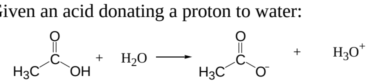
Acidity and Basicity

Quantitative Reflection of Acid Strength

Given an acid donating a proton to water:



HA A$^-$

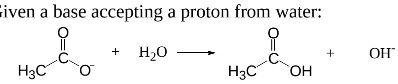
The extent of that reaction at equilibrium is quantitated by the K_a:

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

•Since the products of the reaction are in the numerator, larger K_a values are observed for stronger acids.
•Also, since pK_a = -log K_a, smaller pK_a values are observed for stronger acids.

Quantitative Reflection of Base Strength

Given a base accepting a proton from water:



B$^-$ HB

The extent of that reaction at equilibrium is quantitated by the K_b:

$$K_b = \frac{[HB][OH^-]}{[B]}$$

•Since the products of the reaction are in the numerator, larger K_b values are observed for stronger bases.
•Also, since pK_b = -log K_b, smaller pK_b values are observed for stronger bases.

Conjugate Acid/Base Pairs

- Since both K_a and K_b are defined for reactions involving water, their product for conjugate acid/base pairs equals K_w (10^{-14})
- Since $K_a \cdot K_b = 10^{-14}$, $pK_a + pK_b = 14$
- Acid and base strength are therefore conversely related for conjugate acid/base pairs
  - Stronger acids have weaker conjugate bases and vice versa

K_a/K_b and Free Energy (ΔG)

- Any equilibrium constant can be related to the free energy of the reaction:

$$\Delta G = -RT \ln K$$

OR

$$\Delta G = -2.303 RT \log K$$

- High K_a values therefore give more negative ΔG values

Determining Relative Acidity from Structure

- Bronsted acidity depends on:
  - Identity of atom donating the proton
  - Relative stability of starting acid and conjugate base produced
    - Charged vs. neutral
    - Delocalized charge vs. isolated charge
    - Charge delocalization mechanism
      - Resonance vs. induction
    - Hybridization of atom donating the proton

Atom Identity - Problem

- Given your previous knowledge of acidity, rank the following lists of acids from strongest to weakest:
  - List 1: H_2O, HF, NH_3, CH_4
  - List 2: HCl, HBr, HF, HI
- Can you relate the order of acidity in your list to trends in the periodic table?

Relative Stabilities – Charged vs. Neutral

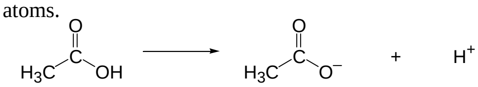
- Given the following two acid dissociation reactions, which acid do you think is stronger?
- Why?

$$H_2O \longrightarrow H^+ \quad + \quad {}^-OH$$

$$H_3O^+ \longrightarrow H^+ \quad + \quad H_2O$$

Relative Stability – Charge Delocalization I

- Both of the following acid dissociation reactions generate charged products with identical donating atoms.

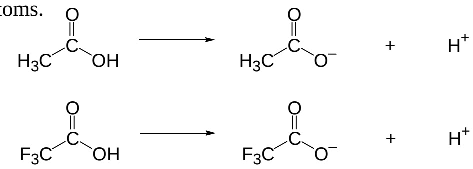


$$CH_3CH_2OH \longrightarrow CH_3CH_2O^- \quad + \quad H^+$$

- Are the charges in either product stabilized in any way?
- Which starting material is a stronger acid?

Relative Stability – Charge Delocalization II

- Both of the following acid dissociation reactions generate charged products with identical donating atoms.

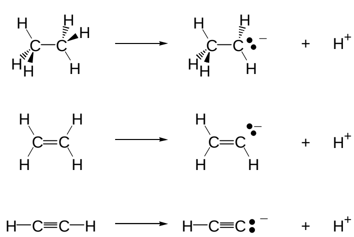


- Are the charges in either product stabilized in any way?
- Which starting material is a stronger acid?

Atom Hybridization

- Hybridization influences acidity because orbitals have differing energy, and electrons closer to the nucleus will be more stable (and thus less reactive)

Which product formed in these acid-base reactions is most stable (and therefore produced by the strongest acid)?



Determining Relative Basicity from Structure

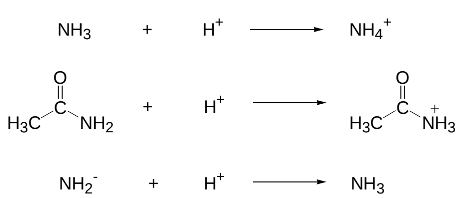
- Bronsted basicity depends on:
  - Identity of atom accepting the proton
  - Relative stability of starting base and conjugate acid produced
    - Charged vs. neutral
    - Delocalized charge vs. isolated charge
    - Charge/electron delocalization mechanism
      - Resonance vs. induction
    - Hybridization of atom accepting the proton

Atom Identity - Problem

- Since acid and conjugate base strength are inversely related, how can you use the periodic table to predict base strength?
- Come up with a list of three bases in order of increasing strength based on the trends you propose.

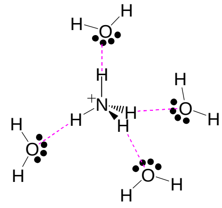
Relative Stability – Problem

- Rank the following bases from most to least basic – consider the relative stabilities of the starting materials, products, and the relative CHANGES in stability from reactants to products



Effect of Solvation on Ionization

- Charged species are generally not stable
- Polar solvents can stabilize charged species



Solvent Leveling

- In any solvent, bases stronger than the conjugate base of the solvent react with the solvent

$$NH_2^- + H_2O \longrightarrow NH_3 + {}^-OH$$

pKa = 15.7 pKa = 38

- Likewise, acids stronger than the conjugate acid of the solvent react with the solvent
- Use of bases stronger than hydroxide requires less acidic solvents than water (such as alkanes or liquid ammonia)

$$NH_2^- + CH_3CH_2CH_2CH_2CH_2CH_3 \longrightarrow \text{no reaction}$$

pKa ~ 50