6.1.3 Carboxylic Acids and Esters

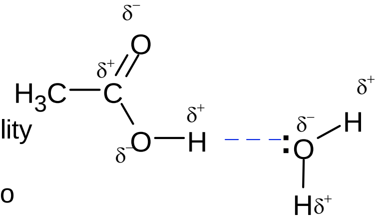
Acidity

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

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

Solubility in Water

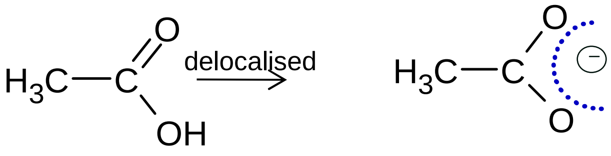
The smaller carboxylic (up to C4) acids dissolve in water in all proportions but after this the solubility rapidly reduces. They dissolve because they can hydrogen bond to the water molecules.



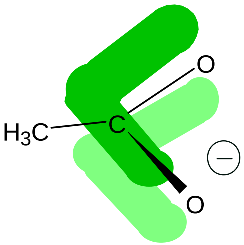
Delocalisation

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

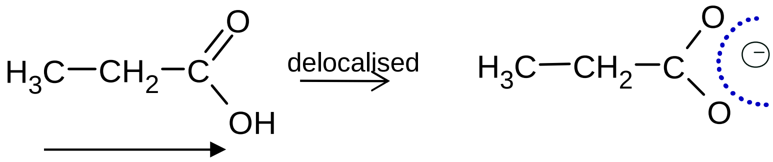
The delocalised ion has equal C-O bond lengths. If delocalisation did not occur, the C=O bond would be shorter than the C-O bond.



The pi charge cloud has delocalised and spread out. The delocalisation makes the ion more stable and therefore more likely to form.



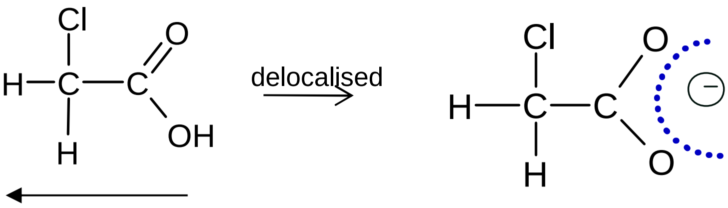
Strength of carboxylic acids



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



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

Salt formation reactions of carboxylic acids

Carboxylic acids can form salts with metals, alkalis and carbonates.

acid + metal (Na) → salt + hydrogen

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

acid + alkali (NaOH) → salt + water

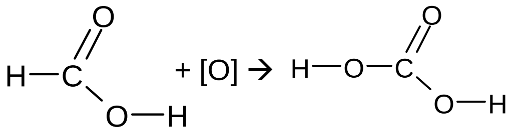
$$CH_3CO_2H + NaOH \rightarrow CH_3CO_2^-Na^+ + H_2O$$

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

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

The effervescence caused by production of CO_2 with carboxylic acids with solid Na_2CO_3 or aqueous $NaHCO_3$ can be used as a functional group test for carboxylic acids

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

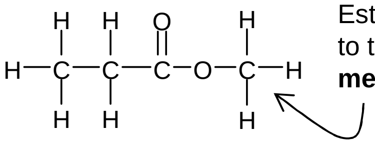


It forms carbonic acid (H_2CO_3) which can decompose to give CO_2

Esterification

Carboxylic acids react with alcohols, in the presence of a strong sulfuric acid catalyst, to form esters and water.

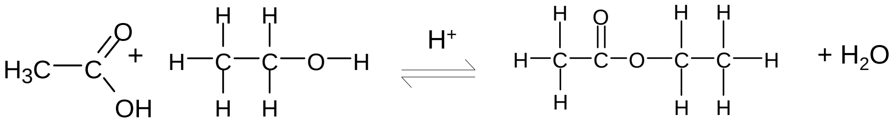
$$\text{Carboxylic Acid + Alcohol} \overset{H^+}{\rightleftharpoons} \text{Ester + water}$$



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

The bit ending in **–anoate** comes from the carboxylic acid and includes the C in the C=O bond.

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



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

Ethanoic acid Ethanol Ethyl Ethanoate

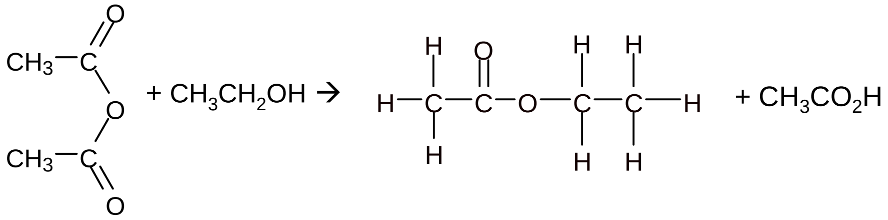
The reaction is reversible. The reaction is quite slow and needs heating under reflux, (often for several hours or days). Low yields (50% ish) are achieved. An acid catalyst (H_2SO_4) is needed.

Esterification using acid anhydrides

Change in functional group**: acid anhydride → ester**
Reagent: **alcohol**
Conditions: **room temp.**

The acid anhydrides are more reactive than carboxylic acids. The reaction is not reversible and a higher yield is achieved.

$$(RCO)_2O + CH_3CH_2OH \rightarrow RCO_2CH_2CH_3 + RCO_2H$$



Hydrolysis of esters

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.

$$CH_3CH_2CO_2CH_2CH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3CH_2CO_2H + CH_3CH_2OH$$

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

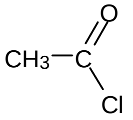
$$CH_3CH_2CO_2CH_3 + NaOH \rightarrow CH_3CH_2CO_2^- Na^+ + CH_3OH$$

methyl propanoate sodium propanoate methanol

This reaction goes to completion.

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.

Acyl Chlorides



ethanoyl chloride

Acyl chlorides are much more reactive than carboxylic acids

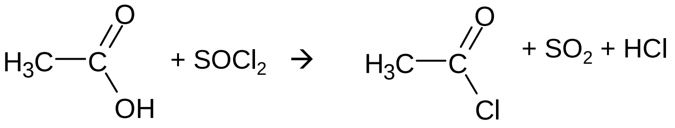
The Cl group is classed as a good leaving groups (to do with less effective delocalisation.) This makes acyl chlorides much more reactive than carboxylic acids and esters.

Formation of acyl chloride from a carboxylic acid

Reaction: carboxylic acid → acyl chloride
Reagent: $SOCl_2$
Conditions: room temp

Sulfur dichloride oxide (thionyl chloride) $SOCl_2$ is a liquid

$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$



Reactions of acyl chlorides

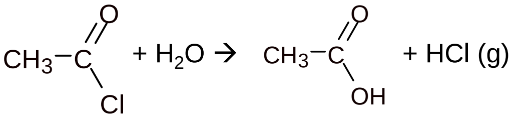
Reaction with water

Change in functional group**: acyl chloride → carboxylic acid**

Reagent: **water**

Conditions: **room temp.**

$RCOCl\ (l) + H_2O \rightarrow RCO_2H + HCl\ (g)$



Observation: Steamy white fumes of HCl are given off

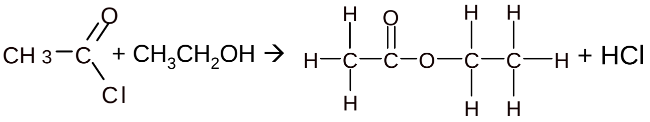
Reaction with alcohol

Change in functional group**: acyl chloride → ester**

Reagent: **alcohol**

Conditions: **room temp.**

$RCOCl\ (l) + CH_3CH_2OH \rightarrow RCO_2CH_2CH_3 + HCl\ (g)$



Observation: Steamy white fumes of HCl are given off

This reaction for making esters is much better than using carboxylic acids as the reaction is much quicker and it is not a reversible reaction

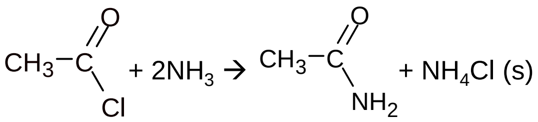
Reaction with ammonia

Change in functional group**: acyl chloride → primary amide**

Reagent: **ammonia**

Conditions: **room temp.**

$RCOCl\ (l) + 2NH_3 \rightarrow RCONH_2 + NH_4Cl\ (s)$



Observation: white smoke of NH_4Cl is given off

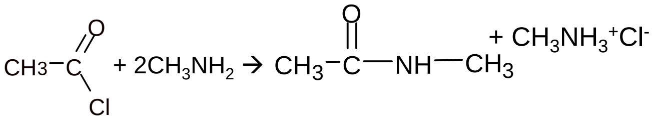
Reaction with primary amines

Change in functional group**: acyl chloride → secondary amide**

Reagent: **primary amine**

Conditions: **room temp.**

$RCOCl + 2CH_3NH_2 \rightarrow RCONHCH_3 + CH_3NH_3^+Cl^-$



N-methylethanamide

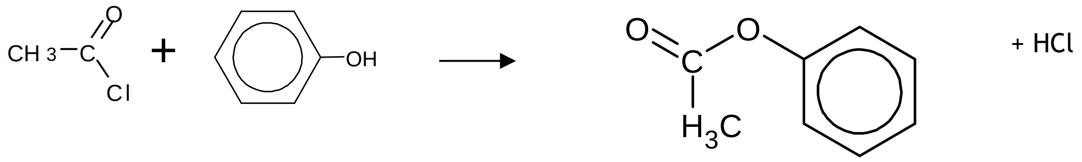
Reaction with phenol

Change in functional group**: acyl chloride → ester**

Reagent: **phenol**

Conditions: **room temp.**

$RCOCl\ (l) + C_6H_5OH \rightarrow RCO_2C_6H_5 + HCl\ (g)$



Observation: Steamy white fumes of HCl are given off

Phenols do not easily form esters with carboxylic acids but do so readily with acyl chlorides