# Edexcel

# AS - Level

# Chemistry

CODE: (WCH11)

# Topic 10

# Organic chemistry: halogenoalkanes, alcohol and spectra

# 10A General principles in organic chemistry

## REACTIONS IN ORGANIC CHEMISTRY

In Topic 4, you learned that there were five different types of organic reaction. In this topic you will learn about two more types. All seven types of reaction are considered here so that you don't have to refer back to Topic 4.

## ADDITION REACTIONS

In this type of reaction, two reactant species combine together to form a single product species. Usually all the species are molecules. A general equation for an addition reaction is:

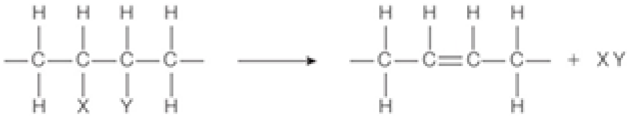
$$A + B \rightarrow C$$

One example is the reaction between ethene and bromine:

$$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$$

## ELIMINATION REACTIONS

This is one of the two new types of reaction you are learning about. In this type, two atoms or groups are removed from a molecule (they are eliminated from the molecule). The atoms or groups are removed from neighbouring carbon atoms. This resul in the formation of a second bond between the two carbon atom A general equation for an elimination reaction is:



X and Y represent atoms or groups of atoms. In this example, the organic product has a double bond between the central carbon atoms and a small molecule, XY, is also formed.

One example you will meet later is the reaction between bromoethane and ethanolic potassium hydroxide:

$$CH_3CH_2Br + KOH \rightarrow CH_2{=}CH_2 + KBr + H_2O$$

## SUBSTITUTION REACTIONS

In this type of reaction, two reactant species combine together to form two product species. Usually all the species are molecules or ions. A general equation for a substitution reaction is:

$$A + B \rightarrow C + D$$

One example is the reaction between bromoethane and potassium hydroxide. Potassium hydroxide is an ionic compound, and as the potassium ion is a spectator ion, the reaction only involves the hydroxide ion. An equation for this reaction is:

$$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$$

In this reaction, the OH group has taken the place of, or *substituted*, the Br atom. You might think that this type of reaction is like the displacement reactions you met in **Topic 8C.2**. The equation for one of these displacement reactions is $Mg + CuSO_4 \rightarrow MgSO_4 + Cu$. However, this equation can be simplified to $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$, which means that electrons are being transferred from Mg to $Cu^{2+}$, so it is a redox reaction. The reaction between bromoethane and the hydroxide ion is not a redox reaction, so it is better not to think of substitution and displacement reactions as being the same type.

## OXIDATION REACTIONS

In this type of reaction, one organic compound is oxidised, usually by an inorganic reagent. This means that the organic compound can either lose hydrogen or gain oxygen. There isn't a suitable general equation that can be used for this type of reaction, but here is one example you will see later in this topic: the oxidation of ethanol by a mixture of potassium dichromate(VI) and sulfuric acid. The equation is not written to include the inorganic reagent because it would be very complicated. Usually the oxygen atoms produced by the oxidising agent are shown using the symbol [O], so the equation then becomes:

$$C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$$

You can now see why this reaction is classified as oxidation: the ethanol molecule loses two hydrogen atoms.

## REDUCTION REACTIONS

In this type of reaction, an organic compound is reduced, sometimes by hydrogen gas and a catalyst and sometimes by an inorganic reagent. This means that the organic compound can either gain hydrogen or lose oxygen.

$C_2H_4 + H_2 \rightarrow C_2H_6$

You can now see why this reaction is classified as reduction: the ethene molecule gains two hydrogen atoms. Note that this is also an example of an addition reaction.

## HYDROLYSIS REACTIONS

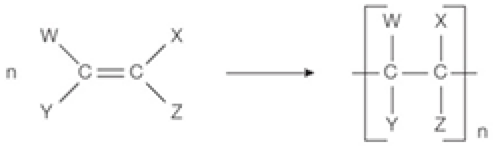
This is another new type of reaction. In hydrolysis reactions, an organic compound reacts with water. The OH group of water replaces an atom or group in the organic compound. A general equation for a hydrolysis reaction is:

$RX + H_2O \rightarrow ROH + HX$

You might think that this is an example of a substitution reaction, and you would be right! Hydrolysis reactions are really substitution reactions in which the OH from a water molecule replaces an atom or group (usually a halogen) in an organic compound.

## POLYMERISATION REACTIONS

At IAS, all the polymerisation reactions you see are examples of addition polymerisation. If you study chemistry in more detail at IAL, you will also meet examples of condensation polymerisation. However, we will not consider these in this topic. In addition polymerisation, very large numbers of a reactant molecule (sometimes of two different reactant molecules) react together to form one very large product molecule. A general equation for a polymerisation reaction is:



A familiar example of this type of reaction is the polymerisation of ethene to poly(ethene).

## REACTION MECHANISMS

You have already learnt about reaction mechanisms in Topics 4 and 5. Just to remind you, a mechanism tries to explain the actual changes that occur during a reaction, especially in the bonding between the atoms. A mechanism is a sequence of two or more steps, each one represented by an equation, that shows how a reaction takes place.

So far in this book, you have met two different types of reaction mechanism:

Mechanism 1 free radical substitution in alkanes
Mechanism 2 electrophilic addition to alkenes
In this topic, you will look at one more:
Mechanism 3 nucleophilic substitution in halogenoalkanes

## HOMOLYTIC AND HETEROLYTIC BOND BREAKING

In mechanism 1, the type of bond breaking is homolytic. This is when a covalent bond breaks, and each atom keeps one electron from the shared pair of electrons in the bond. Free radicals are formed.

In mechanisms 2 and 3, the type of bond breaking is heterolytic, when a covalent bond breaks, and one atom keeps both electrons from the shared pair of electrons in the bond. This atom becomes a negative ion, and can act as a nucleophile. The other atom becomes a positive ion, and can act as an electrophile.

### ELECTROPHILES AND NUCLEOPHILES

In mechanism 1, the attacking species are free radicals, such $Cl^{\circ}$
as
In mechanism 2, the attacking species are electrophiles, such as the H of an HBr molecule.
In mechanism 3, the attacking species are nucleophiles, such as the OH- ion.

### THE ROLE OF BOND POLARITY IN MECHANISMS

In mechanism 1, the reactants are alkanes and halogens, whose bonds are either non-polar or only very slightly polar. This means that the type of bond breaking is most likely to be homolytic. In mechanisms 2 and 3, the reactants are molecules such as hydrogen halides and halogenoalkanes, whose bonds are polar. This means that the type of bond breaking is most likely to be heterolytic.

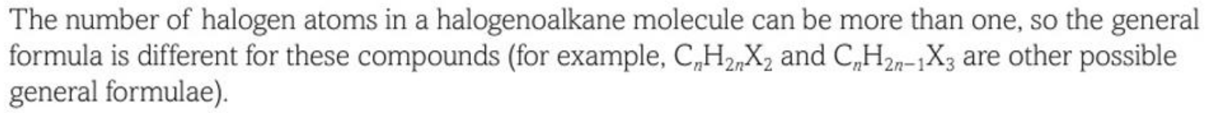
## 10B 1 Halogenoalkanes and hydrolysis reactions

### WHAT ARE HALOGENOALKANES?

The halogenoalkanes are a homologous series of compounds with the general formula $C_nH_{2n+1}X$. Think of them as the result of replacing a hydrogen atom in a hydrocarbon by a halogen atom. X represents a halogen atom - usually bromine or chlorine, but it could also be fluorine or iodine. You have already met halogenoalkanes earlier in this book-chloromethane is a halogenoalkane and is the product of the reaction between methane and chlorine.

The symbol R is often used in organic chemistry to represent any alkyl group (such as methyl or ethyl). The formula of a halogenoalkane could be simplified to RX.

The number of halogen atoms in a halogenoalkane molecule can be more than one, so the general formula is different for these compounds

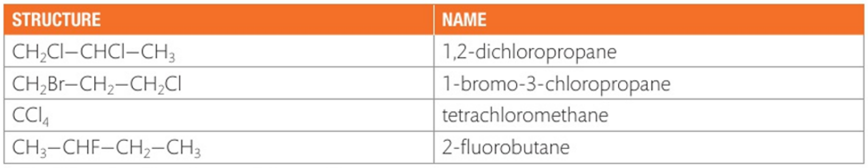


The number of halogen atoms in a halogenoalkane molecule can be more than one, so the general formula is different for these compounds (for example, $C_nH_{2n}X_2$ and $C_nH_{2n-1}X_3$ are other possible general formulae).

**fig A** The most problematic halogenoalkanes are those containing both chlorine and fluorine. They are known as chlorofluorocarbons (CFCs for short) and were used in aerosol cans for decades. We have known for a long time that they damage the ozone layer in the upper atmosphere and, through international agreement, they are mostly no longer used.

## NAMING HALOGENOALKANES

We have already met the names of some halogenoalkanes, but **table A** shows some examples to remind you.

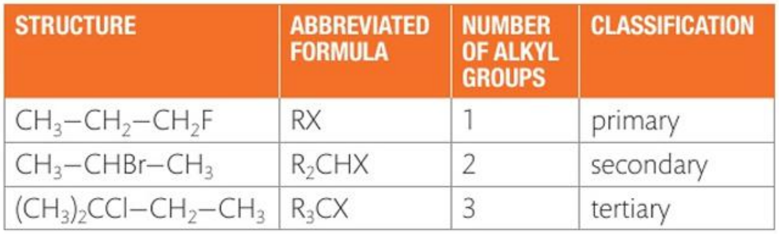


| STRUCTURE | NAME |
|---|---|
| $CH_2Cl-CHCl-CH_3$ | 1,2-dichloropropane |
| $CH_2Br-CH_2-CH_2Cl$ | 1-bromo-3-chloropropane |
| $CCl_4$ | tetrachloromethane |
| $CH_3-CHF-CH_2-CH_3$ | 2-fluorobutane |

**table A** Examples of how to name halogenoalkanes.

## CLASSIFYING HALOGENOALKANES

You have met the terms 'primary', 'secondary' and 'tertiary' in the topic referring to carbocations (see Topic 5A.4). Halogenoalkanes are classified in a similar way, depending on the number of alkyl groups joined to the C atom bonded to the halogen atom. Table B shows some examples.



| STRUCTURE | ABBREVIATED FORMULA | NUMBER OF ALKYL GROUPS | CLASSIFICATION |
|---|---|---|---|
| $CH_3-CH_2-CH_2F$ | RX | 1 | primary |
| $CH_3-CHBr-CH_3$ | $R_2CHX$ | 2 | secondary |
| $(CH_3)_2CCl-CH_2-CH_3$ | $R_3CX$ | 3 | tertiary |

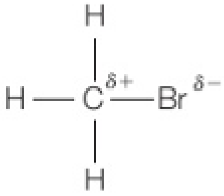
**table B** Examples of how to classify halogenoalkanes.

## WHAT MAKES HALOGENOALKANES REACTIVE?

Hydrocarbons contain only hydrogen and carbon atoms, which have similar electronegativities, so their bonds are almost non-polar.

Halogenoalkanes contain a halogen atom with an electronegativity higher than that of carbon, so the C-X bond is polar. This bond polarity can be indicated using the partial charges 8+ and 8-.

Down Group 7 of the Periodic Table, the electronegativities of the halogens decrease from fluorine to iodine, so the polarity of the C-X bond also decreases.



**Nucleophiles** are species that attract slightly positive or electron-deficient parts of a molecule, causing reactions in halogenoalkanes. These carbon atoms attract negative ions or molecules with a slightly negative atom, using a lone pair of electrons when attacking another species.

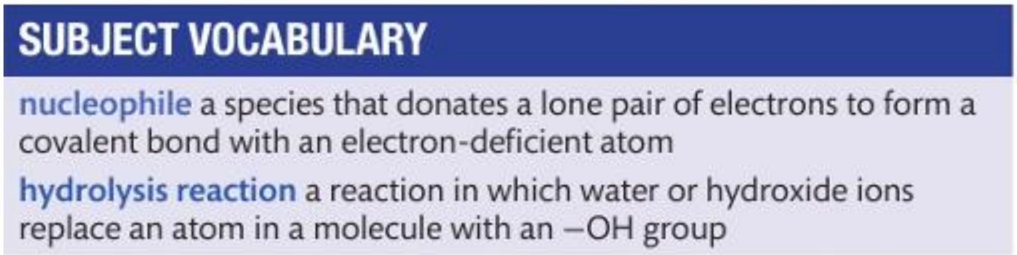
## HYDROLYSIS REACTIONS

When a halogenoalkane is added to water, a reaction begins, but it may take some time to complete. A water molecule contains polar bonds, and the 8- oxygen atom in water is attracted to the 8+ carbon atom in the halogenoalkane.

The reaction that occurs can be represented by the equation below, in which R represents any alkyl group:

$$RX + H_2O \rightarrow ROH + HX \text{ or } RX + H_2O \rightarrow ROH + H^+ + X^-$$

This type of reaction is known as a **hydrolysis reaction**. 'Hydro' refers to water and 'lysis' refers to splitting, so it means splitting with water.



**SUBJECT VOCABULARY**

**nucleophile** a species that donates a lone pair of electrons to form a covalent bond with an electron-deficient atom

**hydrolysis reaction** a reaction in which water or hydroxide ions replace an atom in a molecule with an –OH group

## 10B 2 Comparing the rates of hydrolysis reactions

### PRACTICAL ASPECTS

If instead of adding water in a hydrolysis reaction, silver nitrate solution is added, then the progress of the reaction can be followed. You may remember that silver nitrate can be used in a test for halide ions because the silver ions in silver nitrate react with the halide ions formed in the hydrolysis to give a precipitate:

$$Ag^+ + X^- \rightarrow AgX$$

This means that we can tell how quickly the hydrolysis reaction occurs by observing how quickly the precipitate of AgX forms.

Without going into full practical details, a comparison of the rates of these reactions involves:

- using ethanol as a solvent for the mixture (halogenoalkanes and aqueous silver nitrate do not mix, but form separate layers)
- controlling variables such as temperature and the concentration and quantity of halogenoalkanes timing the appearance of the precipitate (although this is difficult to do accurately because a precipitate may first appear faint, but become thicker with time).

Fig A shows that there is no precipitate in tube (a), a faint cream-coloured precipitate in tube (b) and a thicker pale yellow precipitate in tube (c). These observations are caused by the reaction of a chloroalkane in (a), a bromoalkane in (b) and an iodoalkane in (c).

Two types of comparison can be made. You can:

- compare halogenoalkanes with the same structure but containing different halogens
- compare halogenoalkanes containing the same halogen but with different structures.

Fluoroalkanes are comparatively very unreactive, so reactions involving them are often omitted.

## INTERPRETING THE RESULTS FOR DIFFERENT HALOGENS

Table A shows the trend when the halogen is different.

| SAME STRUCTURE BUT DIFFERENT HALOGEN | RESULT |
|---|---|
| 1-iodobutane | fastest |
| 1-bromobutane | |
| 1-chlorobutane | slowest |

**table A** Examples comparing halogenoalkanes with the same structure but with different halogens.

You might suppose that the halogenoalkane with the most polar bond would be the fastest to be hydrolysed (in this case, 1-chlorobutane) because the $\delta+$ charge on the carbon atom is greatest, so the attacking nucleophile should be attracted more strongly.

This is true, but there is another, more important factor to consider. Bond breaking requires energy, and weaker bonds break more easily than stronger bonds. **Table B** shows (mean) bond enthalpies. You can see that the C—I bond is the weakest and the C—Cl bond is the strongest.

| BOND | BOND ENTHALPY / $kJ\,mol^{-1}$ |
|---|---|
| C—Cl | +346 |
| C—Br | +290 |
| C—I | +228 |

**table B** Mean bond enthalpies.

Under the same conditions, the C—I bond breaks most easily, forming $I^-$ ions, and so a precipitate of AgI forms more quickly.

The C—F bond is much stronger (+467 $kJ\,mol^{-1}$) than any of the others, which explains why fluoroalkanes are not often used in these hydrolysis experiments.

## INTERPRETING THE RESULTS FOR DIFFERENT STRUCTURES

**Table C** shows the trend when the structure is different.

| SAME HALOGEN BUT DIFFERENT STRUCTURE | RESULT |
|---|---|
| 2-bromo-2-methylpropane (tertiary) | fastest |
| 2-bromobutane (secondary) | |
| 1-bromobutane (primary) | slowest |

**table C** Examples comparing halogenoalkanes with the same halogen but with different structures.

To explain why tertiary halogenoalkanes are more rapidly hydrolysed than secondary and primary compounds requires a detailed understanding of two different reaction mechanisms, and is beyond the scope of this book, but will be dealt with in **Topic 15A (Book 2: IAL)**.

# 10B 3 Halogenoalkane reactions and mechanisms

### SUBSTITUTION REACTIONS

The hydrolysis reactions in **Topics 10B.1** and **10B.2** involved replacing a halogen atom (X) with a hydroxyl group (OH). These are substitution reactions, and here is a summary of the four reactions you need to know.

Reaction 1 $RX \xrightarrow{H_2O\text{/warm}} ROH$

Reaction 2 $RX \xrightarrow{KOH\text{/heat under reflux}} ROH$

Reaction 3 $RX \xrightarrow{KCN\text{/heat under reflux}} RCN$

Reaction 4 $RX \xrightarrow{NH_3\text{/heat in sealed tube}} RNH_2$

## REACTION 1

This is the hydrolysis reaction you met in Topic 10B.1.

## REACTION 2

Heating a halogenoalkane with aqueous potassium hydroxide under reflux is one way of making alcohols. The attacking nucleophile is the OH- ion. An example of an equation for this reaction is the conversion of 1-chloropropane into propan-1-ol:

$$CH_3CH_2CH_2Cl + KOH \rightarrow CH_3CH_2CH_2OH + KCl$$

or

$$CH_3CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2OH + Cl^-$$

The advantage of an ionic equation is that the nucleophile is clearly shown.

## REACTION 3

Heating a halogenoalkane with potassium cyanide dissolved in ethanol under reflux is one way of making **nitriles**. The attacking nucleophile is the CN- ion

$$CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$$

or

$$CH_3CH_2Br + CN^- \rightarrow CH_3CH_2CN + Br^-$$

## REACTION 4

Heating a halogenoalkane with ammonia solution under pressure in a sealed tube is one way of making primary amines. The sealed tube is needed because ammonia is a gas and would otherwise escape from the apparatus before it could react. The attacking nucleophile is the NH3 molecule. An example of an equation for this reaction is the conversion of 1-iodobutane into butylamine:

$$CH_3CH_2CH_2CH_2I + NH_3 \rightarrow CH_3CH_2CH_2CH_2NH_2 + HI$$

This equation looks similar to those for Reactions 1–3, but it isn't quite the full story. Like $NH_3$, the organic product is a base, so it would react with the inorganic product, the acid HI, to form a salt. So a better equation is:

$$CH_3CH_2CH_2CH_2I + NH_3 \rightarrow CH_3CH_2CH_2CH_2NH_3^+ + I^-$$

However, this is only the first step because the product is a salt, not a primary amine. To produce a high yield of the amine, the ammonia is used in excess, and some of this excess ammonia reacts in a second step to produce the amine:

$$CH_3CH_2CH_2CH_2NH_3^+I^- + NH_3 \rightarrow CH_3CH_2CH_2CH_2NH_2 + NH_4^+I^-$$

The final products are butylamine and ammonium iodide. These two steps are often combined as:

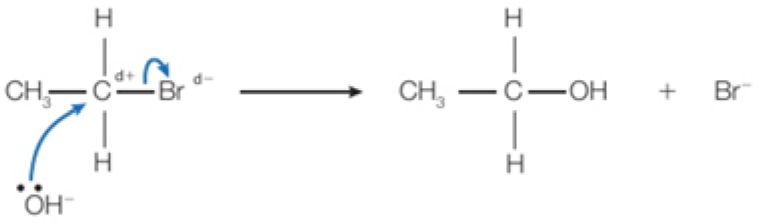
$$CH_3CH_2CH_2CH_2I + 2NH_3 \rightarrow CH_3CH_2CH_2CH_2NH_2 + NH_4^+I^-$$

## NUCLEOPHILIC SUBSTITUTION MECHANISMS

You have already learned about mechanisms for free radical substitution and electrophilic addition; here is a different mechanism to learn about.
In each reaction the attacking species is a nucleophile, so the reaction type is described as **nucleophilic substitution**. You only need to know about mechanisms for primary halogenoalkanes undergoing Reactions 2 and 4.

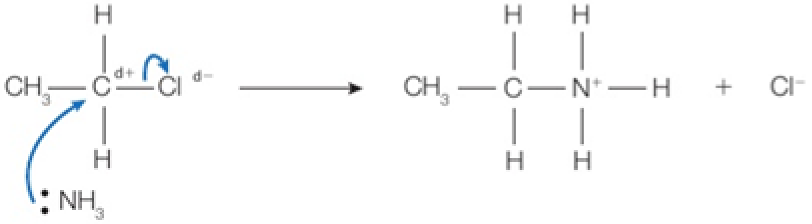
## MECHANISM OF REACTION 2

One example is the reaction between bromoethane and aqueous potassium hydroxide. The reaction starts with the donation of a lone pair of electrons from the oxygen of a hydroxide ion to the electron-deficient carbon atom and the formation of a C-O bond. At the same time, the electrons in the C-Br bond move to the Br atom, resulting in the breaking of the C-Br bond. This type of bond breaking is known as heterolytic fission. 'Hetero' indicates different, and you already know that 'lysis' indicates breaking.

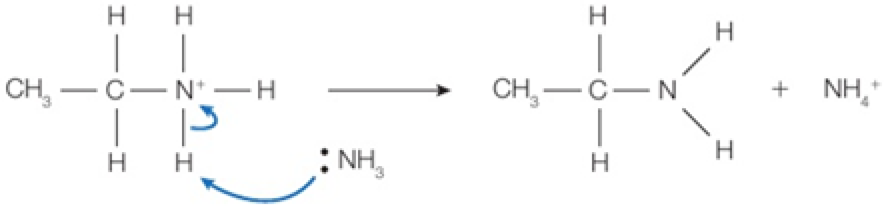


## MECHANISM OF REACTION 4

One example is the reaction between chloroethane and ammonia. The first step of the reaction involves the donation of a lone pair of electrons from the nitrogen of an ammonia molecule to the electron-deficient carbon atom and the formation of a C-N bond. At the same time, the electrons in the C-Cl bond move to the Cl atom, resulting in the breaking of the C-Cl bond.

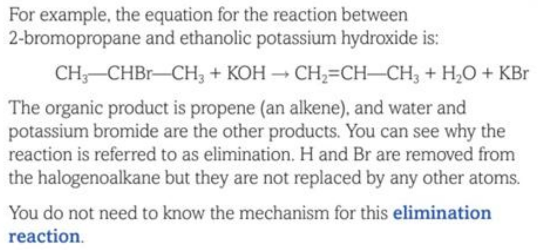


The second step of the reaction involves another ammonia molecule acting as a base and removing a hydrogen ion from the ion formed in the first step.



## ELIMINATION REACTIONS

Reaction 2 above is a nucleophilic substitution reaction, but using a different solvent (ethanol instead of water) causes a different reaction to occur. When a halogenoalkane is heated with **ethanolic** potassium hydroxide, the OH- ion acts as a base and not as a nucleophile.

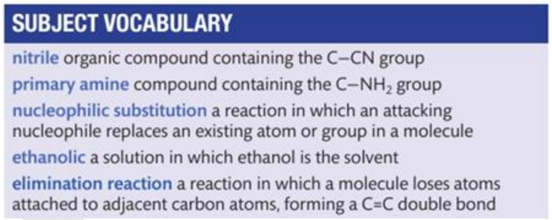


For example, the equation for the reaction between 2-bromopropane and ethanolic potassium hydroxide is:

$$CH_3—CHBr—CH_3 + KOH \rightarrow CH_2{=}CH—CH_3 + H_2O + KBr$$

The organic product is propene (an alkene), and water and potassium bromide are the other products. You can see why the reaction is referred to as elimination. H and Br are removed from the halogenoalkane but they are not replaced by any other atoms.

You do not need to know the mechanism for this **elimination reaction**.



**SUBJECT VOCABULARY**

**nitrile** organic compound containing the C–CN group

**primary amine** compound containing the $C–NH_2$ group

**nucleophilic substitution** a reaction in which an attacking nucleophile replaces an existing atom or group in a molecule

**ethanolic** a solution in which ethanol is the solvent

**elimination reaction** a reaction in which a molecule loses atoms attached to adjacent carbon atoms, forming a C=C double bond

# 10C 1 Alcohols and some of their reactions

## WHAT ARE ALCOHOLS?

The alcohols are a homologous series of compounds with the general formula C,H2n+1OH. Think of them as the result of replacing a hydrogen atom in a hydrocarbon with a hydroxyl group. You have already met alcohols in Topic 10B.1 as the products of the hydrolysis of halogenoalkanes.

The symbol R can be used to represent an alkyl group, as with halogenoalkanes. The formula of an alcohol can be simplified to ROH.

## NAMING ALCOHOLS

We have already discussed how to name alcohols in Topic 4A.4, but table A shows some examples to remind you.

| STRUCTURE | NAME |
|---|---|
| $CH_3–CH(OH)–CH_3$ | propan-2-ol |
| $CH_3–CH_2–CH_2–CH_2OH$ | butan-1-ol |
| $(CH_3)_3C–CH_2OH$ | 2,2-dimethylpropan-1-ol |
| $CH_2(OH)–CH(OH)–CH_2OH$ | propane-1,2,3-triol |

**table A** Examples of how to name alcohols.

**fig A** Sanitising hand gels containing alcohols are used in hospitals to reduce infection risks to patients.

You will have come across the last example in foods, medicines and personal care products. Its common names are glycerol and glycerine. You can see how the IUPAC system can be adapted to name compounds with more than one OH group.

## CLASSIFYING ALCOHOLS

You have met the terms primary, secondary and tertiary applied to carbocations (in Topic 5A.4) and to halogenoalkanes (in Topic 10B.1).

Alcohols are classified in a similar way, depending on the number of alkyl groups joined to the C atom bonded to the hydroxyl group. Table B shows some examples.

| STRUCTURE | ABBREVIATED FORMULA | NUMBER OF ALKYL GROUPS | CLASSIFICATION |
|---|---|---|---|
| $CH_3–CH_2–CH_2OH$ | ROH | 1 | primary |
| $CH_3–CH(OH)–CH_3$ | $R_2CHOH$ | 2 | secondary |
| $(CH_3)_2C(OH)–CH_2–CH_3$ | $R_3COH$ | 3 | tertiary |

**table B** Examples of how to classify alcohols.

## REACTIONS

In this topic, the reactions of alcohols we cover are:

- combustion
- conversions to halogenoalkanes
- dehydration to alkenes.

Reaction mechanisms are not required for any of these reactions.

## COMBUSTION

You have already seen in Topic 4B.3 that alcohols are used as biofuels. If combustion is complete, the products are carbon dioxide and water. This is the equation for the complete combustion of ethanol:

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

## CONVERSIONS TO HALOGENOALKANES

These reactions involve replacing the hydroxyl group in an alcohol molecule with a halogen atom. The reaction is known as halogenation. However, just adding a halogen to an alcohol does not work. A different method is needed for each halogen.

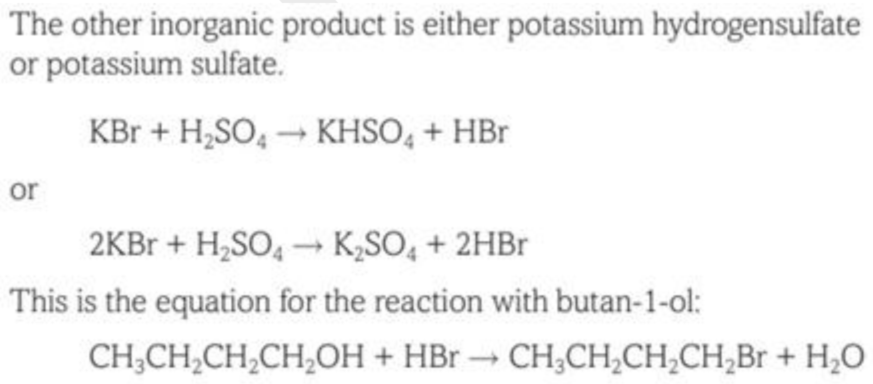
Chlorination is carried out using phosphorus(V) chloride (a white solid, also known as phosphorus pentachloride). The reaction is very vigorous at room temperature, so the alcohol and phosphorus(V) chloride reaction mixture does not need heating. There are also two inorganic products: phosphoryl chloride and hydrogen chloride. This is the equation for the reaction with propan-1-ol:

$$CH_3CH_2CH_2OH + PCl_5 \rightarrow CH_3CH_2CH_2Cl + POCl_3 + HCl$$

Chlorination of tertiary alcohols can be done in a different way, using a method that does not work well for primary and secondary alcohols. The alcohol needs only to be mixed (by shaking) with concentrated hydrochloric acid at room temperature. This is the equation for the reaction with 2-methylpropan-2-ol:

$$(CH_3)_3COH + HCl \rightarrow (CH_3)_3CCl + H_2O$$

Bromination is carried out using a mixture of potassium bromide and about 50% concentrated sulfuric acid. The reaction mixture is warmed with the alcohol. It is better to write two equations, rather than one, as the inorganic reagents first react together to form hydrogen bromide



The other inorganic product is either potassium hydrogensulfate or potassium sulfate.

$$KBr + H_2SO_4 \rightarrow KHSO_4 + HBr$$

or

$$2KBr + H_2SO_4 \rightarrow K_2SO_4 + 2HBr$$

This is the equation for the reaction with butan-1-ol:

$$CH_3CH_2CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2CH_2Br + H_2O$$

This is the equation for the reaction with ethanol:

$$3C_2H_5OH + PI_3 \rightarrow 3C_2H_5I + H_3PO_3$$

The inorganic product is phosphonic acid (often known as phosphorous acid).

### DEHYDRATION TO ALKENES

Dehydration is done by heating the alcohol with concentrated phosphoric acid. The reaction is similar to the elimination reaction of a halogenoalkane, with the OH group and a hydrogen atom from an adjacent carbon atom being removed and a C=C double bond formed in the carbon chain.

You can see why the reaction is described as dehydration, as water is the only inorganic product. These are the equations for a reaction in which there are two possible products, starting with butan-2-ol:

$$CH_3CH(OH)CH_2CH_3 \rightarrow \underset{\text{but-1-ene}}{CH_2{=}CHCH_2CH_3} + H_2O$$

and

$$CH_3CH(OH)CH_2CH_3 \rightarrow \underset{\text{but-2-ene}}{CH_3CH{=}CHCH_3} + H_2O$$

**SUBJECT VOCABULARY**

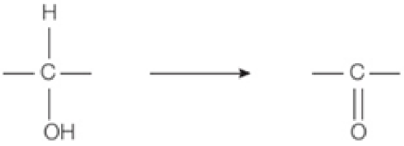
**halogenation** a reaction where the hydroxyl group in an alcohol molecule is replaced by a halogen atom

**dehydration** a reaction where the hydroxyl group from an alcohol molecule, and a hydrogen atom from an adjacent carbon atom, are removed, forming a C=C double bond

## 10C 2 Oxidation reactions of alcohols

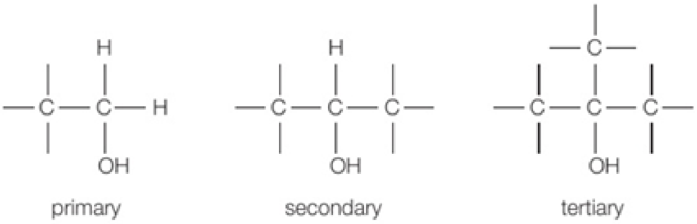
### BACKGROUND

There are different ways of considering oxidation and reduction. In this topic, the best way to consider oxidation is as the loss of hydrogen from an alcohol molecule. Unlike dehydration, covered in Topic 10C.1, oxidation affects only one carbon atom. The atoms removed from an alcohol molecule are the hydrogen of the OH group and a hydrogen atom from the carbon atom joined to the OH group, as shown below.



The organic product contains a C=O group, known as a carbonyl group.

The diagrams below should help you to understand why primary and secondary alcohols, but not tertiary alcohols, can be oxidised in this way.



primary secondary tertiary

Only the primary and secondary structures have a hydrogen atom on the C of the C—OH group – the tertiary structure does not.

## THE PRODUCTS OF OXIDATION

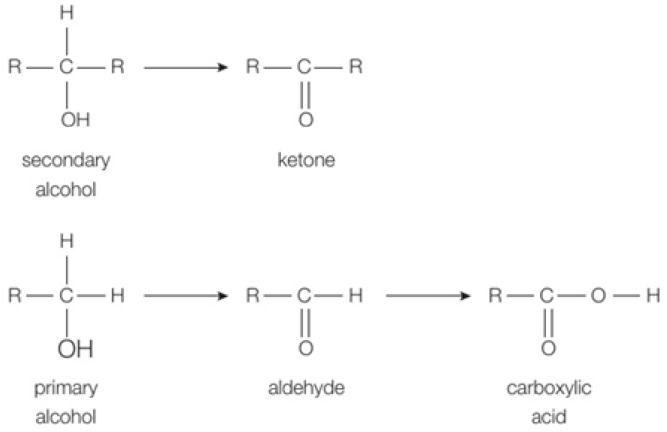
### KETONES

When a secondary alcohol is oxidised, the organic product belongs to a homologous series called **ketones**. A simplified formula for a ketone is RCOR. Using the same symbol R twice suggests that the two alkyl groups are the same (for example, two ethyl groups). This is not necessarily the case, but if the two alkyl groups are meant to be different, then the R symbols can be altered slightly.

### ALDEHYDES AND CARBOXYLIC ACIDS

When a primary alcohol is oxidised, the organic product belongs to a homologous series called **aldehydes**. A simplified formula for an aldehyde is RCHO. This should not be written as RCOH, which would imply that the molecule contains an OH group.

oxygen atom gained goes between the C and H of the CHO group. The organic product belongs to a homologous series called **carboxylic acids**. A simplified formula for a carboxylic acid is RCOOH.



The oxidation reactions typically involve a mixture of potassium dichromate(VI) and dilute sulfuric acid, represented by [O], which changes color from orange to green. Equations for these reactions can be written, but a comprehensive study of organic products is beyond the scope of IAS.

Propan-1-ol to propanal:

$$CH_3CH_2CH_2OH + [O] \rightarrow CH_3CH_2CHO + H_2O$$

Propanal to propanoic acid:

$$CH_3CH_2CHO + [O] \rightarrow CH_3CH_2COOH$$

Propan-2-ol to propanone:

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

You do not need to know the mechanisms of any of these reactions.

### DIFFERENT PRACTICAL TECHNIQUES

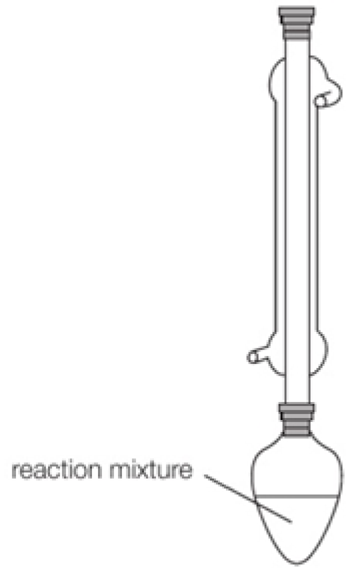
Because of the easier oxidation of aldehydes compared with alcohols, two different techniques are used. These are:

- heating under reflux
- distillation with addition.

### HEATING UNDER REFLUX

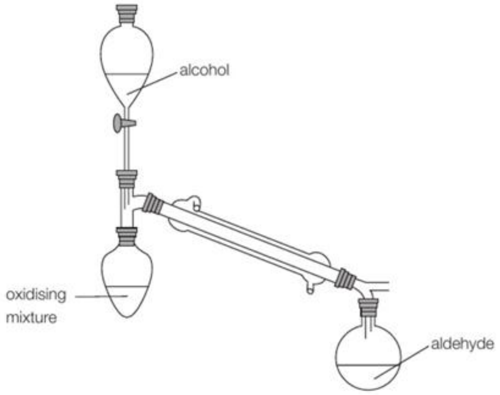
When the oxidation is intended to be complete (to obtain a ketone or a carboxylic acid), the technique used is **heating under reflux**. You can see the apparatus for this technique in the diagram.

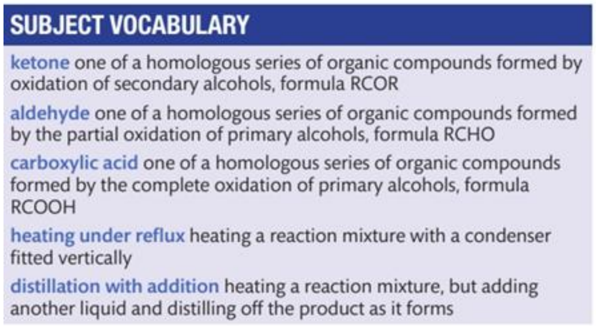
In this apparatus, the products of oxidation stay in the reaction mixture, because if they do boil off, they condense in the vertical condenser and return to the heating flask.



### DISTILLATION WITH ADDITION

When the oxidation is intended to be incomplete (to obtain an aldehyde, and not a carboxylic acid), the technique used is **distillation with addition**. The apparatus for this technique is shown in the diagram.





**SUBJECT VOCABULARY**

**ketone** one of a homologous series of organic compounds formed by oxidation of secondary alcohols, formula RCOR

**aldehyde** one of a homologous series of organic compounds formed by the partial oxidation of primary alcohols, formula RCHO

**carboxylic acid** one of a homologous series of organic compounds formed by the complete oxidation of primary alcohols, formula RCOOH

**heating under reflux** heating a reaction mixture with a condenser fitted vertically

**distillation with addition** heating a reaction mixture, but adding another liquid and distilling off the product as it forms

## 10C 3 Purifying an organic liquid

### BACKGROUND

So far, you have met many different reactions that can be used in the preparation of organic compounds. In most cases the intended organic product is not pure. It could be contaminated with:

- unreacted starting materials
- other organic products
- the inorganic reagents used, or the inorganic products formed from them
- water.

This means that organic chemists need to use several techniques to separate the intended product from a reaction mixture. These techniques will be different, depending on whether the intended product is a gas, a liquid or a solid. In this topic, we consider only the techniques used to purify an organic liquid.

The techniques we consider are:

- simple distillation
- fractional distillation
- solvent extraction
- drying
- boiling point determination.

## APPARATUS

Chemistry textbooks often depict apparatus used in organic chemistry, but not all labs can set up every piece. In simple experiments, glassware connected by tubing and corks or bungs is inexpensive and easy to use. Organic compounds pose a problem due to their flammability, toxicity, and potential attack on corks and bungs. A solution is glass-based apparatus with ground-glass joints.

**Fig A** shows a selection of this type of apparatus. Using these eight pieces of apparatus, you can create a wide variety of experimental set-ups.

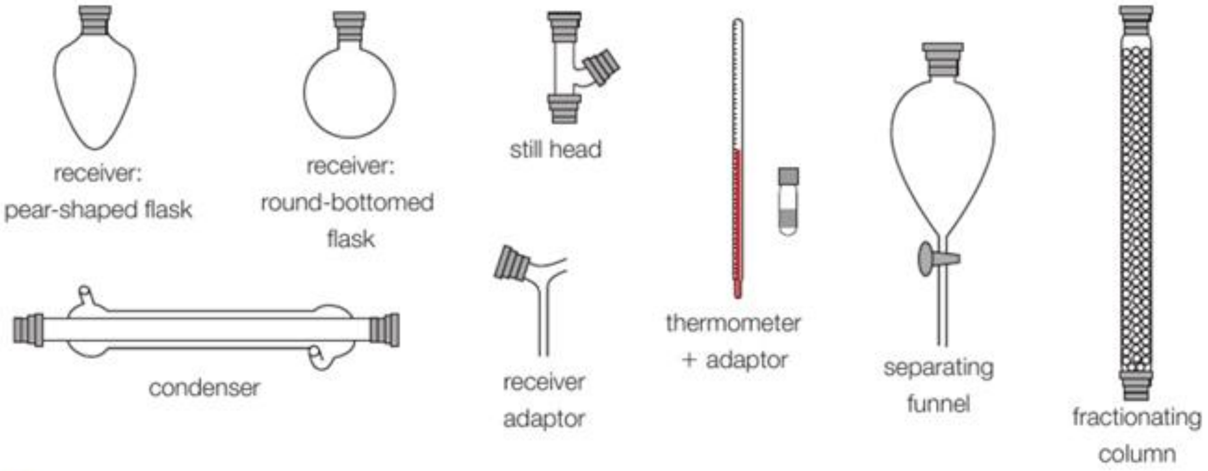


**fig A** A selection of apparatus made mainly of glass, ideal for experiments using organic compounds.

## SIMPLE DISTILLATION

Here is a summary of the process of simple distillation.

- Distillation of an impure liquid involves heating the liquid in a flask connected to a condenser.

- The liquid with the lowest boiling temperature evaporates or boils off first and passes into the condenser first. This means it can be collected in the receiver separately from any other liquid that evaporates later.

- The purpose of the thermometer is to monitor the temperature of the vapour as it passes into the condenser. If the temperature remains steady, this is an indication that one compound is distilling over.

**Fig C** shows the apparatus used for simple distillation.

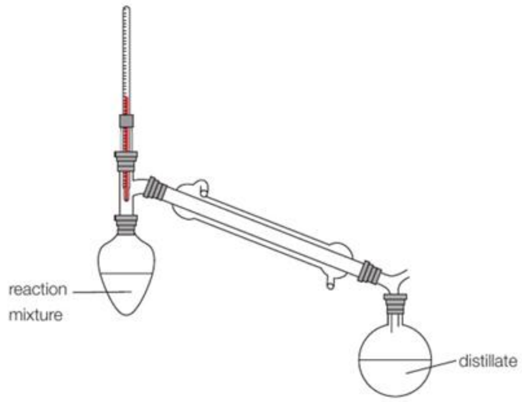


**fig C** Apparatus used for simple distillation.

## FRACTIONAL DISTILLATION

Here is a summary of the process of fractional distillation.

- Fractional distillation uses the same apparatus as simple distillation, but with a fractionating column between the heating flask and the still head (fig D).

• The column is usually filled with glass beads or pieces of broken glass, which act as surfaces on which the vapour leaving the column can condense. It can then be evaporated again as more hot vapour passes up the column.

• Effectively, the vapour undergoes several repeated distillations as it passes up the column. This provides a better separation.

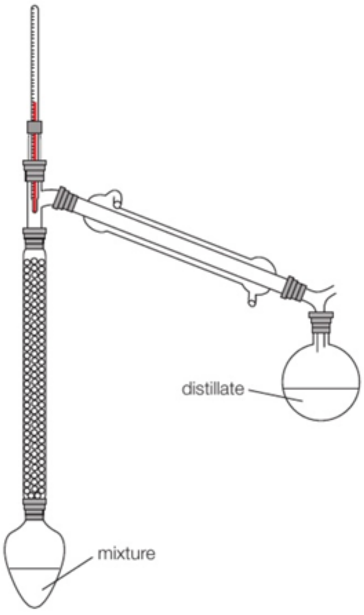


**fig D** Apparatus used for fractional distillation.

## ADVANTAGES AND DISADVANTAGES

Simple distillation is quicker and easier to set up than fractional distillation, but it doesn't separate liquids as well and should only be used for very different boiling temperatures.

## SOLVENT EXTRACTION

As the name suggests, this method involves using a solvent to remove the desired organic product from the other substances in the reaction mixture. There are several solvents that can be used, but the choice depends mainly on these features.

- The solvent added should be immiscible (i.e. does not mix) with the solvent containing the desired organic product.
- The desired organic product should be much more soluble in the solvent added than in the reaction mixture.
- Here is a summary of the process of solvent extraction. Place the reaction mixture in a separating funnel, and then add the chosen solvent - it should form a separate layer.
- Place the stopper in the neck of the funnel and gently shake the contents of the funnel for a while.
- Allow the contents to settle into two layers.
- Remove the stopper and open the tap to allow the lower layer to drain into a flask. Then pour the upper layer into a separate flask.

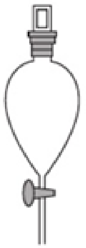


**fig E** Apparatus used for solvent extraction.

If a suitable solvent is used and the method is followed correctly, most of the desired organic product will have moved into the added solvent. It is better to use the solvent in small portions than in a single large volume (for example, four portions of 25 cm3 rather than one portion of 100 cm3) because this is more efficient.

## DRYING

Organic liquids are prepared using inorganic reagents in aqueous solutions. Water may dissolve in the liquid, requiring removal by a drying agent. Common agents include anhydrous metal salts like calcium sulfate, magnesium sulfate, and sodium sulfate, which form hydrated salts and absorb water when in contact with water.

Here is a summary of how to dry an organic liquid.

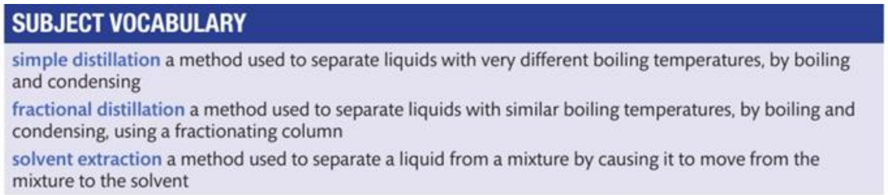
• The drying agent is added to the organic liquid and the mixture is swirled or shaken, and then left for a period of time.

• Before use, a drying agent is powdery, but after absorbing water it looks more crystalline.

- If a bit more drying agent is added, and it remains powdery, this is an indication that the liquid is dry.
- The drying agent is removed either by decantation (pouring the organic liquid off the solid drying agent), or by filtration.

### TESTING FOR PURITY

To determine the purity of an organic compound, measure its boiling temperature. Impurities can raise the temperature, so measuring it accurately is crucial. Data books and online resources provide accurate boiling temperatures for pure compounds. However, this test may not be conclusive as the thermometer may read too low or too high. Different compounds can have the same boiling temperature, such as 1-chloropentane and 2-methylpropan-1-ol.



**SUBJECT VOCABULARY**

**simple distillation** a method used to separate liquids with very different boiling temperatures, by boiling and condensing

**fractional distillation** a method used to separate liquids with similar boiling temperatures, by boiling and condensing, using a fractionating column

**solvent extraction** a method used to separate a liquid from a mixture by causing it to move from the mixture to the solvent

## 10D 1 Mass spectrometry of organic compounds

### BACKGROUND TO MASS SPECTROMETRY

You have already come across the principles of mass spectrometry in Topic 2A.2. We will now look at how this technique can be used to determine the relative molecular mass of organic compounds. We will also determine the structures of some of these compounds.

### THE MOLECULAR ION PEAK

The obvious thing to do when first looking at the mass spectrum of an organic compound is to find the peak furthest to the right. This is the one with the greatest m/z value (mass to charge ratio). This peak is the **molecular ion peak** - the result of the organic molecule losing an electron in the mass spectrometer. The equation for this process, using butane as an example, is:

$$C_4H_{10} + e^- \rightarrow C_4H_{10}^{+} + 2e^-$$

An electron collides with a butane molecule and knocks out an electron, so forming a positive ion from the molecule. The m/z value of the C,Hit peak (58) indicates the relative molecular mass of butane.

### OTHER PEAKS

The spectrum may show a small peak near the M+1 peak due to the presence of a naturally occurring carbon isotope (13C). This isotope is radioactive and used in radiocarbon dating. Smaller m/z values result from fragmentation, rearrangement reactions, and electron loss. Rearrangement is unpredictable but helps explain the large number of peaks in some spectra.

### FRAGMENTATION IN HYDROCARBONS

**Fragmentation** is very common and can often be used to work out the structure of an organic molecule. Consider the breaking of a carbon-carbon bond in the molecular ion formed from a hydrocarbon. Two species are formed. They are:

- another positive ion
- a neutral species (usually a free radical).

EXAMPLES OF FRAGMENTATION

A very simple example of fragmentation is the molecular ion of ethane, which can fragment to form a methyl cation and a methyl radical:

$$(CH_3\text{–}CH_3)^+ \rightarrow CH_3^+ + CH_3$$

The ethane molecule is symmetrical, and there is only one carbon-carbon bond in ethane, so you can imagine that the right-hand carbon is just as likely to become the positive ion. The equation for this fragmentation would be:

$$(CH_3\text{–}CH_3)^+ \rightarrow CH_3 + CH_3^+$$

You can see that the products are identical, so the spectrum does not depend on how the bond breaks - there will be a peak at m/z = 15.

Sometimes the free radical formed is shown with a dot
(representing the unpaired electron), and the molecular ion is shown with a dot as well as a positive charge, as in this example:

$$(CH_3\text{–}CH_3)^{+\bullet} \rightarrow CH_3\bullet + CH_3^+$$

Now consider propane. There are two carbon-carbon bonds, but they are equivalent - they can both be described as the bond between the central carbon and one of the two terminal carbons. However, there are now two possible fragment ions that can form:

$$(CH_3\text{–}CH_2\text{–}CH_3)^+ \rightarrow CH_3^+ + CH_2\text{–}CH_3$$

$$(CH_3\text{–}CH_2\text{–}CH_3)^+ \rightarrow CH_3 + (CH_2\text{–}CH_3)^+$$

You would therefore expect to see peaks at m/z = 15 (the methyl cation) and m/z = 29 (the ethyl cation) in its spectrum. These peaks are present, although there are several others that are difficult to explain and are of no help in deducing the structure.

Free radicals are not detected in a mass spectrometer, so all the peaks formed by fragmentation are caused by positive ions.

## POSSIBLE INFORMATION

Here is the information you could be given in exam questions.

- A complete mass spectrum - the disadvantage of this is the possible large number of peaks that cannot be used to work out the structure and would be distracting. Another possibility is a complete mass spectrum, but with only the m/z values of the useful peaks marked on the spectrum.

- A simplified mass spectrum showing only the peaks that will help you work out a structure.

- A list of the m/z values of the useful peaks.

With practice, you will be able to work out the structure of an organic compound from this information.

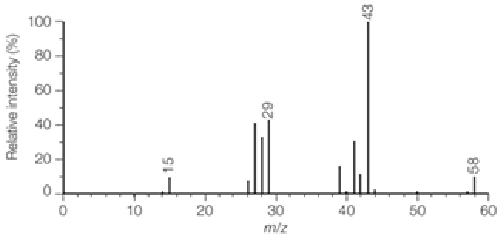
## A TYPICAL MASS SPECTRUM

The traditional way to present a mass spectrum is to label the vertical axis as relative intensity (%), always from 0% to 100%. The horizontal axis is labelled m/z (with no units). The horizontal axis usually, but not necessarily, starts from zero and continues to just beyond the molecular ion peak.

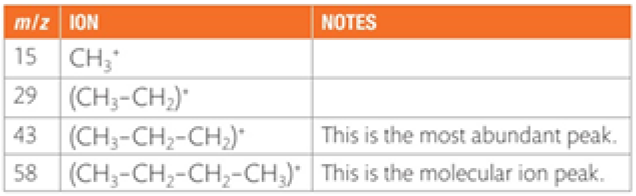
The tallest peak is sometimes referred to as the **base peak**.

This base peak represents the ion with the highest abundance, and is shown with a relative intensity of 100%. It represents the most stable fragment.

This is the mass spectrum of butane:

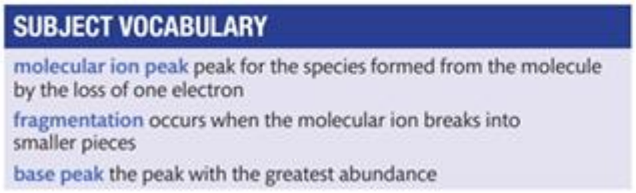


Among the visible peaks are those labelled 15, 29, 43 and 58. **Table A** shows the origin of these peaks.



| m/z | ION | NOTES |
|---|---|---|
| 15 | $CH_3^+$ | |
| 29 | $(CH_3-CH_2)^+$ | |
| 43 | $(CH_3-CH_2-CH_2)^+$ | This is the most abundant peak. |
| 58 | $(CH_3-CH_2-CH_2-CH_3)^+$ | This is the molecular ion peak. |

**table A** The origin of the peaks in the mass spectrum of butane.



**SUBJECT VOCABULARY**

**molecular ion peak** peak for the species formed from the molecule by the loss of one electron

**fragmentation** occurs when the molecular ion breaks into smaller pieces

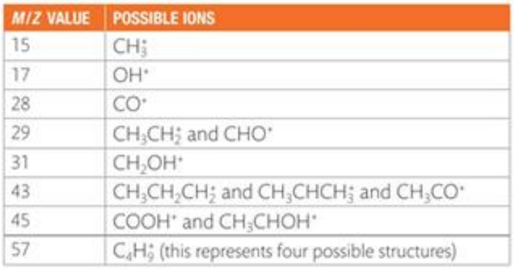
**base peak** the peak with the greatest abundance

# 10D 2 Deducing structure from mass spectra

## FRAGMENTATION IN OTHER ORGANIC COMPOUNDS

So far, we have looked only at the mass spectra of alkanes. Now let's look at other organic compounds - those containing oxygen. In this topic, we will look at two examples of simplified mass spectra and see how they can be used to work out the structures of the compounds responsible for them.

Oxygen is present in many organic compounds, so you need to be familiar with other m/z values. You may also come across compounds containing nitrogen (amines) and halogens (halogenoalkanes).



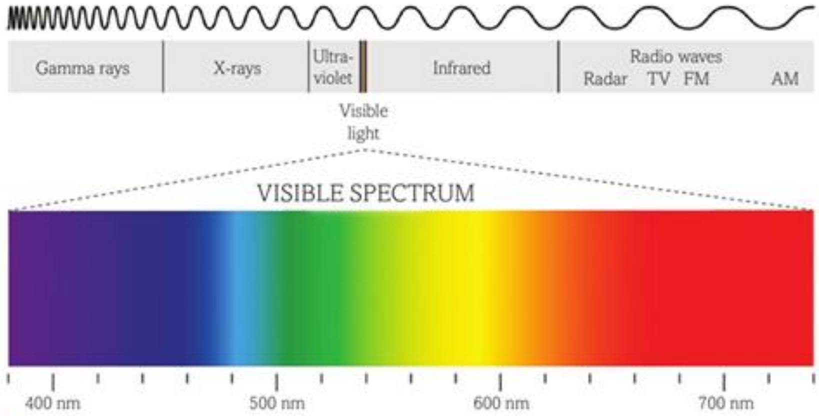
| M/Z VALUE | POSSIBLE IONS |
|---|---|
| 15 | $CH_3^+$ |
| 17 | $OH^+$ |
| 28 | $CO^+$ |
| 29 | $CH_3CH_2^+$ and $CHO^+$ |
| 31 | $CH_2OH^+$ |
| 43 | $CH_3CH_2CH_2^+$ and $CH_3CHCH_3^+$ and $CH_3CO^+$ |
| 45 | $COOH^+$ and $CH_3CHOH^+$ |
| 57 | $C_4H_9^+$ (this represents four possible structures) |

**table A** Common m/z values and the possible ions responsible for these peaks.

# 10D 3 Infrared spectroscopy

## INFRARED RADIATION

The electromagnetic spectrum of radiation shown in fig A includes infrared radiation. The 'infra' part of "infrared' comes from the Latin for "below", so this radiation has a frequency below, or less than, that of red light.

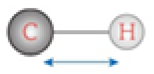


▲ **fig A** You can see how infrared radiation fits into the wider electromagnetic spectrum, next to the red part of the visible spectrum.

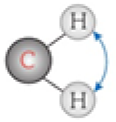
## WHAT HAPPENS WHEN MOLECULES ABSORB INFRARED RADIATION

The importance of infrared radiation in chemistry is that it is absorbed by molecules and causes two possible effects, both described as vibrations. These effects are:

- **stretching** - where the bond length increases and decreases
- bending - where the bond angle increases and decreases.



The C–H bond stretches when it absorbs infrared radiation.



The C–H bond bends when it absorbs infrared radiation.

In this book, only stretching vibrations will be considered.

When a molecule absorbs infrared radiation, the amount of energy absorbed depends on:

- the length of the bond
- the strength of the bond
- the mass of each atom involved in the bond.

The absorption of infrared radiation is linked to changes in the polarity of the molecule, so simple non-polar molecules (such as H2 and Cl2) do not absorb infrared radiation.

## WHAT DOES AN INFRARED SPECTRUM LOOK LIKE?

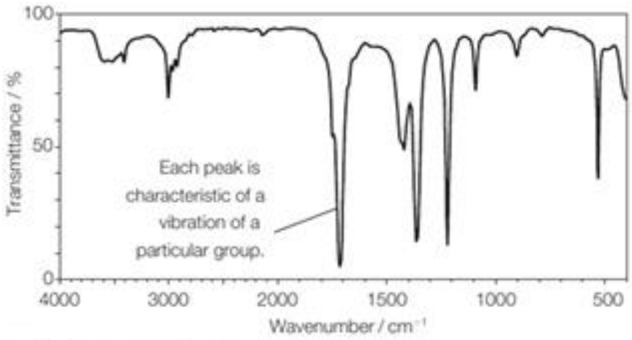
When a compound is irradiated by infrared radiation, the bonds in the molecules absorb radiation from some parts of the spectrum, but not from others.

### AXES

The spectrum is normally shown with the vertical axis labelled **transmittance**, shown as a percentage from 0 to 100. A value of 100% transmittance means that 100% of the radiation is transmitted and none is absorbed.

The horizontal axis could be labelled either as frequency or wavelength, but a different unit is used: **wavenumber**. This is the reciprocal of the wavelength, and so it represents frequency. It is usually quoted in the unit cm1. The numerical scale normally starts at 4000 cm1 and ends at 500 cm1.

**Fig B** is an example of a typical infrared spectrum.



▲ **fig B** A typical infrared spectrum.

## ABSORPTIONS AND THEIR INTENSITIES

You can see that some of the spectrum consists of a wavy but almost horizontal line close to 100%, but at specific wavenumbers there are dips or troughs. These are referred to as absorptions (or sometimes as peaks). The actual transmittance value of an absorption is not very important, but its intensity is.

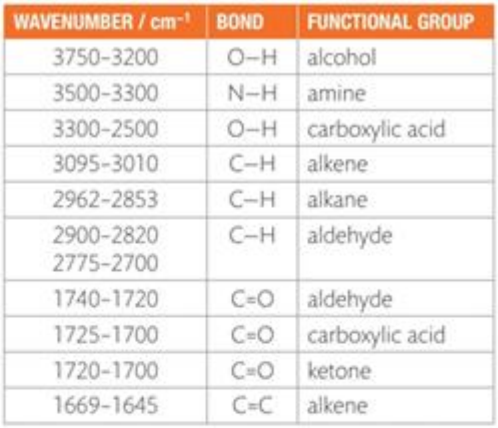
Weak intensities refer to high transmittance values, and strong intensities to low transmittance values.

## WAVENUMBER VALUES

The wavenumber values are also very important. The spectrum in fig B shows that the absorption with the lowest transmittance occurs at about 1700 cm1. Sometimes, another important feature to note is whether the absorption is sharp (i.e. a narrow wavenumber range) or broad (a wide wavenumber range).

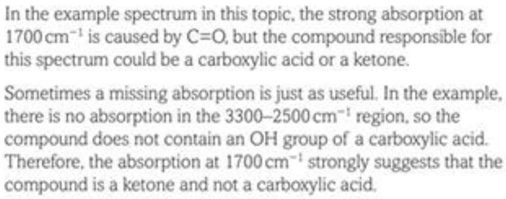
## CHARACTERISTIC ABSORPTIONS

You do not need to remember any of the information in table A, as it will be provided in an exam. However, it is important to be familiar with how to use it when interpreting infrared spectra.



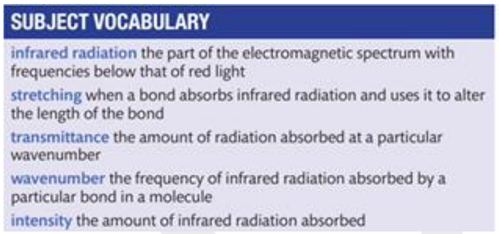
| WAVENUMBER / cm$^{-1}$ | BOND | FUNCTIONAL GROUP |
|---|---|---|
| 3750–3200 | O–H | alcohol |
| 3500–3300 | N–H | amine |
| 3300–2500 | O–H | carboxylic acid |
| 3095–3010 | C–H | alkene |
| 2962–2853 | C–H | alkane |
| 2900–2820<br>2775–2700 | C–H | aldehyde |
| 1740–1720 | C=O | aldehyde |
| 1725–1700 | C=O | carboxylic acid |
| 1720–1700 | C=O | ketone |
| 1669–1645 | C=C | alkene |

**table A** Information to help interpret an infrared spectrum.



In the example spectrum in this topic, the strong absorption at 1700 cm$^{-1}$ is caused by C=O, but the compound responsible for this spectrum could be a carboxylic acid or a ketone.

Sometimes a missing absorption is just as useful. In the example, there is no absorption in the 3300–2500 cm$^{-1}$ region, so the compound does not contain an OH group of a carboxylic acid. Therefore, the absorption at 1700 cm$^{-1}$ strongly suggests that the compound is a ketone and not a carboxylic acid.



**SUBJECT VOCABULARY**

**infrared radiation** the part of the electromagnetic spectrum with frequencies below that of red light

**stretching** when a bond absorbs infrared radiation and uses it to alter the length of the bond

**transmittance** the amount of radiation absorbed at a particular wavenumber

**wavenumber** the frequency of infrared radiation absorbed by a particular bond in a molecule

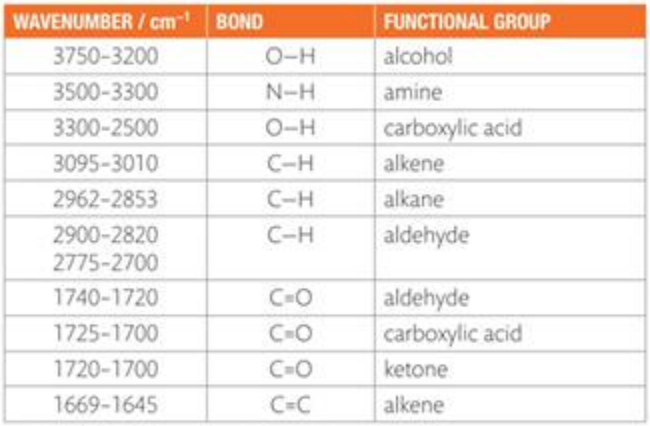
**intensity** the amount of infrared radiation absorbed

# 10D 4 Using infrared spectra

## DIFFERENT WAYS OF USING INFRARED SPECTRA

There are three main ways your understanding of infrared spectra could be tested, and you need to become familiar with all of them. They are:

- predicting the absorptions in the spectrum of an organic compound
- deducing the functional groups in a compound from a list of wavenumbers
- deducing the structure of a compound from wavenumbers and molecular formula.



| WAVENUMBER / cm$^{-1}$ | BOND | FUNCTIONAL GROUP |
|---|---|---|
| 3750–3200 | O–H | alcohol |
| 3500–3300 | N–H | amine |
| 3300–2500 | O–H | carboxylic acid |
| 3095–3010 | C–H | alkene |
| 2962–2853 | C–H | alkane |
| 2900–2820<br>2775–2700 | C–H | aldehyde |
| 1740–1720 | C=O | aldehyde |
| 1725–1700 | C=O | carboxylic acid |
| 1720–1700 | C=O | ketone |
| 1669–1645 | C=C | alkene |

**table A** Information to help interpret an infrared spectrum.

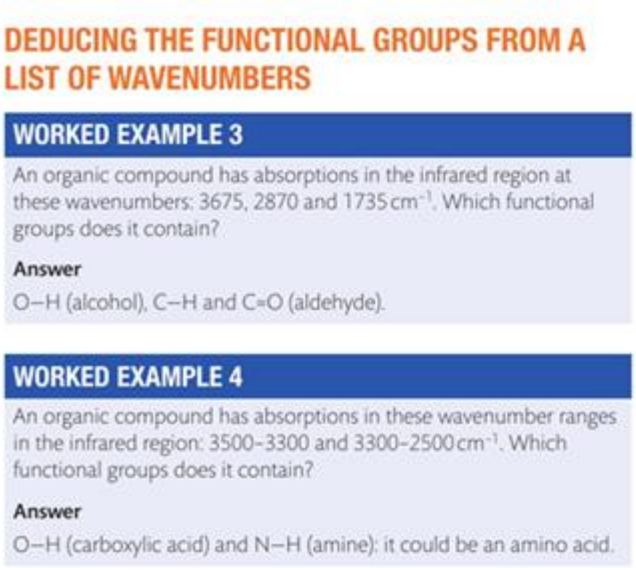
These all require the use of wavenumber data, like the data shown in Topic 10D.3. This will either be provided in the question, or you can use information from the Data booklet provided in the exam. Table A is the table from Topic 10D.3 reproduced here for your convenience.

## FINGERPRINT REGION

The 'fingerprint region' refers to the infrared region between 1500 and 500 cm, where absorptions occur due to bending vibrations or bonds not listed in the wavenumbers table. This region acts like a fingerprint, slightly different for similar molecules, despite individual absorptions being difficult to recognize.

## PREDICTING THE SPECTRUM OF AN ORGANIC COMPOUND

Suppose you are given the identity of an organic compound. This might be a formula (displayed, skeletal or structural) or a name. You should then be able to predict the wavenumber ranges of the compound's infrared spectrum.



### DEDUCING THE FUNCTIONAL GROUPS FROM A LIST OF WAVENUMBERS

**WORKED EXAMPLE 3**

An organic compound has absorptions in the infrared region at these wavenumbers: 3675, 2870 and 1735 cm$^{-1}$. Which functional groups does it contain?

**Answer**

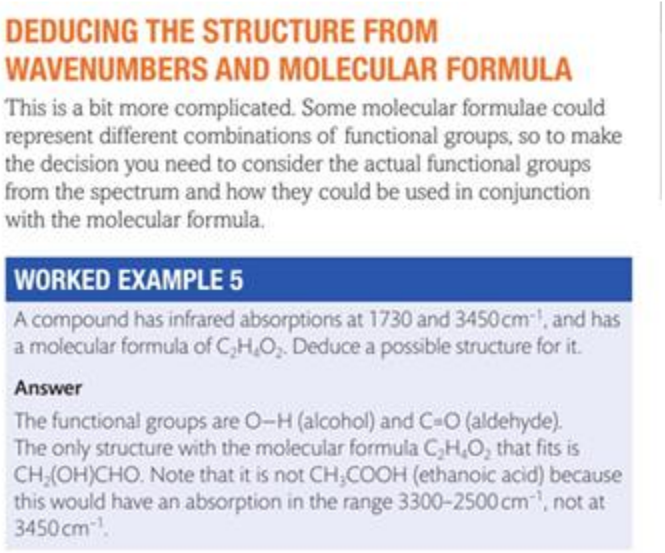
O–H (alcohol), C–H and C=O (aldehyde).

**WORKED EXAMPLE 4**

An organic compound has absorptions in these wavenumber ranges in the infrared region: 3500–3300 and 3300–2500 cm$^{-1}$. Which functional groups does it contain?

**Answer**

O–H (carboxylic acid) and N–H (amine): it could be an amino acid.



### DEDUCING THE STRUCTURE FROM WAVENUMBERS AND MOLECULAR FORMULA

This is a bit more complicated. Some molecular formulae could represent different combinations of functional groups, so to make the decision you need to consider the actual functional groups from the spectrum and how they could be used in conjunction with the molecular formula.

**WORKED EXAMPLE 5**

A compound has infrared absorptions at 1730 and 3450 cm$^{-1}$, and has a molecular formula of $C_2H_4O_2$. Deduce a possible structure for it.

**Answer**

The functional groups are O–H (alcohol) and C=O (aldehyde). The only structure with the molecular formula $C_2H_4O_2$ that fits is $CH_2(OH)CHO$. Note that it is not $CH_3COOH$ (ethanoic acid) because this would have an absorption in the range 3300–2500 cm$^{-1}$, not at 3450 cm$^{-1}$.

## Revision questions

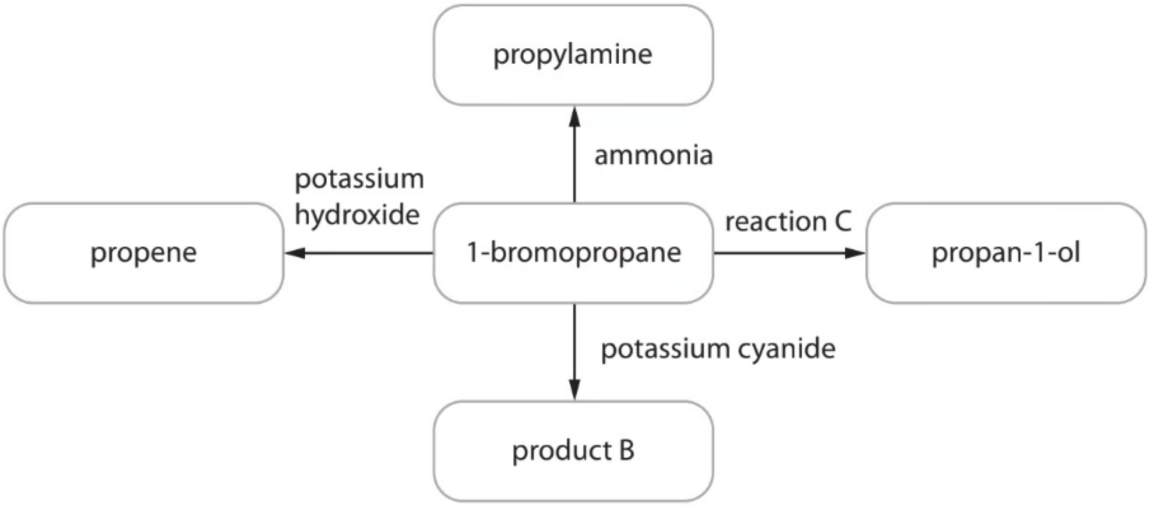
### 1.a.

1–bromopropane is used for spot removal when 'dry cleaning' clothes.

1–bromopropane does not occur naturally but can be made from propan–1–ol.
Identify the reagent or reagents you would use to make 1–bromopropane from propan–1–ol.

b.

Some reactions of 1–bromopropane are shown.



c.

i) Give the conditions for the formation of propene.

**(1)**

ii) Give the **molecular** formula of product B.

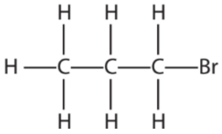
**(1)**

iii) Name the type and mechanism of the reaction taking place in reaction C.

**(2)**

iv) Complete the mechanism for the reaction that occurs between ammonia and 1–bromopropane to form propylamine, $CH_3CH_2CH_2NH_2$ .
Include curly arrows, and relevant lone pairs and dipoles.

**(4)**



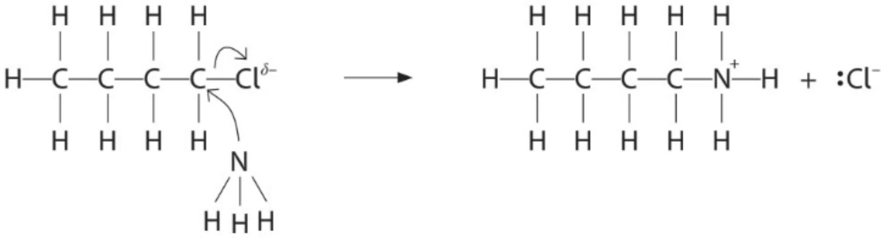
2.a)

Ammonia reacts with 1-chlorobutane.

State the type and mechanism of this reaction.

b.

A student drew the first step of the mechanism for the reaction.



i) Identify **two** omissions in the student's mechanism.

**(2)**

ii) To obtain butylamine, sodium hydroxide solution is added. Complete the next step of the mechanism to form butylamine, showing curly arrows, relevant lone pairs and the reaction products.

**(3)**

**c.**

The reactions of ammonia and of hydroxide ions with halogenoalkanes are similar.

Compare the rate of reaction of ammonia with 1-chlorobutane and with 2-bromo-2-methylpropane.
Justify your answer.

**3.a)**

This question is about halogenoalkanes.

The rates of hydrolysis of 1–chloropropane, 1–bromopropane and 1–iodopropane in reactions with aqueous silver nitrate solution were compared.

i) State what would be measured in the experiment to compare the rates of hydrolysis.

**(1)**

ii) State which of these halogenoalkanes would hydrolyse the fastest. Justify your answer.

**(2)**

**b.**

The equation for the hydrolysis of 1–chloropropane by aqueous hydroxide ions is shown.

$$CH_3CH_2CH_2Cl + OH^- \rightarrow CH_3CH_2CH_2OH + Cl^-$$

Give the mechanism for this hydrolysis. Include curly arrows, and relevant dipoles and lone pairs.

**c.**

The boiling temperatures of some halogenoalkanes are shown.

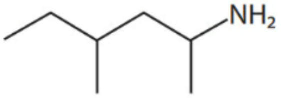
| **Halogenoalkane** | **Boiling temperature / °C** |
|---|---|
| 1–chloropropane | 47 |
| 1–bromopropane | 71 |
| 1–iodopropane | 103 |

Explain the trend in boiling temperature of these halogenoalkanes by comparing the intermolecular forces involved.

Detailed explanations of the forces involved are not required.

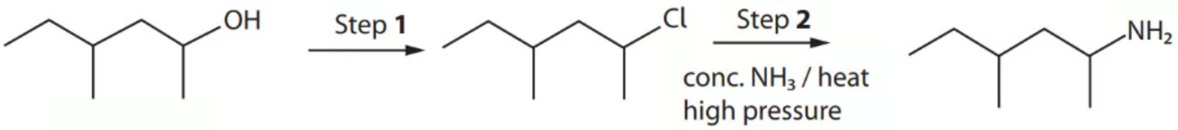
**4.**

The compound DMAA was originally synthesised as a decongestant.



DMAA

A suggested synthetic route for DMAA is shown.



compound **A**

i) Give the systematic name of compound **A**.

**(1)**

ii) Identify, by name or formula, a suitable reagent for Step **1**.

**(1)**

iii) Give the mechanism for the reaction in Step **2**.

Include curly arrows, and any relevant dipoles and lone pairs.

**(4)**

**5.**

DMAA is only slightly soluble in water but dissolves readily in hydrochloric acid to form an aqueous solution.

DMAA

i) Explain the type of bonding that occurs between the nitrogen atom and the hydrogen ion, when the positive ion forms.

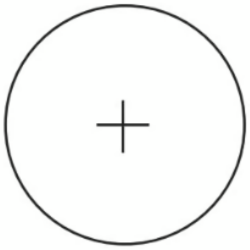
**(3)**

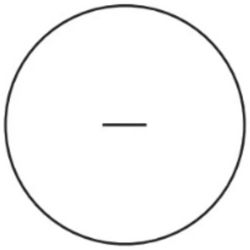
ii) Complete the diagrams to show how the ions formed in the reaction between DMAA and hydrochloric acid interact with water molecules.

**(3)**

ii) Complete the diagrams to show how the ions formed in the reaction between DMAA and hydrochloric acid interact with water molecules.

**(3)**

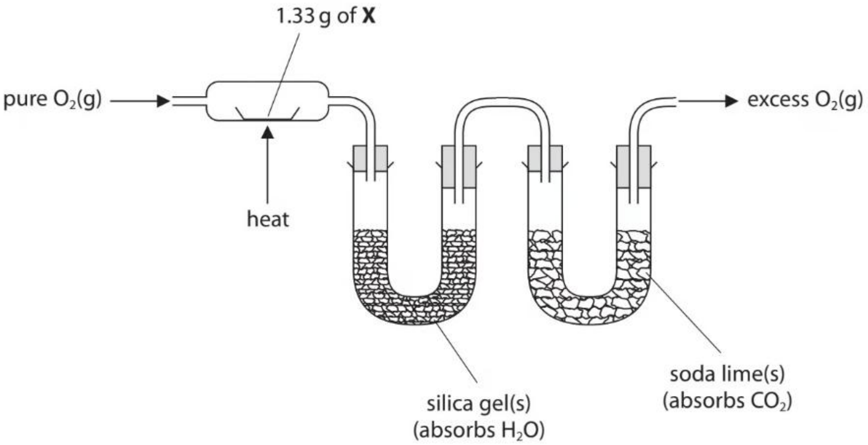




**6. a.**

This question is about two organic compounds, **X** and **Y.** Both are liquids which contain carbon, hydrogen and oxygen only.

The mass of hydrogen and of carbon present in 1.33 g of **X** were determined by passing its combustion products through the apparatus shown.



**b.**

i) State the **measurements** that should be made.

**(2)**

ii) Give **two** reasons why pure $O_2$(g), and **not** air, should be used.

**(2)**

iii) The experiment showed that 1.33 g of **X** contains 0.14 g of hydrogen and 0.63 g of carbon.

Calculate the empirical formula of **X**, using these data.

You **must** show your working.

**(3)**

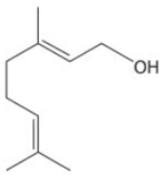
**7.a.**

Geraniol is used in perfumes and can be extracted from many plants.

Data on geraniol are shown.

| Solubility in water | Melting temperature/°C | Boiling temperature/°C | Density / g cm$^{-3}$ |
|---|---|---|---|
| insoluble | –15 | 230 | 0.889 |

The structure of geraniol is shown.



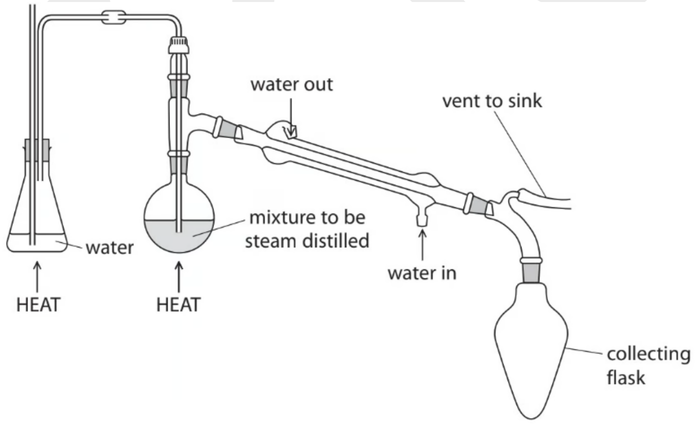
Geraniol has **two** different types of functional group.

**Name** the functional groups, giving a chemical test and its positive result to show the presence of each group.

First functional group:

Second functional group:

**b.**



The steam distillation product is geraniol and water. The water may contain dissolved impurities which have similar boiling temperatures to geraniol.

The contents of the collecting flask are transferred to a piece of apparatus used to separate the geraniol from the water layer.

Draw a labelled diagram of this apparatus and its contents.