Cambridge

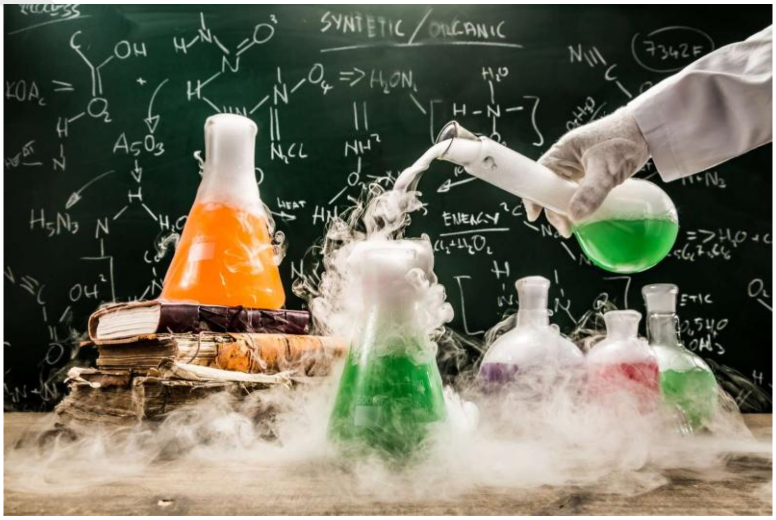
AS Level

Chemistry

CODE: (9701)

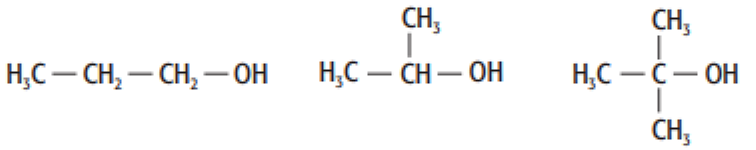
Chapter 17 and 18

Alcohols, esters and carboxylic acids and carbonyl compounds



The homologous series of alcohols

Alcohols are organic molecules with hydroxyl groups, $C_nH_{2n+1}OH$, and are named by adding '-anol' to the alkane stem. They have three or more carbon atoms, with the hydroxyl group position indicated by a number.



propan-1-ol
primary alcohol

propan-2-ol
secondary alcohol

2-methylpropan-2-ol
tertiary alcohol

Figure 17.2 Note that the numbering to show the position of the OH group in an alcohol starts from the end of the molecule that gives the smaller number.

Propan-1-ol is classified as **a primary alcohol**. The carbon atom bonded to the --OH group is attached to one other carbon atom (alkyl group). Propan-2-ol is a **secondary alcohol** as the carbon atom bonded to the --OH group is attached to two other carbon atoms (alkyl groups). With three alkyl groups attached, 2-methylpropan-2-ol is an example of a **tertiary alcohol.**

Reactions of the alcohols

1 Combustion

When ignited, the alcohols react with oxygen in the air. The products of complete combustion are carbon dioxide and water

$$\text{alcohol} + \text{oxygen} \longrightarrow \text{carbon dioxide} + \text{water}$$

$$\underset{\text{ethanol}}{C_2H_5OH} + 3O_2 \longrightarrow 2CO_2 + 3H_2O$$

Brazil's limited oil reserves can be utilized to produce sugar cane, which can be fermented to produce ethanol, a fuel used in various forms. Sugar cane absorbs CO_2 as it grows, making it a carbon-neutral biofuel. Despite the CO_2 produced during cultivation, it is better for the environment to use bio-ethanol than petrol or diesel from crude oil.

Figure 17.3 The fuel called 'gasohol' is a mixture of ethanol and petrol.

2 Substitution to form a halogenoalkane

In this substitution reaction with a hydrogen halide, such as hydrogen chloride, the OH group in the alcohol is replaced by a halogen atom to produce a halogenoalkane.

The carbon atom bonded to the hydroxyl group in the alcohol will carry a partial positive charge (as oxygen is more electronegative than carbon). This makes the carbon atom open to nucleophilic attack.

The initial attack on the alcohol is by the partially negative halogen atom in the hydrogen halide:

$$\overset{\delta+}{H} \rightarrow \overset{\delta-}{X} \quad \text{where X = halogen atom}$$

alcohol + hydrogen halide ⟶ halogenoalkane + water

For example:

$$\underset{\text{ethanol}}{CH_3CH_2OH} + HCl \longrightarrow \underset{\text{chloroethane}}{CH_3CH_2Cl} + 3H_2O$$

The dry hydrogen chloride gas for this reaction can be made *in situ* (in the reaction vessel). Sodium chloride and concentrated sulfuric acid are used for this:

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

Sulfur dichloride oxide, $SOCl_2$, can also be used to substitute a chlorine atom into an alcohol molecule, as shown below:

$$C_2H_5OH + SOCl_2 \longrightarrow C_2H_5Cl + HCl + SO_2$$

Note that in this reaction the two byproducts of the reaction (HCl and SO_2) are both gases. These escape from the reaction mixture, leaving the halogenoalkane, without the need to distil it off as in the hydrogen halide reaction.

We can also use phosphorus halides to provide the halogen atoms for this substitution reaction.

For chloroalkanes we can use solid phosphorus(V) chloride, PCl_5:

$$C_2H_5OH + PCl_5 \xrightarrow{\text{room temperature}} C_2H_5Cl + HCl + POCl_3$$

The release of acidic hydrogen chloride gas from this reaction can be used as a test for the hydroxyl group. The HCl gas causes acidic 'steamy fumes' to be observed.

Phosphorus(III) chloride can also be used to halogenate an alcohol, but this reaction does require heating.

For bromoalkanes and iodoalkanes we can make the phosphorus(III) halide, PBr_3 or PI_3, *in situ* using red phosphorus and bromine or iodine. These are warmed with the alcohol. For example:

$$3C_2H_5OH + PI_3 \longrightarrow \underset{\text{iodoethane}}{3C_2H_5I} + H_3PO_3$$

3 Reaction with sodium metal

In the reaction with hydrogen halides, the C O bond in the alcohol breaks. However, in some other reactions the O H bond in the alcohol breaks. The reaction with sodium metal is an example

$$\underset{\text{ethanol}}{C_2H_5OH} + \underset{\text{sodium}}{Na} \longrightarrow \underset{\text{sodium ethoxide}}{C_2H_5O^-Na^+} + \underset{\text{hydrogen}}{H_2}$$

Figure 17.5 Sodium reacting with ethanol. The pink colour is from a colourless phenolphthalein indicator that has been added to the ethanol, showing the basic nature of the sodium ethoxide formed.

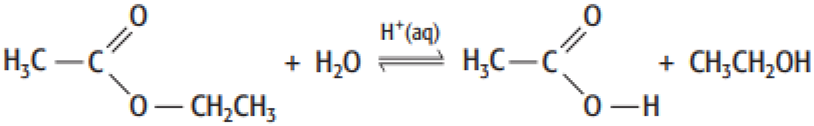
Other alcohols react in a similar way with sodium. For example, propan-1-ol would produce sodium propoxide plus hydrogen gas. In general:

alcohol + sodium ⟶ sodium alkoxide + hydrogen

4 Esterification

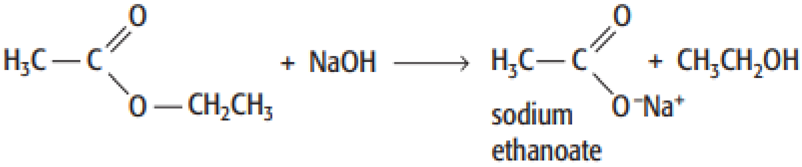
Hydrolysis of esters

Esters can be hydrolysed by heating under reflux with either an acid or a base. Refluxing with an acid simply reverses the preparation of the ester from an alcohol and a carboxylic acid. The acid catalyses the reaction.



$$CH_3COOCH_2CH_3 + H_2O \xrightleftharpoons{H^+(aq)} CH_3COOH + CH_3CH_2OH$$

. An alcohol and the sodium salt of the carboxylic acid are formed. The equation for the base hydrolysis of ethyl ethanoate is:



$$CH_3COOCH_2CH_3 + NaOH \longrightarrow CH_3COO^-Na^+ + CH_3CH_2OH$$

sodium ethanoate

5 Dehydration

Alcohols can also undergo elimination reactions in which water is lost and alkenes are formed. As the small molecule removed from the alcohol molecule is H_2O, this reaction is also known as dehydration.

$$\text{alcohol} \xrightarrow{\text{catalyst}} \text{alkene} + \text{water}$$

The reaction takes place when alcohol vapour is passed over a hot catalyst of aluminium oxide powder. Pieces of porous pot or pumice also catalyse the reaction.
For example:

$$\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow{Al_2O_3\text{ catalyst}} \underset{\text{ethene}}{CH_2{=}CH_2} + \underset{\text{water}}{H_2O}$$

Figure 17.7 shows how the ethene gas formed can be collected.

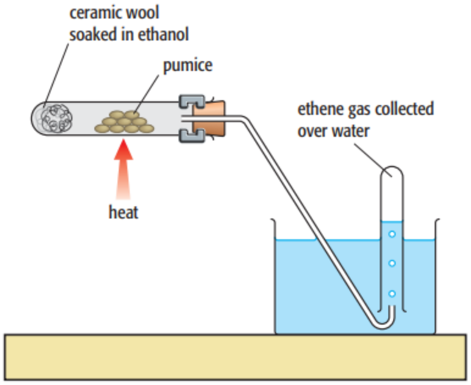


Figure 17.7 The dehydration of ethanol to give ethene.

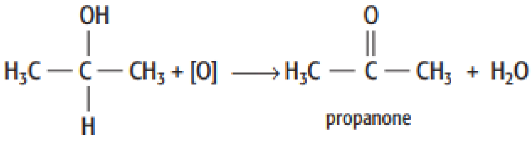
6 Oxidation

For many of their reactions, the class of alcohol makes no difference to the type of products formed. In organic chemistry, we can usually generalise for the whole homologous series. However, when alcohols are oxidised, different products are obtained from primary, secondary and tertiary alcohols.

The product formed when an alcohol is oxidised can be used to distinguish between primary, secondary and tertiary alcohols. You can learn about the chemical tests for the products.

■■ With tertiary alcohols, a mixture of the tertiary alcohol, dilute sulfuric acid and potassium dichromate(VI) solution remains orange when warmed. No reaction takes place under these relatively mild conditions.

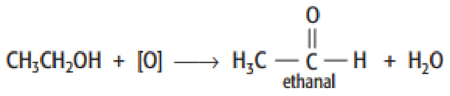
■■ A secondary alcohol, such as propan-2-ol, will be oxidised to form a ketone. In this case propanone is formed and the reaction mixture turns green:



$$CH_3CH(OH)CH_3 + [O] \longrightarrow CH_3COCH_3 + H_2O$$

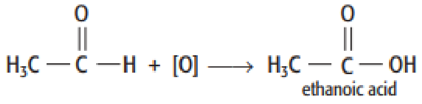
propanone

■ With a primary alcohol, such as ethanol, the alcohol is oxidised to an aldehyde. Ethanol is oxidised to ethanal:



$$CH_3CH_2OH + [O] \longrightarrow \underset{\text{ethanal}}{H_3C-\overset{\overset{\large O}{\|}}{C}-H} + H_2O$$

The ethanal formed can be further oxidised to form ethanoic acid, a carboxylic acid. This is achieved by refluxing with excess acidified potassium dichromate(VI):



$$H_3C-\overset{\overset{\large O}{\|}}{C}-H + [O] \longrightarrow \underset{\text{ethanoic acid}}{H_3C-\overset{\overset{\large O}{\|}}{C}-OH}$$

DISTINGUISHING TERTIARY ALCOHOLS

Given three unknown alcohols, one primary, one secondary and one tertiary, it would be easy to distinguish the tertiary alcohol. Figure 17.8 shows the results of warming each class of alcohol with a solution of acidified potassium dichromate(VI). More details of these reactions are given on page 236.

Figure 17.8 Before warming with the labelled alcohol, each of these tubes contained orange acidified potassium dichromate(VI) solution. After warming, the orange dichromate(VI) ions have been reduced to green chromium(III) ions by the primary and secondary alcohols. This shows that both the primary and secondary alcohols have been oxidised but the tertiary alcohol, 2-methylpropan-2-ol, has not.

Carboxylic acids

Reactions that form carboxylic acids

We have already seen how primary alcohols can be oxidised to aldehydes and then further oxidation of the aldehyde formed yields the carboxylic acid

Carboxylic acids are also made from nitriles, R—C≡N. When a nitrile is refluxed with dilute hydrochloric acid hydrolysis occurs, and the —C≡N group at the end of the hydrocarbon chain is converted to the —COOH group, forming a carboxylic acid (see page 237). For example:

$$\underset{\text{propanenitrile}}{CH_3CH_2CN} + HCl + 2H_2O \longrightarrow \underset{\text{propanoic acid}}{CH_3CH_2COOH} + NH_4Cl$$

Reacting as acids

Carboxylic acids are described as weak acids because their molecules do not dissociate (ionise) completely when added to water

However a small proportion of the molecules do dissociate, releasing the H+(aq) ions that characterise all acidic solutions with a pH value less than 7. For example, ethanoic acid forms aqueous hydrogen ions and ethanoate ions in water:

$$\underset{\text{ethanoic acid}}{CH_3COOH(aq)} \rightleftharpoons \underset{\text{ethanoate ion}}{CH_3COO^-(aq)} + H^+(aq)$$

You can learn more about the dissociation of carboxylic acids in Chapter 26 (pages 394–5).

The presence of $H^+(aq)$ ions in solutions of carboxylic acids means that they undergo all the usual reactions of acids. They react with

- alkalis to form a salt and water:
  $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$
- reactive metals to form a salt and hydrogen gas:
  $2CH_3COOH + Mg \longrightarrow (CH_3COO)_2Mg + H_2$
- carbonates to form a salt, water and carbon dioxide gas:
  $2CH_3COOH + K_2CO_3 \longrightarrow 2CH_3COOK + H_2O + CO_2$

Reduction of carboxylic acids

Carboxylic acids can be reduced to their corresponding primary alcohol by using the reducing agent lithium tetrahydridoaluminate, $LiAlH_4$, in dry ether at room temperature. Dry ether is used because $LiAlH_4$ reacts violently with water

In the simplified reduction equation, the symbol [H] can be used to represent the hydrogen atoms from the reducing agent (remember that in organic chemistry, reduction can be thought of as the addition of hydrogen atoms). So for ethanoic acid being reduced to ethanol, we can show the reaction as:

$$CH_3COOH + 4[H] \longrightarrow CH_3CH_2OH + H_2O$$

Chapter 18 - carbonyl compounds

The homologous series of aldehydes and ketones

You have met aldehydes and ketones, the main classes of carbonyl compounds, in Chapter 17. Remember:

- aldehydes can be formed from the oxidation of primary alcohols
- ketones can be formed from the oxidation of secondary alcohols

Preparation of aldehydes and ketones

Name	**Structural formula**
methanal	$HCHO$
ethanal	CH_3CHO
propanal	CH_3CH_2CHO
butanal	$CH_3CH_2CH_2CHO$
pentanal	$CH_3CH_2CH_2CH_2CHO$

Table 18.1 The names of aldehydes are derived from the name of the equivalent alkane, with the '-e' at the end of the name replaced by '-al'. Note that numbers are not needed when naming aldehydes, as the carbonyl group is always at the end of the carbon chain.

Name	**Structural formula**
propanone	CH_3COCH_3
butanone	$CH_3COCH_2CH_3$
pentan-2-one pentan-3-one	$CH_3COCH_2CH_2CH_3$ $CH_3CH_2COCH_2CH_3$

Table 18.2 Ketones are named by replacing the '-e' with '-one'. However, in ketone molecules larger than butanone we need to indicate the position of the carbonyl group.

1 OXIDATION OF A PRIMARY ALCOHOL

The general equation for the reaction in which an aldehyde is made from a primary alcohol is:

primary alcohol + oxygen atom from oxidising agent ⟶ aldehyde + water

For example:

$$\underset{\text{propan-1-ol}}{CH_3CH_2CH_2OH} + [O] \longrightarrow \underset{\text{propanal}}{CH_3CH_2CHO} + H_2O$$

The oxidising agent used is a solution of potassium dichromate(VI), which is orange, acidified with dilute sulfuric acid. To make the aldehyde, the primary alcohol is heated gently with acidified dichromate solution. The reaction mixture turns green as the orange dichromate ions, $Cr_2O_7^{2-}(aq)$, are reduced to green $Cr^{3+}(aq)$ ions.

The oxidising agent is added one drop at a time to the warm alcohol. The aldehyde made needs to be distilled off as it forms in the reaction vessel. This can be done because the aldehyde product will always have a lower boiling point than its corresponding alcohol. If the aldehyde is not distilled off as soon as it is formed, further heating

1 OXIDATION OF A PRIMARY ALCOHOL (CONTINUED)

with acidified dichromate solution will oxidise the aldehyde produced to a carboxylic acid. The apparatus used to prepare a sample of ethanal is shown in Figure 18.2.

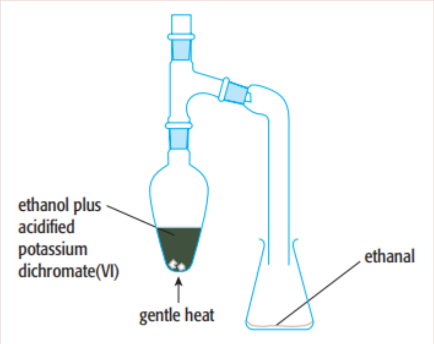


Figure 18.2 Distilling off and collecting the aldehyde, ethanal, formed in the mild oxidation of a primary alcohol, ethanol. The aqueous ethanal formed smells like rotting apples.

2 OXIDATION OF A SECONDARY ALCOHOL

The general equation for making a ketone is:

secondary alcohol + oxygen atom from oxidising agent ⟶ ketone + water

For example:

$$\underset{\text{propan-2-ol}}{CH_3CH(OH)CH_3} + [O] \longrightarrow \underset{\text{propanone}}{CH_3COCH_3} + H_2O$$

Once again, the oxidising agent used is a solution of potassium dichromate(VI), acidified with dilute sulfuric acid. To produce a ketone, this oxidising agent must be heated with a secondary alcohol. The ketone formed cannot be further oxidised, even if we reflux the reaction mixture and add excess oxidising agent. Therefore we do not need to distil out the ketone product immediately.

Reduction of aldehydes and ketones

Chemical reduction of an aldehyde or ketone produces an alcohol

aldehyde + reducing agent ⟶ primary alcohol
ketone + reducing agent ⟶ secondary alcohol

The reduction reaction is carried out by either:

■■ warming the aldehyde or ketone with an aqueous alkaline solution of sodium tetrahydridoborate

■■ adding lithium tetrahydridoaluminate dissolved in a dry ether, such as diethyl ether, at room temperature. The organic solvent has to be dry because lithium tetrahydridoaluminate is a more powerful reducing agent than sodium tetrahydridoborate and reacts vigorously in water.

Look at the equations below used to summarise these reduction reactions:

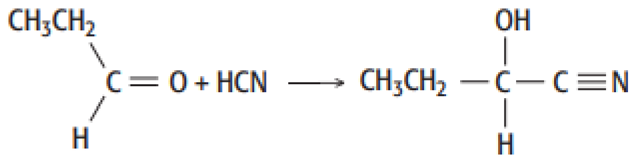
$$\underset{\text{ethanal}}{CH_3CHO} + 2[H] \longrightarrow \underset{\text{ethanol}}{CH_3CH_2OH}$$

$$\underset{\text{propanone}}{CH_3COCH_3} + 2[H] \longrightarrow \underset{\text{propan-2-ol}}{CH_3CH(OH)CH_3}$$

Nucleophilic addition with HCN

The addition reactions we have met so far have involved electrophilic addition across the C=C bond in alkene molecules

However, the attack is by a nucleophile, not an electrophile. We can show this using the **nucleophilic addition** reaction of propanal with HCN.



propanal 2-hydroxybutanenitrile

This is a useful reaction in synthetic chemistry, as it increases the length of the hydrocarbon chain in the original aldehyde molecule by one carbon atom.

The nitrile group ($-C{\equiv}N$) can then be easily:

- hydrolysed to a carboxylic acid
- reduced to an amine.

The hydrolysis can be carried out by refluxing with dilute hydrochloric acid:

$$-CN + H^+ + H_2O \longrightarrow -COOH + NH_4^+$$

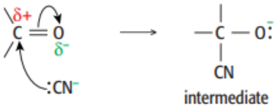
The reduction of the nitrile group to an amine can be carried out using sodium and ethanol:

$$-CN + 4[H] \longrightarrow -CH_2NH_2$$

Mechanism of nucleophilic addition

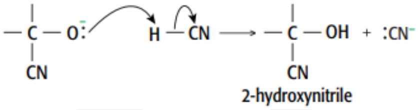
The carbonyl group, C=O, in aldehydes and ketones is polarised due to the high electronegativity of the oxygen atom. The electrons in the C=O bond are drawn nearer to the O atom, giving it a partial negative charge and leaving the C atom with a partial positive charge

First step



The negatively charged intermediate formed in the first step in the mechanism is highly reactive and quickly reacts with an H^+ ion (from HCN, from dilute acid or from water present in the reaction mixture). This forms the **2-hydroxynitrile** product.

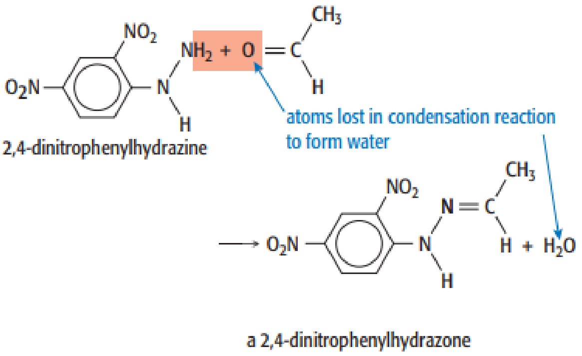
Second step



Testing for aldehydes and ketones

Testing for the carbonyl group

The reaction of an aldehyde or ketone with 2,4-dinitrophenylhydrazine is an example of a **condensation reaction**

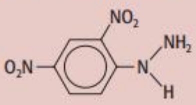


TESTING WITH 2,4-DNPH

The presence of a carbonyl group in an aldehyde or ketone can be easily tested for by adding a solution of 2,4-dinitrophenylhydrazine (often abbreviated to 2,4-DNPH). If an aldehyde or ketone is present, a deep-orange precipitate is formed (Figure 18.3).

Figure 18.3 The orange precipitate formed from 2,4-DNPH in a test with propanone, a ketone.

The structure of 2,4-dinitrophenylhydrazine is:



The precipitate formed can be purified by recrystallisation and its melting point can be measured experimentally. The identity of the compound that precipitated out can then be found by referring to melting point data. From this, the specific aldehyde or ketone used in the test can be identified.

Distinguishing between aldehydes and ketones

aldehydes can be further oxidised to form carboxylic acids, but ketones cannot be oxidised easily. We can use this difference to distinguish between an aldehyde and a ketone in simple chemical tests. The two tests most commonly used involve Tollens' reagent and Fehling's solution.

TESTING WITH TOLLENS' REAGENT

Tollens' reagent is an aqueous solution of silver nitrate in excess ammonia solution, sometimes called ammoniacal silver nitrate solution. The silver ions, Ag^+, in the solution act as a mild oxidising agent. When warmed, the Ag^+ ions will oxidise an aldehyde to form a carboxylate ion.

Under alkaline conditions any carboxylic acid formed is immediately neutralised to the carboxylate ion, $—COO^-$, as H^+ is removed from —COOH and a salt is formed.

In the redox reaction with an aldehyde, the Ag^+ ions themselves are reduced to silver atoms. The silver atoms form a 'mirror' on the inside of the tube, giving a positive test for an aldehyde (Figure 18.4).

There will be no change observed when a ketone is warmed with Tollens' reagent as no redox reaction takes place. It remains a colourless mixture in the test tube.

Figure 18.4 The 'before' and 'after' observations when Tollens' reagent is warmed with an aldehyde, such as ethanal.

TESTING WITH FEHLING'S SOLUTION

Fehling's solution is an alkaline solution containing copper(II) ions. When warmed with an aldehyde, the Cu^{2+} ions act as an oxidising agent. The aldehyde is oxidised to a carboxylate ion while the Cu^{2+} ions are reduced to Cu^+ ions. The clear blue Fehling's solution turns an opaque red/orange colour as a precipitate of copper(I) oxide forms throughout the solution (Figure 18.5).

Once again, ketones are not oxidised, so the Fehling's solution remains blue when warmed.

Figure 18.5 The 'before' and 'after' observations when Fehling's solution is warmed with an aldehyde, such as ethanal.

Reactions to form tri-iodomethane

Tri-iodomethane (iodoform) forms as a yellow precipitate with methyl ketones, i.e. compounds containing the CH_3CO group (Figure 18.6). Note that ethanal, CH_3CHO, an aldehyde, also contains the CH_3CO group.

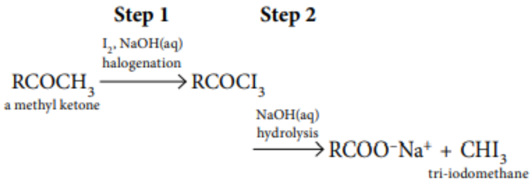
The reaction involves two steps:

1 the carbonyl compound is halogenated – the three hydrogen atoms in the CH_3 group are replaced by iodine atoms

2 the intermediate is hydrolysed to form the yellow precipitate of tri-iodomethane, CHI_3

Figure 18.6 The yellow precipitate of tri-iodomethane forming.

Here R is an alkyl group in a methyl ketone:



Testing for the $CH_3CH(OH)—$ group

The tri-iodomethane test can also be used to identify the presence of a secondary alcohol group on the carbon atom adjacent to a methyl group. This $CH_3CH(OH)—$ group is firstly oxidised by the alkaline iodine solution. This oxidation forms a methyl ketone, $RCOCH_3$, which then reacts via the two steps shown above to give the yellow tri-iodomethane precipitate, CHI_3.

You should note that there are two organic products formed in this reaction: one is tri-iodomethane and the other is the sodium salt of a carboxylic acid.

Infra-red spectroscopy

In **infra-red spectroscopy** a sample being analysed is irradiated with electromagnetic waves in the infra-red region of the electromagnetic spectrum. The machine used is called a spectrophotometer, and it detects the intensity of the wavelengths of infra-red radiation that passes through the sample.

If we irradiate the molecules with energy that corresponds to this frequency, it stimulates larger vibrations and energy is absorbed. This is called the **resonance frequency** of that vibration

These values will usually be given to you. You can see that absorption bands overlap considerably. That is why we need to use a **variety of techniques**.

Using the data in Table 18.3, note the broad bands in Figures 18.8 and 18.9 arising from the O H groups involved in hydrogen bonding in the alcohol and in the carboxylic acid. Contrast the width of these peaks with the sharp peak of the carbonyl group in the ester, ethyl ethanoate in Figure 18.10.

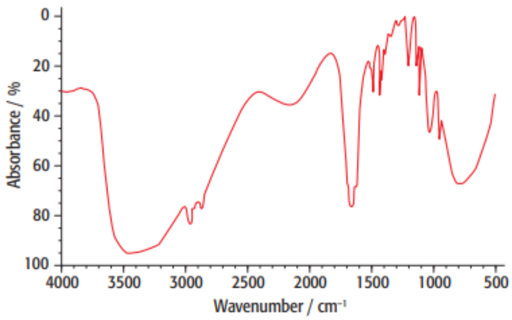


Figure 18.7 The infra-red spectrum of ethylamine, $CH_3CH_2NH_2$. Note that the percentage absorbance and the wavenumbers on the axes both get smaller in magnitude along each axis.

Bond	Functional groups containing the bond	Absorption range (in wavenumbers) / cm^{-1}	Appearance of peak (*s* = strong, *w* = weak)
C—O	alcohols, ethers, esters	1040–1300	*s*
C═C	aromatic compounds, alkenes	1500–1680	*w* unless conjugated
C═O	amides ketones and aldehydes esters	1640–1690 1670–1740 1715–1750	*s* *s* *s*
C≡C	alkynes	2150–2250	*w* unless conjugated
C≡N	nitriles	2200–2250	*w*
C—H	alkanes, CH_2—H alkenes/arenes, ═C—H	2850–2950 3000–3100	*s* *w*
N—H	amines, amides	3300–3500	*w*
O—H	carboxylic acids, RCO_2—H H-bonded alcohol, RO—H free alcohol, RO—H	2500–3000 3200–3600 3580–3650	*s* and very broad *s* *s* and sharp

Table 18.3 Some characteristic infra-red absorbance bands and their intensities.

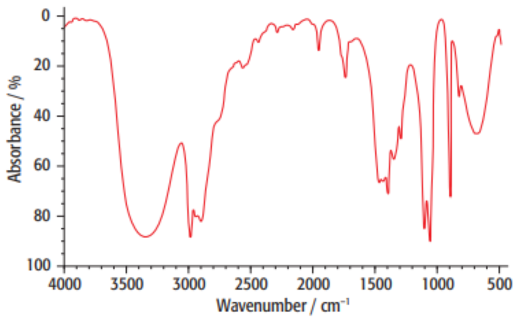


Figure 18.8 The infra-red spectrum of ethanol, CH_3CH_2OH.

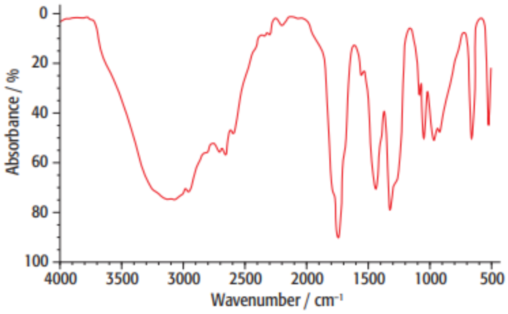


Figure 18.9 The infra-red spectrum of ethanoic acid, CH_3COOH.

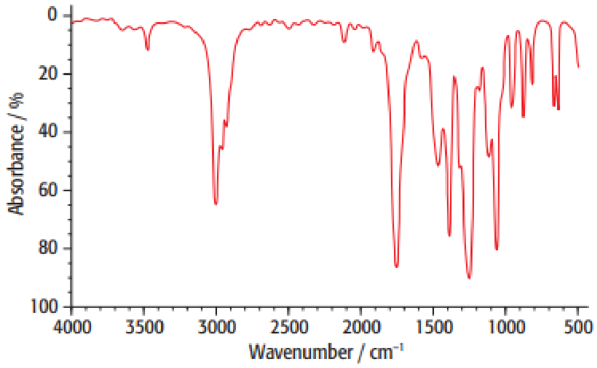
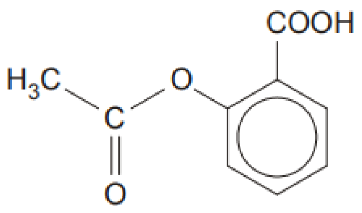


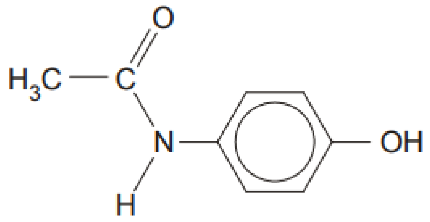
Figure 18.10 The infra-red spectrum of ethyl ethanoate, $CH_3COOCH_2CH_3$.

Revision questions

1. Aspirin and paracetamol are commonly available painkillers.



aspirin



paracetamol

Aspirin and paracetamol can be prepared using ethanoic anhydride, $(CH_3CO)_2O$.

Some examples of the reactions of ethanoic anhydride are shown below.

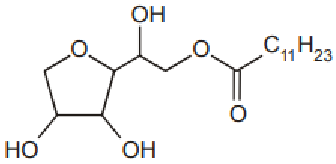
reaction 1 $(CH_3CO)_2O + CH_3OH \rightarrow CH_3COOCH_3 + CH_3COOH$

reaction 2 $(CH_3CO)_2O + CH_3NH_2 \rightarrow CH_3CONHCH_3 + CH_3COOH$

reaction 3 $(CH_3CO)_2O + C_6H_5OH \rightarrow CH_3COOC_6H_5 + CH_3COOH$

Draw the structure of a compound that could react with ethanoic anhydride to form aspirin.

2. The demand for 'natural' shampoos and detergents has led to the development of more biodegradable detergents such as sorbitan monolaurate, which is made from plants.



sorbitan monolaurate

(i) Suggest a type of reaction that could break down sorbitan monolaurate when it is washed into drains and rivers. Explain your answer and state the type of organic products formed.

(ii) Suggest one other reason why detergents such as sorbitan monolaurate are regarded as 'environmentally friendly'.

3. An ester **D** with the formula, $CH_3CH_2COOCH_2CH(CH_3)_2$, is used in rum flavouring.

(a) Draw a displayed formula of ester **D**.

(b) Outline how you could obtain a sample of ester D, starting with a named carboxylic acid and a named alcohol. Include any essential reaction conditions and write an equation for the reaction. You do not need to include any details of the separation or purification of the ester.

(c) State a spectroscopic method that could be used to confirm that a sample of ester D has a molecular mass of 130. Explain how you would obtain the molecular mass of D from the spectrum.

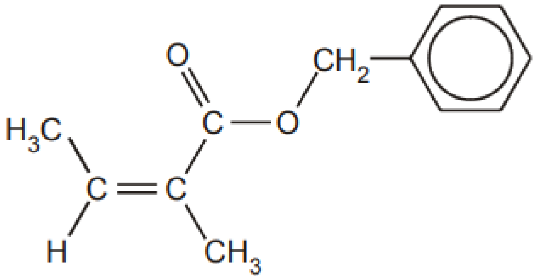
4. Linoleic acid, $C_{17}H_{31}COOH$, is an unsaturated fatty acid found in triglycerides from sunflower oil.

(i) Draw the structure of the triglyceride made from linoleic acid, $C_{17}H_{31}COOH$, and propane-1,2,3-triol. Show clearly all the bonds in the ester groups.

(ii) Deduce the number of carbon to carbon double bonds in a molecule of the triglyceride.

5. Explain why triglycerides are soluble in non-polar solvents and not in water.

6. Compound **A** is used to add the flavour of mushrooms to foods.



compound **A**

(a) (i) Apart from the benzene ring, name the two functional groups in compound **A**.

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(ii) Draw the skeletal formula of compound **A**.

(iii) Deduce the molecular formula of compound A

(b) Compound B is a stereoisomer of compound A. Explain what is meant by the term stereoisomerism. Use compounds A and B to illustrate your answer.

(c) If the food is cooked for a long time, naturally occurring acids catalyse the hydrolysis of compound A. Draw structures to show the two organic compounds formed by the acid hydrolysis of compound A

(d) The hydrolysis of compound A can be monitored by sampling the mixture at regular intervals, separating the components, and recording their infra-red spectra.

(i) State two absorptions that would be expected in the infra-red spectrum of compound A, and identify the parts of the molecule responsible for each.

(ii) Suggest a wavenumber range within the spectrum that could be used to clearly distinguish compound A from the products formed by the hydrolysis reaction. Explain your answer.

7. Glyceryl trihexanoate is a triglyceride that can be made from glycerol (propane-1,2,3-triol) and hexanoic acid, $C_5H_{11}COOH$.

Draw the structure of glyceryl trihexanoate. Show every bond in the functional groups.

8. As a wine ages, some of the acids slowly react with ethanol in the wine to produce esters.

(i) Draw a displayed formula to show the structure of the ester formed when **lactic acid** reacts with ethanol.

(ii) Suggest what effect this process might have on the flavour of the wine. Explain your reasoning.

9. Reaction of geraniol with ethanoic acid can be used to make ester Z, which is used in chewing gum and desserts.

(i) Suggest why esters are used in the manufacture of foods.

(ii) State the conditions needed to make ester Z from geraniol and ethanoic acid.

(iii) Complete the equation for the formation of ester **Z**.

$$+ \quad C_9H_{15}CH_2OH \quad \rightarrow$$