

TOPIC 10 ORGANIC CHEMISTRY: HALOGENOALKANES, ALCOHOLS AND SPECTRA

A GENERAL PRINCIPLES | B HALOGENOALKANES |
C ALCOHOLS | D MASS SPECTRA AND IR

In Topics 4 and 5, you learned about the basics of organic chemistry and about two homologous series, alkanes and alkenes. In this topic, you will learn about two more homologous series, halogenoalkanes and alcohols. There is also a new reaction mechanism to consider, nucleophilic substitution.

Although you have already learned something about mass spectrometry, we will build on this knowledge to see how the technique was developed to become a useful tool to discover the structures of organic compounds. A new technique, infrared spectroscopy, is introduced to show another way to discover different information about the structures of organic compounds.

MATHS SKILLS FOR THIS TOPIC

- Use ratios to construct and balance equations
- Represent chemical structures using angles and shapes in 2D and 3D structures





What prior knowledge do I need?

Topic 1D

- Calculation of empirical and molecular formulae

Topic 4

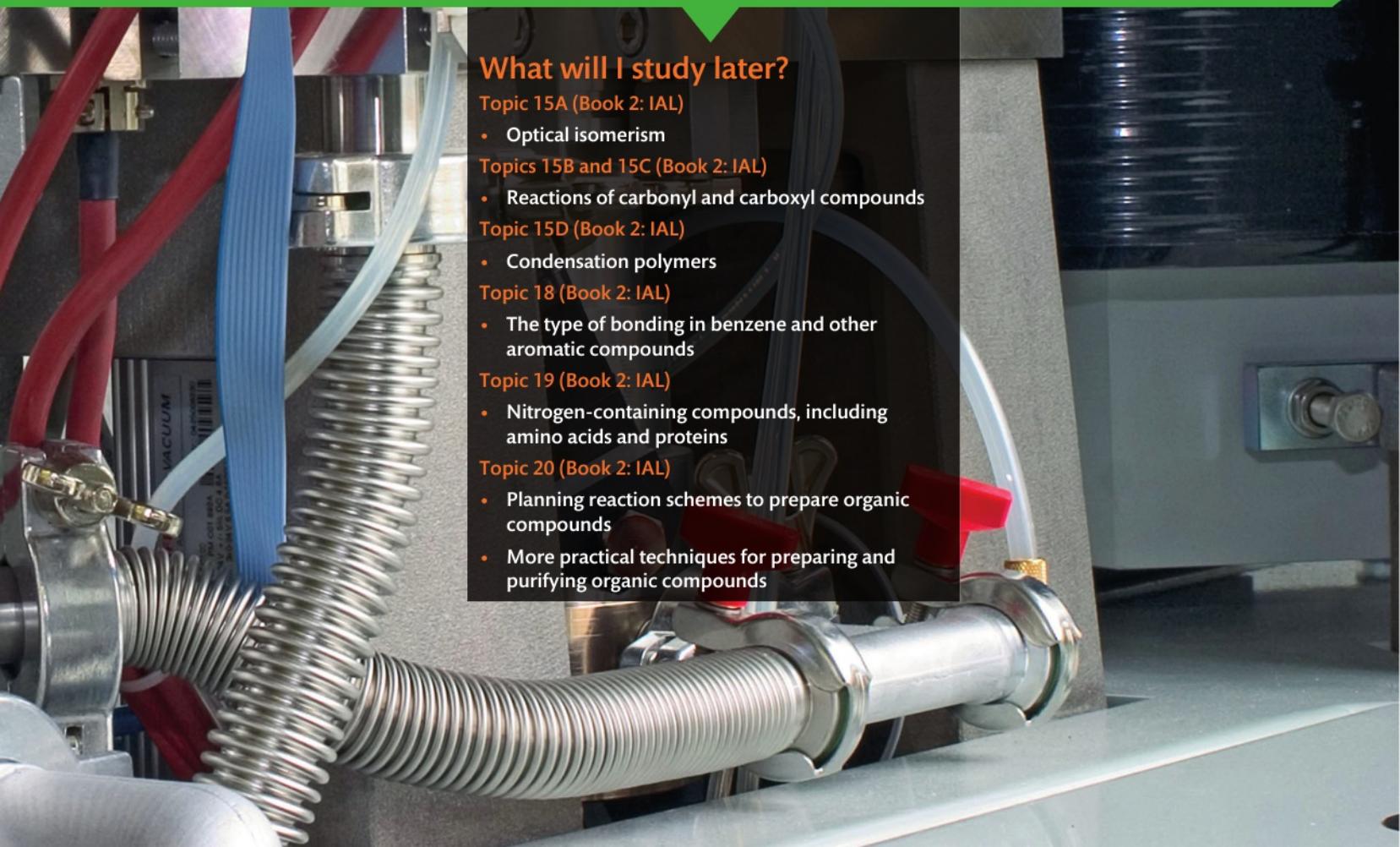
- The names of simple organic compounds
- Homologous series and general formula
- Representing organic compounds by structural formulae

Topics 4B and 5

- Alkanes and alkenes

What will I study in this topic?

- The hydrolysis reactions of halogenoalkanes and how to compare their rates experimentally
- Explaining the different rates of hydrolysis reactions of halogenoalkanes
- Substitution and elimination reactions of halogenoalkanes
- Oxidation and hydration reactions of alcohols
- Converting alcohols to halogenoalkanes
- Practical techniques used to prepare and purify organic compounds
- How fragmentation in mass spectrometry can give information about organic structures
- How infrared spectroscopy can give information about bonds in organic structures



What will I study later?

Topic 15A (Book 2: IAL)

- Optical isomerism

Topics 15B and 15C (Book 2: IAL)

- Reactions of carbonyl and carboxyl compounds

Topic 15D (Book 2: IAL)

- Condensation polymers

Topic 18 (Book 2: IAL)

- The type of bonding in benzene and other aromatic compounds

Topic 19 (Book 2: IAL)

- Nitrogen-containing compounds, including amino acids and proteins

Topic 20 (Book 2: IAL)

- Planning reaction schemes to prepare organic compounds
- More practical techniques for preparing and purifying organic compounds

10A GENERAL PRINCIPLES IN ORGANIC CHEMISTRY

LEARNING OBJECTIVES

- Be able to classify reactions as addition, elimination, substitution, oxidation, reduction, hydrolysis or polymerisation.
- Understand the concept of a reaction mechanism.
- Understand that heterolytic bond breaking results in species that are electrophiles or nucleophiles.
- Understand the link between bond polarity and the type of reaction mechanism a compound will undergo.

REACTIONS IN ORGANIC CHEMISTRY

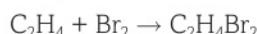
In **Topic 4**, you learned that there were five different types of organic reaction. In this topic you will learn about two more types. All seven types of reaction are considered here so that you don't have to refer back to **Topic 4**.

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:

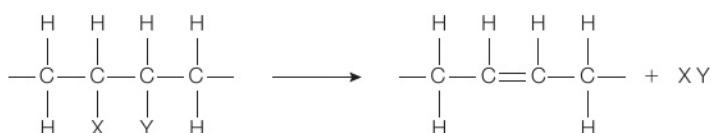


One example is the reaction between ethene and bromine:



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 results in the formation of a second bond between the two carbon atoms. 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:



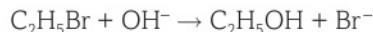
The small molecule eliminated is HBr (the H comes from the left-hand carbon, and the Br from the right-hand carbon). This is not easy to see just by looking at the equation. This is because the H goes to the H₂O molecule and the Br to KBr.

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:



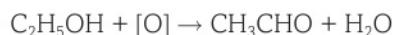
One example is the reaction between bromoethane and potassium hydroxide. Potassium hydroxide is an ionic compound, and as the potassium ion is a spectator ion, the reaction only involves the hydroxide ion. An equation for this reaction is:



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 Cu²⁺, 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:



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

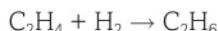
EXAM HINT

It is important to remember that different oxidising agents carry out different oxidation reactions. For example, acidified potassium manganate(VII) will oxidise an alkene to a diol. However, acidified potassium dichromate is needed to oxidise a primary or secondary alcohol.

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. There isn't a suitable general equation that can be used for this type of reaction, but here is one example

you saw in **Topic 5A.3**: the reduction of an alkene to an alkane by hydrogen gas and a nickel catalyst. The equation for the reaction is:



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

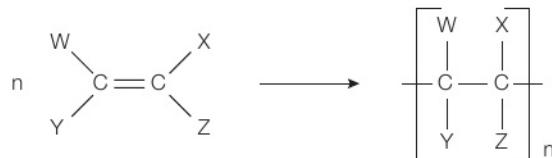
This is another new type of reaction. In hydrolysis reactions, an organic compound reacts with water. The OH group of water replaces an atom or group in the organic compound. A general equation for a hydrolysis reaction is:



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 HETEROOLYTIC 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 as $\text{Cl}\cdot$.

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.

LEARNING TIP

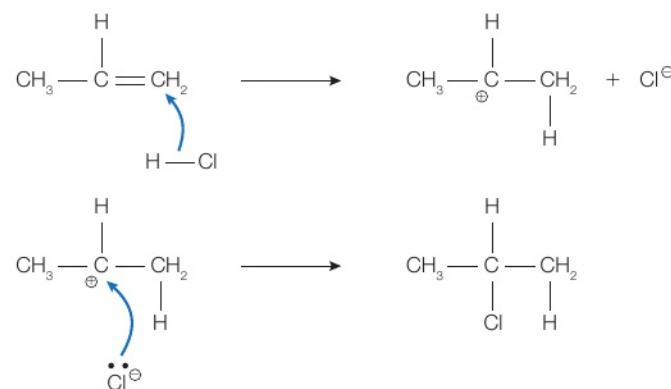
You can often work out the type of an unfamiliar reaction by looking at its equation. Also, some reactions can be classified as more than one type, such as addition and reduction, if they both involve hydrogen reacting with an organic reactant to form a single organic product.

CHECKPOINT

1. The equations for some reactions are given below. Classify each reaction, by looking at the equations.

- $\text{CH}_3\text{CHClCH}_3 + \text{LiOH} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{LiCl}$
- $\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
- $\text{CH}_3\text{CH}_2\text{CHO} + [\text{O}] \rightarrow \text{CH}_3\text{CH}_2\text{COOH}$
- $\text{CH}_3\text{CHClCH}_3 + \text{NaOH} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{NaCl} + \text{H}_2\text{O}$

2. A student wrote a mechanism for the reaction between propene and hydrogen chloride:



Identify the mistakes in the student's mechanism.

10B 1 HALOGENOALKANES AND HYDROLYSIS REACTIONS

10.4 10.6 10.7

LEARNING OBJECTIVES

- Understand the nomenclature of halogenoalkanes and be able to draw their structural, displayed and skeletal formulae.
- Understand the distinction between primary, secondary and tertiary halogenoalkanes.
- Know the definition of the term 'nucleophile'.

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 (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.

EXAM HINT

Practise drawing skeletal formulae for halogenoalkanes. This will help you identify the different isomers for a given molecular formula.

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.

If there are two or more different halogens, then the prefixes used to represent the halogens appear in alphabetical order. As with other homologous series, the longest carbon chain is the basis of the name, and when the prefix numbers are added together the total should be as small as possible.

CLASSIFYING HALOGENOALKANES

You have met the terms ‘primary’, ‘secondary’ and ‘tertiary’ in the topic referring to carbocations (see **Topic 5A.4**).

Haloalkanes 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 ₂ F	RX	1	primary
CH ₃ —CHBr—CH ₃	R ₂ CHX	2	secondary
(CH ₃) ₂ CCl—CH ₂ —CH ₃	R ₃ CX	3	tertiary

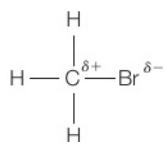
table B Examples of how to classify haloalkanes.

WHAT MAKES HALOGENOALKANES REACTIVE?

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

Haloalkanes 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 $\delta+$ and $\delta-$.

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.



The carbon atom joined to the halogen is always the slightly positive ($\delta+$) or electron-deficient part of the molecule, and this is what makes haloalkanes react as they do.

These carbon atoms attract other species called **nucleophiles**. ‘Nucleo’ indicates positive and ‘phile’ indicates liking, so nucleophiles are species that are attracted to slightly positive or electron-deficient parts of a molecule. Nucleophiles are either negative ions or molecules with a slightly negative atom, but they always use a lone pair of electrons when attacking another species.

We will look at the mechanisms of haloalkane reactions in **Topic 10B.3**, but first let us take a look at a reaction that can be used to compare the reactivities of different haloalkanes.

HYDROLYSIS REACTIONS

When a haloalkane is added to water, a reaction begins, but it may take some time to complete. A water molecule contains polar bonds, and the $\delta-$ oxygen atom in water is attracted to the $\delta+$ carbon atom in the haloalkane. The reaction that occurs can be represented by the equation below, in which R represents any alkyl group:



The product ROH is an alcohol and, as both organic substances are usually colourless liquids, no colour change can be seen. You can see from this simple equation that the C—X bond breaks, so the RX molecule breaks into two parts (R and X), although the R group then combines with the OH group of water.

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.

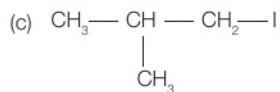
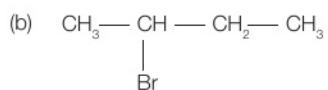
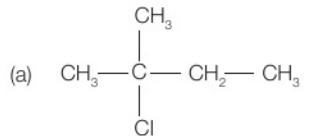
LEARNING TIP

In an organic formula, the symbol R can be used to represent any alkyl group, such as methyl or ethyl.

This should not be confused with the same symbol R used in a completely different context for the gas constant in the equation $pV = nRT$.

CHECKPOINT

1. Write the IUPAC name for each of these haloalkanes and classify them as primary, secondary or tertiary.



2. Why are nucleophiles more strongly attracted to fluoroalkanes than to chloroalkanes?

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 $—\text{OH}$ group

10B 2 COMPARING THE RATES OF HYDROLYSIS REACTIONS

LEARNING OBJECTIVES

- Understand that experimental observations and data can be used to compare the relative rates of hydrolysis of primary, secondary and tertiary structural isomers of a halogenoalkane, and primary chloro-, bromo- and iodo-alkanes, using aqueous silver nitrate in ethanol.
- Know the trend in reactivity of primary, secondary and tertiary halogenoalkanes.
- Understand, in terms of bond enthalpy, the trend in reactivity of chloro-, bromo- and iodo-alkanes.

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:



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).

In an experiment, three tubes containing silver nitrate dissolved in ethanol are left at the same temperature for several minutes. Each tube contains a different halogenoalkane. **Fig A** shows the tubes after several minutes.

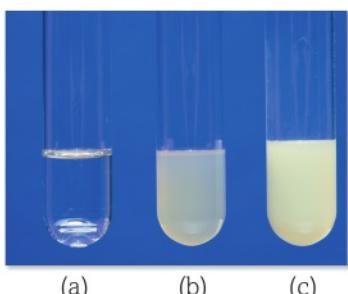


Fig A Three tubes containing silver nitrate dissolved in ethanol, with a different halogenoalkane added to each one.

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)**.

LEARNING TIP

Molecules with partial charges ($\delta+$ and $\delta-$) are not ions. They are molecules with no overall charge but with electron-rich and electron-deficient parts.

CHECKPOINT

1. 2-bromopropane and 2-iodopropane are put into separate test tubes and warmed with water. Explain which one is hydrolysed more quickly.
2. Why are fluoroalkanes not readily hydrolysed compared with chloroalkanes?

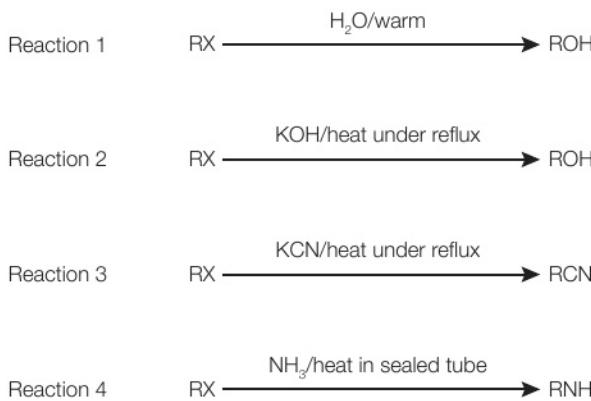
10B 3 HALOGENOALKANE REACTIONS AND MECHANISMS

LEARNING OBJECTIVES

- Understand the reactions of halogenoalkanes with aqueous potassium hydroxide, aqueous silver nitrate in ethanol, potassium cyanide, ammonia and ethanolic potassium hydroxide.
- Understand the mechanisms of the nucleophilic substitution reactions between primary halogenoalkanes and aqueous potassium hydroxide and ammonia.

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

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:



or

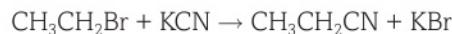


The advantage of an ionic equation is that the nucleophile is clearly shown.

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. An example of an equation for this reaction is the conversion of bromoethane into propanenitrile:



or



Note that the organic product contains one more carbon atom than the starting material. This reaction is a useful way of increasing the length of the carbon chain. It is also an important way of synthesising more complex compounds.

EXAM HINT

If you were to carry out this reaction in the lab then there would need to be a very careful risk assessment. KCN is highly toxic!

REACTION 4

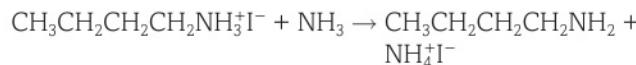
Heating a halogenoalkane with ammonia solution under pressure in a sealed tube is one way of making **primary amines**. The sealed tube is needed because ammonia is a gas and would otherwise escape from the apparatus before it could react. The attacking nucleophile is the NH_3 molecule. An example of an equation for this reaction is the conversion of 1-iodobutane into butylamine:



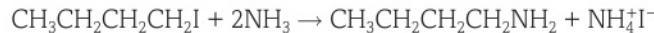
This equation looks similar to those for Reactions 1–3, but it isn't quite the full story. Like NH_3 , the organic product is a base, so it would react with the inorganic product, the acid HI, to form a salt. So a better equation is:



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:



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



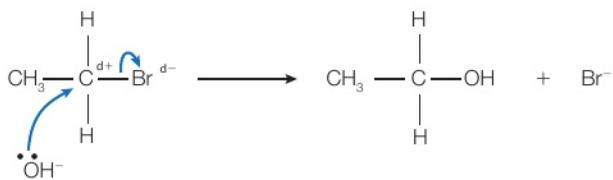
NUCLEOPHILIC SUBSTITUTION MECHANISMS

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.

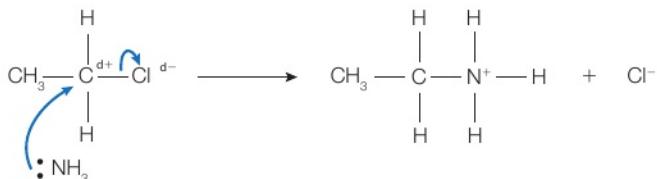
MECHANISM OF REACTION 2

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.

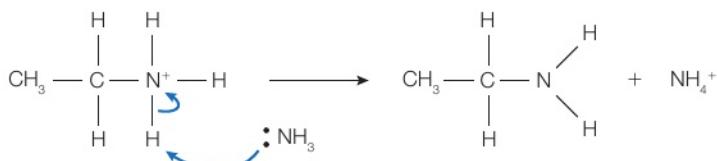


MECHANISM OF REACTION 4

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. You know that a base reacts with a hydrogen ion (H⁺), but in the case of a halogenoalkane, the hydrogen that reacts with the OH⁻ ion is the one attached to a carbon atom next to the C in the C—Br bond.

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



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**.

EXAM HINT

The fact that the same reagents can give different products depending on which solvent you use highlights the need for you to make sure that you know both reactants *and* conditions for an organic synthesis.

LEARNING TIP

Both the hydroxide ion and the ammonia molecule can act as nucleophiles and as bases.

CHECKPOINT

1. Chloromethane is heated with:

- (a) ammonia
- (b) potassium cyanide dissolved in ethanol.

Give the name of the organic product formed in each case.

2. 2-chlorobutane is heated with:

- (a) aqueous potassium hydroxide
- (b) ethanolic potassium hydroxide.

State the mechanism of each reaction and explain why there are two different organic products in (b).

SUBJECT VOCABULARY

nitrile organic compound containing the C—CN group

primary amine compound containing the C—NH₂ 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

SPECIFICATION
REFERENCE

10.15 10.16

10.17 CP6

LEARNING OBJECTIVES

- Understand the nomenclature of alcohols and be able to draw their structural, displayed and skeletal formulae.
- Understand the distinction between primary, secondary and tertiary alcohols.
- Understand the combustion, halogenation and dehydration reactions of alcohols.

WHAT ARE ALCOHOLS?



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

The alcohols are a homologous series of compounds with the general formula $C_nH_{2n+1}OH$. 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.

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

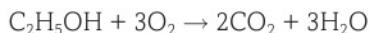
In this topic, the reactions of alcohols we cover are:

- 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:



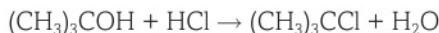
CONVERSIONS TO HALOGENOALKANES

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:



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:



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.



or



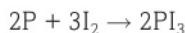
This is the equation for the reaction with butan-1-ol:



EXAM HINT

The sulfuric acid must be no more concentrated than a 50% solution. More concentrated sulfuric acid would oxidise bromide ions to bromine and so result in different products.

Iodination is carried out using a mixture of red phosphorus and iodine. The reaction mixture, including the alcohol, is heated under reflux. As with bromination, it is better to write two equations, as the inorganic reagents first react to form phosphorus(III) iodide:



This is the equation for the reaction with ethanol:

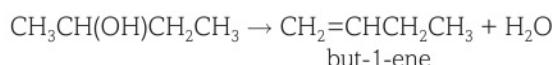


The inorganic product is phosphonic acid (often known as phosphorous acid).

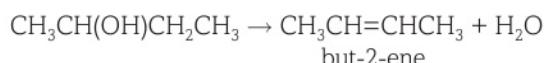
DEHYDRATION TO ALKENES

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:



and



Remember that but-2-ene actually exists as a pair of *E-Z* (*cis-trans*) isomers. It is therefore more correct to state that there are three products – but-1-ene and the two isomeric forms of but-2-ene.

The formula for phosphoric acid does not appear in the equation. This is because the water formed in the reaction mixes with the concentrated phosphoric acid to dilute the acid.

LEARNING TIP

When you balance an equation for the combustion of an alcohol, remember that there is already one atom of oxygen in an alcohol molecule.

CHECKPOINT

SKILLS REASONING

- Write an equation for the complete combustion of butanol, $\text{C}_4\text{H}_9\text{OH}$.
- When butan-2-ol is dehydrated, there is more than one organic product. Explain why there is only one pair of *E/Z* isomers when pentan-3-ol is dehydrated.

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

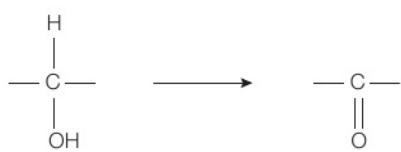
10C 2 OXIDATION REACTIONS OF ALCOHOLS

LEARNING OBJECTIVES

- Understand the oxidation reactions of primary and secondary alcohols by potassium dichromate(VI) to form aldehydes, carboxylic acids and ketones.
 - Understand the techniques of distillation and heating under reflux used to maximise the yields of different products.

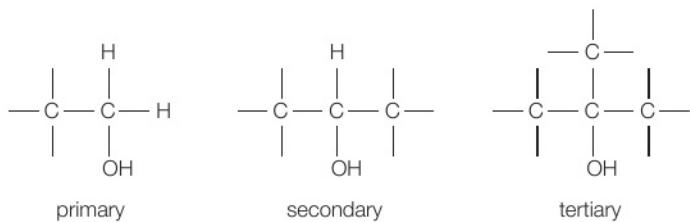
BACKGROUND

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.



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

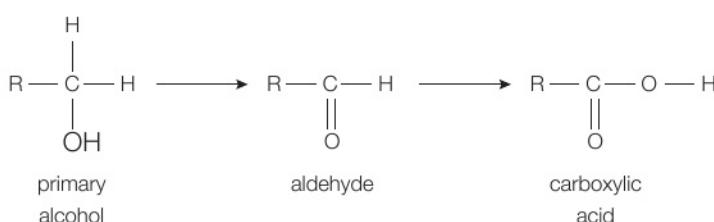
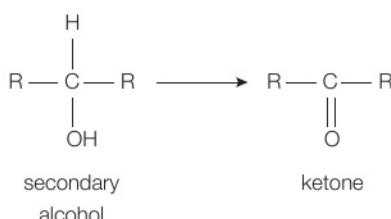
When a secondary alcohol is oxidised, the organic product belongs to a homologous series called **ketones**. A simplified formula for a ketone is RCOR . Using the same symbol R twice suggests that the two alkyl groups are the same (for example, two ethyl groups). This is not necessarily the case, but if the two alkyl groups are meant to be different, then the R symbols can be altered slightly. For example, one could be R and the other could be R' . Another way to show that the alkyl groups are different is for one to be R_1 and the other R_2 .

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.

There is a complication with aldehydes that is not the case with ketones. This is that aldehydes are more easily oxidised than alcohols, so when a primary alcohol is oxidised, the aldehyde formed may be oxidised further. When an aldehyde is oxidised, the process involves the gain of an oxygen atom, not the loss of hydrogen. The 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.

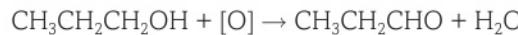
These reactions are summarised below.



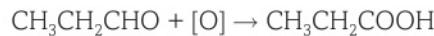
The usual reagent for these oxidation reactions is a mixture of potassium dichromate(VI) and dilute sulfuric acid. Unlike with the inorganic reagents used previously, equations involving this mixture do not need to be written (because they are very complicated). Instead, the oxidising agent is represented by [O]. This symbol simply represents an oxygen atom provided by the oxidising agent. Whenever the mixture of potassium dichromate(VI) and sulfuric acid is used as an oxidising agent, there is a colour change from orange to green.

So now we can write some equations for examples of oxidation reactions. The names of the organic products are given, but a fuller study of these products is outside the scope of IAS.

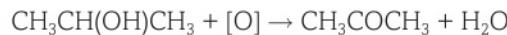
Propan-1-ol to propanal:



Propanal to propanoic acid:



Propan-2-ol to propanone:



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

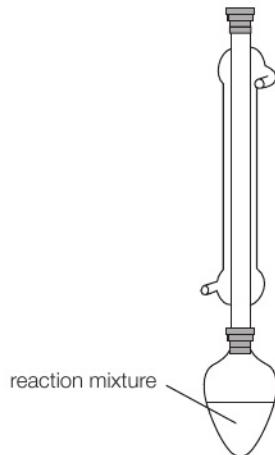
DIFFERENT PRACTICAL TECHNIQUES

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

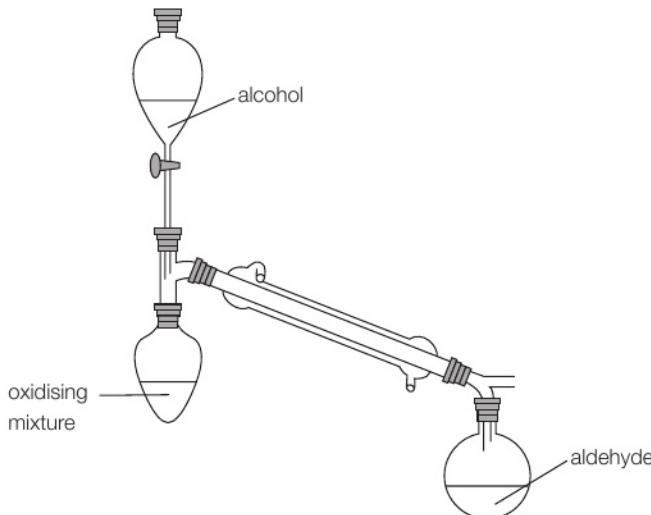
When the oxidation is intended to be complete (to obtain a ketone or a carboxylic acid), the technique used is **heating under reflux**. You can see the apparatus for this technique in the diagram.



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.



In this apparatus, only the oxidising agent is heated, and the alcohol is slowly added to the oxidising agent. When the aldehyde is formed, it immediately distils off (it has a much lower boiling temperature than the alcohol used to make it), and is collected in the receiver.

LEARNING TIP

Practise writing equations to show how a given alcohol can be separately dehydrated and oxidised. This will help you to understand the difference between the two reactions.

CHECKPOINT

1. Butan-1-ol can be dehydrated to form one organic product, but can be oxidised to form two organic products. Give the names and structures of these three products.
2. Pentan-2-ol can be dehydrated to form more than one organic product, but can be oxidised to form only one organic product. Give the names and structures of these products.
3. There are four isomeric alcohols with the formula C_4H_9OH . Draw a structural formula for each isomer and use the formulae to explain which ones can be oxidised by heating with acidified potassium dichromate(VI).

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

LEARNING OBJECTIVES

- Know when and how to use the following techniques in the preparation and purification of a liquid organic compound: simple distillation, fractional distillation, solvent extraction, drying, and boiling temperature determination.

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.

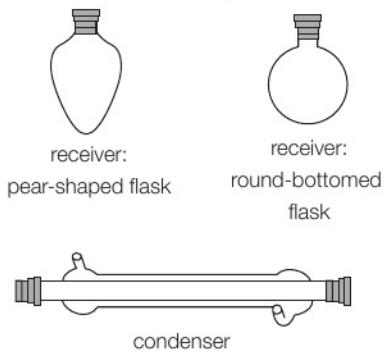
APPARATUS

In a chemistry textbook, you will see many different diagrams of apparatus used in organic chemistry. You will have some of these pieces of apparatus in your laboratory, but you will probably not be able to set up every piece of apparatus you see in the book.

In simple laboratory experiments not involving organic compounds, you are likely to use pieces of glassware connected by tubing and corks or bungs. This kind of apparatus is relatively inexpensive to buy and easy to use. If one of the gases you are using, such as carbon dioxide, leaks from the apparatus, this is not a major problem.

Organic compounds are more of a problem because they may be flammable, or toxic, or both. They may also attack corks and bungs, and so increase the risk of leaks and contamination. One solution to these problems is to use a type of apparatus made only (or mostly) of glass, and which can be fitted together tightly using 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.

Heating is needed in many experiments. You can do this using a Bunsen burner, but often an electric heating mantle or a hot water bath or hot oil bath is preferred for safety reasons.



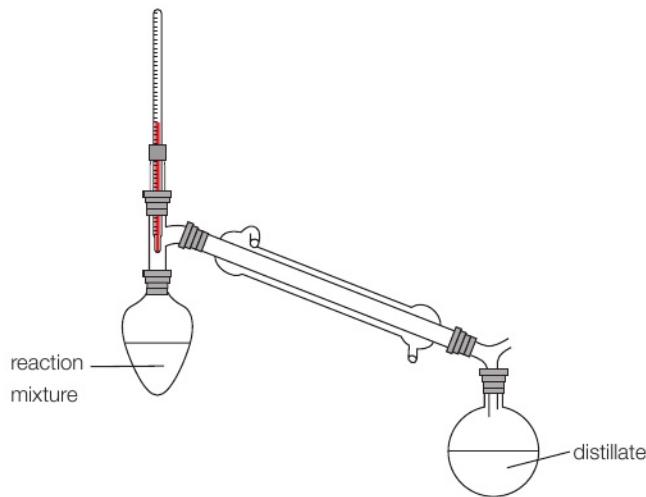
▲ **fig B** This is just one of the many apparatus set-ups using ground-glass joints.

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. If, after a while, the temperature begins to rise, this indicates that a different compound is beginning to distil over.

Fig C shows the apparatus used for simple distillation.

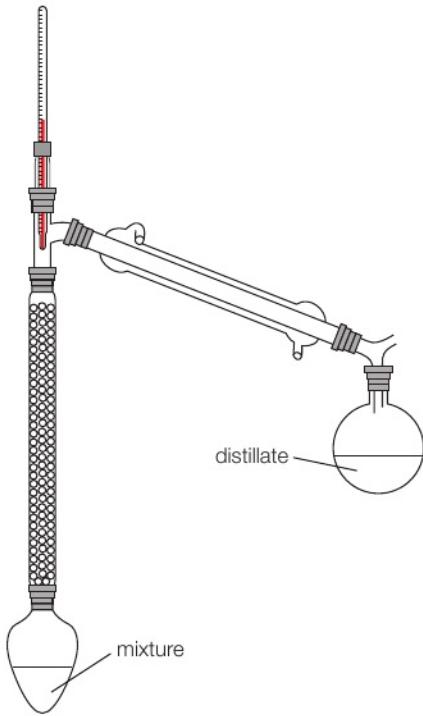


▲ **fig C** Apparatus used for simple distillation.

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.

Fractional distillation takes longer than simple distillation, and is best used when the difference in boiling temperatures is small, and when there are several compounds to be separated from a mixture.

ADVANTAGES AND DISADVANTAGES

The advantages of using simple distillation, rather than fractional distillation, are that it is easier to set up and it is quicker.

The disadvantage is that it does not separate the liquids as well as fractional distillation. Simple distillation should only be used if the boiling temperature of the liquid being purified is very different from the other liquids in the mixture, ideally a difference of more than 25 °C.

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. Using more portions of solvent, but with the same total volume, removes more of the desired organic product.

The desired organic product has been removed from the reaction mixture, but is now mixed with the added solvent. Simple distillation or fractional distillation now has to be used to separate the desired organic product from the solvent used.

DRYING

Many organic liquids are prepared using inorganic reagents, which are often used in aqueous solution. A liquid organic product may partially or even completely dissolve in water, so water may be an impurity that needs to be removed by a drying agent. One important feature of a drying agent is that it does not react with the organic liquid.

There are several drying agents available, but the most common ones are anhydrous metal salts, often calcium sulfate, magnesium sulfate and sodium sulfate. What these compounds have in common is that they form hydrated salts, so when they come into contact with water in an organic liquid they absorb the water as water of crystallisation. Anhydrous calcium chloride can also be used for some organic compounds, although it does react with others and is soluble in alcohols.

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

Using one or more of the purifying techniques, you have purified an organic compound. But is it really pure?

For liquids, there is a simple way to test whether it is pure – measure its boiling temperature. Impurities raise the boiling temperature.

The boiling temperatures of pure organic compounds have been carefully measured and are widely available in data books and online. If you measure the boiling temperature of your organic compound, you can compare it with an accurate value and then make your decision about how pure it is.

The apparatus used depends on the volume of liquid available, and whether it is toxic or flammable. The apparatus used for simple distillation can be used.

A word of caution – this test may not be conclusive, because you may not be able to measure the boiling temperature of your organic compound accurately enough. Your thermometer might read too low or too high, so even if your measured boiling temperature exactly matches the one in the data book or online, you may wrongly assume that your compound is pure.

Also remember that different organic compounds can, by coincidence, have the same boiling temperature. For example, both 1-chloropentane and 2-methylpropan-1-ol boil at 108 °C.

LEARNING TIP

Give examples of when you would use fractional distillation instead of simple distillation. Think back to the advantages and disadvantages of both methods listed above.

CHECKPOINT

1. Describe the apparatus you could use to perform:
 - (a) a simple distillation
 - (b) fractional distillation
 - (c) solvent extraction.
2. What is the purpose of using a thermometer during distillation?
3. What are the limitations of using the measurement of a boiling temperature as a way of assessing the purity of an organic liquid?

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

LEARNING OBJECTIVES

- Be able to interpret data from mass spectra to suggest possible structures of simple 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 mass spectrum of an element often appears very simple, with a very small number of vertical lines, called peaks. Each peak represents an isotope of the element.

In contrast, the mass spectrum of an organic compound often appears complex, with many peaks. If all the peaks are included, there may be more peaks than there are atoms in a molecule of the compound, so something different is happening.

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:



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 $\text{C}_4\text{H}_{10}^+$ peak (58) indicates the relative molecular mass of butane.

OTHER PEAKS

The spectrum may show a very small peak just to the right of the molecular ion peak (sometimes referred to as the *M*+1 peak). This is caused by the presence of a naturally occurring isotope of carbon (^{13}C , rather than the usual ^{12}C isotope) in the molecule. Approximately 99% of all carbon atoms are ^{12}C , with most of the remaining 1% being ^{13}C .

You may have met the ^{14}C isotope, which also occurs naturally in organic compounds. This isotope is radioactive and used in radiocarbon dating. The proportion of ^{14}C atoms in a sample of an organic compound is extremely small and can be ignored in mass spectrometry.

The peaks with smaller *m/z* values result from fragmentation in the mass spectrometer, rearrangement reactions and the loss of more than one electron. Rearrangement is often unpredictable and will not be considered here, but it does help to explain the large number of peaks in some spectra. The breaking of a carbon–hydrogen bond can occur, but this is not usually described as fragmentation.

FRAGMENTATION IN HYDROCARBONS

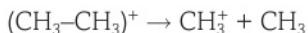
Fragmentation is very common and can often be used to work out the structure of an organic molecule.

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:



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:

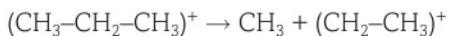


You can see that the products are identical, so the spectrum does not depend on how the bond breaks – there will be a peak at $m/z = 15$.

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:



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:



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.

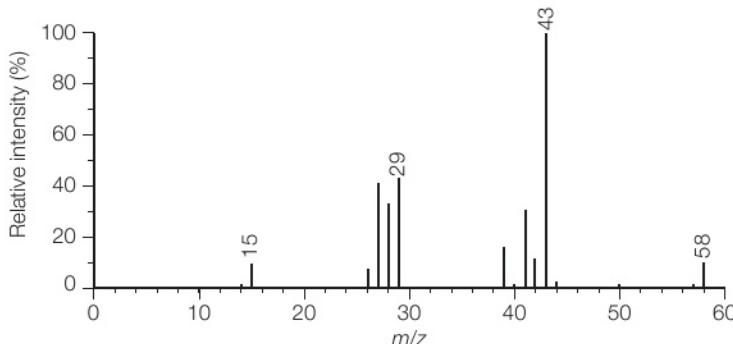
A TYPICAL MASS SPECTRUM

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	$(\text{CH}_3\text{-CH}_2)^+$	
43	$(\text{CH}_3\text{-CH}_2\text{-CH}_2)^+$	This is the most abundant peak.
58	$(\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3)^+$	This is the molecular ion peak.

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

LEARNING TIP

Be clear about the difference between a peak with a large m/z value and a peak with a large abundance.

The m/z value indicates which ion is present, but the height of the peak indicates its abundance.

CHECKPOINT

1. Explain the origin of the $M+1$ peak seen in some mass spectra.
2. Write an equation to show the formation of the base peak in the fragmentation of the molecular ion 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 STRUCTURES FROM MASS SPECTRA

LEARNING OBJECTIVES

- Be able to interpret data from mass spectra to suggest possible structures of simple organic compounds.

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).

Table A shows some common m/z values and possible ions responsible for these peaks.

M/Z VALUE	POSSIBLE IONS
15	CH_3^+
17	OH^+
28	CO^+
29	CH_3CH_2^+ and CHO^+
31	CH_2OH^+
43	$\text{CH}_3\text{CH}_2\text{CH}_2^+$ and $\text{CH}_3\text{CHCH}_3^+$ 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.

LEARNING TIP

It is sometimes worth comparing the m/z values of fragment ions with that of the molecular ion. The difference between the two indicates what has been lost during fragmentation.

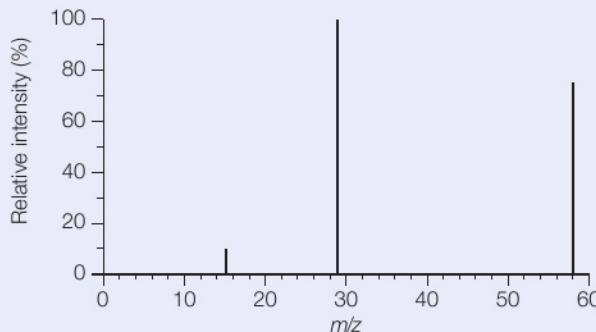
For example, if the molecular ion peak is at $m/z = 60$ and there is a fragment ion with $m/z = 45$, the difference is 15, which suggests the loss of a CH_3 group.

WORKED EXAMPLE 1

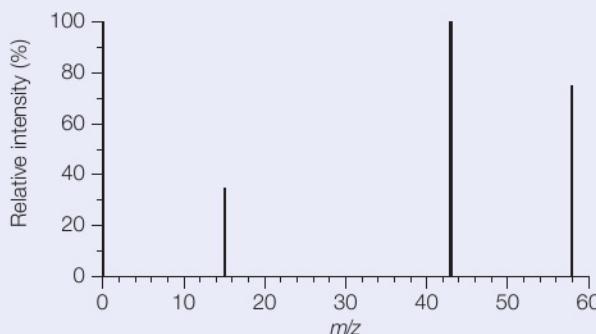
Two compounds, A and B, have the molecular formula C_3H_6O . Their simplified mass spectra are shown below.

Can you deduce the structure of each one?

A



B

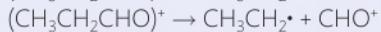
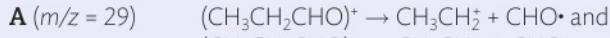
**INTERPRETATION**

Here are the main points that can be deduced from the simplified mass spectra.

- Both mass spectra show a peak at $m/z = 60$. This corresponds to the molecular ion $C_3H_6O^+$ (relative molecular mass of C_3H_6O is 58.0), but this does not help in deducing the structure.
- Both A and B have a peak at $m/z = 15$, which is caused by the CH_3^+ ion. As this is present in both, it does not help to distinguish between the two structures.
- One obvious difference is a major peak at $m/z = 29$ in A, which is not present in B. This could be caused by either $CH_3CH_2^+$ or CHO^+ , or by both of them. The structure CH_3CH_2CHO fits perfectly – this is the aldehyde propanal.
- The other obvious difference is a major peak at $m/z = 43$ in B, which is not present in A. This could not be caused by either $CH_3CH_2CH_2^+$ or $CH_3CHCH_3^+$ because the radical produced at the same time would have a mass of 15 (they must add up to 58), and oxygen has a mass of 16. The other possibility is CH_3CO^+ , which when considered with the peak at $m/z = 15$ (CH_3^+) suggests the structure CH_3COCH_3 – this is the ketone propanone.

You may be asked to write equations to show the formation of the ions you have used in your deduction.

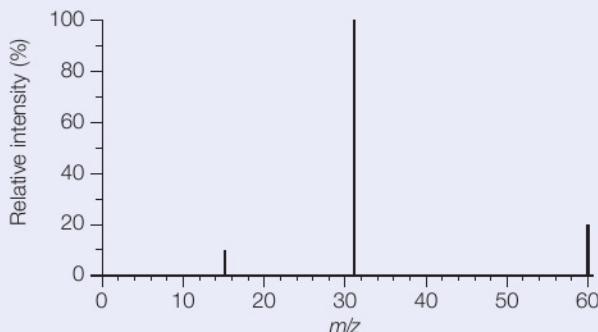
In this example, they are:

**WORKED EXAMPLE 2**

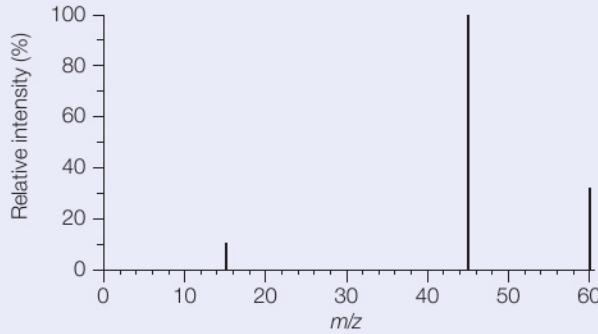
Two compounds, C and D, have the molecular formula C_3H_8O . Their simplified mass spectra are shown below.

Can you deduce the structure of each one?

C



D

**INTERPRETATION**

Here are the main points that can be deduced from the simplified mass spectra.

- Both mass spectra show a peak at $m/z = 60$. This corresponds to the molecular ion $C_3H_8O^+$ (relative molecular mass of C_3H_8O is 60.0), but this information does not help in deducing the structure.
- Both C and D have a peak at $m/z = 15$, which is caused by the CH_3^+ ion. As this is present in both, this information does not help to distinguish between the two structures.
- One obvious difference is a major peak at $m/z = 31$ in C, which is not present in D. This could be caused by CH_2OH^+ . When considered with the peak at $m/z = 15$ (CH_3^+) and a CH_2 group, this suggests the structure $CH_3CH_2CH_2OH$, which is propan-1-ol.
- The other obvious difference is a major peak at $m/z = 45$ in D, which is not present in C. This could not be caused by $COOH^+$ because D contains only 1 oxygen atom. The other possibility is CH_3CHOH^+ , which when considered with the peak at $m/z = 15$ (CH_3^+) suggests the structure $CH_3CH(OH)CH_3$, which is propan-2-ol.

CHECKPOINT

- Write an equation to show the formation of the ethyl cation in the fragmentation of the molecular ion of pentane.
- Write equations to show the formation of the ions used in the deduction of the structures of C and D (from Worked example 2 above).

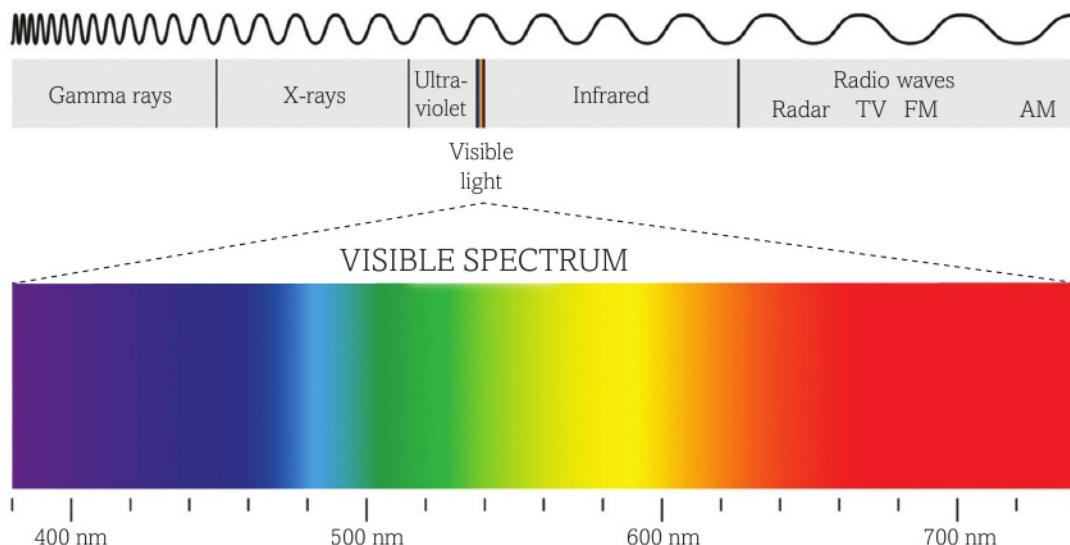
10D 3 INFRARED SPECTROSCOPY

LEARNING OBJECTIVES

- Be able to use infrared spectra to deduce functional groups present in organic compounds.
- Be able to predict infrared absorptions due to familiar functional groups including wavenumber data.

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.

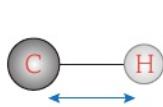


▲ **fig A** You can see how infrared radiation fits into the wider electromagnetic spectrum, next to the red part of the visible spectrum.

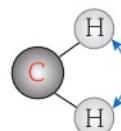
WHAT HAPPENS WHEN MOLECULES ABSORB INFRARED RADIATION

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 H_2 and Cl_2) do not absorb infrared radiation.

WHAT DOES AN INFRARED SPECTRUM LOOK LIKE?

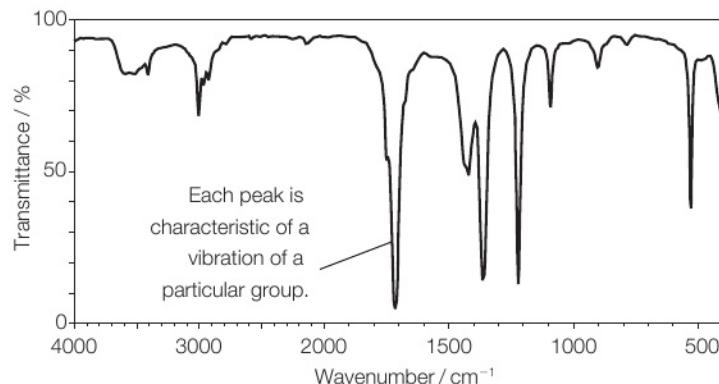
When a compound is irradiated by infrared radiation, the bonds in the molecules absorb radiation from some parts of the spectrum, but not from others.

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 cm^{-1} . The numerical scale normally starts at 4000 cm^{-1} and ends at 500 cm^{-1} . It may seem unusual for the numbers to decrease from left to right, but the left to right direction does represent increasing frequency. Another unusual feature is that the scale changes after 2000 cm^{-1} .

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 cm^{-1} . 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	C–H	aldehyde
2775–2700		
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 $3300\text{--}2500\text{ cm}^{-1}$ 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.

LEARNING TIP

In an infrared spectrum, remember that the horizontal scale uses wavenumber to represent frequency, and that the scale changes at 2000 cm^{-1} .

CHECKPOINT

- Explain why hydrogen fluoride absorbs infrared radiation but fluorine does not.
- A compound has an infrared spectrum that shows a broad absorption centred on 2850 cm^{-1} and a sharp absorption at 1710 cm^{-1} . Suggest what homologous series the compound belongs to.

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

LEARNING OBJECTIVES

- Be able to use infrared spectra to deduce functional groups present in organic compounds.
- Be able to predict infrared absorptions due to familiar functional groups including wavenumber data.

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.

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.

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	C–H	aldehyde
2775-2700		
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.

FINGERPRINT REGION

You may come across the term ‘fingerprint region’. This term is worth explaining. The table of wavenumbers starts at 3750 and ends at 1645 cm⁻¹, even though there are many absorptions in the infrared region between 1500 to 500 cm⁻¹. Most of the absorptions in this region (1500 and 500 cm⁻¹) result from bending vibrations (not considered in this book) or from absorptions by bonds not listed in the table of wavenumbers.

This region is sometimes referred to as the ‘fingerprint region’ because, although individual absorptions are not easily recognised, the whole pattern acts like a fingerprint that is slightly different for similar molecules.

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.

WORKED EXAMPLE 1

What absorptions would you expect to find in the infrared spectrum of propanal?

Once you recognise propanal as an aldehyde, you could predict:

- absorptions in the ranges 2900–2820 and 2775–2700 cm⁻¹ resulting from the C–H bond
- absorption in the range 1740–1720 cm⁻¹ resulting from the C=O bond.

WORKED EXAMPLE 2

What absorptions would you expect to find in the infrared spectrum of $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$?

This compound is an alcohol, so you could predict a broad absorption in the range 3750–3200 cm⁻¹ resulting from the O–H bond.

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 $\text{C}_2\text{H}_4\text{O}_2$. 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 $\text{C}_2\text{H}_4\text{O}_2$ that fits is $\text{CH}_2(\text{OH})\text{CHO}$. 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.

WORKED EXAMPLE 6

An organic compound has a molecular formula of $\text{C}_3\text{H}_6\text{O}_2$. Its infrared spectrum is shown below.

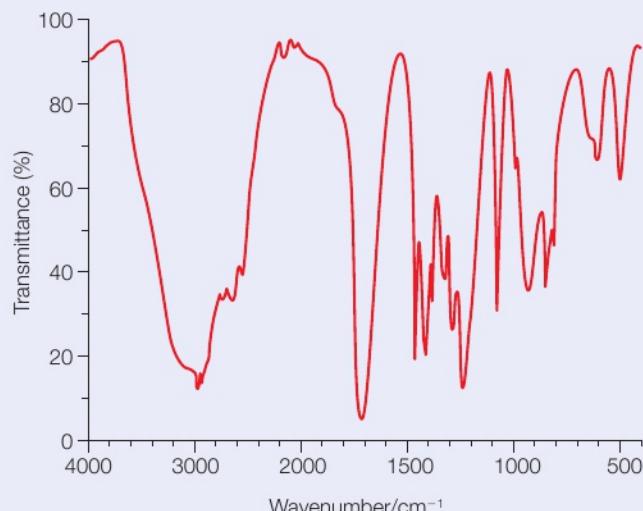


fig A The infrared spectrum of an unknown compound.

Deduce a possible structure for the compound.

Answer

There is a broad absorption at 3000 cm⁻¹ and a narrow absorption at 1700 cm⁻¹. These suggest the presence of O–H (carboxylic acid) and C=O (carboxylic acid). The compound must contain the COOH group, which leaves C_2H_5 to make up the rest of the molecular formula. The only possible structure is $\text{CH}_3\text{CH}_2\text{COOH}$, which is propanoic acid.

LEARNING TIP

Concentrate on the region between 4000 and 1500 cm⁻¹. Practise making predictions of the spectra of molecules in **Topics 4, 5 and 10**.

CHECKPOINT

1. Why is it not easy to use infrared spectra to distinguish between propan-1-ol and propan-2-ol?
2. A compound has the molecular formula $\text{C}_3\text{H}_6\text{O}$. How can its infrared spectrum be used to show that it has the structure $(\text{CH}_3)_2\text{CO}$ and not $\text{CH}_3\text{C}(\text{OH})=\text{CH}_2$?

10 THINKING BIGGER

UNBEATABLE RECORDS

SKILLS

ANALYSIS, INTERPRETATION, CRITICAL THINKING

The following extract comes from an article entitled 'Five rings good, four rings bad'. The article highlights the problem of performance-enhancing drug misuse in sport and, in particular, the use of 'designer' steroids that are not detectable by routine drug testing. This extract focuses on how analytical chemists identified a sample of an unknown steroid as tetrahydrogestrinone (THG).

HOW DON CATLIN'S TEAM CRACKED THG

On 13 June 2003, Don Catlin received a methanolic solution of an unknown steroid, recovered from a hypodermic syringe. He ran standard GC-MS tests on the solution, and synthesised several derivatives. Attempts to identify the steroid failed because the mass spectrum contained a large number of unidentifiable peaks. The only compound that they could identify at this stage was a small amount of another anabolic steroid, norbolethone, evidently present as an impurity.

Catlin suspected that the 'unknown' shared a common carbon skeleton with norbolethone. However, they noted a peak in its mass spectrum with $m/z = 312$, and thought this was the molecular ion. Accurate mass measurement gave 312.2080, from which they deduced the compound had the molecular formula $C_{21}H_{28}O_2$.

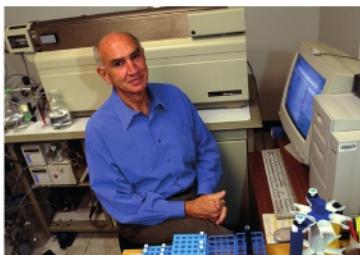


fig A Don Catlin

When they compared the mass spectrum of the unknown with other steroids, it became clear that it shared features with gestrinone and trenbolone.

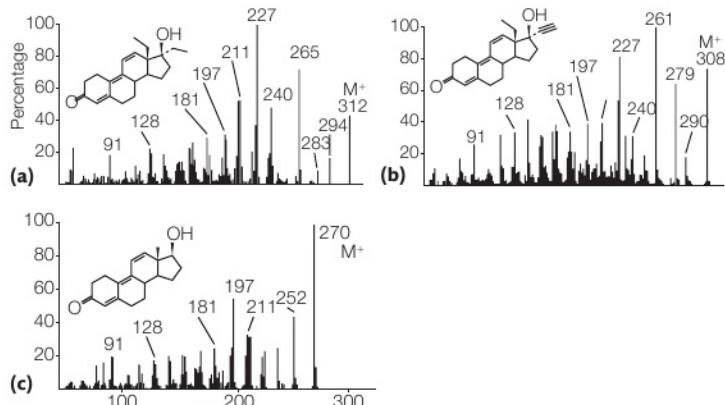


fig B The mass spectra of (a) the unknown substance, (b) gestrinone and (c) trenbolone.

All three compounds had the same fragments with m/z values at 211 and below present, so Catlin deduced that they contained the same A, B and C rings.

Furthermore, when the MS of the unknown was compared with gestrinone, the fragments with m/z above 240 occurred 4 Da higher in the unknown, suggesting that it was gestrinone with four additional hydrogen atoms. A possibility was that the terminal alkyne group in gestrinone had been reduced to an ethyl group.

Having tentatively identified the unknown steroid as tetrahydrogestrinone, the team then prepared an authentic sample of THG by catalytic hydrogenation of gestrinone. This required careful control of conditions (0°C) to prevent hydrogenation of C=C double bonds (see equation in fig C). The retention time and mass spectra of the synthetic THG matched the unknown material exactly.

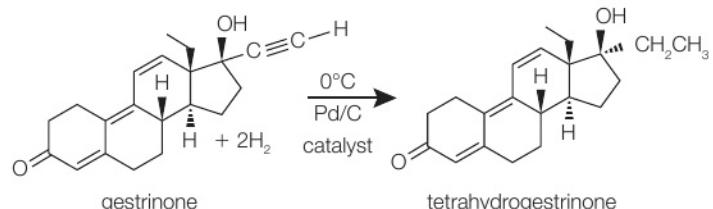


fig C The hydrogenation of gestrinone.

To study the metabolism of THG in mammals, the team gave intravenous doses of THG to a baboon, and collected urine samples from the animal over several days. Detectable amounts of THG were found in urine for many hours after administration.

THG was thus directly detectable in urine samples, though it defies detection by the standard procedure involving derivatisation into the Me_3Si derivatives.

SCIENCE COMMUNICATION

1. (a) Who do you think is the intended audience for this article? Evaluate the ways in which the author has written for them.
- (b) Why do you think value judgements are avoided by the author even though the article considers a very emotive issue?

CHEMISTRY IN DETAIL

2. The analytical techniques of IR spectroscopy and mass spectrometry can be used to identify unknown molecules. Suggest which of these two techniques would be more useful in distinguishing samples of two steroids with similar structures. You should be prepared to justify your choice.
3. The mass spectrum of trenbolone is shown in **fig B**. Suggest how the fragment at $m/z = 252$ is generated.

THINKING BIGGER TIP

The dalton (Da) is the standard unit for indicating mass on an atomic or molecular scale.

ACTIVITY

The online database at NIST Chemistry WebBook allows you to search for a range of organic compounds and related data.

Use the database to find the mass spectrum of one of the following compounds:

- (a) chlorobenzene
- (b) bromoethane
- (c) ethylamine
- (d) cyclohexane.

Prepare a 3–5 minute presentation showing the mass spectrum of your chosen molecule and identifying the most important peaks. Your presentation should include:

- a picture of the mass spectrum of your chosen molecule
- an identification of the main fragment and isotopic abundance peaks of your molecule, explaining how each peak is formed.

SKILLS → ANALYSIS

WRITING SCIENTIFICALLY

An evaluation should review all the information to form a conclusion. You should think about the strengths and weaknesses of the evidence and information, and come to a supported judgement.

DID YOU KNOW?

The women's 800 m record was set in 1983 by the Czech Jarmila Kratochvilová, who ran the distance in 1:53.28. This was before the test for human growth hormone was in routine use at athletics competitions. Since then, only one athlete has managed to come within a second of her record.