CHAPTER 19: Carboxylic Acids and Derivatives I

Learning outcomes:

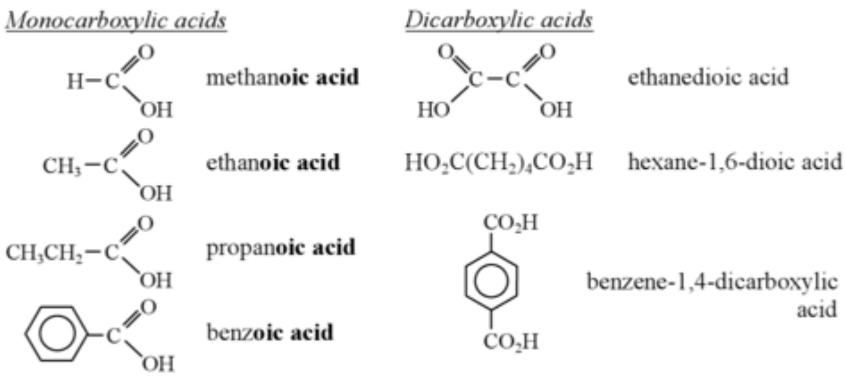
(a) describe the formation of carboxylic acids from alcohols, aldehydes and nitriles.
(b) describe the reactions of carboxylic acids in the formation of:
(i) salts, by the use of reactive metals, alkalis or carbonates.
(ii) esters.
(iii) acyl chlorides.
(c) describe the formation of esters from carboxylic acids, using ethyl ethanoate as an example.
(d) describe the acid and base hydrolysis of esters.
(e) state the major commercial uses of esters, e.g. solvents, perfumes, flavourings.

19.1 Carboxylic Acids

Introduction to carboxylic acids

1) Carboxylic acids are compounds that contain the **-COOH group**.

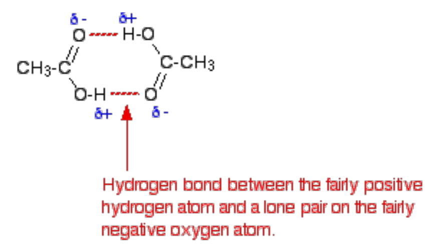
2) Examples of carboxylic acids:



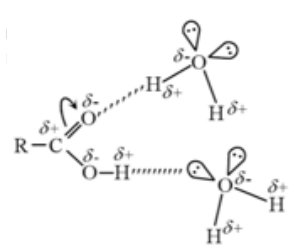
3) Salts of carboxylic acids are called carboxylate salts. The formation of carboxylate salts shows that carboxylic acids are acidic. A carboxylate salt is formed upon the removal of H^+ from -COOH group, leaving $-COO^-$.

Physical properties of carboxylic acids

1) Carboxylic acids have **higher melting and boiling points** than the corresponding alcohols.
   i. This is because in a pure carboxylic acid, **hydrogen bonding** can occur between two molecules of acid to produce a **dimer**.
   ii. This **doubles the size of the molecule**, making the van der Waals' forces stronger.
   iii. Hence more energy is required to overcome these forces of attraction.



2) **Small carboxylic acids are soluble in water**.
   i. This is because carboxylic acid is capable of forming hydrogen bond with water molecule.
   ii. However, the solubility decreases as the number of carbon atoms increases. This is because the presence of long hydrocarbon tail disrupts the effectiveness of hydrogen bonding.



Preparation of carboxylic acids

1) There are **three ways to produce carboxylic acids**:
   i. Oxidation of primary alcohol.
   ii. Oxidation of aldehyde.
   iii. Acidic/alkaline hydrolysis of nitrile.

2) For oxidation of primary alcohol and aldehyde, refer back previous chapters.

3) **Acidic hydrolysis of nitrile**:
   i. When nitrile is **heated under reflux** with a dilute acid such as dilute hydrochloric acid, **carboxylic acid will be formed**.
   ii. Using ethanenitrile as an example, ethanoic acid is formed.

$$CH_3CN + 2H_2O + H^+ \rightarrow CH_3COOH + NH_4^+$$

4) **Alkaline hydrolysis of nitrile**:
   i. When nitrile is **heated under reflux** with an alkali such as sodium hydroxide, **salt of carboxylic acid(carboxylate salt) is produced**. Using ethanenitrile as an example, ethanoate ion is formed.

$$CH_3CN + 2H_2O + OH^- \rightarrow CH_3COO^- + NH_3$$

   ii. Ethanoate ion can be converted to ethanoic acid by the **addition of acid**.

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

19.2 Reactions of Carboxylic Acids

Acidity of carboxylic acids

1) **Carboxylic acids are acidic** because they can donate a proton to form carboxylate ion and hydroxonium ion. The presence of hydroxonium ions makes the solution acidic.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

2) However, **carboxylic acids are only weak acids**. For instance ethanoic acid has a pH of about 2-3.

Reaction with bases

1) Since carboxylic acids are acids, **they will react with a base** such as sodium hydroxide **to produce a carboxylate salt and water**. This is a simple neutralisation reaction.

2) Take ethanoic acid and sodium hydroxide as an example:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

...and the ionic equation is:

$$H^+ + OH^- \rightarrow H_2O$$

Reaction with metals

1) Carboxylic acids **will react with reactive metals** such as sodium **to produce a carboxylate salt and hydrogen gas**.

2) Take ethanoic acid and sodium metal as an example:

$$2CH_3COOH + 2Na \rightarrow 2CH_3COONa + H_2$$

Reaction with carbonates and hydrogencarbonates

1) Carboxylic acids **will react with carbonates and hydrogencarbonates to produce a carboxylate salt, carbon dioxide gas and water**.

2) Take ethanoic acid and sodium carbonate as an example:

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

...and the ionic equation is:

$$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$$

3) Take ethanoic acid and sodium hydrogencarbonate as an example:

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$$

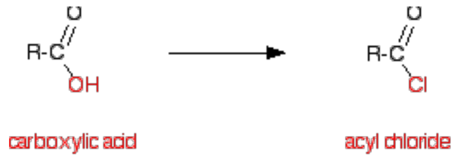
...and the ionic equation is:

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O$$

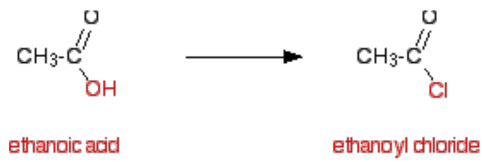
4) This is a useful **test to distinguish carboxylic acids from alcohols and phenols**. This is because alcohols and phenols are not acidic enough to react with these.

Converting carboxylic acids to acyl chlorides

1) Acyl chlorides have the -OH in the -COOH group of the carboxylic acid replaced by chlorine.



2) Take ethanoic acid as an example, ethanoyl chloride is produced.



3) Acyl chlorides are very reactive and can be used to produce a range of other organic compounds.

4) There are **three methods to produce acyl chlorides** from carboxylic acids:

i. Reaction with **phosphorus(III) chloride, PCl_3**.

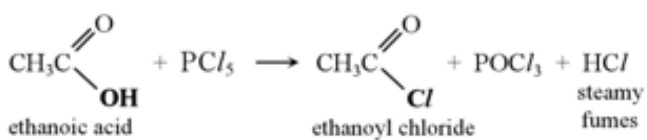
- Take ethanoic acid as an example, the equation is:

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_4$$

ii. Reaction with **phosphorus(V) chloride, PCl_5**.

- Take ethanoic acid as an example, the equation is:

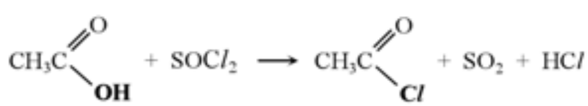
$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$



iii. Reaction with **thionyl chloride, $SOCl_2$**.

- Take ethanoic acid as an example, the equation is:

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

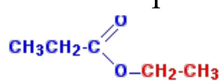


- This method is generally preferred because SO_2 and HCl are both gases, and can be separated from the mixture easily.

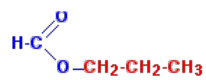
19.3 Esters

Introduction to esters

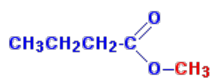
1) Esters are derivatives of carboxylic acids. In an ester, the hydrogen from the -COOH group of carboxylic acid is replaced by an alkyl group. The alkyl group came from the alcohol/phenol. Some common esters and their naming:



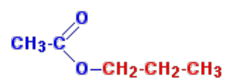
ethyl propanoate



propyl methanoate



methyl butanoate



propyl ethanoate

2) Note that the name of an ester is **'alcohol + carboxylic acid'**.

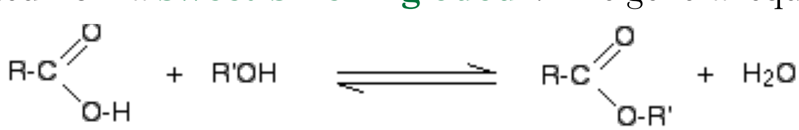
3) Physical properties of esters:
   i. Esters have **lower melting and boiling points than carboxylic acids**. This is because they are not capable of forming intermolecular hydrogen bonding.
   ii. Esters are **insoluble in water** and often identified by their **strong fruity smell**.

4) Unlike carboxylic acids, **esters are neutral**. This is because they cannot donate or accept a proton.

Preparation of esters

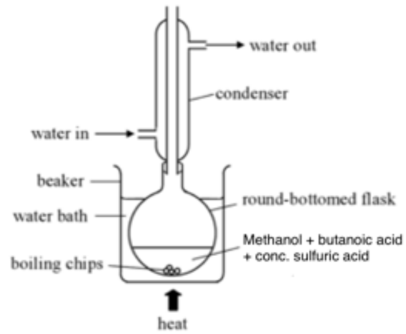
1) Esters can be prepared from the **reaction between alcohol and carboxylic acid(AS)**.

2) Between alcohol and carboxylic acid:
   i. To prepare an ester from carboxylic acid and alcohol, both them are heated under reflux in the presence of concentrated sulfuric acid as catalyst. Esters can be detected from a **sweet-smelling odour**. The general equation:



ii. For example, to make methyl butanoate, methanol and butanoic acid are used.

$$CH_3OH + CH_3CH_2CH_2COOH \rightleftharpoons CH_3CH_2CH_2COOCH_3 + H_2O$$



ii. This reaction cannot be used to produce esters when the -OH group is attached to a benzene ring, also known as phenol. In other words, **carboxylic acid cannot react with phenol to produce ester**.

Hydrolysis of esters

1) **Acidic hydrolysis of esters**:

i. When ester is **heated under reflux** with a dilute acid such as dilute hydrochloric acid, **the corresponding carboxylic acid and alcohol will be formed**.

ii. Using methyl propanoate as an example, propanoic acid and methanol is formed.

$$\underset{\text{methyl propanoate}}{CH_3CH_2COOCH_3} + H_2O \xrightleftharpoons{H^+(aq)} \underset{\text{propanoic acid}}{CH_3CH_2COOH} + \underset{\text{methanol}}{CH_3OH}$$

iii. This is just the reverse process of esterification.

2) **Alkaline hydrolysis of esters**:

i. When ester is **heated under reflux** with a base such as sodium hydroxide solution, **the corresponding carboxylate salt and alcohol will be formed**.

ii. Using methyl propanoate as example, sodium propanoate and methanol is formed.

$$\underset{\text{methyl propanoate}}{CH_3CH_2COOCH_3} + NaOH \longrightarrow \underset{\text{sodium propanoate}}{CH_3CH_2COONa} + \underset{\text{methanol}}{CH_3OH}$$

iii. The sodium propanoate can be converted to propanoic acid by adding dilute acid.

Uses of esters

1) **As solvents**:

i. Small esters such as methyl ethanoate, ethyl ethanoate and butyl ethanoate are very widely used as solvents.

2) **As perfumes and flavourings**:

i. The smell and taste of fruits such as oranges, apples, pears, raspberries, strawberries, and so on, are due to naturally occurring esters. Many foods will have those same esters added to them to simulate the smell and taste of real fruit.

ii. Flower and other smells are also produced by naturally occurring esters.

iii. Perfumes will have the same esters added. Benzyl ethanoate, for example, is used to produce jasmine or gardenia fragrances.