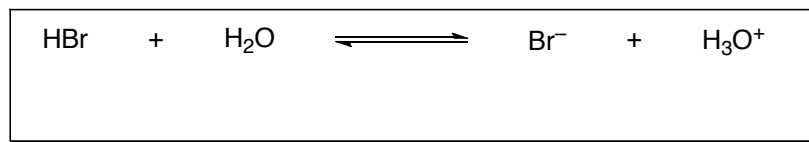
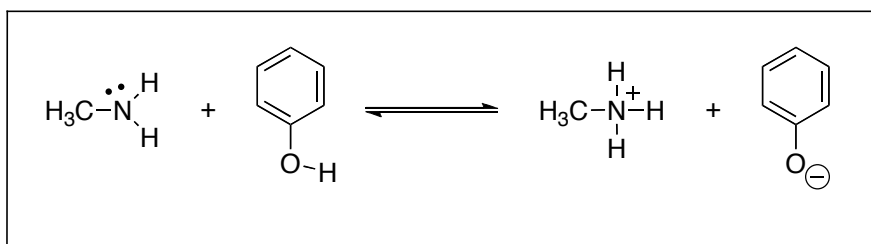
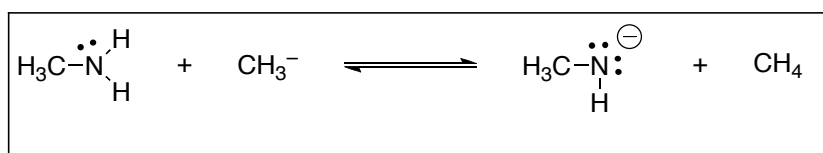
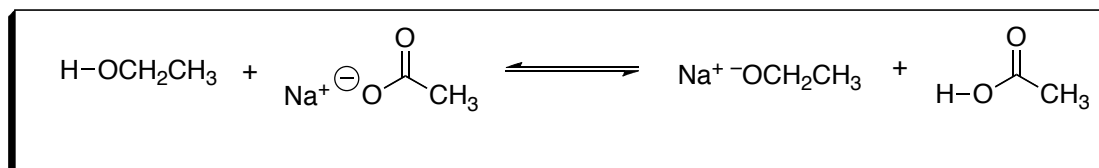
The stronger the acid, the smaller the pKa

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 (quantitative) if ΔpKa of acid/conj acid is > 3

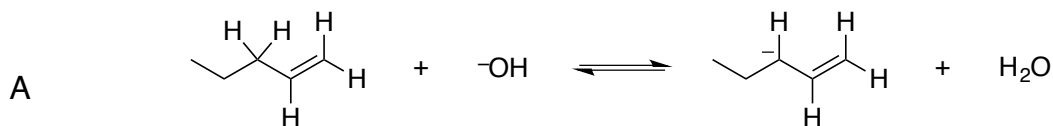
Examples:**Amines: think organic base****Amines can also be acids:****Carboxylic acids...the organic acids:**

7. (40 pts) For the following reactions:

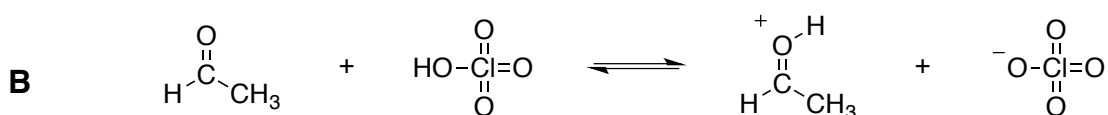
a) Circle the acids and conjugate acids.

b) Estimate the pKa values for each. The table below may be of some help.

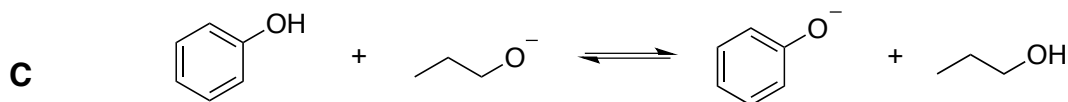
c) Use your pKa values to determine the direction of equilibrium. Indicate whether the reaction is quantitatively to the left, mostly left, 50:50, mostly right or quantitatively to the right. Quantitative means >100:1.



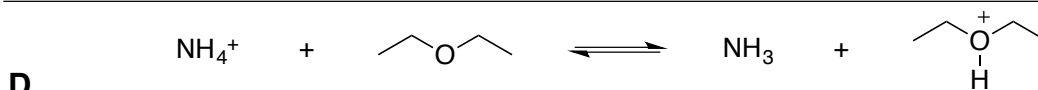
Circle 1: quant. left mostly left 50:50 mostly right quant. right



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



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



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:

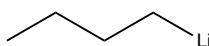
- Resonance
- Electronegativity/Element Effect
- Inductive (through bond) effects
- Hybridization

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

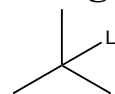
Acid	Conj. Base	pKa	
H ₂ SO ₄	HSO ₄ ⁻	-3	} Resonance stabilization
HNO ₃	NO ₃ ⁻	-1.3	
CH ₃ CO ₂ H	CH ₃ CO ₂ ⁻	4.76	
HCl	Cl ⁻	-7	} Electronegative stabilization The atom effect
HF	F ⁻	3.18	
H ₂ O	HO ⁻	14	
NH ₃	NH ₂ ⁻	38	
CH ₄	CH ₃ ⁻	48	
CH ₃ CO ₂ H	CH ₃ CO ₂ ⁻	4.76	} Inductive effect stabilization
ClCH ₂ CO ₂ H	ClCH ₂ CO ₂ ⁻	2.86	
FCH ₂ CO ₂ H	FCH ₂ CO ₂ ⁻	2.59	
F ₃ CCO ₂ H	F ₃ CCO ₂ ⁻	-0.26	

Strongest Bases that are routinely used in Organic Chemistry

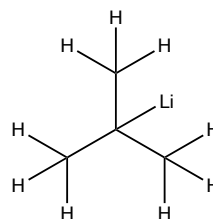
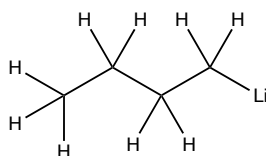
C₄H₉Li



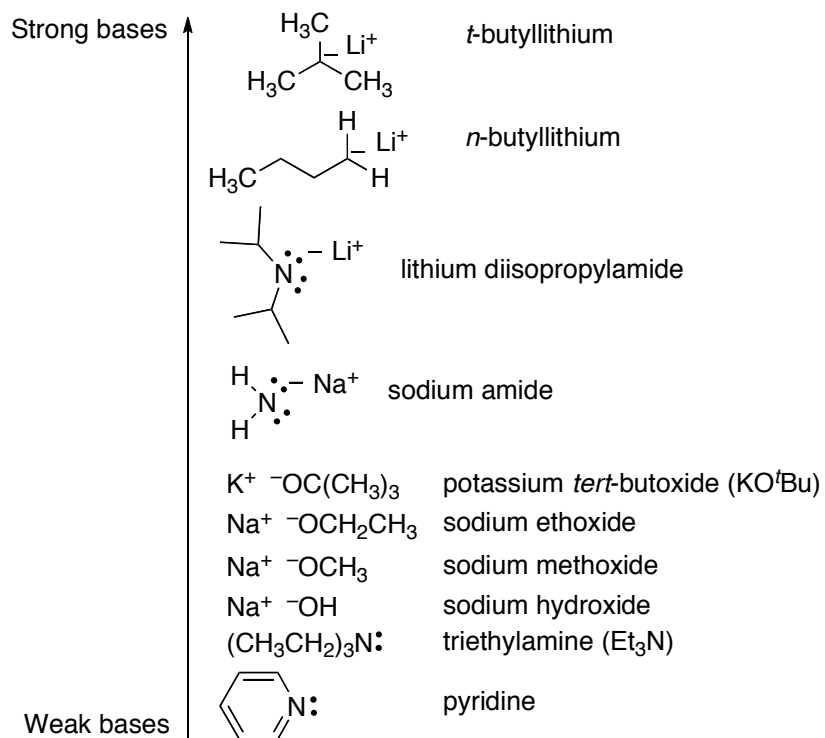
n-butyl lithium (ⁿBuLi)



tert-butyl lithium (^tBuLi)



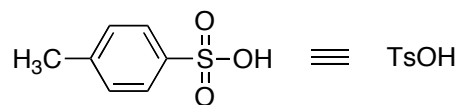
Common Bases used by Organic Chemists



Common Acids used by Organic Chemists

- Strong acids:**

The mineral acids (HBr, HCl, H₂SO₄, HNO₃, etc)



para-toluenesulfonic acid

- Weak acids:**

Carboxylic acids and phenols

