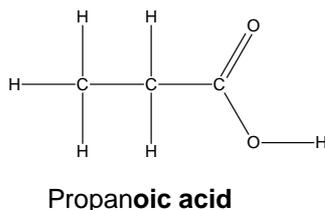


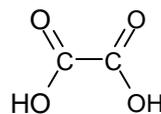
19 Carboxylic Acids and Derivatives

Naming Carboxylic acids

These have the ending **-oic acid** but no number is necessary for the acid group as it must always be at the end of the chain. The numbering always starts from the carboxylic acid end



If there are carboxylic acid groups on both ends of the chain then it is called a -dioic acid



Ethanedioic acid

Note the **e** in this name

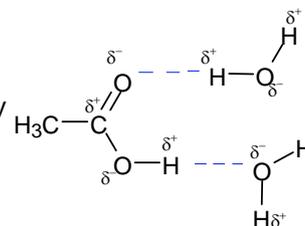
Acidity

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



Solubility in Water

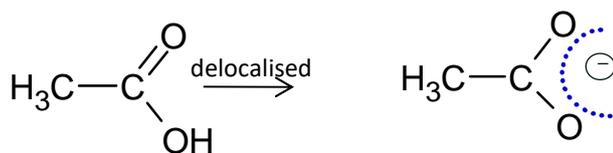
The smaller carboxylic (up to C4) acids dissolve in water in all proportions but after this the solubility rapidly reduces. They dissolve because they can hydrogen bond to the water molecules.



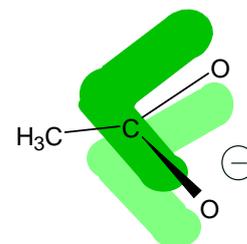
Delocalisation

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

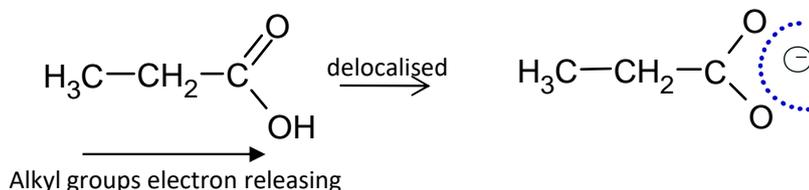
The delocalised ion has equal C-O bond lengths. If delocalisation did not occur, the C=O bond would be shorter than the C-O bond.



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

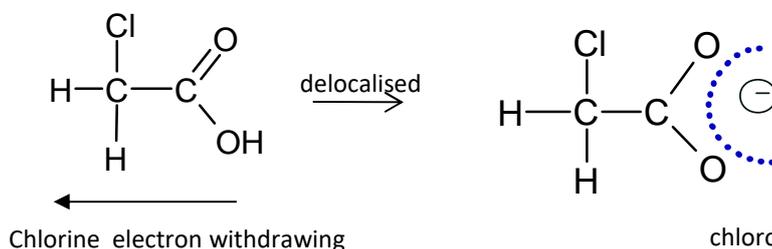


Strength of carboxylic acids



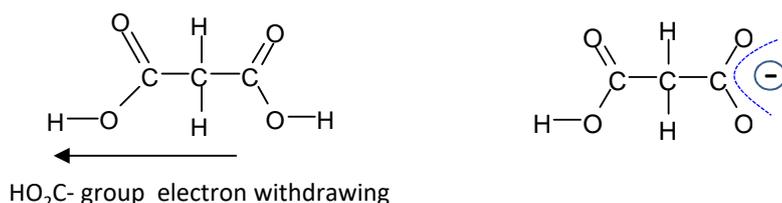
Increasing chain length pushes electron density on to the COO^- ion, making it more negative and less stable. This makes the acid less strong.

Propanoic acid less acidic than ethanoic acid



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

chloroethanoic acid more acidic than ethanoic acid



In a dibasic acid the second HO_2C - group withdraws electron density from the COO^- ion, making it less negative and more stable and weakens the O-H bond. This makes the acid more strong.

Methods of preparing carboxylic acids

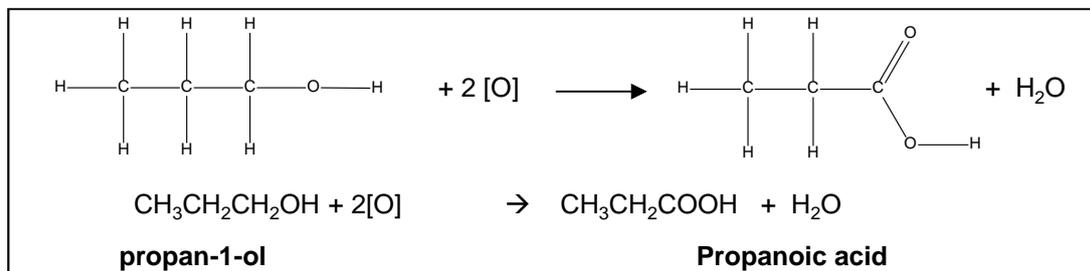
Full Oxidation of Primary Alcohols

Reaction: primary alcohol \rightarrow carboxylic acid

Reagent: potassium dichromate(VI) solution and dilute sulphuric acid

Conditions: use an excess of dichromate, and **heat under reflux**: (distill off product after the reaction has finished)

Observation: the orange dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) reduces to the green Cr^{3+} ion

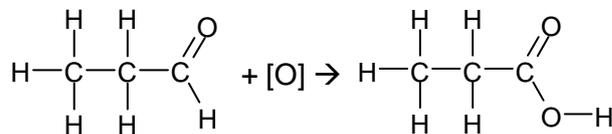


Oxidation of Aldehydes

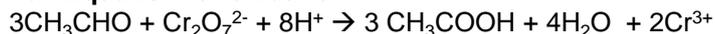
Reaction: aldehyde \rightarrow carboxylic acid

Reagent: potassium dichromate (VI) solution and dilute sulphuric acid.

Conditions: heat under reflux



Full Equation for oxidation

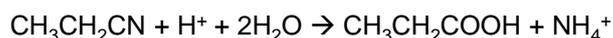


Hydrolysis of Nitriles

Reaction: Nitrile \rightarrow carboxylic acid

Reagent: dilute hydrochloric/ sulphuric acid.

Conditions: heat under reflux

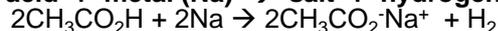


The Reactions of Carboxylic Acids

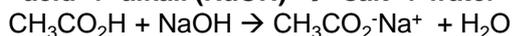
Salt formation reactions of carboxylic acids

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

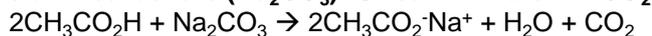
acid + metal (Na) \rightarrow salt + hydrogen



acid + alkali (NaOH) \rightarrow salt + water



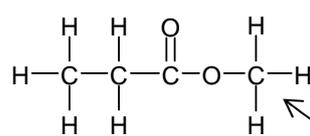
acid + carbonate (Na_2CO_3) \rightarrow salt + water + CO_2



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

Esterification

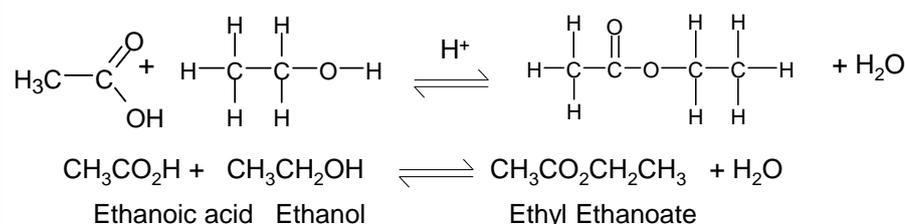
Carboxylic acids react with alcohols, in the presence of a strong acid catalyst, to form esters and water.



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.



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.

Reduction of carboxylic acids to alcohols

Lithium tetrahydridoaluminate (LiAlH_4) is a strong reducing agent

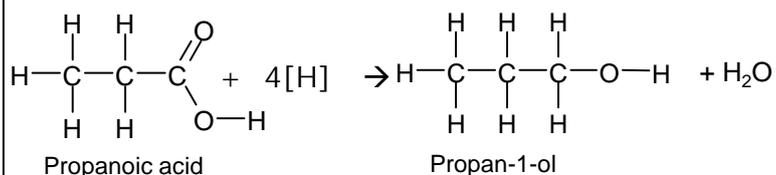
Reagents: LiAlH_4 In dry ether

Conditions: Room temperature and pressure

Type of reaction: Reduction

Role of reagent: Reducing agent

Carboxylic acids will be reduced to primary alcohols



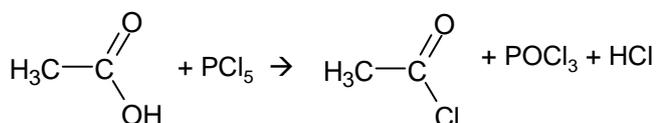
Reaction of carboxylic acid with phosphorous (V) chloride

Reaction: carboxylic acid \rightarrow acyl chloride

Reagent: PCl_5 phosphorous(v)chloride

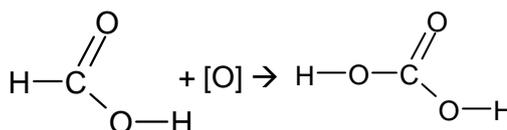
Conditions: room temp

This reaction with PCl_5 (phosphorous(v)chloride) can be used as a test for carboxylic acids. You would observe misty fumes of HCl produced.



Oxidation of methanoic acid

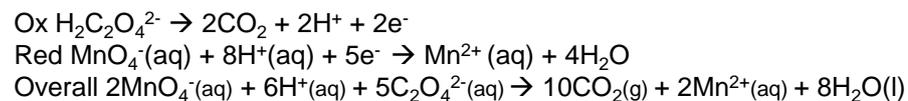
Carboxylic acids cannot be oxidised by using oxidising agents but methanoic acid is an exception as its structure has effectively an aldehyde group. It can be oxidised by Fehling's solution and Tollen's Reagent



It forms carbonic acid (H_2CO_3) which decomposes to give $\text{CO}_2 + \text{H}_2\text{O}$

Oxidation of ethanedioic acid

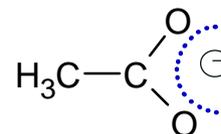
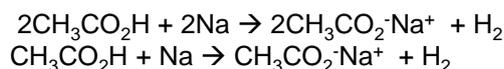
Ethanedioic acid can be oxidised by potassium manganate (VII). The ethanedioic acid is oxidised to carbon dioxide gas. This reaction can be done as a quantitative titration.



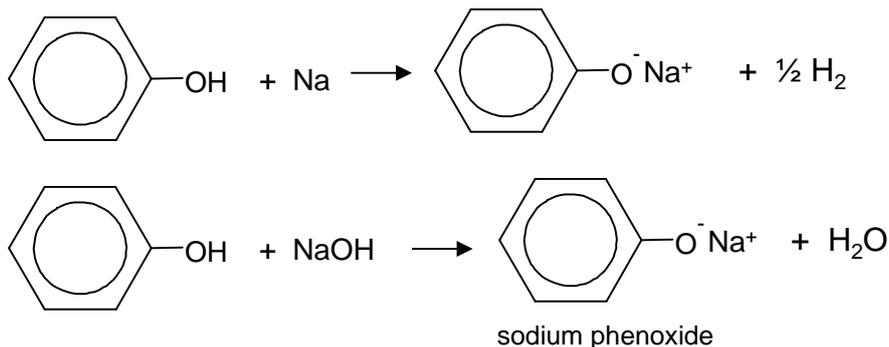
The reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ is slow to begin with (as the reaction is between two negative ions). To do as a titration the conical flask can be heated to 60°C to speed up the initial reaction.

Relative acidities of carboxylic acids, phenols and alcohols

Carboxylic acids are acidic enough to react with sodium, sodium hydroxide, and sodium carbonate. As mentioned earlier the carboxylic acid salts are stabilised by delocalisation, which makes the formation of the salts more likely. Delocalisation spreads out the negative charge which makes it more stable

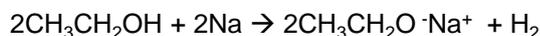


Phenols are very weakly acidic. They are weaker acids than carboxylic acids. Phenols will react with sodium metal and sodium hydroxide, but are not strong enough an acid to react with sodium carbonate. In phenol the lone pair of electrons on the oxygen is delocalised with the electron charge cloud of the arene ring. The delocalised bonding stabilises the formation of the phenoxide ion. The delocalisation is less effective than that in a carboxylate ion



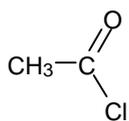
Alcohols have almost no acidity. They do not react with sodium hydroxide or sodium carbonate. They can react with sodium metal.

There is no delocalisation within an alcohol so the formation of a stable ethoxide ion from ethanol is not possible except with the reaction with sodium. The negative charge stays on the oxygen atom which makes it very unstable



Carboxylic acid derivatives: Acyl Chlorides

Acyl Chlorides



ethanoyl chloride

Acyl chlorides are much more reactive than carboxylic acids

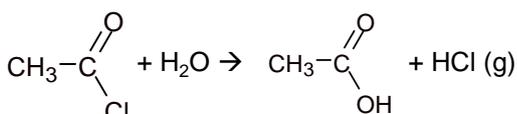
The Cl groups are classed as good leaving groups (to do with less effective delocalisation.) This makes acyl chlorides more reactive than carboxylic acids and esters

Reaction with water

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

Reagent: **water**

Conditions: **room temp.**



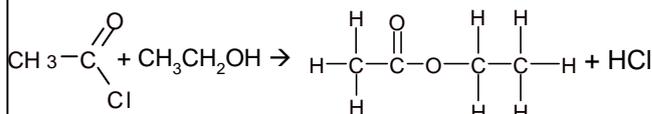
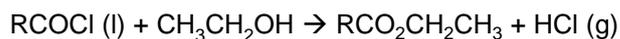
Observation: Steamy white fumes of HCl are given off

Reaction with alcohol

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

Reagent: **alcohol**

Conditions: **room temp.**



Observation: Steamy white fumes of HCl are given off

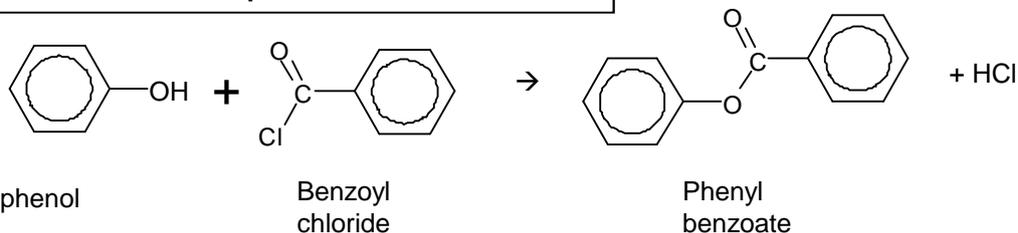
This reaction for making esters is much better than using carboxylic acids as the reaction is much quicker and it is not a reversible reaction

Reaction with phenol

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

Reagent: phenols

Conditions: **room temp.**

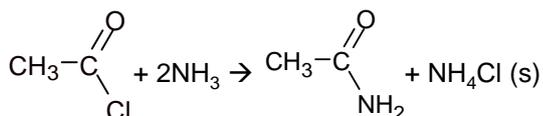


Reaction with ammonia

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

Reagent: **ammonia**

Conditions: **room temp.**



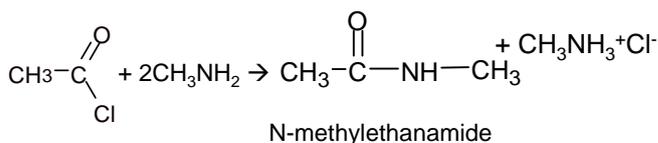
Observation: white smoke of NH_4Cl is given off

Reaction with primary amines

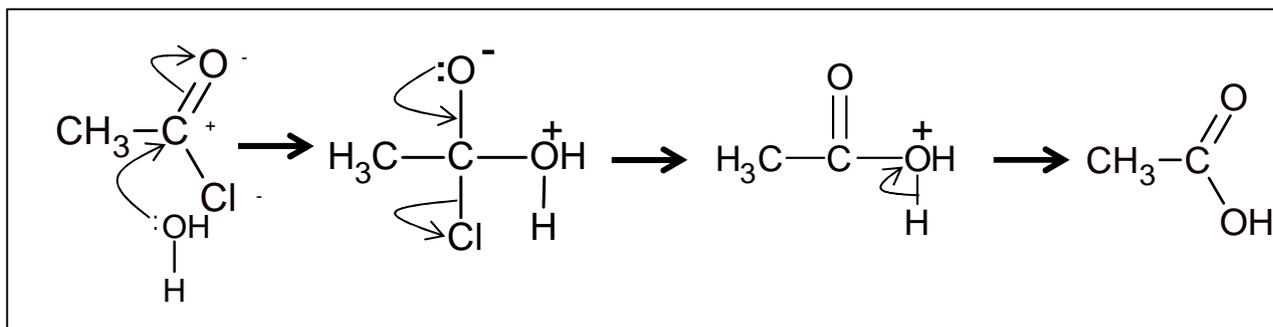
Change in functional group: **acyl chloride** → **secondary amide**

Reagent: **primary amine**

Conditions: **room temp.**

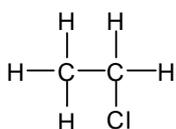


Nucleophilic Addition Elimination Mechanism

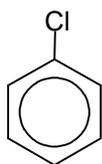


Relative ease of hydrolysis

Acyl chlorides hydrolyse at room temperature with both water and sodium hydroxide. The carbon in the acyl chloride is particularly electron deficient as it is attached to two electronegative atoms (O and Cl) so it is attractive to nucleophiles such as water. Also the C-Cl bond is weakest in the acyl chloride



Alkyl halogenoalkanes will undergo nucleophilic substitution hydrolysis reactions to produce alcohols. They won't do this at room temperature though so are less reactive than acyl chlorides. The carbon attached to the Cl is positive due to the electronegativity difference but is less positive than the carbon in the acyl chloride. They will hydrolyse if heated with water or sodium hydroxide.



chlorobenzene

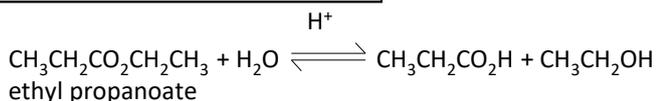
Aryl halogenoalkanes will **not** undergo nucleophilic substitution hydrolysis reactions. The delocalisation in the benzene ring will extend to include the lone pairs on the Cl. This strengthens the C-Cl bond and stops it from breaking

Hydrolysis of esters

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

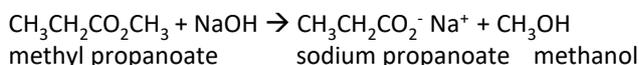
i) with acid
reagents: dilute acid (HCl)
conditions: heat under reflux

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



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



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.

Uses of Esters

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

Esters can have pleasant smells

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.

Esters can be used as **solvents** for polar organic substances
Ethyl ethanoate is used as a solvent in glues and printing inks

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