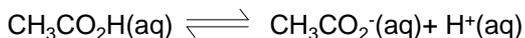


## 6.1.3 Carboxylic Acids and Esters

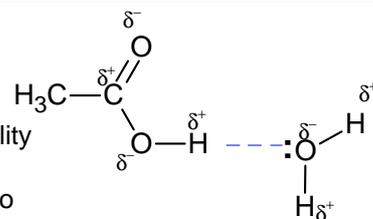
### Acidity

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

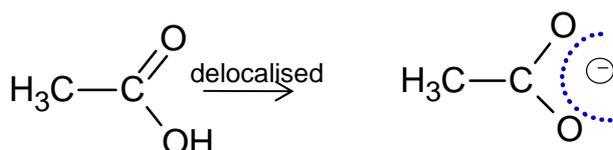
The smaller carboxylic (up to C4) acids dissolve in water in all proportions but after this the solubility rapidly reduces. They dissolve because they can hydrogen bond to the water molecules.



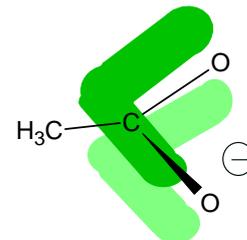
### Delocalisation

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

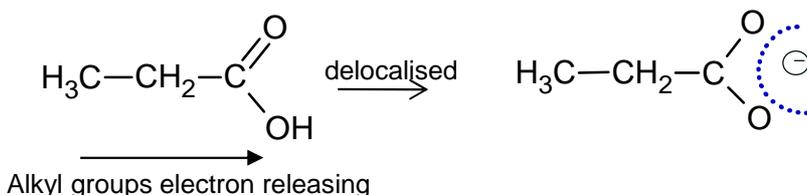
The delocalised ion has equal C-O bond lengths. If delocalisation did not occur, the C=O bond would be shorter than the C-O bond.



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

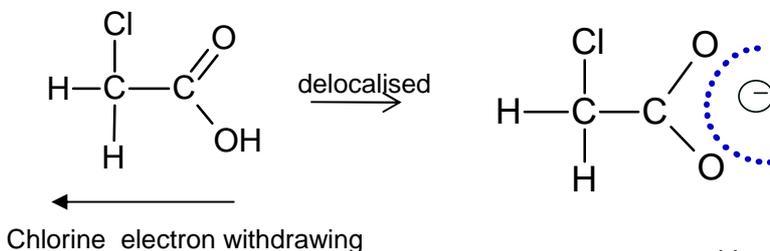


### Strength of carboxylic acids



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

Propanoic acid less acidic than ethanoic acid

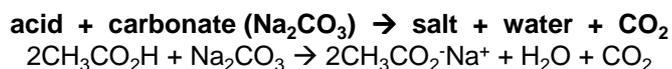
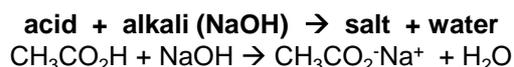
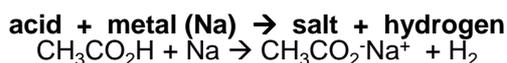


Electronegative chlorine atoms withdraw electron density from the COO<sup>-</sup> ion, making it less negative and more stable. This makes the acid more strong.

chloroethanoic acid more acidic than ethanoic acid

### Salt formation reactions of carboxylic acids

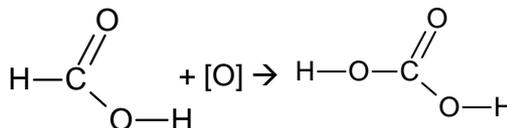
Carboxylic acids can form salts with metals, alkalis and carbonates.



The effervescence caused by production of CO<sub>2</sub> with carboxylic acids with solid Na<sub>2</sub>CO<sub>3</sub> or aqueous NaHCO<sub>3</sub> can be used as a functional group test for carboxylic acids

### Oxidation of methanoic acid

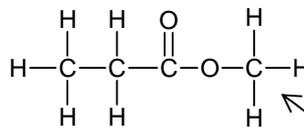
Carboxylic acids cannot be oxidised by using oxidising agents but methanoic acid is an exception as its structure has effectively an aldehyde group



It forms carbonic acid ( $\text{H}_2\text{CO}_3$ ) which can decompose to give  $\text{CO}_2$

### Esterification

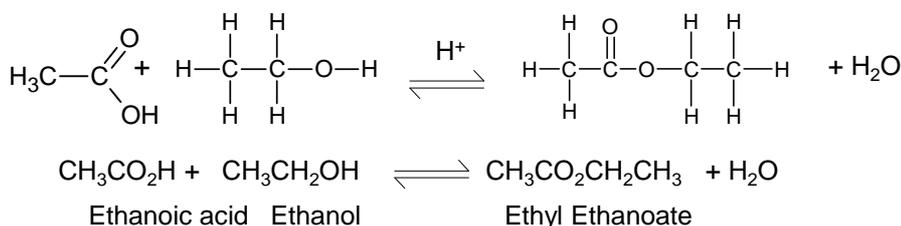
Carboxylic acids react with alcohols, in the presence of a strong sulphuric acid catalyst, to form esters and water.



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 ( $\text{H}_2\text{SO}_4$ ) is needed.

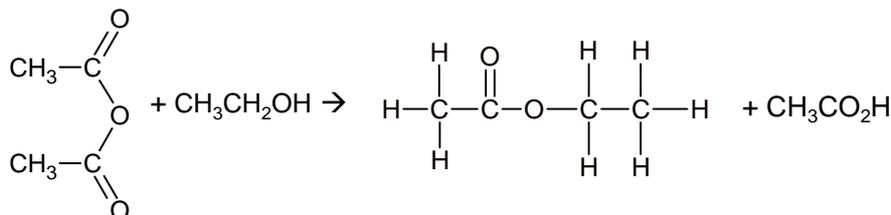
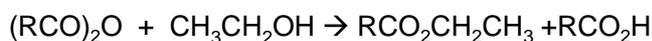
### Esterification using acid anhydrides

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.

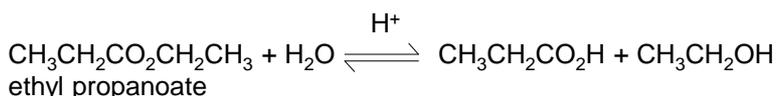


### Hydrolysis of esters

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

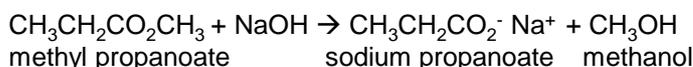
i) with acid  
reagents: dilute acid (HCl)  
conditions: heat under reflux

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.

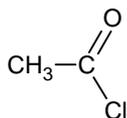
ii) with sodium hydroxide  
reagents: dilute sodium hydroxide  
conditions: heat under reflux



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.

## Acyl Chlorides



ethanoyl chloride

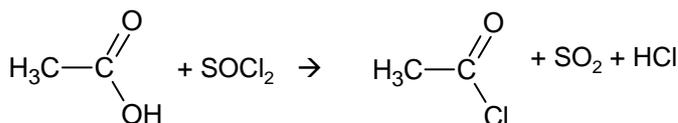
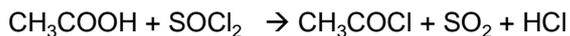
Acyl chlorides are much more reactive than carboxylic acids

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  $\rightarrow$  acyl chloride  
**Reagent:**  $\text{SOCl}_2$   
**Conditions:** room temp

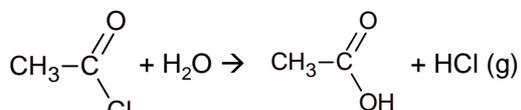
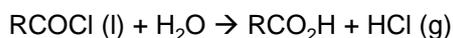
Sulphur dichloride oxide (thionyl chloride)  $\text{SOCl}_2$  is a liquid



## Reactions of acyl chlorides

### Reaction with water

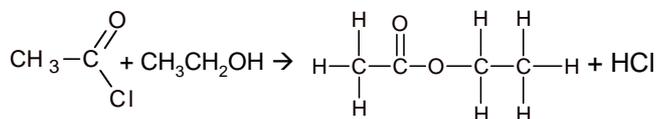
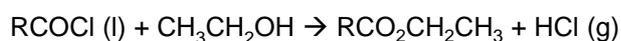
Change in functional group: **acyl chloride  $\rightarrow$  carboxylic acid**  
Reagent: **water**  
Conditions: **room temp.**



Observation: Steamy white fumes of HCl are given off

### Reaction with alcohol

Change in functional group: **acyl chloride  $\rightarrow$  ester**  
Reagent: **alcohol**  
Conditions: **room temp.**

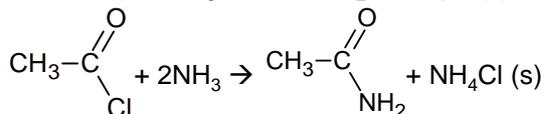


Observation: Steamy white fumes of HCl are given off

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 ammonia

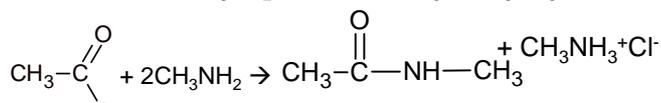
Change in functional group: **acyl chloride  $\rightarrow$  primary amide**  
Reagent: **ammonia**  
Conditions: **room temp.**



Observation: white smoke of  $\text{NH}_4\text{Cl}$  is given off

### Reaction with primary amines

Change in functional group: **acyl chloride  $\rightarrow$  secondary amide**  
Reagent: **primary amine**  
Conditions: **room temp.**



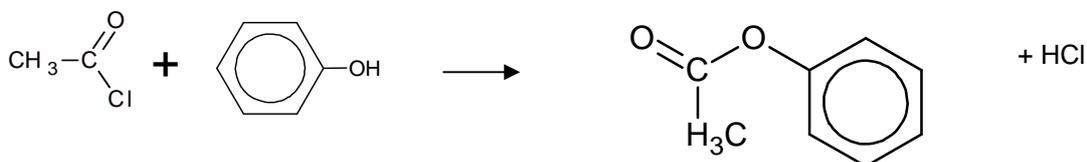
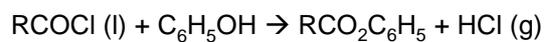
N-methylethanamide

## Reaction with phenol

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

Reagent: **phenol**

Conditions: **room temp.**



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