CH203 Lecture 4

September 14, 2010

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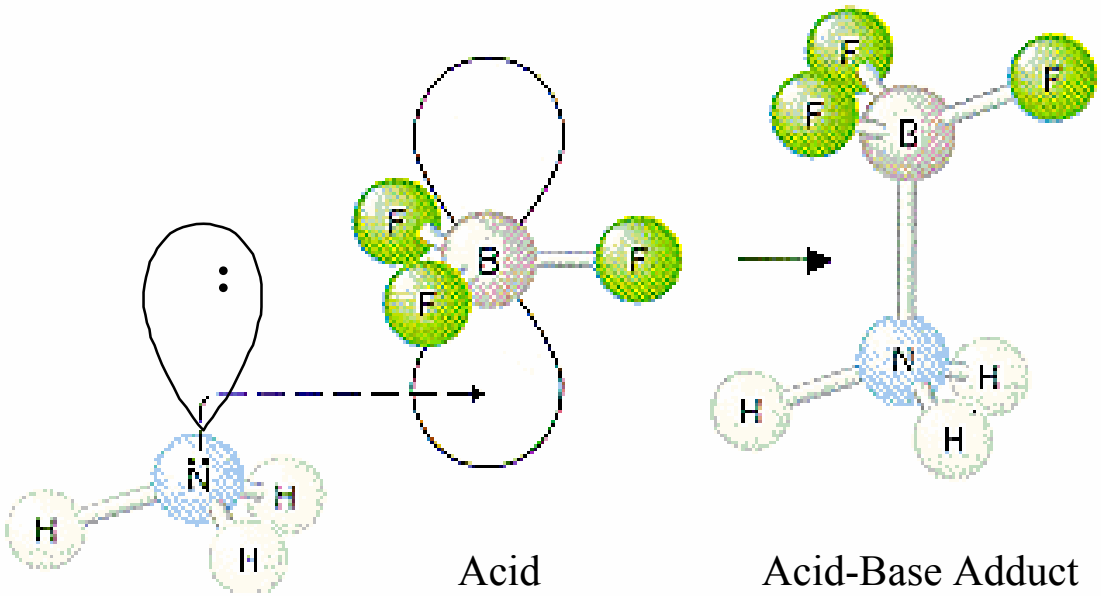
Review: pKa

- The Ka value is a value used to describe the tendency of compounds or ions to dissociate.
- The pKa value is related to the Ka value as the negative log value.
- http://www2.lsdiv.harvard.edu/labs/evans/pdf/evans_pKa_table.pdf
- http://people.uleth.ca/~dibble/sorrtd.pka.jpg
- http://www.chem.wisc.edu/areas/reich/pkatable/

$$F_3B \quad + \quad :NH_3 \longrightarrow \quad F_3B\text{---}NH_3$$

Boron trifluoride



Base Acid Acid-Base Adduct

CH 203 Lecture 4 9/14/10

Review acidity (Ch. 2)

$HA \rightleftharpoons A^- + H^{\oplus}$

$K_a = \dfrac{[A^-][H^+]}{[HA]}$

K_a describes tendency of compounds to dissociate

$pK_a = -\log_{10} K_a$

↳ indicates strength acid

larger value weaker acid

pKa table handout (website)

H_2O < CH_3CO_2H < CF_3CO_2H < HCl

15.7 4.75 0 −7 pKa

Incr. acid strength →

$\overset{\delta+}{H}-\overset{\delta-}{A}$

H-F H-Cl H-Br H-I

pKa 3.2 −7 −9 −10

I val bonding e⁻s farther away from nucleus

CH_3-H NH_2-H H-O-H F-H

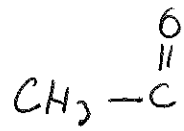
pKa 48 38 15.7 3.2

Dec

∴ main consideration is EN of A bound to H

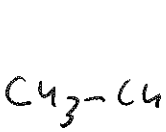
Acidity of Carboxylic acids

organic acids



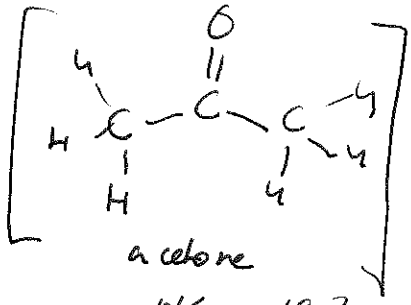
Acetic acid

pKa = 4.75



ethanol

pKa = 16

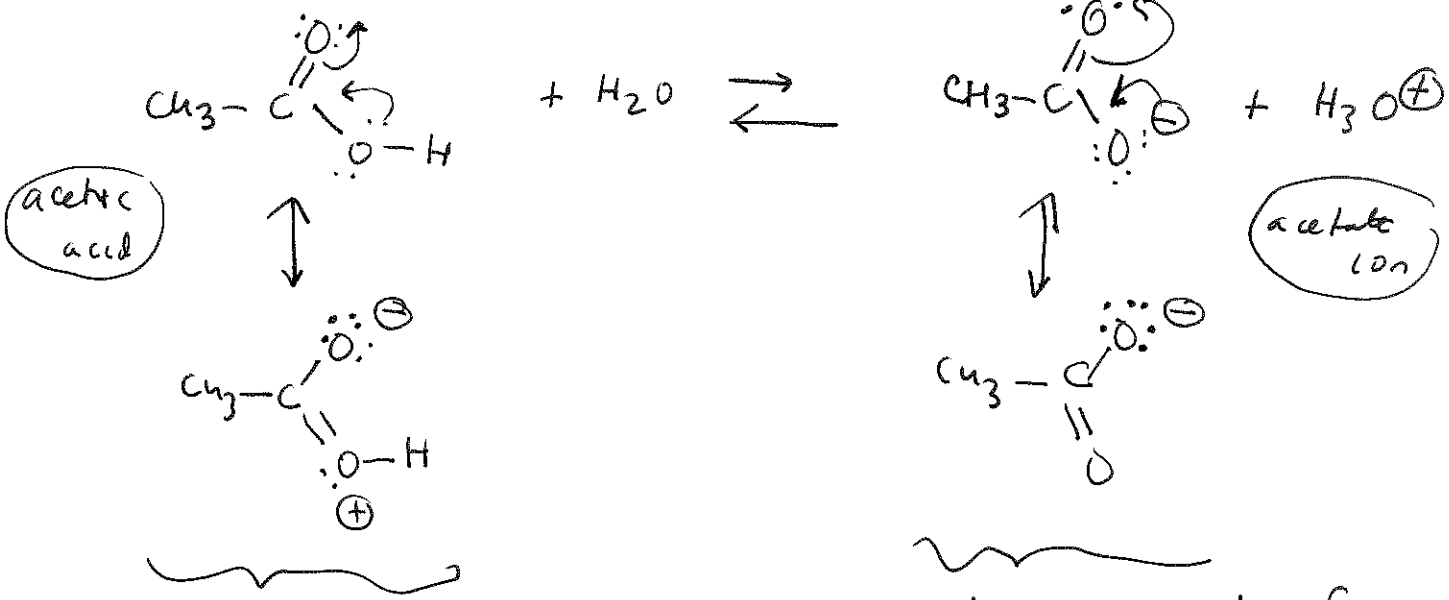


acetone

pKa = 19.3

How do we explain the greater acidity of Carboxylic acids rel. to alcohols?

1) Resonance effects



Small res. stab.

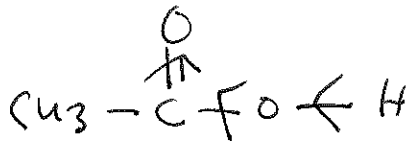
not equivalent, charge sep.

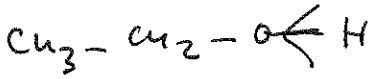
larger res. stab of anion

equivalent structures, no chg. sep.

Acidity of carboxylic acids

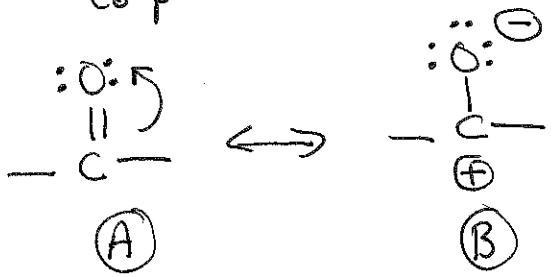
Inductive effects





powerful e^- - attracting induc. effect of the C=O

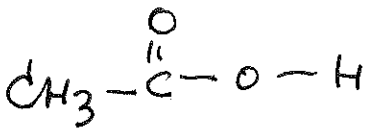
compared to CH_2



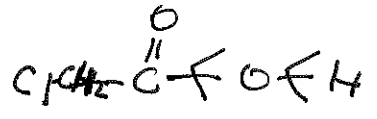
carbon of C=O bears a large ⊕ charge because the second res. structure (B) is an impt. contrib. to the res hybrid

makes C–OH proton more ⊕ than CH_2–OH

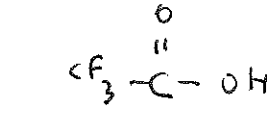
Inductive effects of other grps



pKa = 4.75



pKa = 2.86

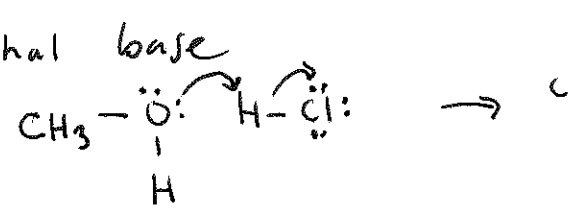


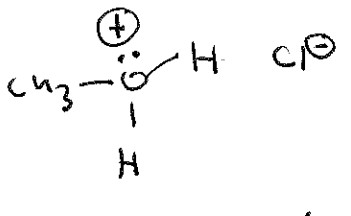
pKa = 1

extra e^- attracting inductive effect of EN Cl atom

Organic cpds as Bases

* Compound w atom w an unshared e^- pair is a potential base





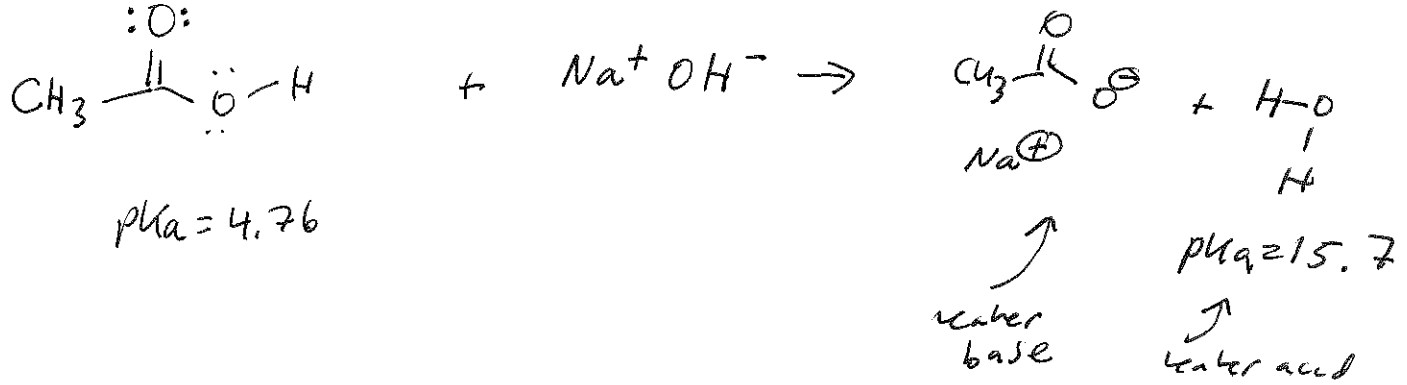
• l.p can bond to H^+

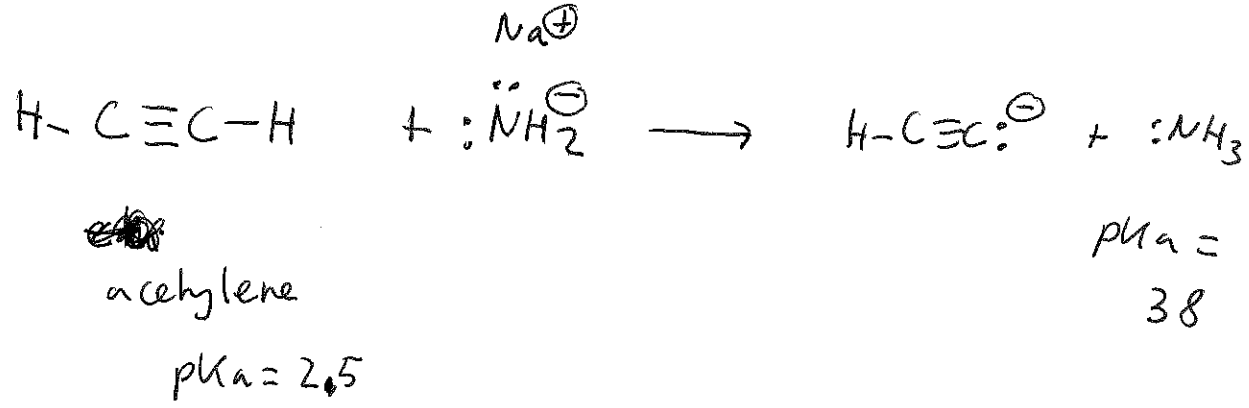
$Et-\ddot{O}-Et$ (ethers)

oxonium ion (protonated) alcohol

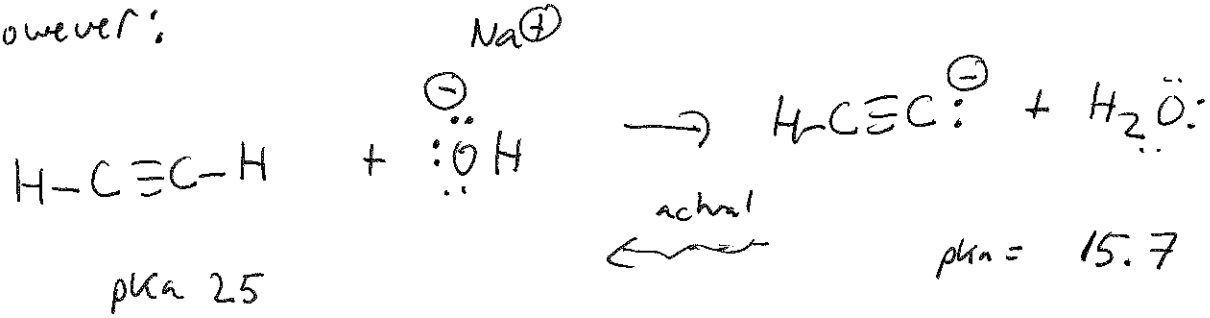
Predicting the Outcome of Acid-Base Reactions

general principle: Acid-base reactions always favor formation of the weaker acid & the weaker base

1) 

2) 

However:



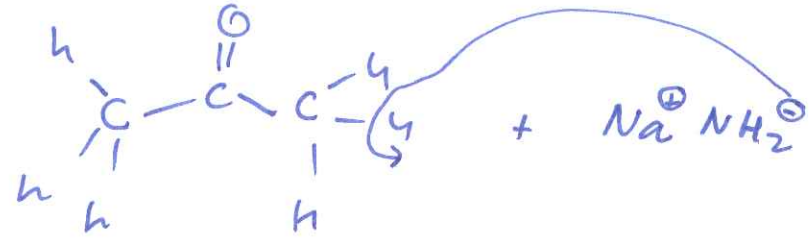
3) $CH_3CH_2-O-H + Na^+OH^- \rightarrow CH_3CH_2O^- + H_2O$

pka 15.9

conj. base

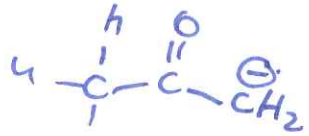
conj acid pka 15.7

Rx will proceed but not quantitatives

4)  + $Na^{\oplus}NH_2^{\ominus} \rightarrow NH_3$ + 33

acetone

pk 19.3

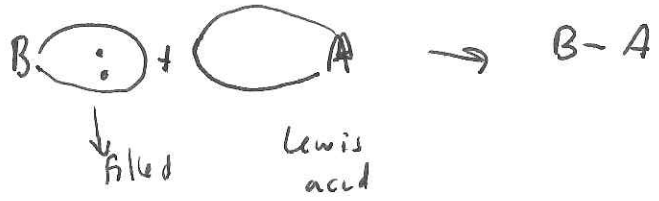


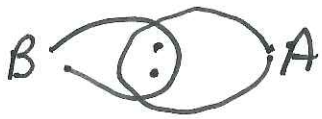
Conj. base

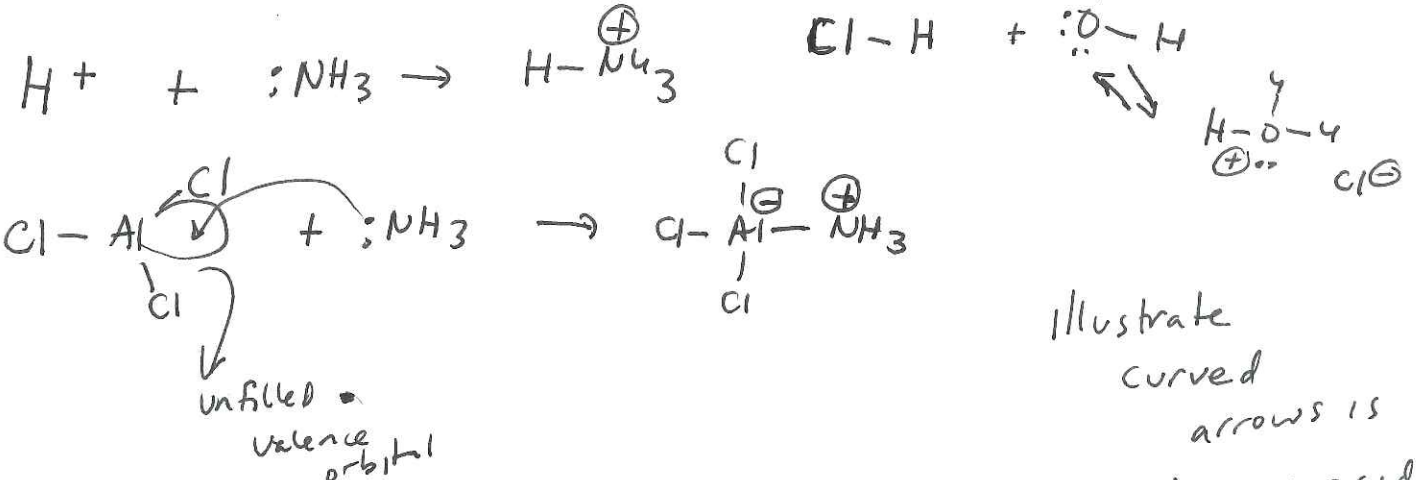
rx will proceed.

The Lewis definition of Acids & Bases

1923: G.N. Lewis ; not limited to substances that donate or accept protons



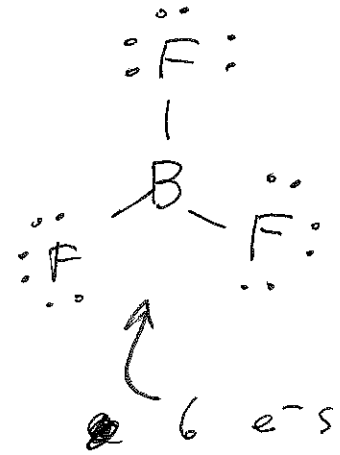




Illustrate curved arrows is Lewis acid-base reactions

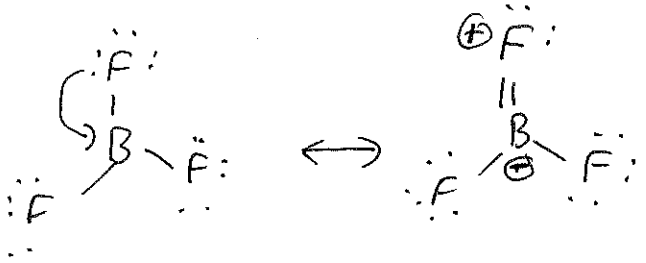
- e⁻ lone pair on acetone
- Use curved arrow to show movement of a pair toward the H atom of the acid

Consider the structure of BF_3 (Lewis acid)



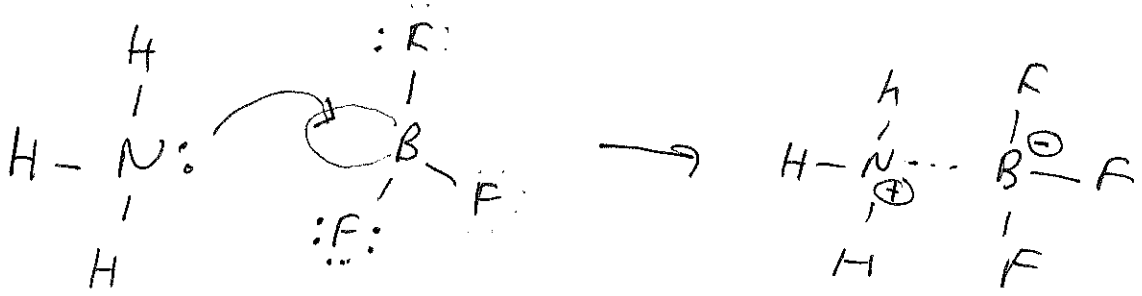
- one exception to octet rule
- B, 3 e⁻s each should form one bond with F

6 e⁻s in outer shell



- central B now has an octet
- F shares e⁻s with B

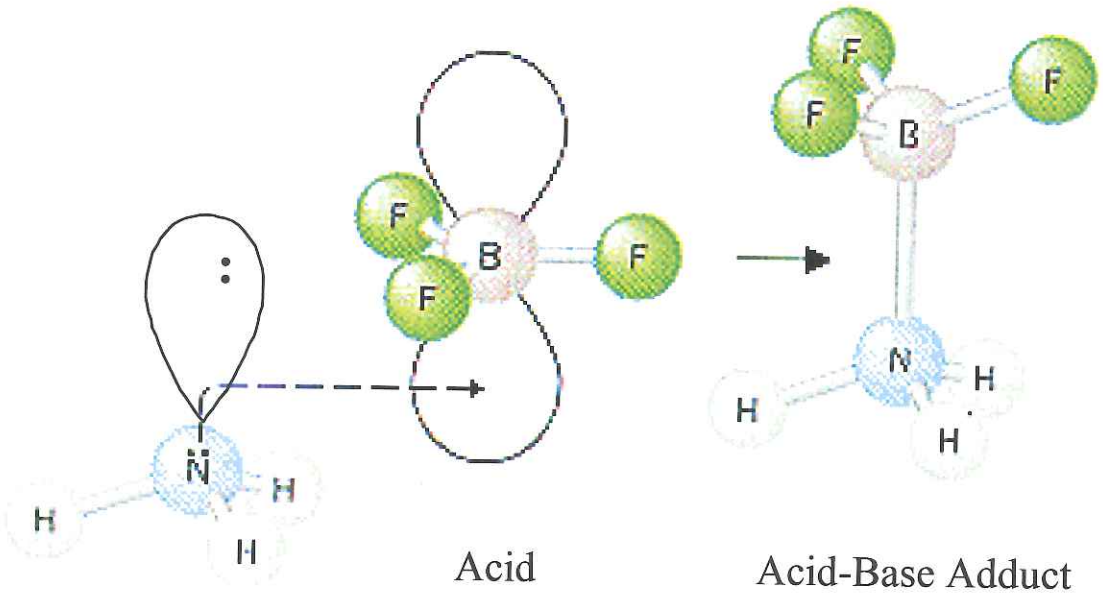
In this case F would have + partial charge, B (−) partial charge, inconsistent with eneg of B + F



BF_3 reacts strongly with compounds which have an unshared pair of e⁻s

$$F_3B \quad + \quad :NH_3 \longrightarrow \quad F_3B\text{---}NH_3$$

Boron trifluoride



Base

Acid

Acid-Base Adduct

- trigonal planar hybridization corresponds to 120° angle, sp^2

Chapter 3 Problems

1, 12, 21, 24, 34, 38,

40, 42, 43, 44, 46,

50 & 52

Skip section 3.5

(Properties of Alkanes)