

II. Acidity of Organic Molecules

A. Bronsted-Lowry Acids and Bases

1. Brønsted-Lowry Definition
2. pK_a Definition
3. Predicting pK_a Values
 - a. identity of conjugate base
 - b. hybridization
 - c. inductive effects
 - d. resonance stabilization

B. Lewis Acids and Bases

Reading: McMurray 2.7 - 2.11

Additional Problems: 2.20-2.23, 2.25-2.26, 2.32-2.41, 2.43-2.47, 2.54-2.56

Stability and Reactivity

Strong acid

- relatively unstable acid
- relatively stable conjugate base

Weak acid

- relatively stable acid
- relatively unstable conjugate base

Strong base

- relatively unstable base
- relatively stable conjugate acid

Weak base

- relatively stable base
- relatively unstable conjugate acid

Effect of Structure on pK_a

1. Charged vs. noncharged species

a charged molecule is more acidic than a neutral molecule



2. Electronegativity of the atom attached to H

the more EN the attached atom, the more acidic the molecule

$\text{C} < \text{N} < \text{O} < \text{F}$
relative
electronegativity

$^-\text{CH}_3 < ^-\text{NH}_2 < \text{HO}^- < \text{F}^-$
relative stability
of conjugate bases

$\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$
relative acidity



$pK_a = 15.5$

$pK_a = 40$

Effect of Structure on pK_a

3. Size of attached atom

the larger the attached atom, the more acidic (down column)



relative
size



relative stability
of conjugate bases

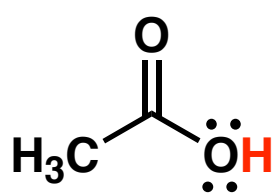


relative acidity

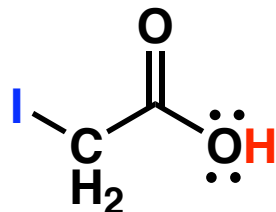
4. Inductive electron withdrawal

a. Magnitude of electronegativity (the more EN, the more acidic)

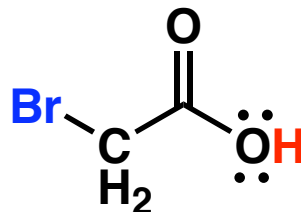
b. Distance away from (-) charged conjugate base (closer = more acidic)



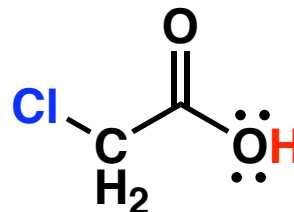
$pK_a = 4.76$



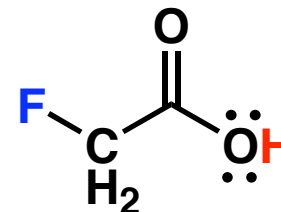
$pK_a = 3.15$



$pK_a = 2.86$

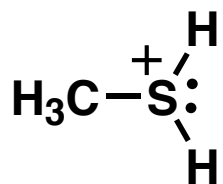


$pK_a = 2.81$

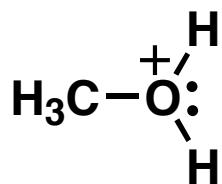


$pK_a = 2.66$

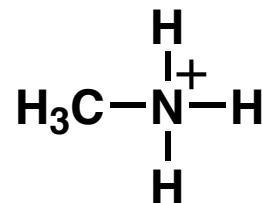
Example: N vs O vs S



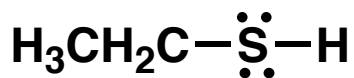
$$pK_a = -6.8$$



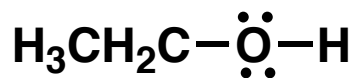
$$pK_a = -2.4$$



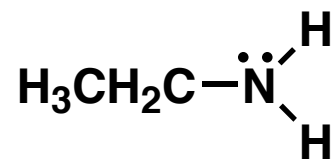
$$pK_a = 9.8$$



$$pK_a = 10.6$$



$$pK_a = 15.9$$



$$pK_a = 35$$

Nitrogen is most effective at stabilizing a positive charge and least effective at stabilizing a negative charge

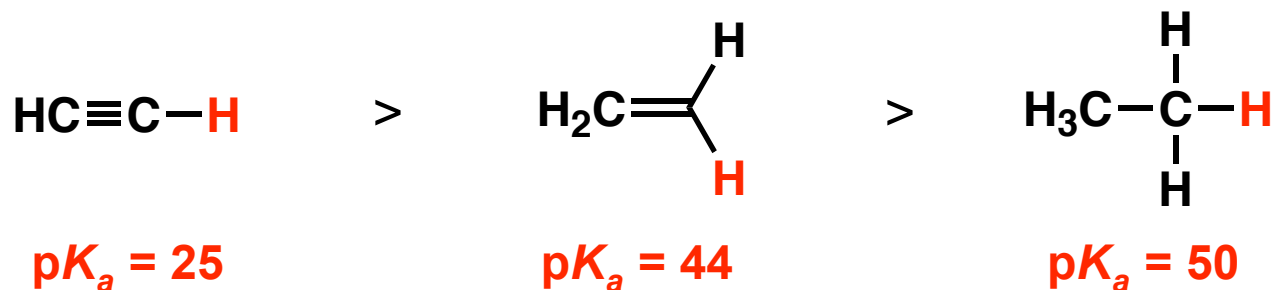
Sulfur is most effective at stabilizing a negative charge and least effective at stabilizing a positive charge

Effect of Structure on pK_a

5. Hybridization (sp , sp^2 , sp^3)

Relative Acidity

sp 50% s character > sp^2 33% s character > sp^3 25% s character

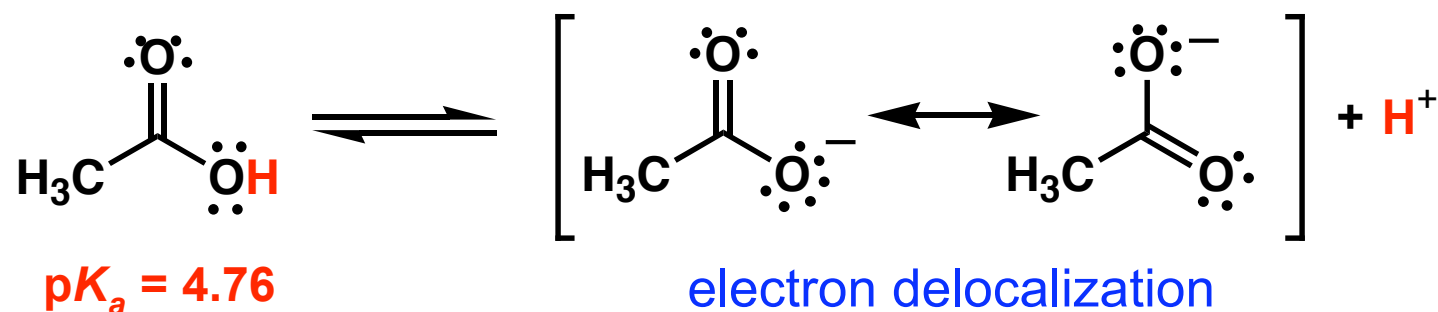
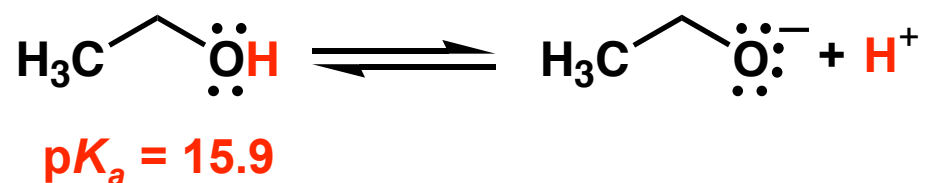


Conjugate base has negative charge, which is stabilized by orbitals with greater s character

Effect of Structure on pK_a

6. Resonance

resonance stabilizes the negative charge of the conjugate base
the more resonance contributors, the more stable the molecule



Summary

1. Series of Neutral Acids
 - a. Deprotonate to find the conjugate bases
 - b. Compare the stability of the conjugate bases
 - c. The more stable the conjugate base, the stronger the acid
2. Series of Charged Acids (+1)
 - a. Compare the stability of the charged acids
 - b. The more stable the charged acid, the weaker it is
3. Series of Neutral Bases
 - a. Protonate to find the conjugate acids
 - b. Compare the stability of the conjugate acids
 - c. The more stable the conjugate acid, the stronger the base
4. Series of Charged Bases (-1)
 - a. Compare the stability of the charged bases
 - b. The more stable the charged base, the weaker it is