Course Chem 343 Lecturer Gellman 11AM

Day Monday Date 9-19-2011

Notes Taken By Derek Salter Total # of Pages 5

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Recall: Lewis Acid-Lewis Base rxns...

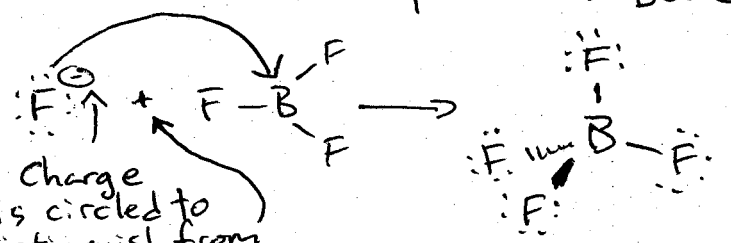
Ex:

$BF_3 + :\ddot{F}:^{\ominus} \rightleftharpoons BF_4^{\ominus}$

LA LB Adduct

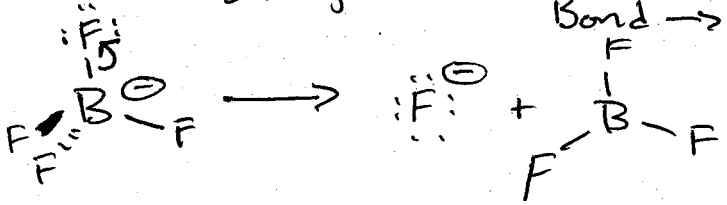
Curved arrows to indicate $e^{\ominus}$ flow

Lone pair → Bond



Reverse

Bond → Lone pair



"Curved Arrow" depiction of proton transfer

(Brønsted-Lowry Acid Base Theory)

Ex: $NH_4^{\oplus} + :\ddot{O}H^{\ominus} \rightleftharpoons \ddot{N}H_3 + H_2\ddot{O}:$

$NH_4^{\oplus}$ → Brønsted Acid

$:\ddot{O}H^{\ominus}$ → Brønsted base

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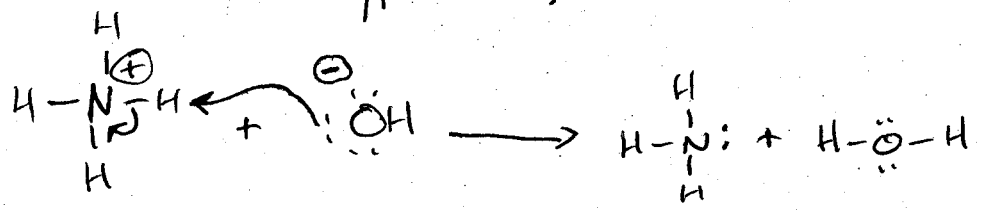
"Mechanism" (hypothesis)



"e⊖ pair displacement" (Bonding e⊖ pair + Lone e⊖ pair → Lone e⊖ pair + Bonding e⊖ pair)

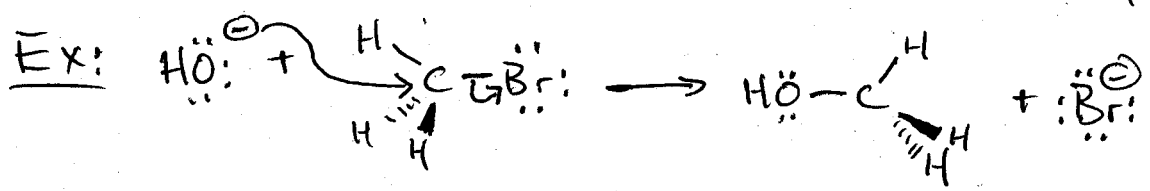
Lewis vs. Brønsted-Lowry (BL) - comments

1). BL acid-base rxn - always convert one acid base pair to a different acid-base pair.

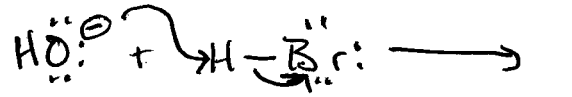
2). BL base is always a Lewis base, and a BL acid is always a Lewis acid, BUT a Lewis acid is not necessarily a BL acid (BF_3, no proton, but functions as Lewis acid)

Analogy: BL acid-base rxn and "Nucleophilic displacement"

Ex:



Consider a BL rxn:



Note the mechanistic similarity - e⊖ pair displacement → lonepair becomes bonding pair & vice versa

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Terminology:

$:\ddot{O}H^-$ is Brønsted base, or Nucleophile

nucleus loving

H-Br is (Brønsted) acid, CH_3-Br is an "electrophile" (electron loving)

$:\ddot{Br}:^-$ is a "leaving group" in context of nucleophilic displacement (conjugate base in context of BL acid-base Reaction)

Strengths of Brønsted acids:

Recall: $H\text{-}A + H_2O \rightleftharpoons A:^- \; H_3O^+$

$K_{eq} = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$ if you leave out $[H_2O]$, no longer K_{eq}, but K_a $\quad K_a = \frac{[A^-][H_3O^+]}{[HA]}$

finally, $pK_a = -\log[K_a]$

Stronger acid means lower pka

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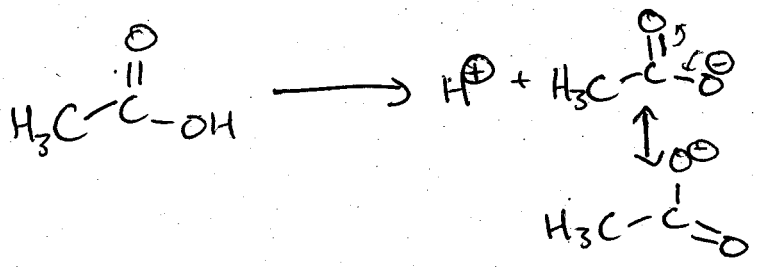
Ex: $H\text{-}OH \longrightarrow H^{\oplus} + {}^{\ominus}OH$ Pka 16

$H_3C\text{-}OH$, $H_3CCH_2\text{-}OH$ ← water and aliphatic alcohols have similar pkas (alkyl)



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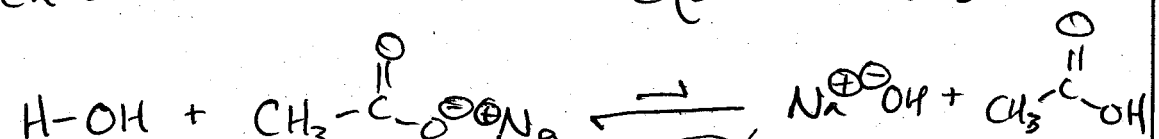
$H\text{-}Cl \longrightarrow H^{\oplus} {}^{\ominus}Cl$ -6

Predict which side of BL acid-base equilibrium is favored.



(equilibrium lies to left)

- Judge which of 2 bases is more basic.

$^{\ominus}OH$ is much more basic than acetate ($CH_3\text{-}C(=O)\text{-}O^{\ominus}$) because H_2O is less acidic than $CH_3\text{-}C(=O)\text{-}OH$

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Note: Amphoteric acids - multiple protons - don't be confused about pka values...

Ex: H_2O can be acid and base!

$$H_2O + H\text{-}Cl \rightleftharpoons H_3O^{\oplus} + {}^{\ominus}Cl$$ H_2O functions as base

$$H_2O + :B \rightleftharpoons HO^{\ominus} + H\text{-}B$$

↑ generic base

H-OH pka = 16

$H\text{-}\overset{\oplus}{O}H_2$ pka = -2

↑ much more acidic.

Relationships between molecular structure & pka (qualitative)

1). periodic ~~tables~~ trends

(a) other things being comparable, pka ~~increases~~ decreases left to right ~~↑~~ along a row

	$H_3C\text{-}H$	~~$HO\text{-}H$~~ $H_2N\text{-}H$	$HO\text{-}H$	$F\text{-}H$
pka	~55	~35	~16	~3

This trend is based on electronegativity