Carboxylic Acids I

General

Naming

Acid/ Base Properties

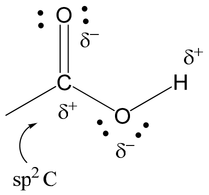
Ref 18: 1 - 2I

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

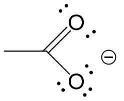
Adv Rdg 18: 2J - 4

General

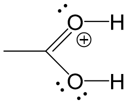
$-CO_2H$



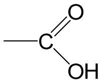
B.L. acid $\xrightarrow{-H^+}$



B.L. base $\xrightarrow{+H^+}$

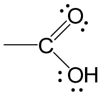


Lewis acid:



π* MO of C=O is electrophilic

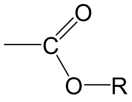
Lewis base:



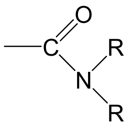
lone pairs on C=O are nucleophilic

Acid Derivatives

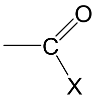
–OH replaced by other e/n atoms (groups); most important



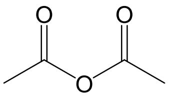
ester



amide



acyl halide



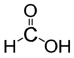
acid anhydride

—C≡N nitrile (cyanide)

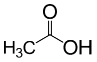
Occurrence

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

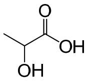
formic acid



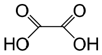
acetic



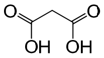
lactic



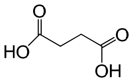
oxalic



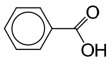
malonic



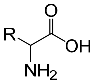
succinic



benzoic



α-aminoacids



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

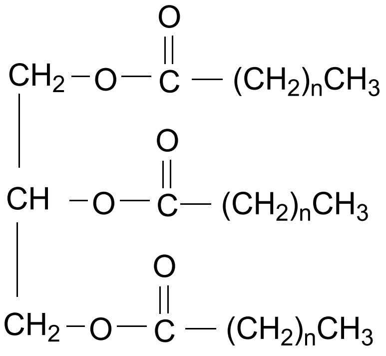
Fats

(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:



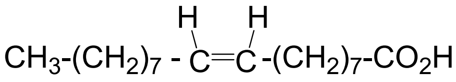
chains may be identical or different

Examples

sat^d fatty acid: stearic acid

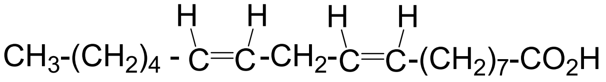
$CH_3\text{-}(CH_2)_{16}\text{ -}CO_2H$

"cis" unsaturated fatty acid: oleic acid



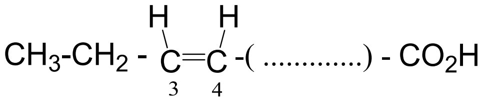
$CH_3\text{-}(CH_2)_7\text{ - }\overset{H}{C}{=}\overset{H}{C}\text{-}(CH_2)_7\text{-}CO_2H$

poly unsaturated acid (PUFA), linoleic acid



$CH_3\text{-}(CH_2)_4\text{ - }\overset{H}{C}{=}\overset{H}{C}\text{-}CH_2\text{-}\overset{H}{C}{=}\overset{H}{C}\text{-}(CH_2)_7\text{-}CO_2H$

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

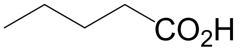


$CH_3\text{-}CH_2\text{ - }\underset{3}{\overset{H}{C}}{=}\underset{4}{\overset{H}{C}}\text{ -(............) - }CO_2H$

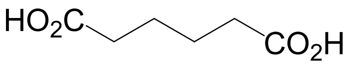
Systematic Naming

- ending: -oic acid
- "2 acid F.G.'s: -edioic acid
- on rings: -carboxylic acid
- group has highest priority in numbering
- salts: -oate

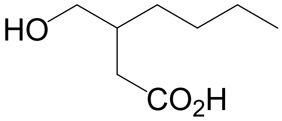
Practice



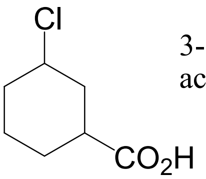
pentanoic acid



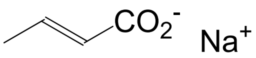
hexanedioic acid



3-butyl-4-hydroxybutanoic acid



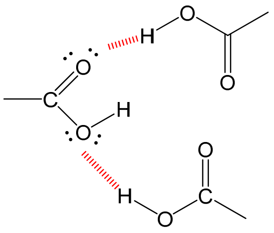
3-chlorocyclohexanecarboxylic acid



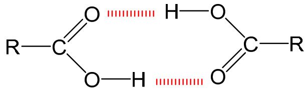
sodium 2-butenoate

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

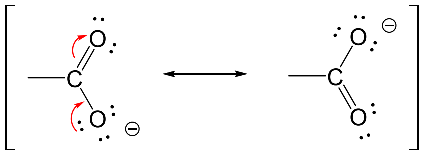
- weaker than mineral acids (HCl, H_2SO_4, ...)
- much stronger than alcohols etc. (see pK_a Tables; esp. HT Data Sheet)
- recall: small pK_a = strong acid

Illustration:

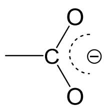
- CH_3CO_2H ≈ 1% ionized
- CH_3CH_2OH ≈ 1×10^{-5} % ionized

Explanation

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

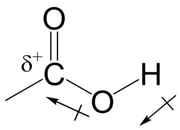


or



neg. charge delocalised

2.) inductive effect of carbonyl group



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

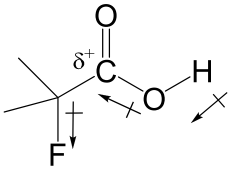
Effect of Substituents on α, β, C's

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

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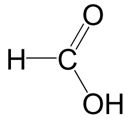
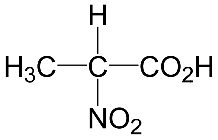
Practice

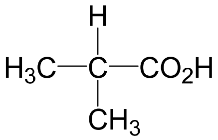
compare acidity of the following w/ that of CH_3CO_2H



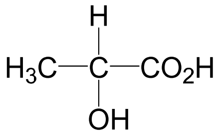
stronger



stronger



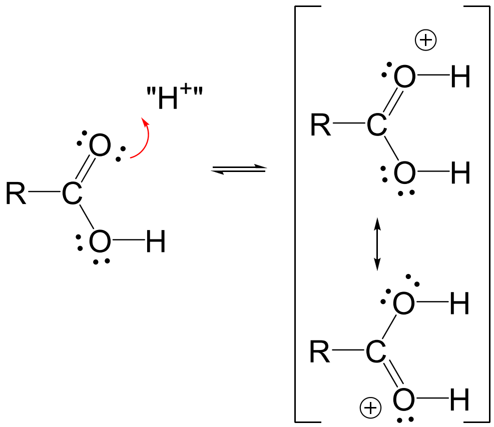
weaker



stronger

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)