LEC ⑫ CHEM 30A Oct 28th

ACIDS & BASES

① INTRO

② PROTONATING ORGANIC STRUCTURES

③ ACID/BASE EQUILIBRIA

④ STRUCTURE & ACIDITY

Read Ch4, Problems 4.1 - 4.47

MIDTERM: LOW 5 HIGH 98, MEAN = 55

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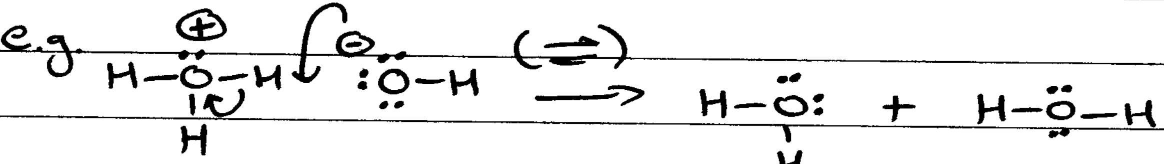
① INTRO

BRONSTED/LOWRY ⇒ ACID ⇒ H^+ DONOR
BASE ⇒ H^+ ACCEPTOR

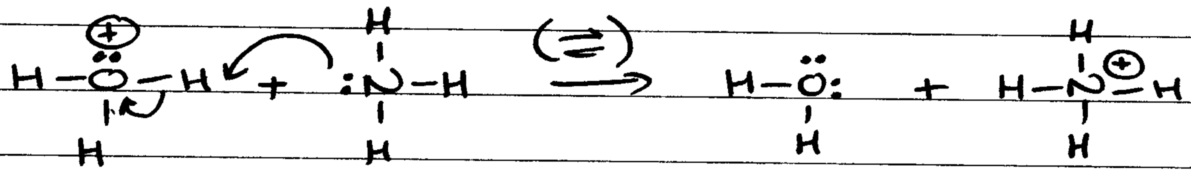
e.g.



$H_3O^+ + {}^-OH \rightleftharpoons H_2O + H_2O$

ACID (H^+ DONOR) BASE (H^+ ACCEPTOR)

hydronium ion hydroxide ion

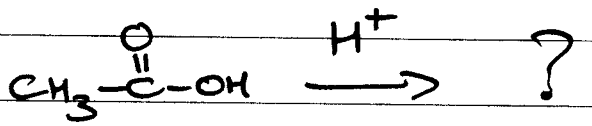


$H_3O^+ + NH_3 \rightleftharpoons H_2O + NH_4^+$

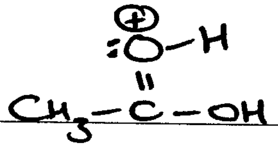
ACID BASE CONJUGATE BASE CONJUGATE ACID

② PROTONATING ORGANIC STRUCTURES

(i)

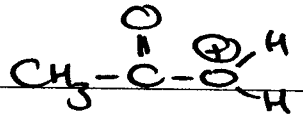


$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{H^+} ?$



Ⓐ

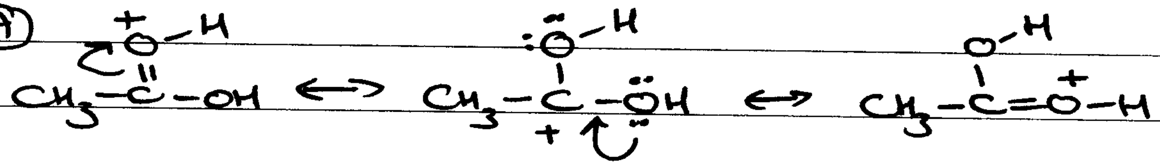
or



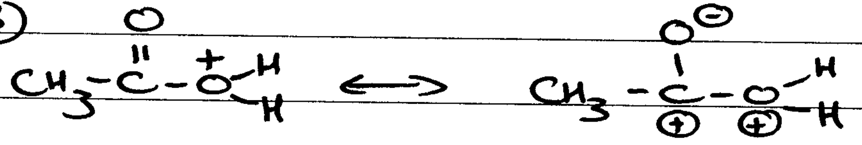
Ⓑ

consider RESONANCE

Ⓐ



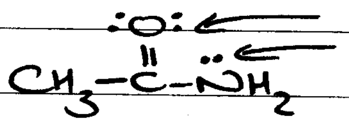
Ⓑ



not good!

$\overset{O}{\overset{\|}{C}}$ more basic than C–OH in $-\overset{O}{\overset{\|}{C}}-OH$

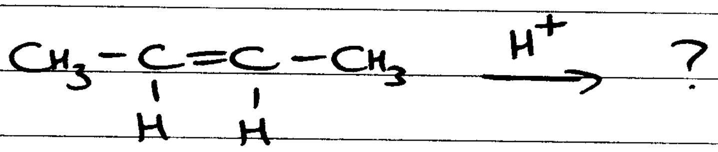
HMK



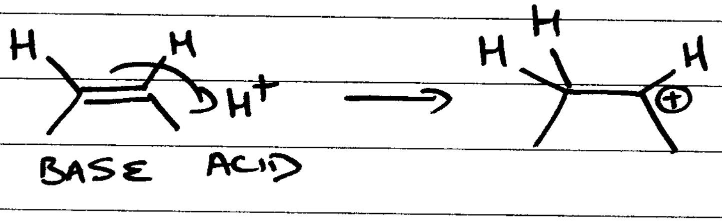
$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$

which is more basic?

(ii)



$CH_3-\underset{H}{C}=\underset{H}{C}-CH_3 \xrightarrow{H^+} ?$



CARBOCATION

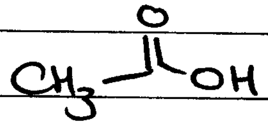
③ ACID/BASE EQUILIBRIA

(quantify acid strength → acid dissociation constants)

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \leftarrow$$ changes very little (huge xs)

$$K_a = k_{eq}[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

e.g. acetic acid 

$CH_3-\overset{O}{\overset{\|}{}}-OH$

$K_a = 1.74 \times 10^{-5}$

Most organic acids have a K_a with a -ve exponent => hard to compare

$pK_a = -\log_{10} K_a$ pK_a (acetic acid) $= 4.76$

LARGER pK_a ⟶ WEAKER ACID

STRONG ACID => WEAK CONJUGATE BASE
WEAK ACID => STRONG CONJUGATE BASE

Scan through pK_a table in the book.

POSITION of EQUILIBRIUM

$$HA + B^{\ominus} \rightleftharpoons A^{\ominus} + HB$$

Competition between $B^{\ominus}$ and $A^{\ominus}$ for $H^{\oplus}$

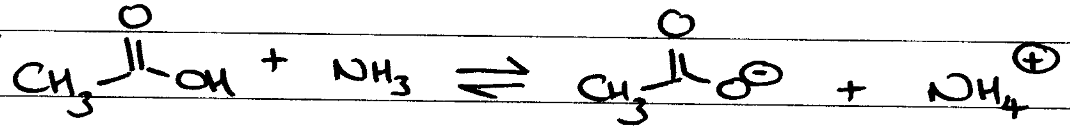
$$K_{eq} = \frac{[A^-][HB]}{[HA][B^-]} \quad \text{multiply by} \quad \frac{[H_3O^+]}{[H_3O^+]}$$

$$K_{eq} = \frac{[A^-][H_3O^+]}{[HA]} \times \frac{[HB]}{[B^-][H_3O^+]}$$

$$K_{eq} = \frac{K_{HA} \text{ (acid)}}{K_{HB} \text{ (conjugate acid)}}$$

$$pK_{eq} = pK_{HA} - pK_{HB}$$

e.g.



$$CH_3\overset{O}{\overset{\|}{C}}OH + NH_3 \rightleftharpoons CH_3\overset{O}{\overset{\|}{C}}O^{\ominus} + NH_4^{\oplus}$$

	ACID	BASE	CONJUGATE BASE	CONJUGATE ACID
pKa	4.76			9.24

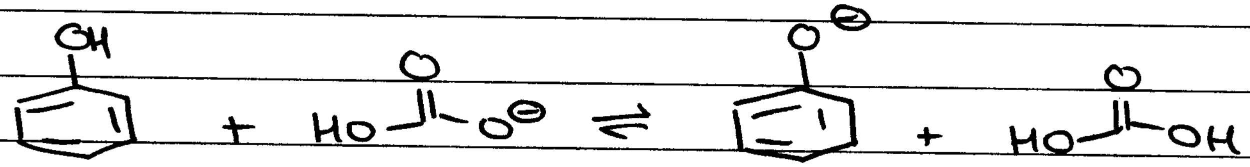
$$\text{So } pK_{eq} = 4.76 - 9.24$$
$$= -4.48$$

$$K_{eq} = 10^{-pK_{eq}} = 3 \times 10^4$$

STRONGER ACID and STRONGER BASE react to give WEAKER ACID and WEAKER BASE

If stronger acid on left, $K_{eq} > 1$
If stronger acid on right, $K_{eq} < 1$

For example:



pka ~ 10 pka ~ 6.4

STRONGER ACID

$K_{eq} = 10^{-3.6}$ ↓

④ STRUCTURE AND ACIDITY

$HA \rightleftharpoons H^+ + \boxed{A^-}$ all about A^-

The more stable A^-, the more acidic HA

a) ELECTRONEGATIVITY (within a row)

consider:

CH_3CH_2-H $CH_3-N{<}^{H}_{H}$ CH_3-O-H

51 38 16 pka

⟶ INCREASING ACIDITY

$CH_3\ddot{C}H_2^{\ominus}$ $CH_3-\ddot{N}{<}^{H}_{\ominus}$ $CH_3-\ddot{\underset{\cdot\cdot}{O}}:^{\ominus}$ conjugate bases

⟵ INCREASING BASICITY

C 2.5 N 3.0 O 3.5 EN

Greater EN, electrons held more tightly, A^- more stable

b) ATOM SIZE

consider:

CH_3-S-H vs CH_3-O-H

7 16 pka

$CH_3-S^{\ominus}$ $CH_3O^{\ominus}$

more stable

Negative charge spread over a larger volume (lower charge density)

So, for HALOGEN acids:

$HI > HBr > HCl > HF$ acidity.

because $I^- > Br^- > Cl^- > F^-$ size.

next up...

RESONANCE & the INDUCTIVE EFFECT.