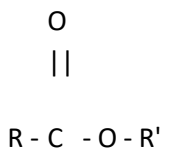
Esters and Esterification

Key Concepts

Esters have the general formula :



in which R and R' represent alkyl groups.

Esters (alkyl alkanoates) are prepared by reacting an alkanol with an alkanoic acid:

alkanol	+	alkanoic acid	→	alkyl alkanoate (ester)	+	water
R'OH	+	RCOOH	→	R**COO**R' (ester)	+	H_2O

Preparation of Esters:

Reflux
The reaction mixture consisting of the alkanol, the alkanoic acid and a small amount of concentrated sulfuric acid is heated in a vessel with a water-cooled condenser (Liebig condenser) to prevent loss of volatile material.

Separation
After heating, the reaction mixture is then poured into a separating funnel.
Calcium carbonate ($CaCO_3$), or a similar neutralizing agent, is added to the mixture to react with any unreacted acid present in the mixture.

calcium carbonate + acid → water soluble salt + carbon dioxide gas + water

The less dense organic layer floats on top of the more dense aqueous layer.
The stop cock on the separating funnel is opened to allow the more dense aqueous layer to be run off, leaving the less dense organic layer containing the ester in the separating funnel.

Purification
The organic layer separated in the separating funnel above contains the ester. This organic layer is distilled to obtain the pure ester. A sharp boiling point is an indication of the purity of the ester.

Examples of Esters

methyl butanoate (apple) :

methanol + butanoic acid → methyl butanoate (ester) + water

CH_3OH + C_3H_7COOH → $C_3H_7COOCH_3$ (ester) + H_2O

ethyl methanoate (rum essence) :

ethanol + methanoic acid → ethyl methanoate (ester) + water

C_2H_5OH + $HCOOH$ → $HCOOC_2H_5$ (ester) + H_2O

ethyl butanoate (pineapple) :

ethanol + butanoic acid → ethyl butanoate (ester) + water

C_2H_5OH + C_3H_7COOH → $C_3H_7COOC_2H_5$ (ester) + H_2O

pentyl ethanoate (banana) :

pentanol + ethanoic acid → pentyl ethanoate (ester) + water

$C_5H_{11}OH$ + CH_3COOH → $CH_3COOC_5H_{11}$ (ester) + H_2O

pentyl butanoate (apricot) :

pentanol + butanoic acid → pentyl butanoate (ester) + water

$C_5H_{11}OH$ + C_3H_7COOH → $C_3H_7COOC_5H_{11}$ (ester) + H_2O

octyl butanoate (orange) :

octanol + butanoic acid → octyl butanoate (ester) + water

$C_8H_{17}OH$ + C_3H_7COOH → $C_3H_7COOC_8H_{17}$ (ester) + H_2O

methyl ethanoate (solvent) :

methanol + ethanoic acid → methyl ethanoate (ester) + water

CH_3OH + CH_3COOH → CH_3COOCH_3 (ester) + H_2O

ethyl ethanoate (solvent) :

ethanol + ethanoic acid → ethyl ethanoate (ester) + water

C_2H_5OH + CH_3COOH → $CH_3COOC_2H_5$ (ester) + H_2O

5. Esterification

Extract from Chemistry Stage 6 Syllabus (Amended October 2002). © Board of Studies, NSW. [Edit: 11Jun10]

Background: Living things store much of their energy as esters, known as fats or oils. Many of the flavours and odours of fruits are esters. The formation and breakdown of esters are reactions that occur frequently in living things.

describe the differences between the alkanol and alkanoic acid functional groups in carbon compounds

Background

A functional group is an atom or group of atoms that reacts in a characteristic way in different carbon compounds.

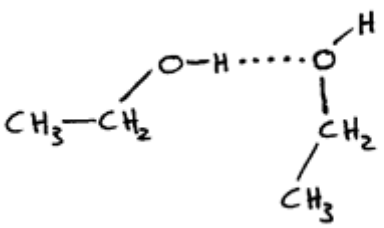
- The hydroxy functional group,-OH, in alkanols provides their characteristic properties, such as high melting points and boiling points.
- The carboxylic acid functional group, -COOH, in alkanoic acids can lose a hydrogen ion and behave as a weak acid.

explain the difference in melting point and boiling point caused by straight-chained alkanoic acid and straight-chained primary alkanol structures

Background

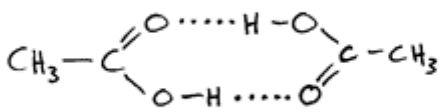
Straight-chained structures do not have any branches on the hydrocarbon chain.
A primary alkanol has the -OH group at the end of the hydrocarbon chain.

- The high melting points and boiling points in alkanols is due to hydrogen bonding between the O in one molecule and the H of an-OH in a nearby molecule.



- The ability of the-COOH group to be involved in two hydrogen bonds gives an alkanoic acid an even higher boiling point than that of a similar sized

alkanol. Two hydrogen bonds can occur between a pair of alkanoic acid molecules.



identify data, plan, select equipment and perform a first-hand investigation to prepare an ester using reflux

- Use a chemical data book to **identify** the boiling points of the alkanol, alkanoic acid, ester and water.
- **Plan** the investigation by considering if the boiling points of the reactants and products are sufficiently different for you to easily separate the ester from the rest of the reaction mixture by fractional distillation. Consider the effect of using more than a few drops of concentrated sulfuric acid catalyst and how this might complicate the separation. Consider if you would be better off using differences in densities and water solubility of the components to separate the ester.
- **Choose suitable reflux equipment**:

  A large test tube fitted with a cork through which a pipette has been passed upside-down. The test tube could be heated in hot water; air circulating around the pipette acts as a condenser.

  Ground-glass joint equipment, including a water-cooled condenser, positioned vertically, and a reaction vessel heated by an electric heater.
- **Perform** the investigation, making sure you identify and use safe work practices. For instance, if using the first method above, make sure the pipette is not blocked by pieces of cork, otherwise you risk an explosion!

identify esterification as the reaction between an acid and an alkanol and describe, using equations, examples of esterification

- An acid, containing the-COOH functional group, can react with an alkanol, containing the-OH functional group, to produce an ester and water.

$$\underset{\text{alkanol}}{R\text{-}OH} + \underset{\text{acid}}{HOOC\text{-}R^{!}} \rightleftharpoons \underset{\text{ester}}{R\text{-}OOC\text{-}R^{!}} + \underset{\text{water}}{H_2O}$$

- If an oxygen-18 isotope, **O**, is used in the alkanol only, it is found in the ester, but not in the water product. Use of this tracer shows that the O in water comes from the acid.

$$\underset{\text{alkanol}}{R\text{-}\mathbf{O}H} + \underset{\text{acid}}{HOOC\text{-}R^{!}} \rightleftharpoons \underset{\text{ester}}{R\text{-}\mathbf{O}OC\text{-}R^{!}} + \underset{\text{water}}{H_2O}$$

- The reaction is reversible and comparable quantities of alkanol, acid, ester and water are present at equilibrium.

- Common names, rather than systematic names, are often used to obtain the ester name:

$$CH_3OH + HOOCCH_3 \rightleftharpoons CH_3OOCCH_3 + H_2O$$

Common: methyl alcohol acetic acid methyl acetate water
Systematic: methanol ethanoic acid methyl ethanoate

$$CH_3CH_2OH + HOOCH \rightleftharpoons CH_3CH_2OOCH + H_2O$$

Common: ethyl alcohol formic acid ethyl formate water
Systematic: ethanol methanoic acid ethyl methanoate

identify the IUPAC nomenclature for describing the esters produced by reactions of straight-chained alkanoic acids from C1 to C8 and straight-chained primary alkanols from C1 to C8

The naming of esters follows a straight forward pattern using IUPAC nomenclature.

The table below will give you a start. Copy it and attempt to complete it.

Alkanol	**Alkanoic acids**							
	methanoic acid	**ethanoic acid**	**propanoic acid**	**butanoic acid**	**pentanoic acid**	**hexanoic acid**	**heptanoic acid**	**octanoic acid**
methanol	methyl methanoate	methyl ethanoate	methyl propanoate		methyl pentanoate			methyl octanoate
ethanol	ethyl methanoate							
propanol	propyl methanoate							
butanol	butyl methanoate		butyl propanoate					

pentanol								
hexanol			hexyl propanoate					
heptanol								
octanol				octyl butanoate				octyl octanoate

There is no need to learn all the ester names. Just remember the naming pattern you used.

Did you note that the alkanol always forms the first part of the ester's name having its ending changed from '...anol' to '...yl' and the alkanoic acid forms the second part of the ester's IUPAC name with its ending changing from '...oic acid' to '... oate'?

naming Alkanols ▸ AUS-e-TUTE

describe the purpose of using acid in esterification for catalysis

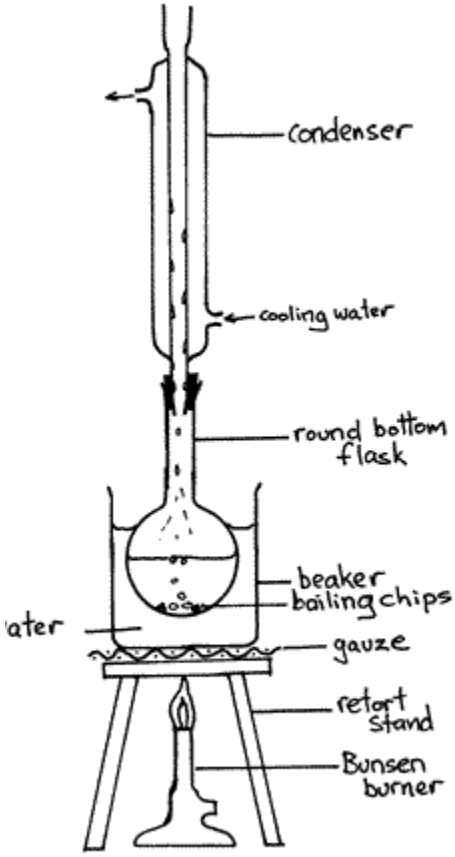
- Esterification is catalysed by the addition of a small amount of acid. Esterification is called a *condensation reaction* because a water molecule condenses out.
- Only a few drops of concentrated acid needs to be added to a mixture of alkanol and alkanoic acid to catalyse the reaction.
- If concentrated sulfuric acid is added in large amounts, say 5% to 10% of the reaction volume, it can have a significant effect on the position of equilibrium. Concentrated sulfuric acid is a dehydrating agent, that is, it has a strong affinity for water. If a significant amount of sulfuric acid is present, it will shift the equilibrium position to the right by absorbing water.

  alcohol + acid $\rightleftharpoons$ ester + water

  This increases the yield of ester. However using large amounts of sulfuric acid is wasteful, uneconomic and complicates the separation of ester from the reaction mixture.

explain the need for refluxing during esterification

- Esterification requires heat for the reaction to reach equilibrium within an hour, rather than after many days. When the reaction mixture is heated, volatile components, such as the reactant alcohol and the product ester, could escape. This problem is overcome by refluxing the reaction mixture.



- A condenser is placed on top of the reaction vessel so that any volatile components pass into the condenser. The condenser can be water or air-cooled and causes the volatile components to condense back to liquid and fall back into the reaction mixture.

- Refluxing also improves the safety of the operation, as the volatile components are flammable.

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process information from secondary sources to identify and describe the uses of esters as flavours and perfumes in processed foods and cosmetics

- You can **process** information from the labels on processed food containers and cosmetics. You should be able to recognise and record the names of esters they contain. Remember the name of an ester is usually in two words:
  - the first word is derived from the alcohol and ends in *-yl*
  - the second word is derived from the acid and ends in *-oate*.

- Alternatively, you could look in a list of food additives or cosmetic ingredients and try to recognise ester names.

- Having identified the names of some esters, you should then use a chemical dictionary, chemical encyclopedia or Internet search engine to find uses of those esters.

outline some examples of the occurrence, production and uses of esters

- Use a chemical dictionary, chemical encyclopedia or Internet search engine to find occurrence, production and uses of esters.