CAIE Chemistry A-level

18: Carboxylic Acids and Derivatives

Notes

Carboxylic Acids

Carboxylic acids are organic compounds with the functional group -COOH.

Formation of Carboxylic Acids

Carboxylic acids can be produced from alcohols, aldehydes and nitriles.

Formation from Alcohols and Aldehydes

Primary alcohols are oxidised to **aldehydes**. Aldehydes are further oxidised to **carboxylic acids**.

Acidified potassium dichromate(VI) is used as an oxidising agent when producing carboxylic acids from alcohols and aldehydes. During oxidation, potassium dichromate(VI) changes colour from **orange** to **green**. In the following equations, [O] denotes the oxidising agent.

Primary alcohols are **partially oxidised** to **aldehydes**:

$$RCH_2OH + [O] \rightarrow RCHO + H_2O$$

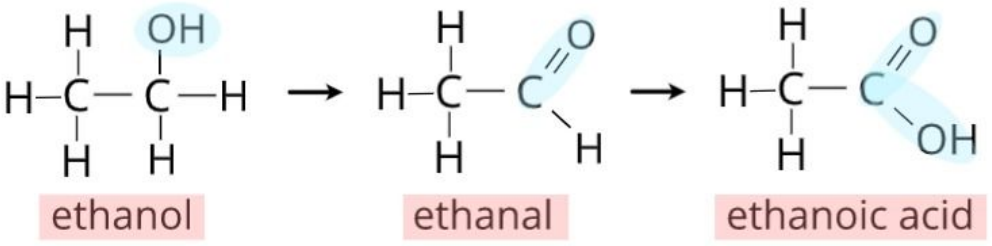
If the aldehyde undergoes **further oxidation**, **carboxylic acids** are produced:

$$RCHO + [O] \rightarrow RCOOH + H_2O$$

The full oxidation reaction can be written as:

$$RCH_2OH + 2[O] \rightarrow RCOOH + 2H_2O$$

For oxidation to occur, the alcohol or aldehyde is heated under **reflux** with acidified potassium dichromate(VI). Below is a diagram showing the oxidation process of ethanol to ethanoic acid:



Formation from Nitriles

Nitriles can undergo **hydrolysis** to form **carboxylic acids**. The C≡N nitrile bond reacts with water to produce the carboxylic acid.

- *Acid hydrolysis*
  The nitrile is heated under **reflux** with a dilute acid (such as **hydrochloric acid**). A **carboxylic acid** and a **salt** are produced.
  The reaction of propanenitrile with a dilute acid:

$$CH_3CH_2CN + 2H_2O + HCl \rightarrow CH_3CH_2COOH + NH_4Cl$$

- *Alkaline hydrolysis*
  The nitrile is heated under **reflux** with an alkali (such as **sodium hydroxide**). This produces a **carboxylic acid** and **ammonia**. The reaction takes place in two stages. First, carboxylate ions are produced (e.g. **sodium carboxylate** forms if sodium hydroxide is used). A **strong acid** must then be added to provide hydrogen ions to liberate the carboxylic acid. Hydrochloric acid is commonly used.

The formation of propanoic acid from propanenitrile:

Stage 1: $CH_3CH_2CN + NaOH + H_2O \rightarrow CH_3CH_2COONa + NH_3$

Stage 2: $CH_3CH_2COONa + HCl \rightarrow CH_3CH_2COOH + NaCl$

Reactions of Carboxylic Acids

Formation of Salts

A salt is produced when carboxylic acids react with **metals**, **alkalis** or **carbonates**.

- *Reactions with metals:*
  Carboxylic acids react with reactive metals to produce a **salt** and bubbles of **hydrogen gas**. Since carboxylic acids are **weak acids**, the reaction rates are a lot **slower** than the reactions involving strong acids like hydrochloric acid. Remember salts are ionic compounds so the charges of each ion must balance when writing equations and formulae.

  Example 1: $2CH_3COOH + 2Na \rightarrow 2CH_3COONa + H_2$

  Example 2: $2CH_3COOH + Mg \rightarrow (CH_3COO)_2Mg + H_2$
- *Reactions with alkalis:*
  When carboxylic acids react with alkalis, a simple **neutralisation** reaction takes place, since carboxylic acids are weak acids. The ionic equation is: $H^+ + OH^- \rightarrow H_2O$

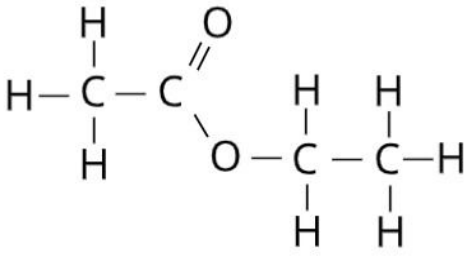
  $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

  $2HCOOH + Mg(OH)_2 \rightarrow (HCOO)_2Mg + 2H_2O$
- Reactions with carbonates:
  When carboxylic acids react with carbonates, a **salt**,**carbon dioxide** and **water** are formed.

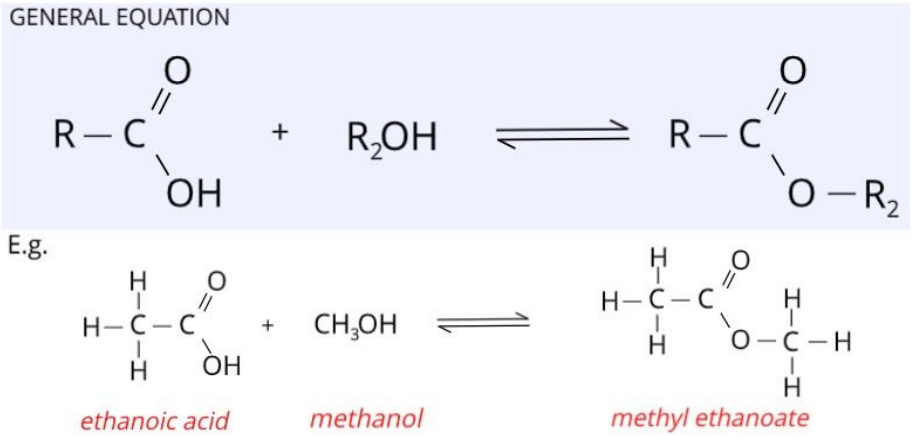
$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + CO_2 + H_2O$$

Formation of Alkyl Esters

Esters are produced when **carboxylic acids** and **alcohols** are heated in the presence of an **acid catalyst** (typically concentrated sulfuric acid). The process is known as **esterification**.



The diagram on the left shows an ester. The **left side** of the compound is derived from the **carboxylic acid** and the **right side** from the **alcohol**. This compound has been formed from ethanoic acid and ethanol and is called **ethyl ethanoate**. 'Ethyl' from the alcohol and 'ethanoate' from the carboxylic acid.



Formation of Alcohols

Carboxylic acids can be **reduced** to primary alcohols using **$LiAlH_4$**. The reduction process occurs in **two stages** because the carboxylic acid is converted into an **aldehyde** before becoming a **primary alcohol**. The symbol [H] is used in equations to represent the reducing agent. The overall equation for this reaction is:

$$RCOOH + 4[H] \rightarrow RCH_2OH + H_2O$$

Esters

Acid and Base Hydrolysis of Esters

Acid Hydrolysis

When esters react with water an **acid catalyst** is required. This reaction is **reversible** so **excess water** must be used to ensure the position of equilibrium is shifted as far towards the products as possible. This reaction can occur when the ester is mixed with dilute acid.

$$CH_3CH_2COOCH_3 + H_2O \rightleftharpoons CH_3CH_2COOH + CH_3OH$$

Alkali Hydrolysis

An ester can be hydrolysed by **heating it under reflux** with a dilute alkali (such as sodium hydroxide). These reactions are not reversible so the products are easier to separate.

$$CH_3CH_2COOCH_3 + NaOH \rightarrow CH_3CH_2COONa + CH_3OH$$

To convert the carboxylate salt product into a **carboxylic acid**, **excess strong dilute acid** can be added to the salt (after the alcohol has been removed from the products by distillation).

Commercial Uses of Esters

Esters are commonly used commercially as **solvents**, **perfumes** and **flavourings**. Many foods contain esters to artificially create the smell and taste of fruit.