FACTFILE:
GCE CHEMISTRY

4.9 CARBOXYLIC ACIDS AND DERIVATIVES

Rewarding Learning

Learning Outcomes

Students should be able to:

4.9.1 recall that derivatives of carboxylic acids include esters and acyl chlorides;

4.9.2 recall the molecular and structural formulae of monoesters and of acyl chlorides

4.9.3 explain the boiling points and solubility of monoesters by making reference to intermolecular forces;

4.9.4 recall that esters can be formed from alcohols using carboxylic acids or acyl chlorides;

4.9.5 recall the laboratory preparation of a liquid ester from a carboxylic acid and an alcohol;

4.9.6 recall the structure of fats and oils as esters of propane-1,2,3-triol (glycerol) and fatty acids;

4.9.7 recall the trans-esterification reactions of esters with alcohols and carboxylic acids and the use of these reactions to produce biodiesel and margarines;

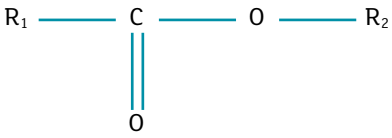
4.9.8 recall that margarines/spreads are produced from the hardening of oils by catalytic hydrogenation using finely divided nickel;

4.9.9 recall the reactions of acyl chlorides with water and alcohols;

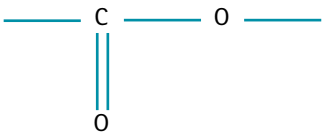
Derivatives of Carboxylic acids

Acid derivatives such as acyl chlorides and esters are compounds which are related to carboxylic acids; the OH group has been replaced by something else.

Esters are carboxylic acid derivatives and have the general structure.

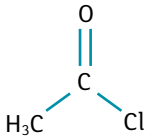


The functional group of an ester is the –COO– group which is called simply an ester group or an ester linkage.



The name of an ester is an **alkyl carboxylate**. When naming, the alcohol provides the **alkyl** part of the name and the carboxylic acid provides the **carboxylate** part of the name. For example the ester made from methanol and propanoic acid is methyl propanoate, $CH_3CH_2COOCH_3$, and the ester made from butanoic acid and ethanol is ethyl butanoate $CH_3CH_2CH_2COOCH_2CH_3$.

Acyl chlorides are carboxylic derivatives – the OH of the acid is replaced by a Cl. The structure of ethanoyl chloride is shown below.



Physical properties of esters

Esters are polar and have permanent dipole-dipole attractions and van der Waals' forces between the molecules. They do not form hydrogen bonds between their molecules so their boiling points are lower than carboxylic acids with the same number of carbon atoms.

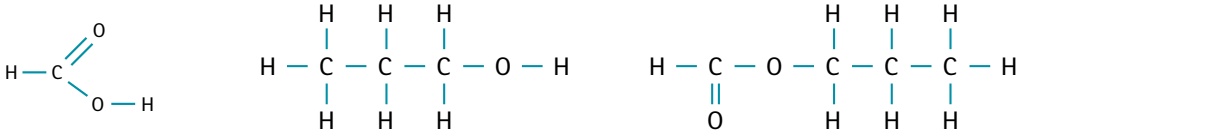
The small esters are fairly soluble in water but solubility in water decreases as the hydrocarbon chain length increases. Esters which are soluble in water form hydrogen bonds with water.

Preparation of esters

1. by reaction of carboxylic acid and alcohol
   Carboxylic acids react with alcohols to produce esters, in an equilibrium reaction.

For example:

$HCOOH + CH_3CH_2CH_2OH \rightleftharpoons HCOOCH_2CH_2CH_3 + H_2O$



methanoic acid | propan-1-ol | propyl methanoate | water

Condition: A catalyst of concentrated sulfuric acid is used and the mixture is heated.
Observation: sweet smell detected

2. by reaction of acyl chloride and alcohol

For example:

$CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$

ethanoyl chloride | ethanol | ethyl ethanoate | hydrogen chloride

condition: room temperature

observation: A vigorous reaction which produces steamy/misty fumes of HCl(g) and mixture warms up

This is a suitable way of producing an ester from an alcohol because it occurs at room temperature, is irreversible and the hydrogen chloride is removed as a gas, shifting the equilibrium to the right and forming more of the ester. This method is not commonly used in the laboratory due to the volatile and corrosive nature of the acid chlorides. The normal laboratory preparation of an ester uses an alcohol and a carboxylic acid and needs heat, a catalyst and is reversible so it is more difficult to get a high yield of ester.

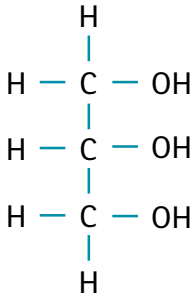
The Laboratory preparation of a liquid Ester from a Carboxylic Acid and an Alcohol

- Place a mixture of the alcohol and concentrated sulfuric acid in a pear shaped/round bottomed flask.
- Add a mixture of the alcohol and carboxylic acid slowly from a dropping funnel.
- Swirl the mixture (e.g. using a magnetic stirrer).
- Add some anti-bumping granules and heat under reflux
- Arrange the apparatus for distillation, heat the mixture gently and collect the distillate around the boiling point
- Place the crude ethyl ethanoate in a separating funnel and shake with sodium carbonate solution to remove traces of unreacted ethanoic acid and the concentrated sulfuric acid. Invert the funnel and open the tap occasionally to release pressure due to any carbon dioxide gas produced. Remove the stopper and allow the layers to separate and discard the lower aqueous layer .
- Add some calcium chloride solution to the ethyl ethanoate, to remove any ethanol impurities, shake, and run off the lower aqueous layer into a boiling tube.
- Add a spatula of anhydrous calcium chloride/ sodium sulfate/magnesium sulfate (a drying agent which removes water) and stopper the boiling tube and shake. Repeat until the ester is clear.
- Filter to remove calcium chloride.
- Redistill to remove any remaining organic impurities, collecting the fraction at the boiling point.
- Esters can be hydrolysed in acid or alkaline conditions to form alcohols and carboxylic acids or salts of carboxylic acids.

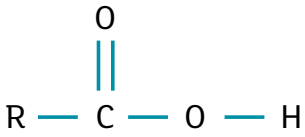
Fats

Vegetable oils and animal fats are **esters** of propane-1,2,3-triol (a tri-alcohol) and a long chain carboxylic acid called a fatty acid.

Propane-1,2,3-triol (also known as **glycerol**) has the structure shown.

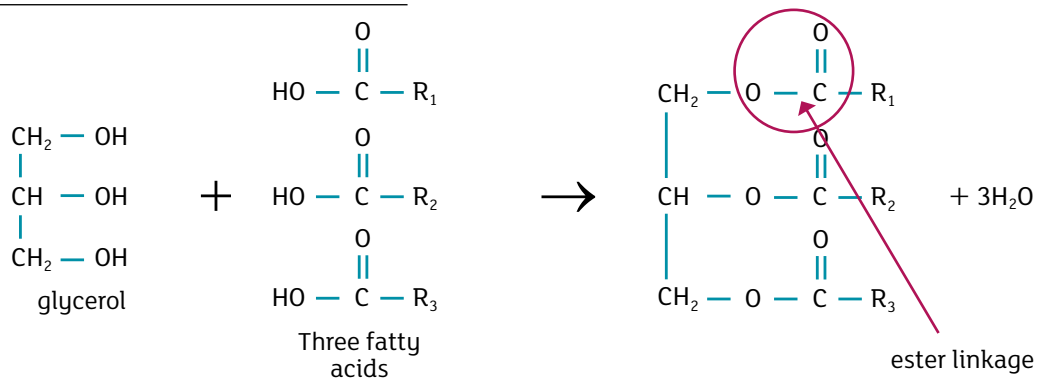


Fatty acids generally have the structure:



The R is hydrogen or an alkyl group.
Two common fatty acids are stearic acid $CH_3(CH_2)_{16}COOH$, a saturated (no C=C in chain) fatty acid containing 18 carbon atoms and oleic acid $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ an unsaturated fatty acid containing 18 carbon atoms

The fats formed in the condensation reaction between fatty acids and glycerol are triesters and are often referred to as triglycerides. Propane-1,2,3-triol has three OH groups and so it reacts with three fatty acids to form a triglyceride.



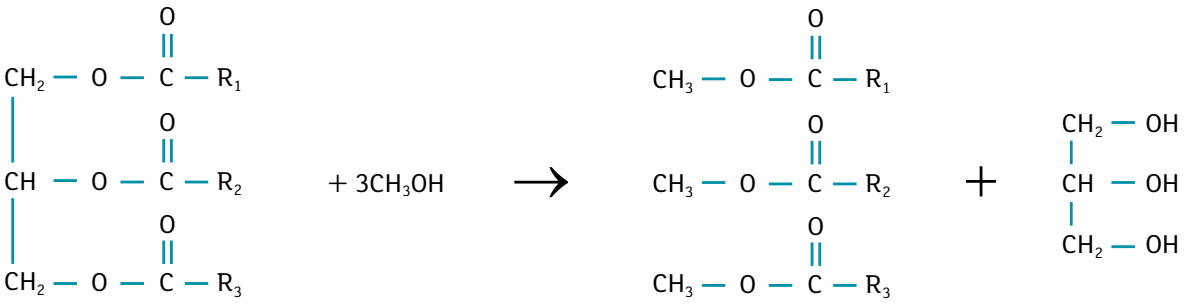
There is a triester linkage in the triglyceride. The three fatty acids which form the lipid may be the same (e.g. three stearic acids) or they may be different. A **triglyceride** is an ester of propane-1,2,3-triol (glycerol) and three fatty acid molecules.

Transesterification

Biodiesel is a fuel, similar to diesel, which is made from vegetable sources. e.g. from the reaction of rape seed oil with methanol.

It is a renewable fuel which consists of a mixture of methyl esters of long-chain carboxylic acids (fatty acids).It is produced by heating vegetable oils (triglycerides) with methanol or ethanol in the presence of an acid catalyst. The process can be called **trans-esterification** – reacting a ester with an alcohol to produce a different ester and a different alcohol.

Trans-esterification is a reaction where the alkyl group of an ester is exchanged with the alkyl group of an alcohol.



The alkyl groups R_1, R_2 and R_3 can be the same or different. The reaction is reversible so an excess of methanol is used to drive the equilibrium to the right, and under appropriate conditions this process can produce a 98% yield.

Hardening of oils

Unsaturated fats (oils) can be catalytically hydrogenated to form saturated fats such as margarines. The saturated fats formed are solid due to the extra hydrogen added, resulting in a larger formula mass and so stronger van der Waals' forces between the molecules.

The conditions are

- Bubble in hydrogen
- At 180°C
- In the presence of a finely divided nickel catalyst.

Acyl chlorides

1. With water

$$R\text{-}COCl + H_2O \rightarrow R\text{-}COOH + HCl$$

e.g. CH_3CH_2COCl + H_2O → CH_3CH_2COOH + HCl

propanoyl chloride · water · propanoic acid · hydrogen chloride

observation: a vigorous reaction producing steamy/ misty fumes of hydrogen chloride, mixture warms up

The pipetted addition of ethanoyl chloride to the water in the beaker has formed ethanoic acid and fumes of HCl. A glass rod dipped in concentrated ammonia solution and applied to the gas will produce white fumes of ammonium chloride.

© Andrew Lambert Photography / Science Photo Library

2. with alcohols – see preparation of esters above.

This reaction is not as vigorous is the reaction of acyl chloride with water.

Revision Questions

1 Butan-1-ol was reacted with an excess of propanoic acid in the presence of a small amount of concentrated sulfuric acid. 6.0 g of the alcohol produced 7.4 g of the ester. Which one of following is the percentage yield of the ester?

A 57%

B 70%

C 75%

D 81%

[1]

2 Methyl propanoate may be prepared in the laboratory by the reaction of propanoic acid and methanol.

(i) Write the equation for the preparation of methyl propanoate..

..... [2]

(ii) Concentrated sulfuric acid is added to the reaction mixture.
State **one** function of this acid in the preparation.

.....

..... [1]

(iii) Propanoic acid has a boiling point of 141°C, while that of methyl propanoate is only 79°C despite its higher relative formula mass.
Explain the difference in the two boiling points.

.....

.....

..... [2]

(iv) Propanoyl chloride may be used in place of propanoic acid for this preparation. State **two** advantages of using the acyl chloride.

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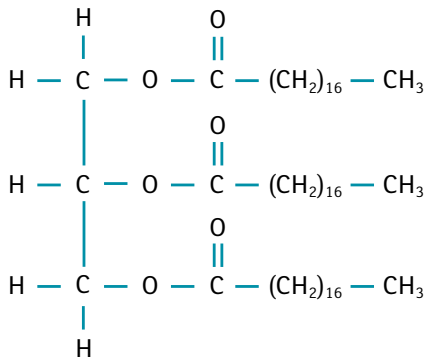
..... [2]

3 The following fat, stearin, is present in lard:



stearin

a) When refluxed with potassium hydroxide stearin produces the potassium salt of stearic acid (potassium stearate) and only one other product.

(i) Using the R– to represent $CH_3(CH_2)_{16}$–, write an equation for the reaction of stearin with excess potassium hydroxide.

..... [2]

(ii) State the systematic name of the other product.

..... [1]

b) The methyl ester of stearic acid is present in biodiesel.

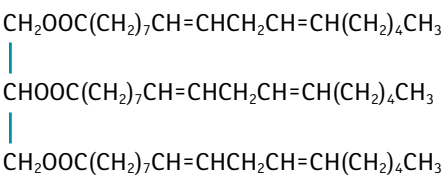
(i) Give the molecular formula of the ester.

..... [1]

(ii) Give the equation for the complete combustion of this ester.

..... [2]

4 Trilinolein (rape seed oil) may be represented as:



$CH_2OOC(CH_2)_7CH=CHCH_2CH=CH(CH_2)_4CH_3$

$CHOOC(CH_2)_7CH=CHCH_2CH=CH(CH_2)_4CH_3$

$CH_2OOC(CH_2)_7CH=CHCH_2CH=CH(CH_2)_4CH_3$

[1]

a) Write an equation for the formation of trilinolein from 3 molecules of the fatty acid linoleic acid and glycerol, representing linoleic acid as $C_{17}H_{31}COOH$.

[2]

b) Explain why trilinolein is described as an unsaturated fat.

.....

..... [1]

c) Rapeseed oil can be converted into biodiesel by reaction with methanol. Draw the structure of this biodiesel molecule.

[2]

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