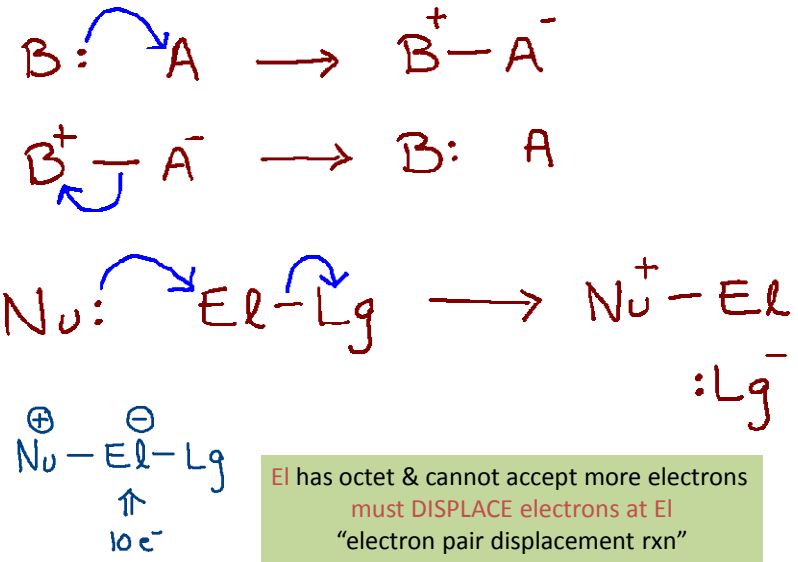
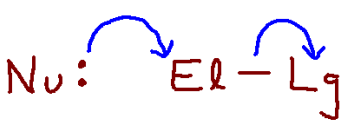
1. Electron Pair Rxns & MO Model
2. K_{eq} & Brønsted-Lowry Acid-Base

Loudon 3.2 & 3.4

Electron Pairs in Reactions



El has octet & cannot accept more electrons
must DISPLACE electrons at El
"electron pair displacement rxn"



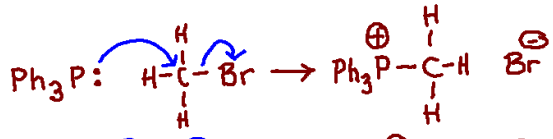
participants in "electron pair displacement" rxns

Nu = Nucleophile ⇐ includes Lewis base & Brønsted base

El = Electrophile ⇐ includes Lewis acid

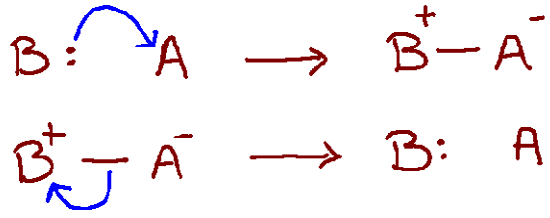
Lg = Leaving Group

Examples



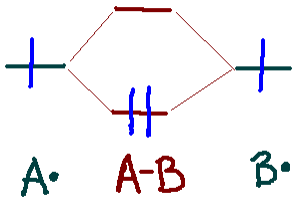
El = H
Nu = base
Lg = conj. base

Electron Pairs in Reactions

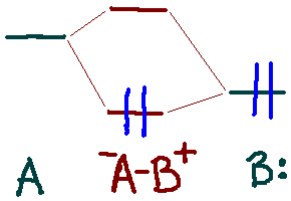


How do we make MO models for bonds in chemical reactions?

MO View: Lewis A-B Association



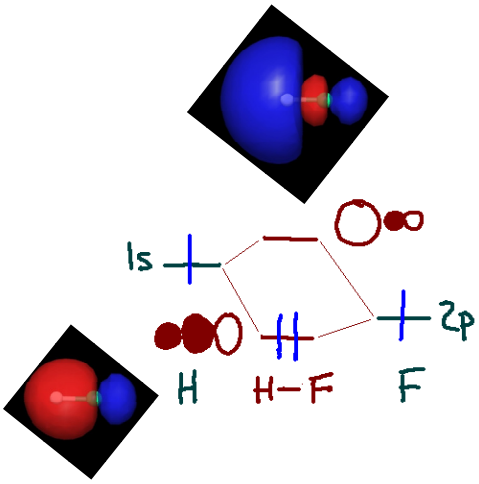
Need (for large E_{stab})
- Good AO overlap
- Similar AO energies (and usually ARE)



Need (for large E_{stab})
- Good AO overlap
- Similar AO energies (and usually ARE NOT)

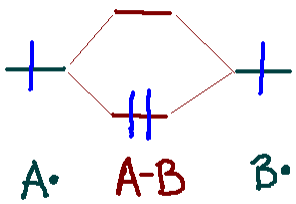
This has consequences !!!

Unequal AO Energies = Polar MO/Bond



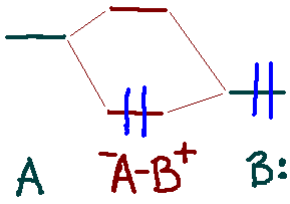
- ABMO
  - dominated by hi E AO
  - empty → no effect on electron location, energy
- BMO
  - dominated by low E AO
  - electrons prefer one atom, e.g., F
  - polar bond

MO View: Lewis A-B Dissociation



AO similar energy

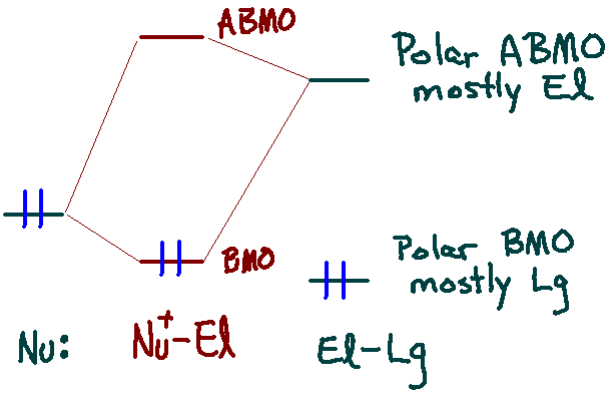
electrons separate, one w/ each atom



AO different energy

electrons slide to atom with low energy AO

MO View: Electron Pair Displacement



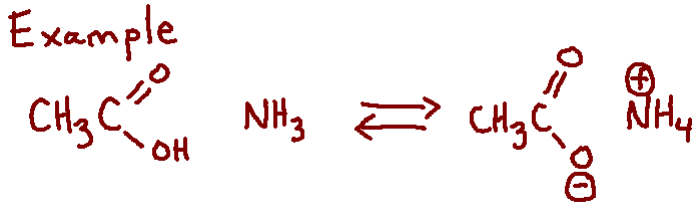
New Nu-El BMO combines
- Nu AO (lone pair)
- El-Lg ABMO

Electrons occupying new BMO
- make Nu-El bond & break El-Lg bond

MO Models Make Predictions

- Bond Polarity
  - Polar bond → Polar BMO + Reverse Polar ABMO
- Two types of bond breaking rxns
- Electron Donors
  - "High" energy filled AO (Nu, Lewis & Bronsted base)
- Electron Acceptors
  - Empty VALENCE AO (Lewis acid)
  - "Low" energy polar ABMO (El-Lg, Bronsted acid)

K_{eq} for Brønsted- Lowry Acid-Base



- Which side dominates at equilibrium?
- 2 strategies
  - Deduction. Theory produces answer
  - Induction. Data (expel observations) produce answer
    - What data needed?

K_{eq} from 2 K_a

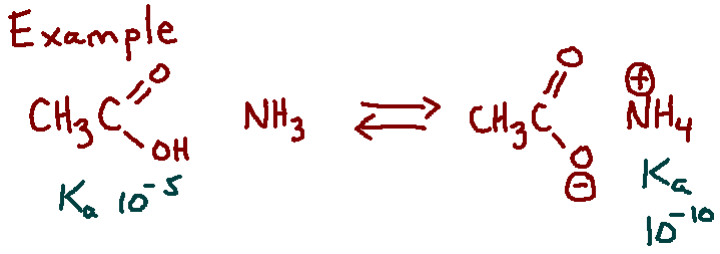
$$K_a^{HA} = \frac{[A^-][H_3O^+]}{[HA]}$$

$$K_a^{HB} = \frac{[B^-][H_3O^+]}{[HB]}$$

$$K_{eq} = K_a^{HA}/K_a^{HB} = \frac{[A^-][HB]}{[HA][B^-]}$$

Application

Example



$$K_{eq} = 10^{-5}/10^{-10} = 10^{-5} \times 10^{10} = 10^5$$

Induction is powerful, but only if you know K_a values

Using pK_a Values

$$K_{eq} = K_a^{HA} / K_a^{HB}$$

$$\log K = \log K^{HA} - \log K^{HB}$$

$$= -pK_a^{HA} + pK_a^{HB}$$

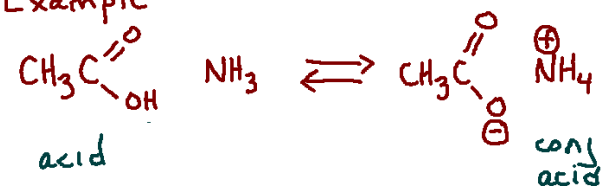
$$\Rightarrow \boxed{10^{\log K} = K}$$

$$\boxed{K_{eq} = 10^{pK_a^{HB} - pK_a^{HA}}}$$

- Hard to remember?
- Shortcut?
  - K_{eq} favorable if
  - pK (HB) > pK(HA)
  - HA stronger acid
- Bottom-line(s)
  - find 2 acids
  - weaker acid favored
  - $K = 10^{\Delta pK}$

Application

Example



acid — conj acid

pK_a 5 — weaker → 10

so ⇌ & $K_{eq} > 1$

$$\boxed{K_{eq} = 10^{10-5} = 10^5}$$

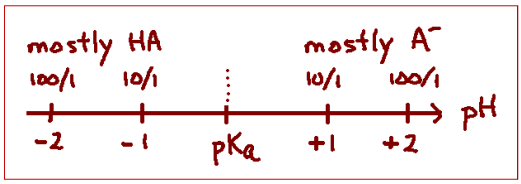
Induction is powerful, but only if you know pK_a values

Ionization State at Specific pH

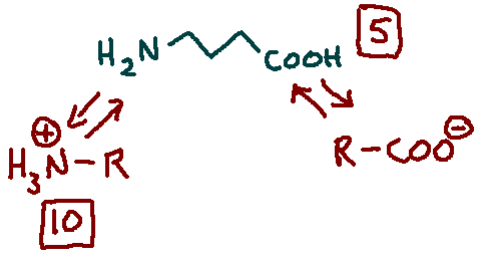
$$\frac{K_a}{[H_3O^+]} = \frac{[A^-]}{[HA]}$$

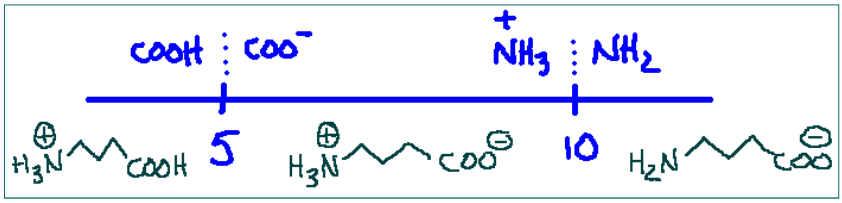
$[H_3O^+] > K_a$ → mostly HA

$[H_3O^+] < K_a$ → mostly A^-



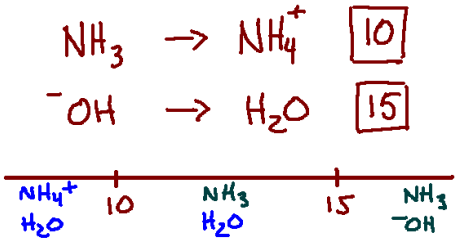
Application





What About Base Strength?

- Look at conjugate acid



- Strong conjugate acid → weak base
- Weak conjugate acid → strong base