Carboxylic Acids I

General

Naming

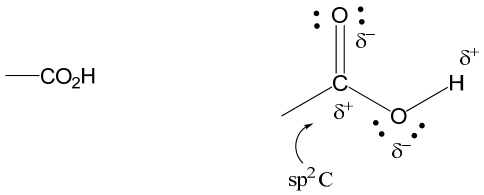
Acid/ Base Properties

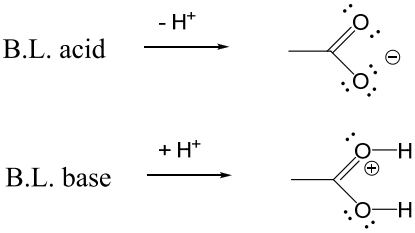
Ref 18: 1 - 2I

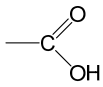
Prob 18: 1, 2 (19, 20 some)

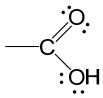
Adv Rdg 18: 2J - 4

General



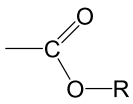


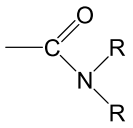
Lewis acid:  π* MO of C=O is electrophilic

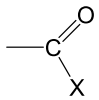
Lewis base:  lone pairs on C=O are nucleophilic

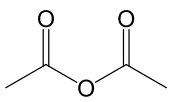
Acid Derivatives

–OH replaced by other e/n atoms (groups); most important



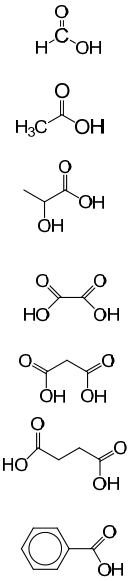


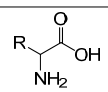




Occurrence

- occur widely; “stable” , known for long time
- many common names exist



α-aminoacids 

R variable; building blocks of proteins, such as muscle, enzymes, some hormones, antibodies, ...

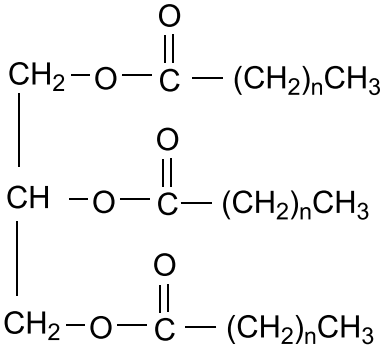
Fats

(for see details, see Solomons 23.2)

• "fatty acid" = long, unbranched acid;
most common: C_{16}, C_{18}

• are parts of fats ; i.e. multi-ester of glycerol
"triglyceride"

Illustration:



chains may be identical or different

Examples

sat^{d} fatty acid: stearic acid

"cis" unsaturated fatty acid: oleic acid

poly unsaturated acid (PUFA), linoleic acid

omega-3 (ω-3) fatty acid, linolenic acid

Systematic Naming

• ending: -oic acid

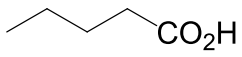
• "2 acid F.G.'s: -edioic acid

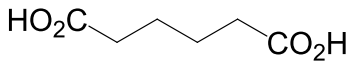
• on rings: -carboxylic acid

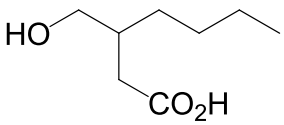
• group has highest priority in numbering

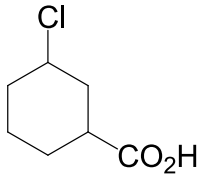
• salts: -oate

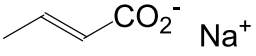
Practice





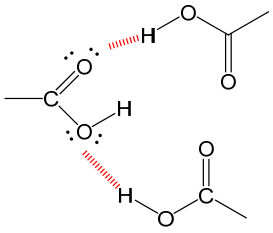




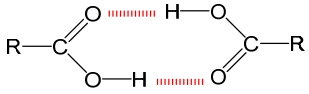


H – Bonding

• similar to ROH, but more variety exists



• dimers are prominent, if "neat" (*no solvent*)



Note:

can H-bond to other molecules,

such as ROH, H_2O, A/K's, amines ...

H-Bonding ...

Consequences

• b.p. ↑

• soluble in other H-bond forming substances

• "partially" responsible fo 2°, 3° structure

("folding") of large biomoecules;

e.g., prioteins, DNA, carbohydrates, ...

Acidity

• weaker than mineral acids (HCl, H_2SO_4, ...)

• much stronger than alcohols etc.

(see pK_a Tables; esp. HT Data Sheet)

• recall: small pK_a = strong acid

Illustration:

- CH_3CO_2H ≈ 1% ionized
- CH_3CH_2OH ≈ 1×10^{-5} % ionized

Explanation

1.) conj. base resonance stabilized, therefore more easily formed, and acid stronger

2.) inductive effect of carbonyl group

- pos. C polarizes O–H bond further;
- "H^+" lost more easily

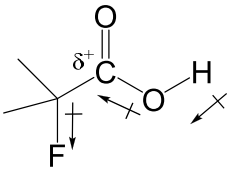
Effect of Substituents on α, β, C's

Polarity of O–H bond
influenced by inductive effect

EWG's acidity ↑

EDG's acidity ↓

Illustration:



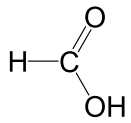
- the closer the EWG, the more acidic the acid
- more EWG's present, more acidity
- important EWG's: $-NO_2$, –X (–F), –OH

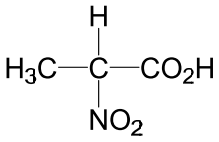
- EDG's (mainly alkyl groups) decrease acidity, explanation somewhat controversial

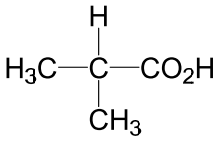
Practice

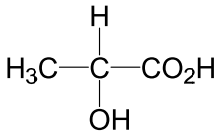
compare acidity of the following w/ that of

CH_3CO_2H









Basicity

expressed w/ strong acids (HCl, ...)

- H^+ preferentially attaches to C=O oxygen, since resulting cation is resonance stabilized
- mech. involved in many acid catalyzed rxns, (see later)