LEC (12) CHEM 30A Feb 7th

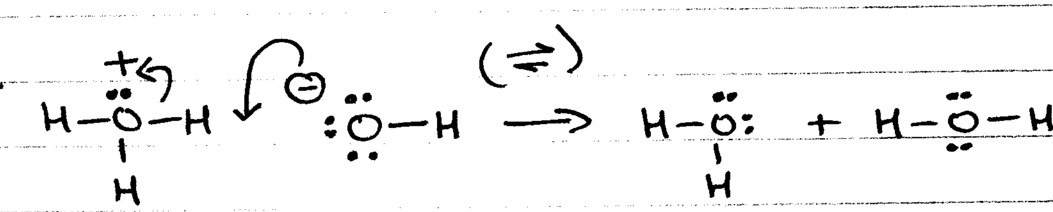
ACIDS & BASES

1. INTRO
2. ACID/BASE EQUILIBRIA
3. STRUCTURE AND ACIDITY
4. PROTONATING ORGANIC STRUCTURES
5. LEWIS ACIDS/BASES

READ Ch4, PROBLEMS 4.1 → 4.45

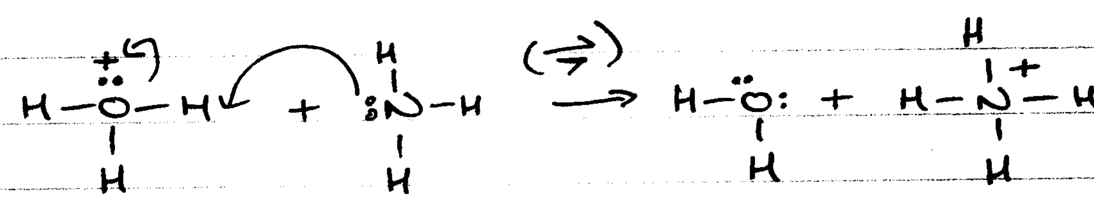
(1) BRONSTED LOWRY ⇒ ACID H^+ DONOR
BASE H^+ ACCEPTOR

e.g.



ACID
H^+ DONOR
hydronium ion

BASE
H^+ ACCEPTOR
hydroxide ion



ACID | BASE | CONJUGATE BASE | CONJUGATE ACID

(2) ACID | BASE EQUILIBRIA

acid dissociation constants
→ quantify acid strength

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

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

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

e.g. for acetic acid 

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

most organic acids have Ka values with -ve exponents, so we often compare pKa values

$$pK_a = -\log_{10} K_a$$

$$pK_a (CH_3CO_2H) = 4.76$$

LARGER pKa VALUE → WEAKER ACID

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

Scan through table on page 141

POSITION OF ACID BASE EQUILIBRIA

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

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

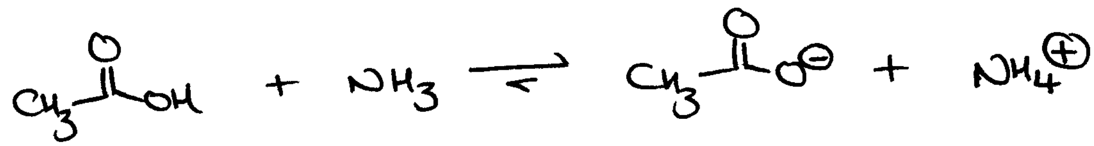
$$k_{eq} = \frac{[A^-][HB]}{[HA][B^-]}$$

multiply by $\frac{[H_3O^+]}{[H_3O^+]}$

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

$$k_{eq} = \frac{K_{HA}}{K_{HB}}$$ (ACID) / (CONJUGATE BASE)

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



ACID | BASE | CONJUGATE BASE | CONJUGATE ACID

pKa 4.76 | | | pKa 9.24

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

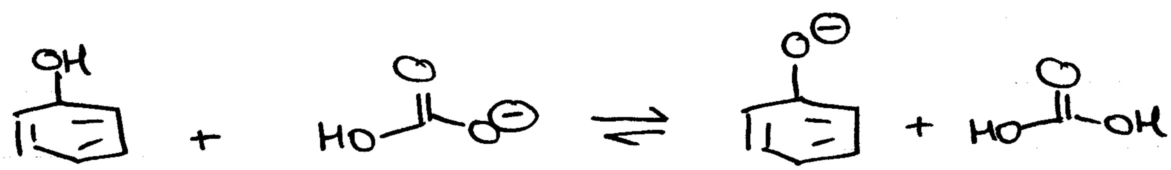
$K_{eq} = 10^{-pK_{eq}}$

$= 3 \times 10^{4}$

STRONGER ACID AND STRONGER BASE REACT TO GIVE WEAKER ACID & 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

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

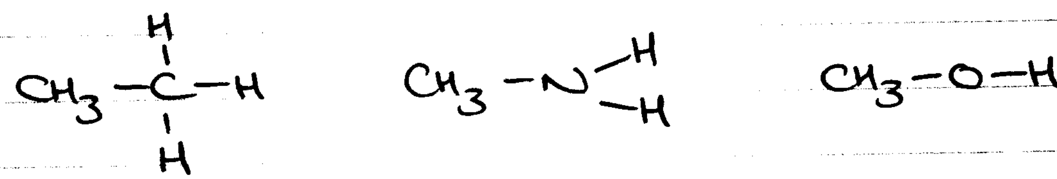
3) STRUCTURE AND ACIDITY

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

The more stable A^-, the more acidic HA is

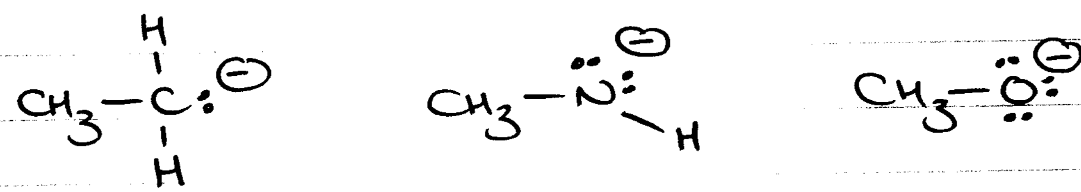
a) ELECTRONEGATIVITY

consider:



pKa: 51 — 38 — 16

⟶ INCREASING ACIDITY



conjugate bases

⟵ INCREASING BASICITY

C	N	O
2.5	3.0	3.5

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

This trend holds across any given row of the periodic table

b) ATOM SIZE

consider:

CH_3-S-H vs CH_3-O-H

pKa 7 16

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

↑ more stable

NEGATIVE CHARGE IS SPREAD OVER A LARGER VOLUME (lower charge density)

So, for HALOGEN ACIDS

HI > HBr > HCl > HF

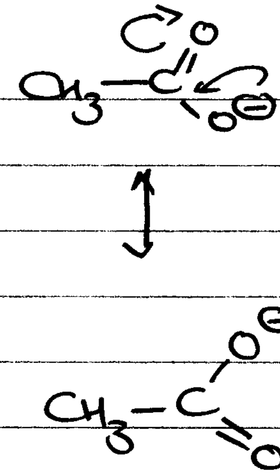
c) RESONANCE

consider:

CH_3CH_2-O-H vs $CH_3-C(=O)-OH$

pKa 16 5

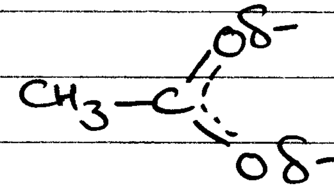
$CH_3CH_2-O^{\ominus}$ vs



⇑

charge localized on ONE atom

charge delocalized ⟹



DELOCALIZATION ≡ STABILITY

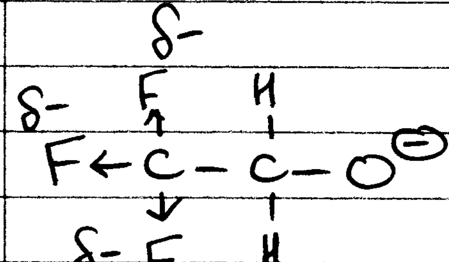
(hot potato analogy)

d) INDUCTIVE EFFECT

consider: CH_3CH_2-O-H CF_3CH_2-O-H

pKa 15.9 12.4

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

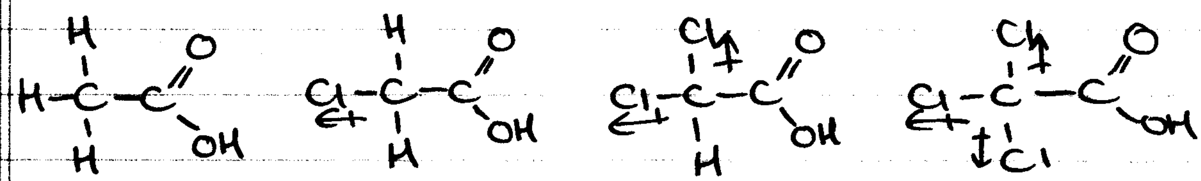


THROUGH BOND EFFECT

falls off rapidly w/ distance

	CF_3CH_2OH	$CF_3CH_2CH_2OH$	$CF_3CH_2CH_2CH_2OH$
pKa	12.4	14.6	15.4

Same effect on carboxylic acids



4.75 2.85 1.48 0.64

c) HYBRIDIZATION

CH_3CH_2-H (← sp3) pKa 51

$CH_2=CH-H$ (← sp2) 44

$H-C\equiv C-H$ (← sp) 25

↓ MORE ACIDIC

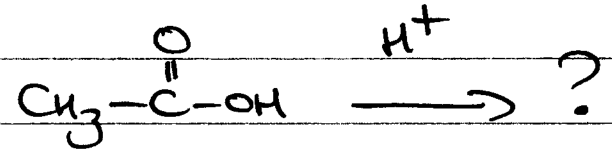
s character of orbitals 25% → 33% → 50%

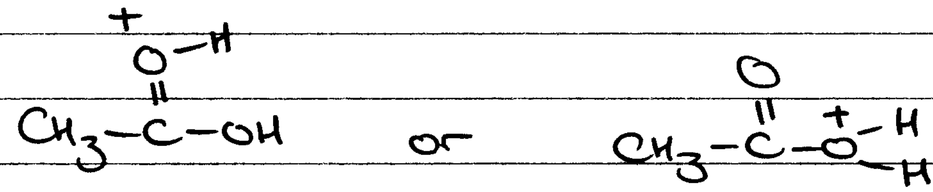
electrons held closer to the nucleus

- more stable anion
- more acidic

(4) ORGANIC STRUCTURES

(i)

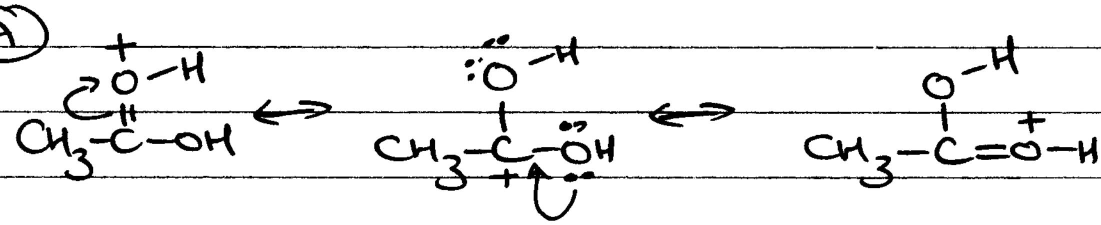




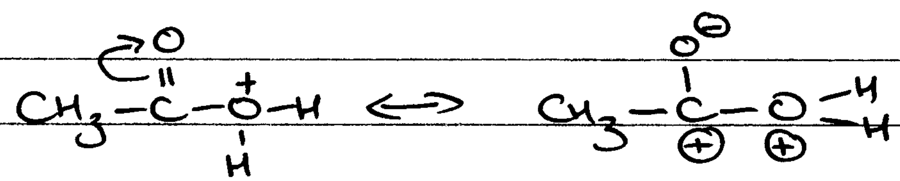
(A) or (B)

consider resonance

(A)



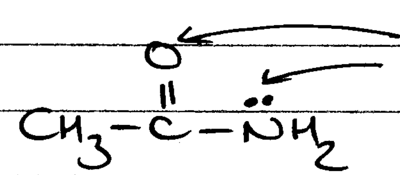
(B)



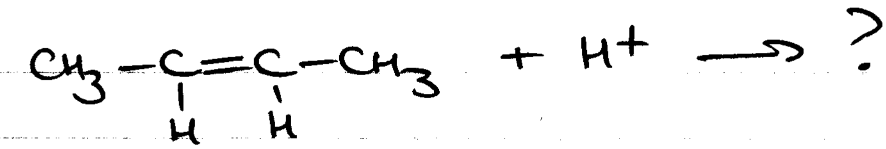
not a good resonance form

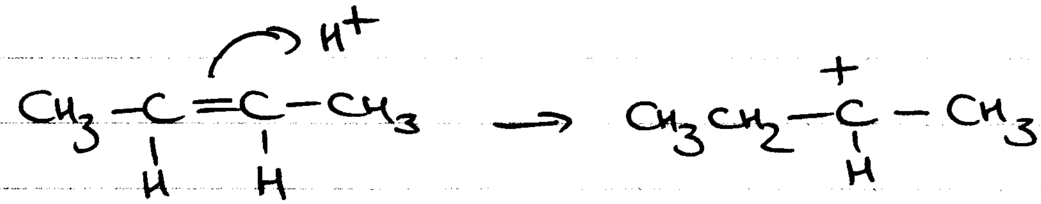
So C=O more basic than C–OH in –C(=O)–OH

HMK



which is more basic

(ii) 



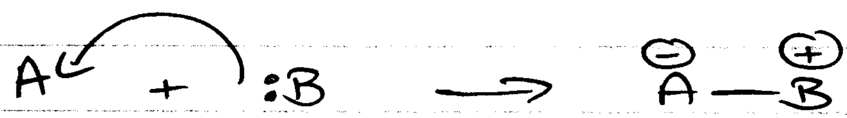
CARBOCATION

(see a lot more of these soon)

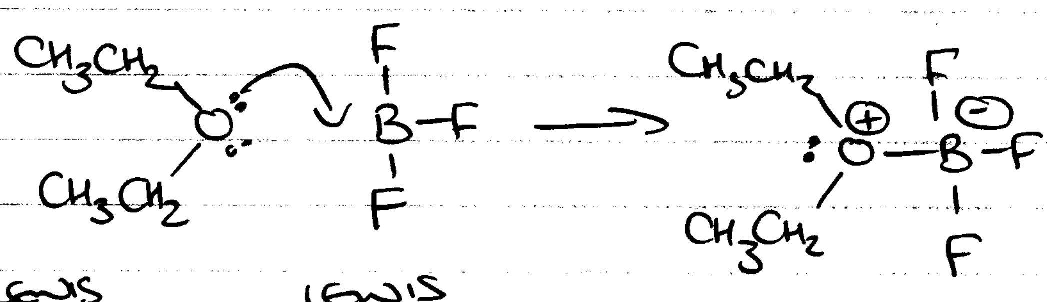
5 LEWIS ACIDS / BASES

about e^- pairs, not H^+

LEWIS ACID accepts an e^- pair
LEWIS BASE donates an e^- pair



LEWIS ACID   LEWIS BASE

e.g. 

LEWIS BASE   LEWIS ACID