3.9 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.

**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.

\[
\text{CH}_3\text{CO}_2\text{H}(aq) \rightleftharpoons \text{CH}_3\text{CO}_2^-(aq) + \text{H}^+(aq)
\]

**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.

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

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

**Strength of carboxylic acids**

Propanoic acid less acidic than ethanoic acid

Chloroethanoic acid more acidic than ethanoic acid
Esterification

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

\[
\text{Carboxylic Acid + Alcohol} \xrightarrow{H^+} \text{Ester + water}
\]

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

- The bit ending in \(\text{-anoate}\) comes from the carboxylic acid and includes the C in the C=O bond.
- The bit ending in \(\text{-yl}\) comes from the alcohol that has formed it and is next to the single bonded oxygen.

Uses of Esters

- 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
- Esters can be used as plasticisers for polymers

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.

\[
\text{H-C-O-H} + [O] \rightarrow \text{H-O-C-O-H}
\]

It forms carbonic acid (\(H_2CO_3\)) which can decompose to give CO₂.

Salt formation reactions of carboxylic acids

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

- acid + metal (Na) → salt + hydrogen
  \[2CH_3CO_2H + 2Na \rightarrow 2CH_3CO_2Na^+ + H_2\]
- acid + alkali (NaOH) → salt + water
  \[CH_3CO_2H + NaOH \rightarrow CH_3CO_2Na^- + H_2O\]
- acid + carbonate (\(Na_2CO_3\)) → salt + water + CO₂
  \[2CH_3CO_2H + Na_2CO_3 \rightarrow 2CH_3CO_2Na^- + H_2O + CO_2\]

The effervescence caused by production of CO₂ with carboxylic acids with solid \(Na_2CO_3\) or aqueous \(NaHCO_3\) can be used as a functional group test for carboxylic acids.
**Fats and oils** are **esters** of glycerol and long chain carboxylic acids (fatty acids).

Vegetable oils and animal fats can be hydrolysed to give soap, glycerol and long chain carboxylic (fatty) acids.

**Soap**

Long chain carboxylic (fatty) acids, produced by the hydrolysis of fats, act as soaps. The polar CO\(_2^-\) end is hydrophilic and mixes with water. The long non-polar hydrocarbon chain is hydrophobic and mixes with grease. So this allows the grease and water to mix and be washed away.

**Biodiesel**

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

It can be argued that the biodiesel produced from this method is classed as carbon-neutral as any carbon dioxide given off when the biofuel is burnt would have been extracted from the air by photosynthesis when the plant grew.

This does not take into account any energy needed to irrigate plants, extract the oil, heat the reaction with methanol mixture or process the fuel. If the energy for this process comes from fossil fuels then the biofuel produced is not carbon neutral.

It also does not take into account the effect on land available for food production.

---

**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
  
  \[
  \text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \xrightarrow{H^+} \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}
  \]

  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 irreversible and does not give a good yield of the products.

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

  \[
  \text{CH}_3\text{CH}_2\text{CO}_2\text{CH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2^-\text{Na}^+ + \text{CH}_3\text{OH}
  \]

  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.

**Glycerol** forms hydrogen bonds very easily and is readily soluble in water. It is used in cosmetics, food and in glues.

**Biodiesel**

Biodiesel is a mixture of methyl esters of long chain carboxylic acids.

It can be argued that the biodiesel produced from this method is classed as carbon-neutral as any carbon dioxide given off when the biofuel is burnt would have been extracted from the air by photosynthesis when the plant grew.

This does not take into account any energy needed to irrigate plants, extract the oil, heat the reaction with methanol mixture or process the fuel. If the energy for this process comes from fossil fuels then the biofuel produced is not carbon neutral.

It also does not take into account the effect on land available for food production.
Carboxylic acid derivatives: Acyl Chlorides and Acid Anhydrides

**Acyl Chlorides**

Acyl chlorides are much more reactive than carboxylic acids.

The \(\text{Cl} \) and \(-\text{OCOCH}_3\) groups are classed as good leaving groups (to do with less effective delocalisation.) This makes acyl chlorides and acid anhydrides much more reactive than carboxylic acids and esters.

**Acid Anhydrides**

Acid anhydrides have a similar reactivity to acyl chlorides and therefore bring about the same changes in functional groups.

The main difference is the by-products. Acyl chlorides mostly give off HCl. Acid anhydrides give off \(\text{RCOOH}\).

**Reaction with water**

<table>
<thead>
<tr>
<th>Change in functional group: acyl chloride (\rightarrow) carboxylic acid</th>
<th>Change in functional group: acid anhydride (\rightarrow) carboxylic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent: water</td>
<td>Reagent: water</td>
</tr>
</tbody>
</table>

\[
\text{RCOCl} (\text{l}) + \text{H}_2\text{O} \rightarrow \text{RCO}_2\text{H} + \text{HCl} (\text{g})
\]

\[
\text{CH}_3\text{C} = \text{O} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{C} = \text{O} + \text{HCl} (\text{g})
\]

Observation: Steamy white fumes of HCl are given off.

**Nucleophilic Addition Elimination Mechanism**

**Reaction with alcohol**

<table>
<thead>
<tr>
<th>Change in functional group: acyl chloride (\rightarrow) ester</th>
<th>Change in functional group: acid anhydride (\rightarrow) ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reagent: alcohol</td>
<td>Reagent: alcohol</td>
</tr>
</tbody>
</table>

\[
\text{RCOCl} (\text{l}) + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{RCO}_2\text{CH}_3\text{CH}_3 + \text{HCl} (\text{g})
\]

\[
\text{CH}_3\text{C} = \text{O} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H} - \text{C} = \text{O} - \text{C} - \text{H} + \text{HCl}
\]

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.

\[
\text{CH}_3\text{C} = \text{O}^5 + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{H} - \text{C} = \text{O} - \text{C} - \text{H} + \text{HCl}
\]

Nucleophilic Addition Elimination Mechanism

N Goalby chemrevise.org
Reaction with ammonia

Change in functional group: acyl chloride → primary amide
Reagent: ammonia
Conditions: room temp.

RCOCI (l) + 2NH₃ → RCONH₂ + NH₄Cl (s)

CH₃-Cl + 2NH₃ → CH₃-C-Cl + NH₄Cl (s)

Observation: white smoke of NH₄Cl is given off

Reagent: ammonia
Conditions: room temp.

RCOCl₂ + 2NH₃ → RCONH₂ + RCO₂⁻NH₄⁺

CH₃-C-Cl + 2NH₃ → CH₃-C-Cl + CH₃CO₂⁻NH₄⁺

Reaction with primary amines

Change in functional group: acyl chloride → secondary amide
Reagent: primary amine
Conditions: room temp.

RCOCI + 2CH₃NH₂ → RCONHCH₃ + CH₃NH₂⁺Cl⁻

CH₃-Cl + 2CH₃NH₂ → CH₃-C-NH-CH₃ + CH₃NH₂⁺Cl⁻

N-methylethanamide

Reagent: primary amine
Conditions: room temp.

(RCO₂)₂O + 2CH₃NH₂ → RCONHCH₃ + RCO₂⁻CH₃NH₃⁺

CH₃-C-C-Å + 2CH₃NH₂ → CH₃-C-NH-CH₃ + CH₃CO₂⁻CH₃NH₃⁺

N-methylethananamide

Nucleophilic Addition Elimination Mechanism
**Practical: Making Aspirin**

Aspirin is made from 2-hydroxybenzoic acid which contains a phenol group. In the reaction the phenol group is turned into an ester by reacting it with the reactive ethanoic anhydride.

Ethanoic anhydride is used instead of acid chlorides because it is cheaper, less corrosive, less vulnerable to hydrolysis, and less dangerous to use.

**Purifying an organic solid: Recrystallisation**

<table>
<thead>
<tr>
<th>Step</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. <strong>Dissolve the impure compound in a minimum volume of hot</strong> (near boiling) <strong>solvent.</strong></td>
<td>An appropriate solvent is one which will dissolve both compound and impurities when hot and one in which the compound itself does not dissolve well when cold. The minimum volume is used to obtain saturated solution and to enable crystallisation on cooling.</td>
</tr>
<tr>
<td>2. <strong>Hot filter</strong> solution through (fluted) filter paper quickly.</td>
<td>This step will remove any insoluble impurities and heat will prevent crystals reforming during filtration.</td>
</tr>
<tr>
<td>3. <strong>Cool</strong> the filtered solution by inserting beaker in ice</td>
<td>Crystals will reform but soluble impurities will remain in solution form because they are present in small quantities so solution is not saturated. Ice will increase the yield of crystals.</td>
</tr>
<tr>
<td>4. <strong>Suction filtrate</strong> with a Buchner flask to separate out crystals</td>
<td>The water pump connected to the Buchner flask reduces the pressure and speeds up the filtration.</td>
</tr>
<tr>
<td>5 Wash the crystals with distilled water</td>
<td>To remove soluble impurities</td>
</tr>
<tr>
<td>6. Dry the crystals between absorbent paper</td>
<td></td>
</tr>
</tbody>
</table>

**Loss of yield in this process**
- Crystals lost when filtering or washing
- Some product stays in solution after recrystallisation
- Other side reactions occurring
Measuring melting point

One way of testing for the degree of purity is to determine the melting "point", or melting range, of the sample.

If the sample is very pure then the melting point will be a sharp one, at the same value as quoted in data books.

If impurities are present (and this can include solvent from the recrystallisation process) the melting point will be lowered and the sample will melt over a range of several degrees Celsius.

Melting point can be measured in an electronic melting point machine or by using a practical set up where the capillary tube is strapped to a thermometer immersed in some heating oil.

In both cases a small amount of the salt is put into a capillary tube. The tube is heated up and is heated slowly near the melting point.

Comparing an experimentally determined melting point value with one quoted in a data source will verify the degree of purity.

Sometimes an error may occur if the temperature on the thermometer is not the same as the temperature in the actual sample tube.