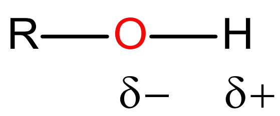
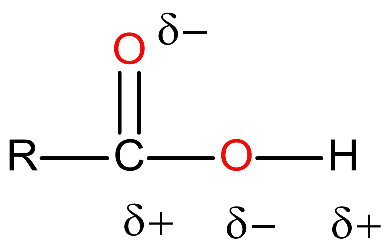
Physical properties of carboxylic acids

- Carboxylic acids are the most polar functional group we have seen so far. The presence of the carbonyl group next to the OH causes the O-H bond to be even more polar.



alcohols

pK_a ~ 16-19



carboxylic acids

pK_a ~ 4-10

This is why -COOH groups are considered to be acidic, while -OH groups are not.

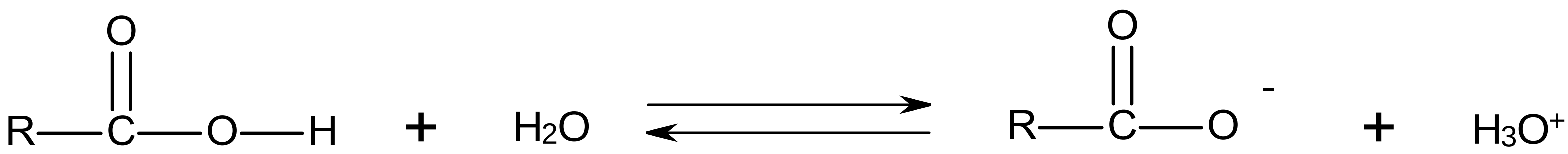
Acidity of carboxylic acids

Acid	K_a	Percent Ionization (0.100 M Solution)
Formic	1.8×10^{-4}	4.2%
Acetic	1.8×10^{-5}	1.3%
Propionic	1.3×10^{-5}	1.2%
Butyric	1.5×10^{-5}	1.2%
Valeric	1.5×10^{-5}	1.2%
Caproic	1.4×10^{-5}	1.2%

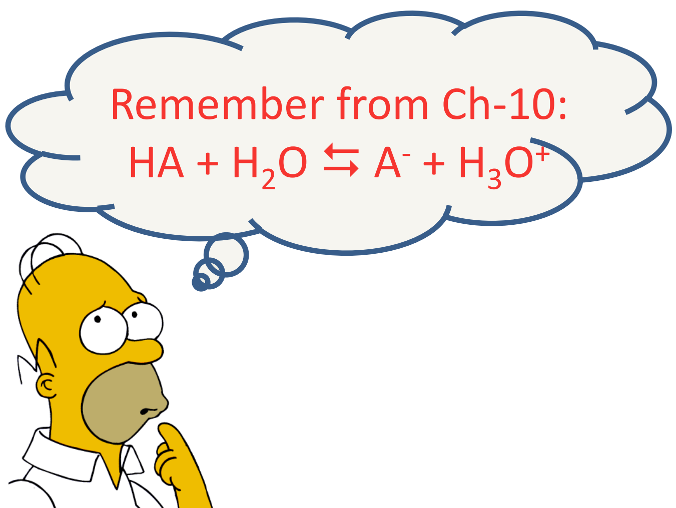
Acidity of carboxylic acids

- When carboxylic acids are placed in water, they undergo de-protonation as discussed in Ch-10:

$$HA \quad + \quad H_2O \rightarrow A^- \quad + \quad H_3O^+$$



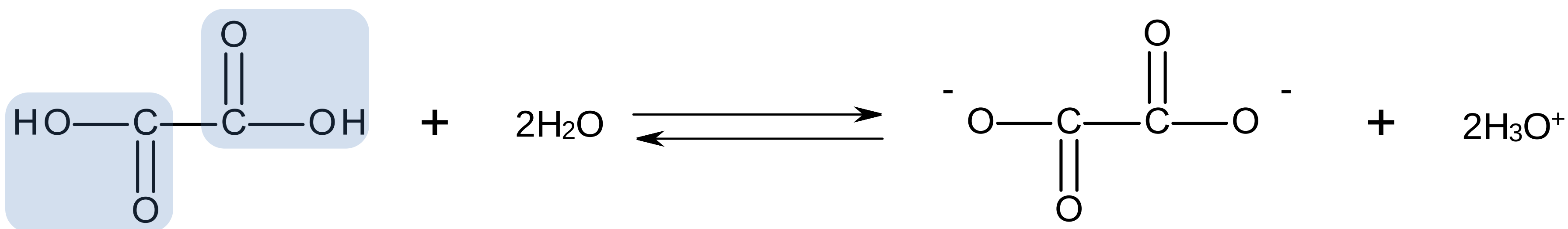
carboxylic acid　　carboxylate ion　　hydronium



Acidity of carboxylic acids

acetic acid
IUPAC: Ethanoic acid

acetate ion
IUPAC: Ethanoate ion



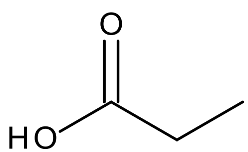
oxalic acid
IUPAC: Ethanedioic acid

oxalate ion
IUPAC: Ethanedioate ion

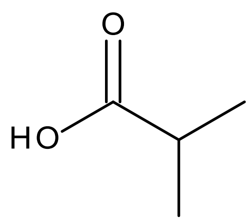
Conjugate bases of carboxylic acid

- The name of the de-protonated carboxylic acid (i.e. the conjugate base) is obtained from the name of the carboxylic acid.
- Remove the "-ic acid" part of the acid's name and replace with "-ate"

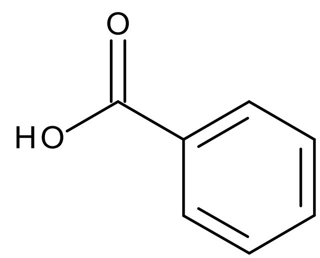
acid



propanoic acid

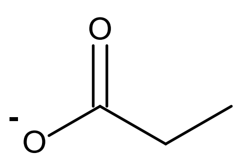


2-methylpropanoic acid

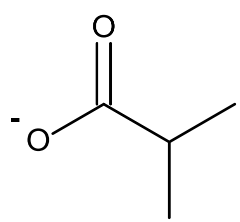


benzoic acid

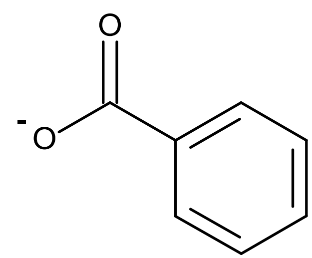
base



propanoate ion



2-methylpropanoate ion



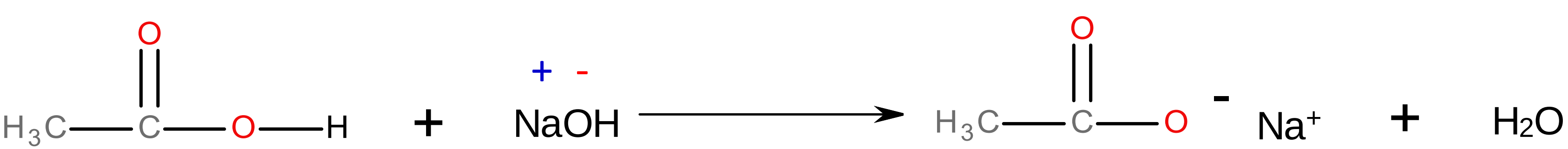
benzoate ion

Carboxylic acid salts

Acid + Base → Salt + H_2O

- When carboxylic acids are reacted with strong bases, they are converted to salts as follows:

carboxylic acid base salt water



acetic acid
IUPAC: Ethanoic acid

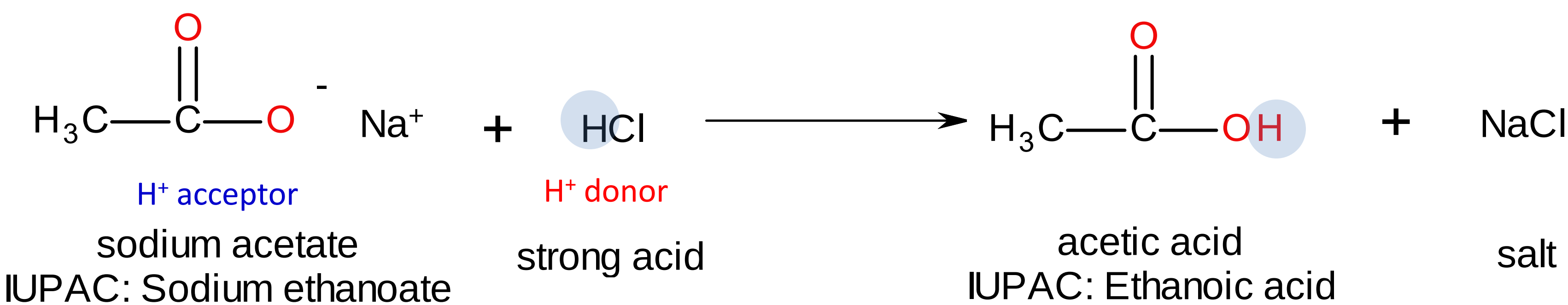
base

sodium acetate
IUPAC: Sodium ethanoate

water

Carboxylic acid salts

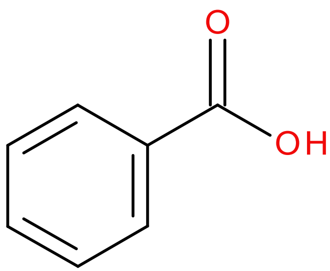
- Salts of carboxylic acids are much more water-soluble than the acids themselves.
- Also, they can be converted back to the acid form by reacting them with a strong acid:



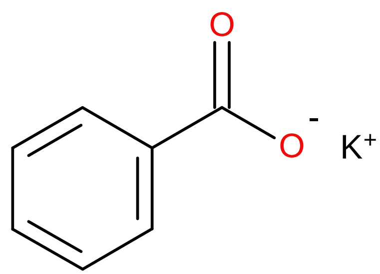
Handy rule: things that are charged tend to be more water-soluble than things that aren't (when comparing two similar structures)

Uses of carboxylic acid salts

- Because of their enhanced solubility in water compared to the acid form, many drugs and medicines that possess acid groups are marketed as carboxylic acid salts (sodium or potassium salts).



Benzoic acid



Potassium benzoate

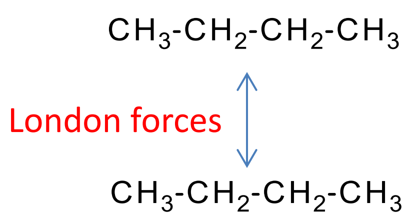
$$CH_3\text{-}CH{=}CH{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}OH$$ sorbic acid

$$CH_3\text{-}CH{=}CH{-}CH{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O^{-}\ Na^{+}$$ sodium sorbate

A brief review of boiling point trends

- Boiling points are determined by attractions between molecules; the stronger the attractions are, the higher the boiling point for the substance

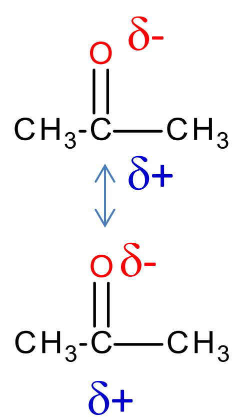
Weakest intermolecular attraction (lowest b.p.)



In simple hydrocarbons (alkanes, alkenes, etc.) there are only non-polar bonds. No dipole-dipole or H-bonding possible. Only **London**

Alkanes, alkenes, alkynes, aromatics

mid-range b.p.

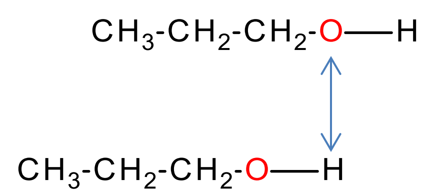


Dipole-dipole forces

Polar molecules have **dipole-dipole** attractive forces, in addition to London forces.

Aldehydes, ketones, esters

Strongest intermolecular attraction (highest b.p.)



H-bonding

In certain molecules, a H-atom may be involved in a bond to an O, N, or F-atom. This kind of H can **H-bond** to O, N, or F-atoms of other molecules.

Alcohols, carboxylic acids, amines, amides

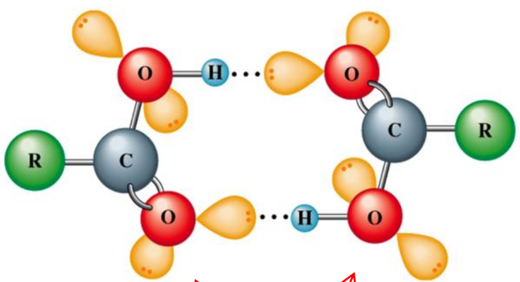
Physical properties of carboxylic acids

- Because of the **very polar** –COOH group, carboxylic acids exhibit strong intermolecular attractions.
- As expected, carboxylic acids of a given number of carbon atoms have higher boiling points than alcohols.

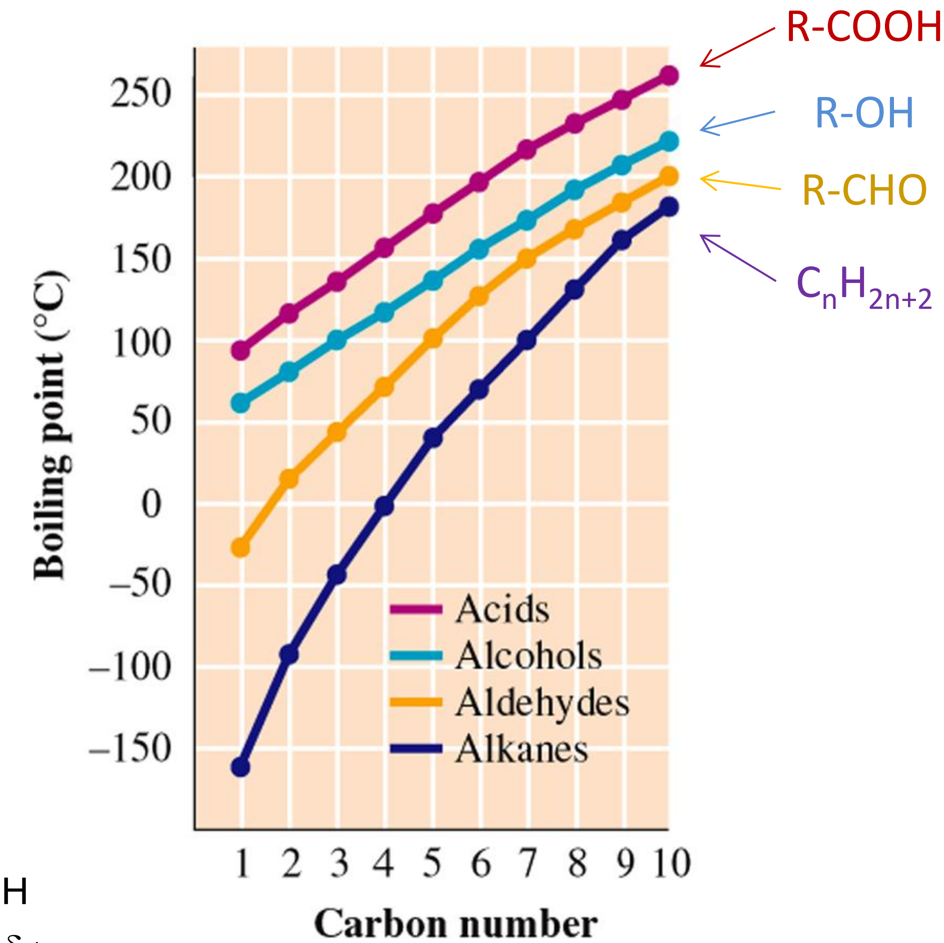
Name	Functional-Group Class	Molecular Mass	Boiling Point (°C)
diethyl ether	ether	74	34
ethyl formate	ester	74	54
methyl acetate	ester	74	57
butanal	aldehyde	72	76
1-butanol	alcohol	74	118
propionic acid	acid	74	141

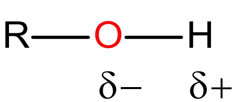
Boiling point trends

stronger H-bond
than between alcohols

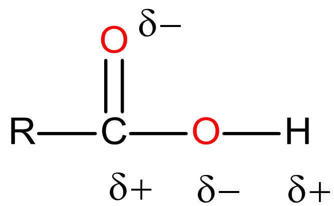


carboxylic acids





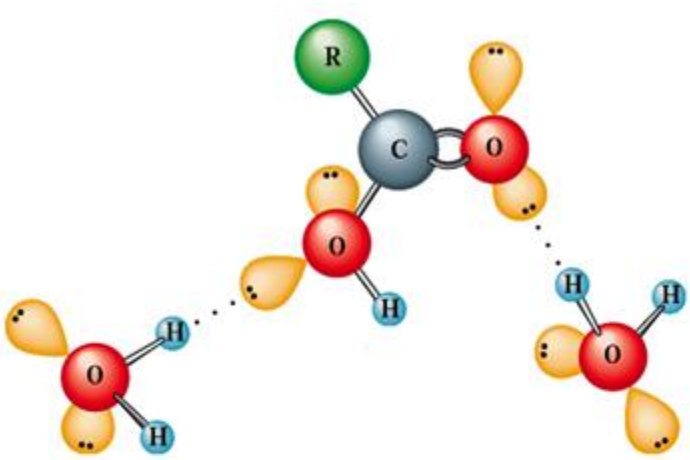
alcohols

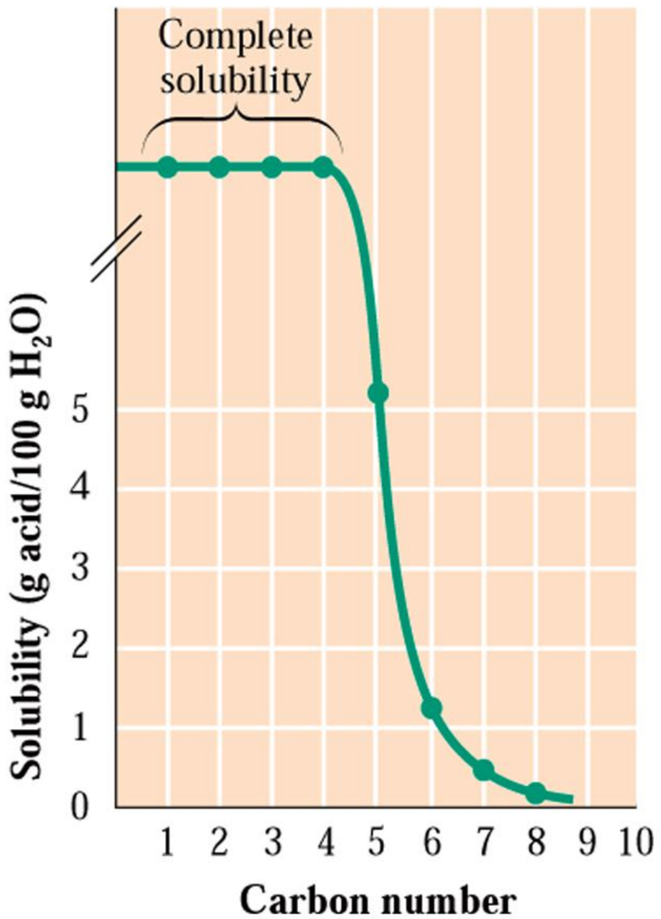


carboxylic acids

Physical properties of carboxylic acids

- In terms of water-solubility, because of H-bonding, carboxylic acids dissolve well in water (up to 4-carbon chains).
- Beyond 4 carbons, water-solubility drops off rapidly.





Water-solubility:
- Is the molecule polar? What about chain length?
- Can it H-bond with water? Can water H-bond to it?