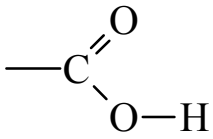
Carboxylic Acids

Three main areas specified by OCR:
1. Formation of Salts
2. Esterification
3. Hydrolysis of Esters

Review of Content from AS Acids

Carboxylic Acids contain the following functional group:



They are named by adding –oic acid onto the end of the carbon skeleton.

Formula	Name
HCOOH	Methanoic Acid
CH_3COOH	Ethanoic Acid
C_2H_5COOH	Propanoic Acid
C_3H_7COOH	Butanoic Acid

- The –COOH group is the section responsible for the chemistry.
- The substituents are named as in other aliphatic compounds
- The carbon in the –COOH group is numbered carbon 1.

Questions

1. Which of the following formulae represent carboxylic acids?
   a) $CH_3CH_2CH(CH_3)COOH$
   b) $(CH_3)_2CHCHO$
   c) CH_3CH_2OH
   d) $C_6H_5CH_2COOH$

2. Draw the displayed formulae for:
   a) Propanoic acid
   b) 2-methylpropanoic acid
   c) 3,3-dimethylbuntanoic acid
   d) 2-methylbenzoic acid

3. Name these acids:
   a) $CH_3CH_2CH_2CH_2COOH$
   b) $CH_3CH_2CH_2COOH$
   c) $CH_3CH(CH_3)CH_2COOH$
   d) $ClCH_2CH_2CH_2CH_2COOH$

Synthesis

Carboxylic acids can be synthesised from 1˚ Alcohols. Using a suitable oxidising agent:

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

- Conditions are reflux.
- Reagent potassium dichromate (VI) $K_2Cr_2O_7/H^+$

Although carboxylic acids look similar to carbonyls, they do have very different chemistry. The carbonyl group is less important in the acid due to the presence of the –OH group.

This synthesis is also possible by hydrolysis of a nitrile:

$$R\text{-}CN(l) + 2H_2O(l) + 2HCl(aq) \rightarrow R\text{-}COOH(aq) + NH_4^+Cl^-(aq)$$

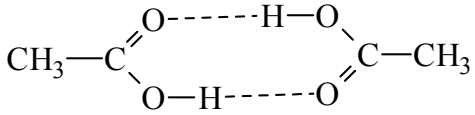
- Conditions are heat
- Reagents as in the equation.

Physical Properties

The physical properties of carboxylic acids are dominated by the ease with which they form hydrogen bonds. This raises the melting point to 17˚C.

They can also hydrogen bond with water which allows the smaller carboxylic acids to mix freely with water.

The main property of interest is the formation of dimers. Two molecules of a carboxylic acid can hydrogen bond together seemingly doubling their relative molecular mass – this only happens in a non-polar solvent.



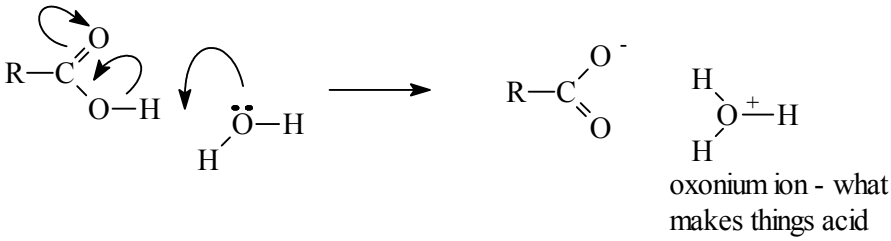
Questions

1. Which of these compounds would you expect to show some degree of hydrogen bonding in the liquid state?
   a) C_6H_6
   b) $(CH_3)_3CC(CH_3)_3$
   c) C_4H_9OH
   d) $C_5H_{11}COOH$

2. The RMM of a carboxylic acid is measured as 244 (in a non-aqueous solvent). Its formula is found to be C_6H_5COOH. Draw a diagram to show why the RMM is double that expected.

Acidic Properties of Carboxylic acids

To some extent all carboxylic acids ionise in water. The presence of the carbonyl group enhances this property



It is the release of the hydrogen ion (proton) to the water molecule that makes these compounds act as acids. Forming $H^+(aq)$ or $H_3O^+(aq)$ in the process.

Reactions of the Acidic nature of carboxylic acids

This release of protons when in water gives the solution a pH of less than 7. The usual reactions of acids are present. The conditions for all these reactions is room temperature.

1. Neutralisation with alkali (e.g. sodium hydroxide)

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO^- Na^+(aq) + H_2O(l)$$

Or more simply as:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

The CH_3COO^- is often called the ethanoate ion.

2. Neutralisation with a base such as copper (II) oxide.

$$2CH_3COOH(aq) + CuO(aq) \rightarrow (CH_3COO^-)_2 Cu^{2+}(aq) + H_2O(l)$$

or more simply as:

$$2CH_3COOH(aq) + O^{2-}(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

3. Reaction with a moderately reactive metal (such as magnesium), sodium is too dangerous.

$$2CH_3COOH(aq) + Mg(s) \rightarrow 2CH_3COO^-(aq) + Mg^{2+}(aq) + H_2O(l)$$

4. Release of carbon dioxide with any carbonate

$$2CH_3COOH(aq) + CO_3^{2-}(aq) \rightarrow 2CH_3COO^-(aq) + CO_2(g) + H_2O(l)$$

You could also include the metal:

$$2CH_3COOH(aq) + CaCO_3(s) \rightarrow 2CH_3COO^-(aq) + Ca^{2+}(aq) + CO_2(g) + H_2O(l)$$

These are specified in the syllabus as need to know reactions.

Carboxylic Acids as Proton Donors

There are many definitions of what makes an acid an acid, ranging back to ancient times when anything with oxygen in was thought to be an acid to the modern Lewis acid theory.

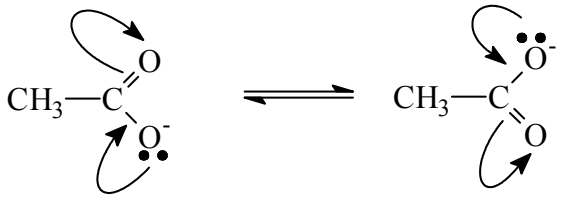
The most commonly accepted theory is that of Brønsted and Lowry who came up with the theory that:

……acids are proton donors and bases are proton acceptors……

In this case the carboxylic acid is acting as a proton donor (giving away its proton (H^+)) and the water is the proton acceptor (acting as a base).

$$CH_3COOH(aq) + H_2O(l) \rightarrow CH_3COO^-(aq) + H_3O^+(aq)$$

The carboxylate anion helps in the understanding of the carboxyl group to release a proton.



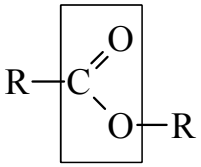
- The extra negative charge can be on either oxygen. It is partially delocalised and adds to the stability of the anion
- This extra stability increased the chances of it being formed.

Questions

Write balanced equations using symbols [H] and [O] in reduction and oxidation reactions where appropriate.

a) ethanol and potassium dichromate in acid solution
b) ethanoic acid and sodium carbonate solution
c) propanal and potassium dichromate in acid solution
d) 2-methylpropanoic acid and aqueous potassium hydroxide solution
e) aqueous propanoic acid and magnesium metal

Esterification reactions



The ester group

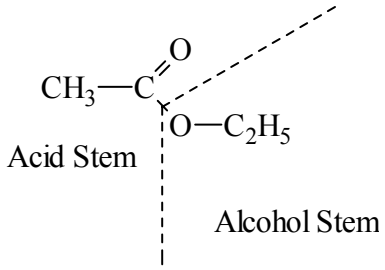
An ester is formed by heating a carboxylic acid and an alcohol in the presence of an acid catalyst – normally concentrated sulphuric acid.

$$CH_3COOH + C_2H_5OH \overset{\text{acid catalyst}}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

You do not need to know the mechanism of Esterification, it is complex, and there are many suggested routes through to completion.

Naming of esters

Esters are named from the acid and alcohol stem.

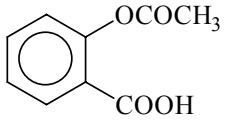
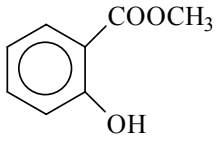


Esters are named as follows:

- the alcohol stem comes at the start of the ester name
- the acid stem provides the second part of the name
- the name of the ester usually ends with *–anoate.*

The above ester is ethyl ethanoate.

Uses of esters

Ethyl 2-methylbutanoate	$CH_3CH_2CH(CH_3)COOCH_2CH_3$	Apple flavour
3-Methylbutyl ethanoate	$CH_3COOCH_2CH_2CH(CH_3)_2$	Pear flavour
1-Methylpropyl ethanoate	$CH_3COOCH(CH_3)CH_2CH_3$	Banana flavour
Ethyl methanoate	$HCOOCH_2CH_3$	Raspberry flavour
Butyl butanoate	$CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3$	Pineapple flavour
Phenylmethyl ethanoate	$CH_3COOCH_2C_6H_5$	Oil of Jasmine
2-Ethanoyloxybenzoic acid (acetylsalicylic acid)		Aspirin
Methyl 2-hydroxybenzoate (methyl salicylate)		Muscle rub
Ethyl ethanoate	$CH_3COOCH_2CH_3$	Glue solvent
Methyl 2-cyanopropenoate	$CH_2=C(CN)COOCH_3$	Superglue
Ethenyl ethanoate	$CH_3COOCH=CH_2$	PVA glue

Esters can be used as adhesives, perfumes, flavourings and even painkillers. OCR specify that you know they can be used as perfumes and flavourings. No examiner however will mark wrong a correct use from above.

Questions

1. Which of the following are acids, esters, alcohols or ethers (ethers contain the –C-O-C- linkage).
   a) $CH_3CH(CH_3)CH(OH)CH_2CH_3$
   b) $CH_3CH_2COOCH(CH_3)CH_3$
   c) $CH_3CH_2OCH_3$
   d) $CH_3CH_2CH_2COOCH_3$

2. Draw the full structures of these esters.
   a) methyl butanoate
   b) propyl 2-methylpropanoate
   c) butyl ethanoate
   d) 1-methylethyl propanoate

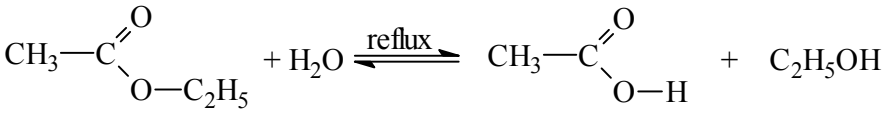
3. Name these compounds
   a) $CH_3CH_2CH_2COOH$
   b) $CH_3(CH_2)_5COOH$
   c) $CH_3C(CH_3)_2COOCH_2CH_3$
   d) $CH_3CH_2COOCH_3$

4. Write balanced equations for the following reactions, including the conditions needed to carry out the reactions. Use [O] and [H] where necessary.
   a) Butanoic acid and $LiAlH_4$
   b) 2-Methylbutanal and acidified potassium dichromate solution
   c) Ethanol and 2-methylpropanoic acid
   d) Butanoic acid and sodium hydroxide solution

Hydrolysis of esters

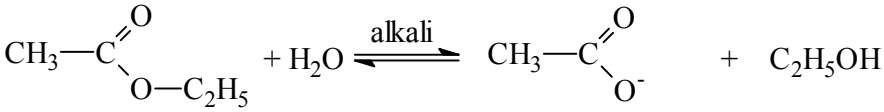
Hydrolysis means the break-up of a molecule using water.

Esters can be hydrolysed by both acids and alkalis. In hydrolysis, the overall result is that a water molecule is added for each ester linkage broken.



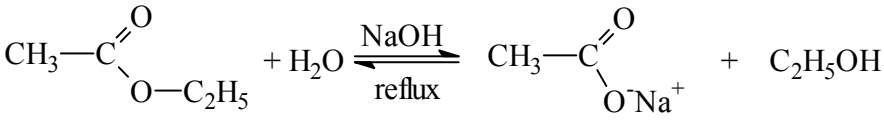
The bond breaks between the C and the O, the OH of the water inserts here.

Acid hydrolysis will give the above products, whereas alkali hydrolysis gives the carboxylate salt.



- Acid hydrolysis leads to equilibrium, the yield of products is never 100%
- Alkaline hydrolysis breaks up the ester completely.

A more accurate way of representing this could be:



This is a major factor in the manufacture of detergents from natural fats or vegetable oils. These are triglycerides – esters of glycerol.