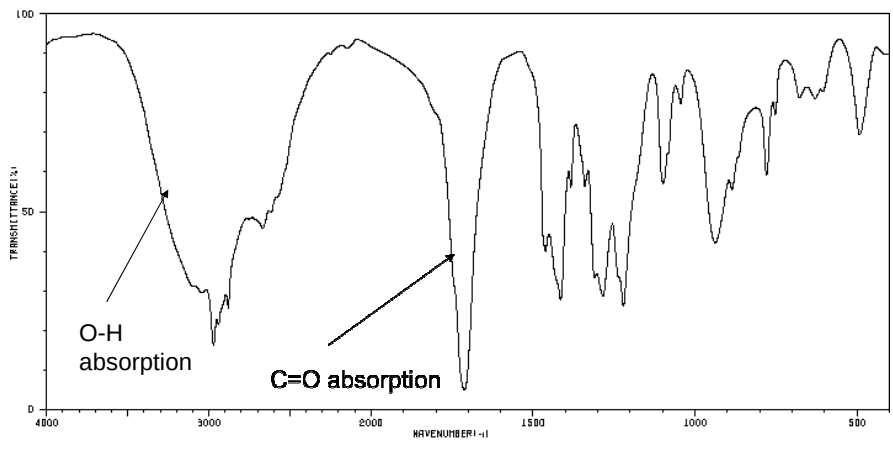
Carboxylic Acids and Esters

N Goalby
Chemrevise.org

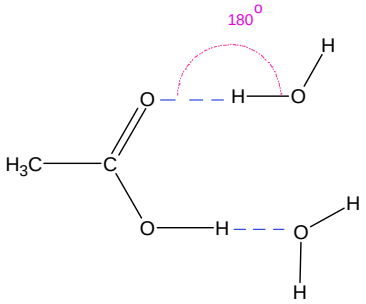


Butanoic acid

IR Spectrum for
Carboxylic acids

Solubility in Water

- The smaller carboxylic (up to C4) acids dissolve in water in all proportions but after this the solubility rapidly reduces. They dissolve because they can hydrogen bond to the water molecules.

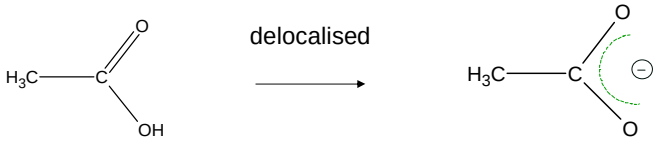


Acidity

The carboxylic acid are only weak acids in water and only partially dissociate, but they are strong enough to displace carbon dioxide from carbonates.

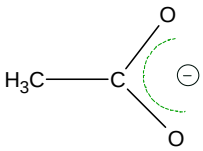
$$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$$

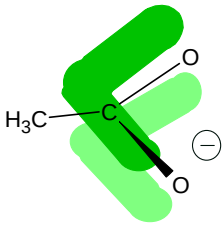
The carboxylic acid salts are stabilised by delocalisation, which makes the dissociation more likely.



Delocalisation

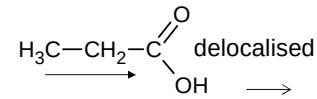
- The delocalised ion has equal C-O bond lengths. If delocalisation did not occur, the C=O bond would be shorter than the C-O bond.



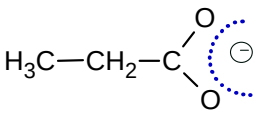


The pi charge cloud has delocalised and spread out. The delocalisation makes the ion more stable and therefore more likely to form. This means it is a stronger acid than phenol.

Strength of Carboxylic acids

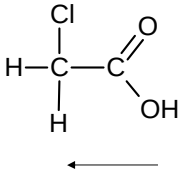


Alkyl groups electron releasing

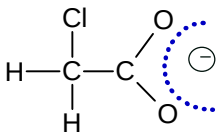


Increasing chain length pushes electron density on to the COO^- ion, making it more negative and less stable. This make the acid less strong.

Propanoic acid less acidic than ethanoic acid



delocalised



Chlorine electron withdrawing

Electronegative chlorine atoms withdraw electron density from the COO^- ion, making it less negative and more stable. This make the acid more strong.

chloroethanoic acid more acidic than ethanoic acid

Examples of salt formation reactions

carboxylic acids can form salts with sodium , sodium hydroxide and sodium carbonate.

acid + metal (Na) → salt + hydrogen

$CH_3CO_2H + Na \rightarrow CH_3CO_2^-Na^+ + H_2$

acid + alkali (NaOH) → salt + water

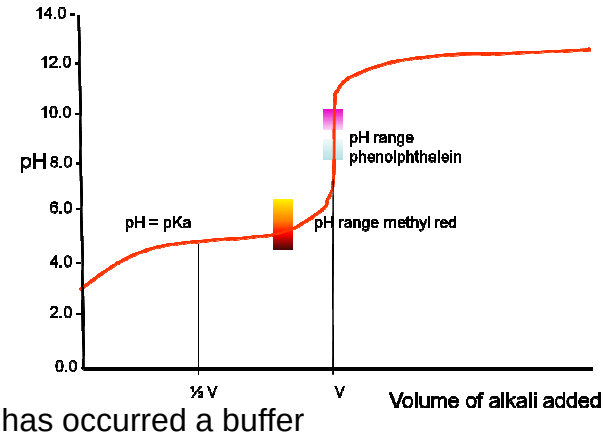
$CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-Na^+ + H_2O$

acid + carbonate (Na_2CO_3) → salt + water + CO_2

$2CH_3CO_2H + Na_2CO_3 \rightarrow 2CH_3CO_2^-Na^+ + H_2O + CO_2$

Reaction with sodium hydroxide

Carboxylic acids neutralise sodium hydroxide. The pH stays steady when small amounts of NaOH are added then rapidly jumps as neutralisation occurs



Before neutralisation has occurred a buffer solution is present as there is a mixture of a weak acid and its salt present:

ethanoic acid + NaOH → sodium ethanoate + water

PH of ethanoate ion

- Sodium ethanoate solution is slightly alkaline so OH^- ions must be present.

Explanation:

Water dissociates into H^+ and OH^- ions.

$$H_2O \rightarrow H^+ + OH^-$$

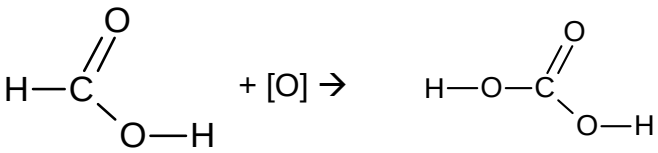
The ethanoate ions can accept H^+ ions and form ethanoic acid, leaving an imbalance in H^+ and OH^- (extra OH^-).

$$CH_3CO_2^- + H^+ \rightarrow CH_3CO_2H$$

extra

Oxidation of methanoic acid

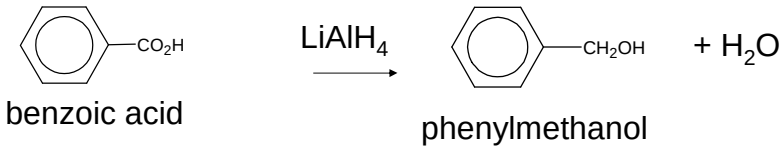
Carboxylic acids cannot be oxidised by using oxidising agents but methanoic acid is an exception as its structure has effectively an aldehyde group



It forms carbonic acid (H_2CO_3)
which can decompose to give CO_2

Reduction of carboxylic acid

Carboxylic acids can be reduced to alcohols by $LiAlH_4$, lithium tetrahydridoaluminate.



benzoic acid

phenylmethanol

The $LiAlH_4$ acts as a nucleophile since H- ions are present.
$LiAlH_4$ can also be used to reduce carbonyls to alcohols

$NaBH_4$ is not strong enough a reducing agent to reduce carboxylic acids but can reduce carbonyls to alcohols.

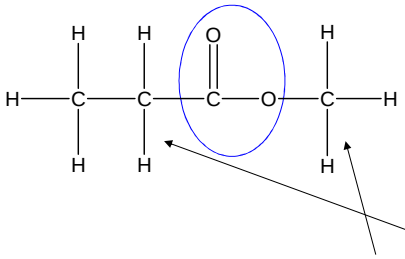
It is not possible to partially reduce a carboxylic acid to a carbonyl.

extra

Esterification

Carboxylic acids react with alcohols to form esters and water.

An Ester



Esters have two parts to their names, eg methyl propanoate.

The bit ending in –yl comes from the alcohol that has formed it and is next to the single bonded oxygen.

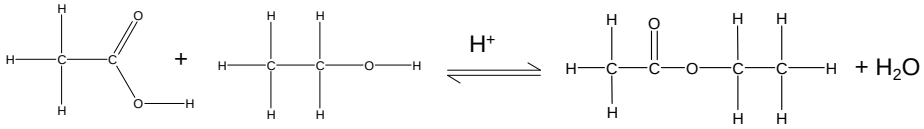
The bit ending in –anoate comes from the carboxylic acid.

key

Ester formation

Carboxylic Acid + Alcohol $\overset{H^+}{\rightleftharpoons}$ Ester + water

The reaction is reversible. The reaction is quite slow and needs heating under reflux, (often for several hours or days). Low yields (50% ish) are achieved. An acid catalyst (H_2SO_4) is needed.



CH_3CO_2H + CH_3CH_2OH $\rightleftharpoons$ $CH_3CO_2CH_2CH_3$ + H_2O

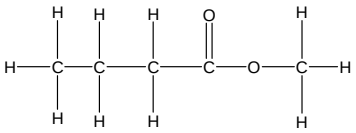
Ethanoic acid Ethanol Ethyl Ethanoate

key

Draw and name the esters formed from the reacting the following alcohols and carboxylic acids

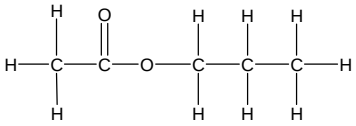
1. Methanol + Butanoic acid

Methyl Butanoate



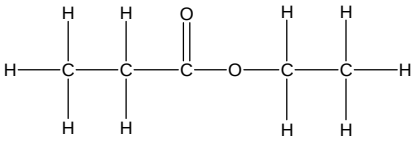
2. Propan-1-ol + Ethanoic acid

Propyl Ethanoate

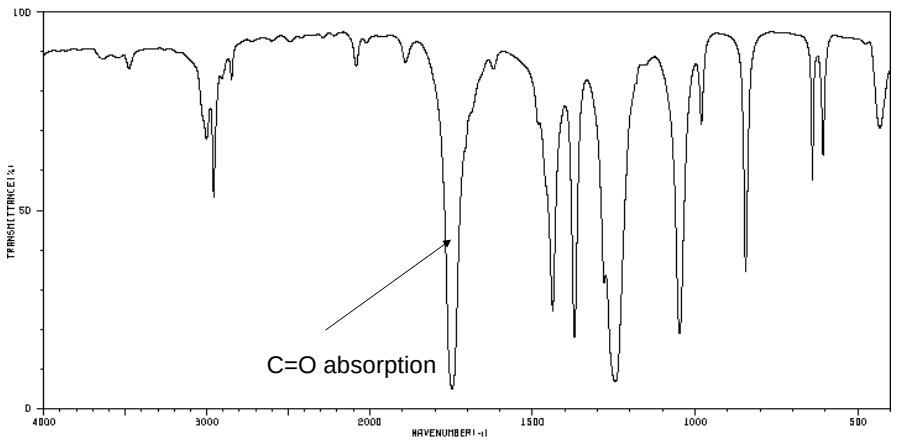


3. Ethanol + Propanoic acid

Ethyl Propanoate



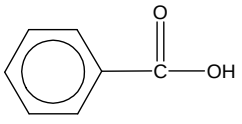
IR Spectrum for an Ester



Mechanism for Esterification

There are two possibilities for the mechanism. Does the single bonded oxygen come from the alcohol or the carboxylic acid?

Experiments were done where a radioactive isotope of oxygen O^{18} was inserted in an alcohol that was used to make an ester.

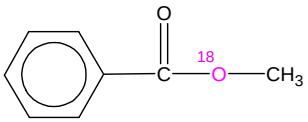


+ $CH_3{}^{18}OH$

There are two possible results and esters

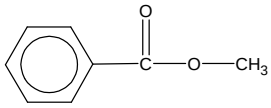
extra

Result 1



+ H_2O

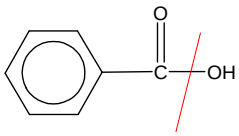
Result 2

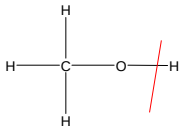


+ $H_2{}^{18}O$

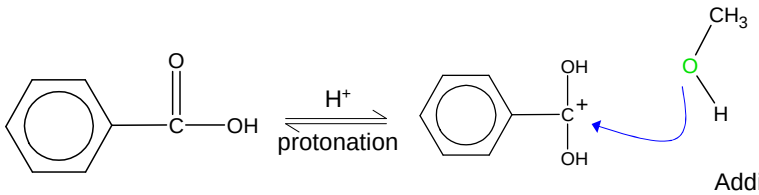
A mass spectrometer showed that the oxygen was found in the ester and not in the water. Result 1 occurs

These bonds must therefore be broken.





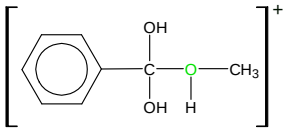
extra



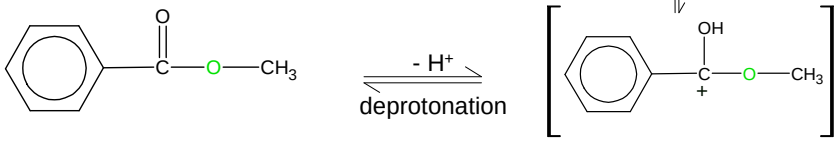
Addition of Alcohol

Mechanism:

Addition - Elimination



$-H_2O$ elimination



extra

Uses of Esters: Solvents

- Although polar, they do not form hydrogen bonds (reason: there is no hydrogen bonded to a highly electronegative atom)
  - thus, much lower b.p. than the hydrogen-bonded carboxylic acids they came from. They are also almost insoluble in water

They will act as solvents, however, for other polar organic substances

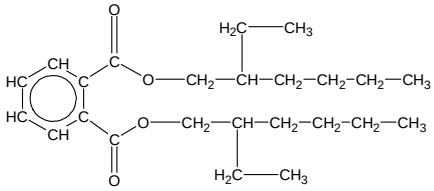
e.g. Ethyl ethanoate is used as a solvent in glues and printing inks

key

Uses of Esters: Plasticisers

- Often pure polymers have limited flexibility because the polymer chains cannot move over each other.
- Incorporating some plasticiser into the polymer allows the chains to move more easily and the polymer can become more flexible.

To make PVC ‘mock leather’ material up to 50% by weight plasticiser must be added.



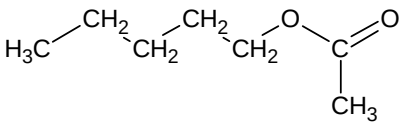
A common ester plasticiser

The plasticiser may evaporate over time making the plastic more brittle as it ages.

key

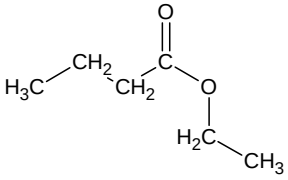
Uses of Esters: food flavourings

Esters are sweet smelling compounds that can be used in perfumes and flavourings.



Pentylethanoate – banana smell

For use in perfumes they need to be non toxic, soluble in solvent such as ethanol, volatile (turns into gas easily), and not react with water.



Ethylbutanoate – pineapple smell

key

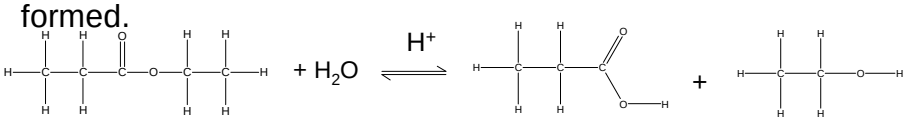
Hydrolysis of esters

key

Esters can be hydrolysed and split up by either heating with acid or with sodium hydroxide.

i) with acid
reagents: dilute acid (HCl)
conditions: heat under reflux

This reaction is the reverse reaction of ester formation. When an ester is hydrolysed a carboxylic acid and an alcohol are formed.



$CH_3CH_2CO_2CH_2CH_3 + H_2O \rightleftharpoons CH_3CH_2CO_2H + CH_3CH_2OH$

ethyl propanoate

This reaction is reversible and does not give a good yield of the products.

ii) with sodium hydroxide
reagents: dilute sodium hydroxide
conditions: heat under reflux

$CH_3CH_2CO_2CH_3 + NaOH \rightarrow CH_3CH_2CO_2^- Na^+ + CH_3OH$

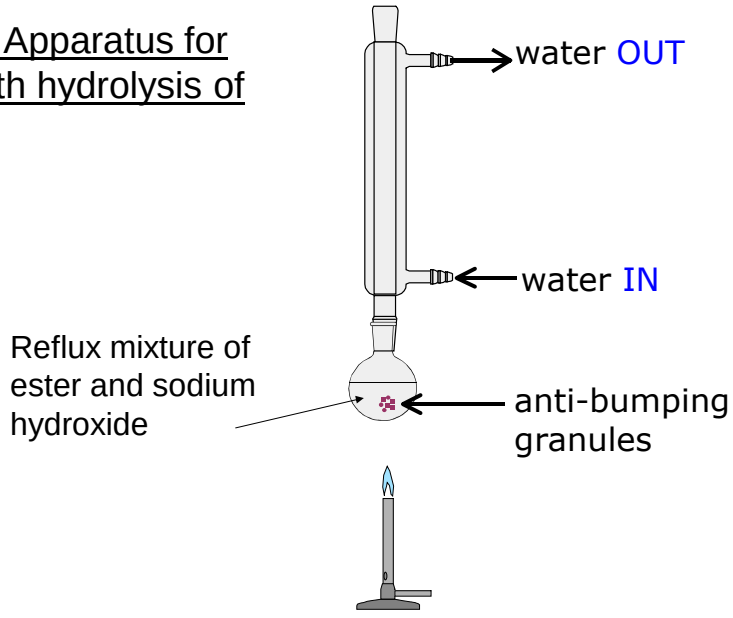
methyl propanoate sodium propanoate methanol

The carboxylic acid salt product is the anion of the carboxylic acid.
The anion is resistant to attack by weak nucleophiles such as alcohols, so the reaction is not reversible.

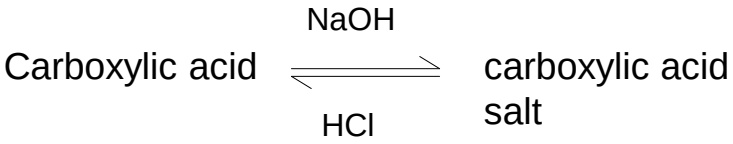
This reaction goes to completion.

key

Reflux Apparatus for use with hydrolysis of esters



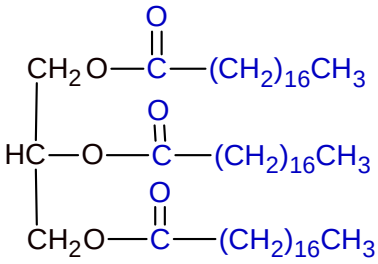
Converting between carboxylic acids and their salts.



After an ester is hydrolysed by reacting with sodium hydroxide, the carboxylic acid salt can be turned into the carboxylic acid by adding hydrochloric acid.

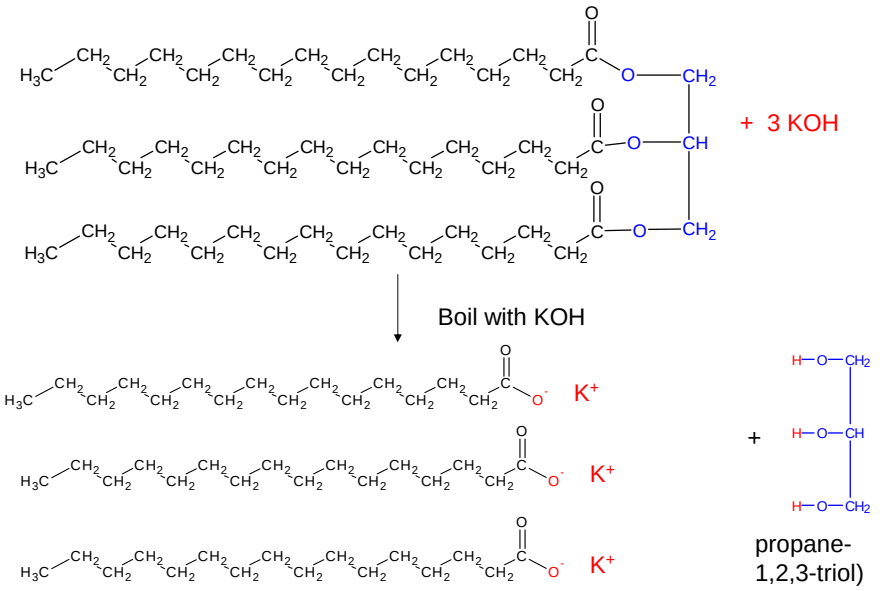
Fats and oils

Fats and oils are ESTERS of glycerol and long chain carboxylic acids (fatty acids)

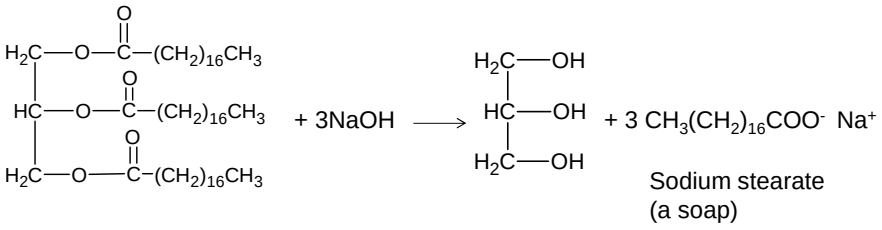


The molecular formula shown above suggests that the fat molecule is shaped like an E, but the molecule is actually shaped more like this:

Hydrolysis of fats



Hydrolysing fats to make Soap

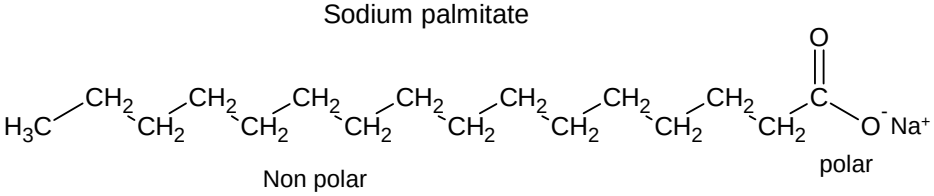


Both the soap and glycerol are useful products

Glycerol form hydrogen bonds very easily. It is used in cosmetics, food and in glues

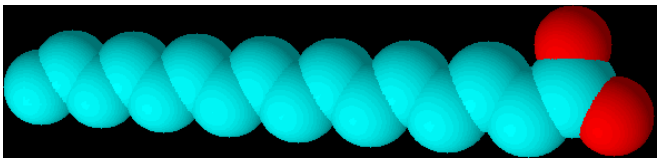
Soap Molecule

Sodium palmitate



Non polar

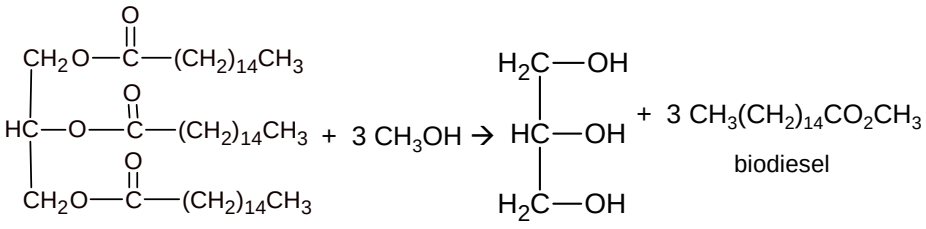
polar



Biodiesel

biodiesel is a mixture of methyl esters of long chain carboxylic acids

Vegetable oils can be converted into biodiesel by reaction with methanol in the presence of a (strong alkali) catalyst



biodiesel