LEC (12) CHEM 30A May 2nd

(1) PROTONATING ORGANIC STRUCTURES
(2) ACID/BASE EQUILIBRIA
(3) STRUCTURE & ACIDITY
(4) LEWIS ACIDS/BASES

MIDTERMS back in DISCUSSION

Read Ch4 Problems 4.1 → 4.45 (3rd)
(4.47) 4th

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(1) PROTONATING ORGANIC STRUCTURES

see last page Lec (11)

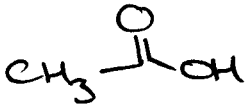
(2) ACID/BASE EQUILIBRIA

Quantify acid strength → acid dissociation constants

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

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

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

e.g. acetic acid 

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

Most organic acids have K_a with -ve exponent
– hard to compare

$pK_a = -\log_{10} K_a$ $\quad pK_a(CH_3CO_2H) = 4.76$

LARGER pK_a → WEAKER ACID

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

Scan through table Pg 141 (3)

– POSITION of EQUILIBRIUM

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

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

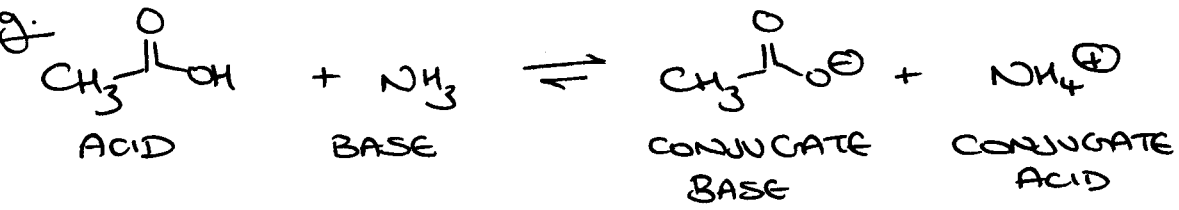
$$K_{eq} = \frac{[A^-][HB]}{[HA][B^-]}$$ multiply by $\frac{[H_3O^+]}{[H_3O^+]}$

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

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

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

eg.



pka 4.76 pka 9.24

So $pK_{eq} = 4.76 - 9.24$

$= -4.48$

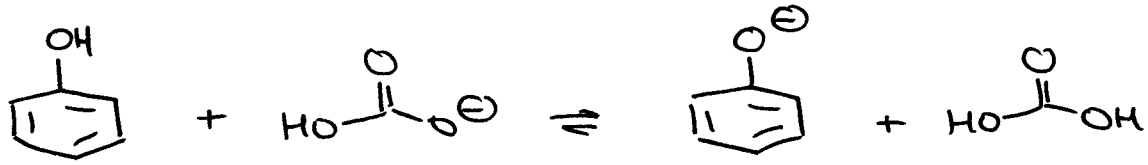
$K_{eq} = 10^{-pK_{eq}}$

$= 3 \times 10^{4}$

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

$K_{eq} = 10^{-3.6}$

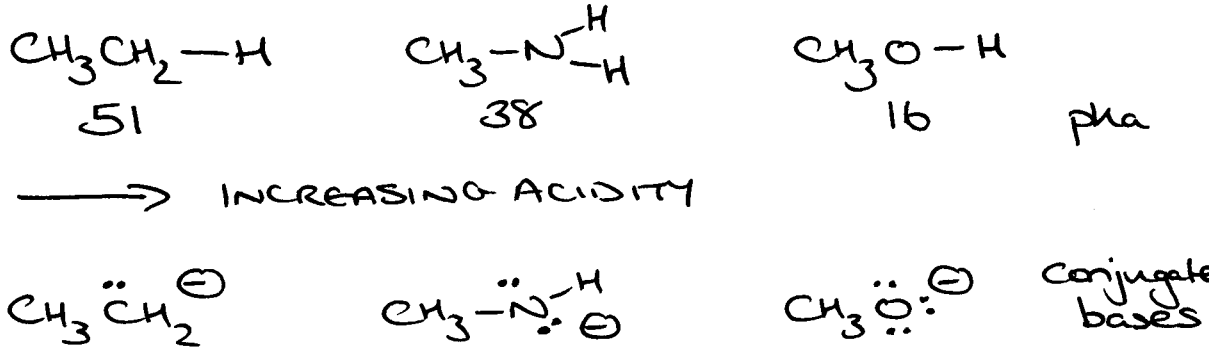
③ STRUCTURE AND ACIDITY

$HA \rightleftharpoons H^+ + A^-$ all about A^-

The more stable A^-, the more acidic HA

a) ELECTRONEGATIVITY (within a row)

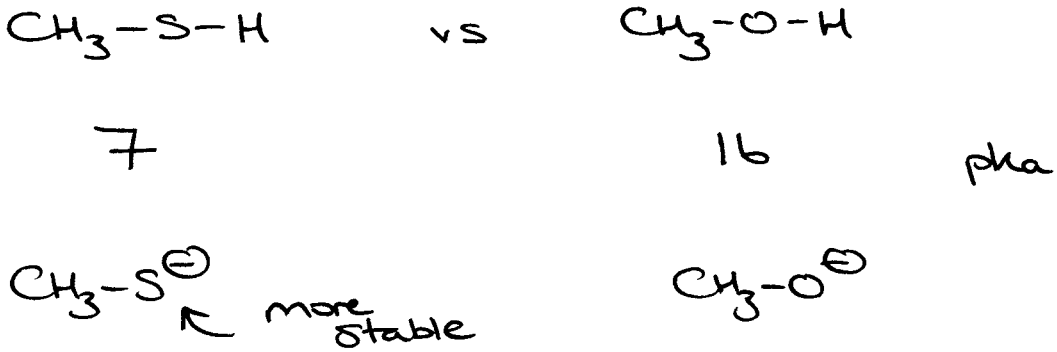
consider:



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

b) ATOM SIZE

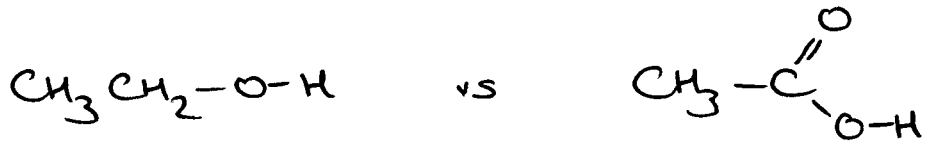
consider



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

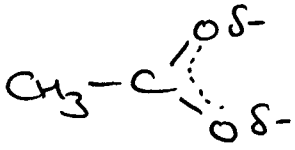
So, for HALOGEN ACIDS, $HI > HBr > HCl > HF$

c) RESONANCE
consider



16 5 pka

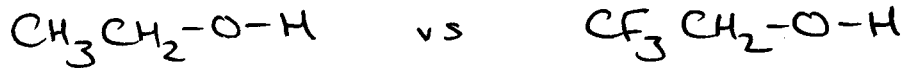
charge localized on one atom



charge delocalized

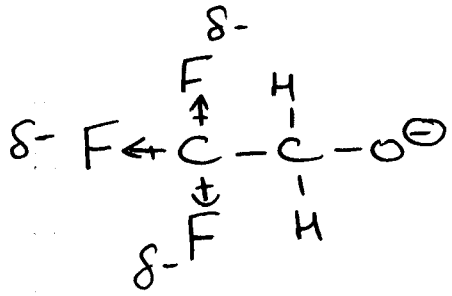
DELOCALIZATION ≡ STABILITY (HOT POTATO)

d) INDUCTIVE EFFECT
consider:



15.9 12.4 pka

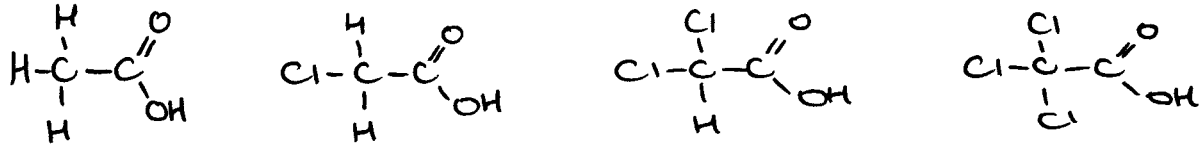
$CF_3CH_2O^{\ominus}$ is more stable than $CH_3CH_2O^{\ominus}$



Through BOND effect, falls off rapidly with distance.

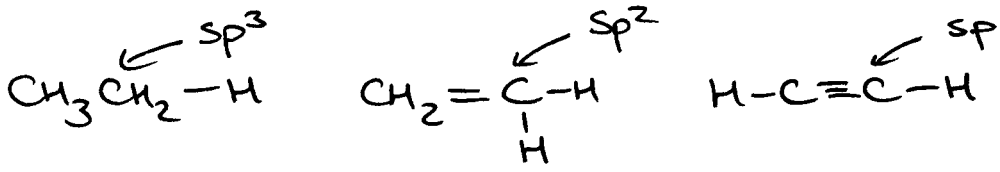
	CF_3CH_2OH	$CF_3CH_2CH_2OH$	$CF_3CH_2CH_2CH_2OH$
pka	12.4	14.6	15.4

Same effect w/ CARBOXYLIC ACIDS



4.75	2.85	1.48	0.64

e) HYBRIDIZATION



51	44	25	pka

⟶ ACIDITY INCREASES

s character of orbital 25% → 33% → 50%

- electrons held closer to the nucleus
  - more stable anion
  - more acidic