

A Level Chemistry OCR

YOUR NOTES

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4. Core Organic Chemistry

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4.1 Basic Concepts

4.1.1 Chemical Names & Formulae

Systematic Nomenclature

- **Systematic nomenclature** can be used to name organic compounds and therefore make it easier to refer to them
- The **alkanes** provide the basis of the naming system and the **stem** of each name indicates how many carbon atoms are in the **longest chain** in one molecule of the compound

Nomenclature of Organic Compounds Table

Number of C atoms	Molecular formula of straight-chain alkane	Name of alkane	Stem used in naming
1	CH ₄	methane	meth-
2	C ₂ H ₆	ethane	eth-
3	C ₃ H ₈	propane	prop-
4	C ₄ H ₁₀	butane	but-
5	C ₅ H ₁₂	pentane	pent-
6	C ₆ H ₁₄	hexane	hex-
7	C ₇ H ₁₆	heptane	hept-
8	C ₈ H ₁₈	octane	oct-
9	C ₉ H ₂₀	nonane	non-
10	C ₁₀ H ₂₂	decane	dec-

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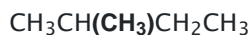
- If there are any side-chains or functional groups present, then the position of these groups is indicated by numbering the carbon atoms in the longest chain

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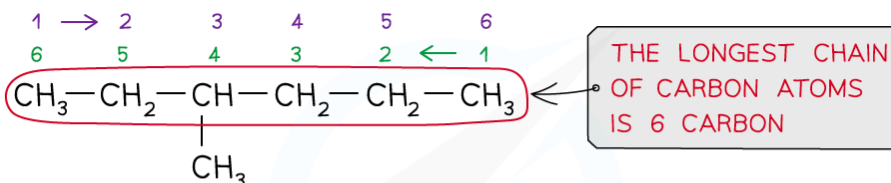
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- starting at the end that gives the lowest possible numbers in the name
- The hydrocarbon **side-chain** is shown in **brackets** in the structural formula



- The side-chain is named by adding '-yl' to the normal alkane **stem**
- This type of group is called an **alkyl** group



COUNTING FROM RIGHT TO LEFT GIVES: 4-METHYL HEXANE

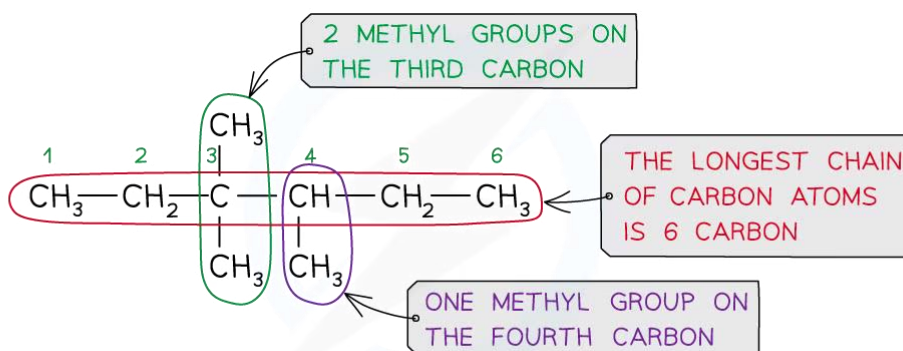
COUNTING FROM LEFT TO RIGHT GIVES: 3-METHYL HEXANE

THE NOMENCLATURE GIVES THE LOWEST POSSIBLE NUMBER IN THE NAME

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Naming Side Chains

- If there are more than one of the same alkyl side-chain or functional groups, **di-** (for two), **tri-** (for three) or **tetra-** (for four) is added in front of its name
- The adjacent **numbers** have a comma between them
- Numbers** are separated from **words** by a hyphen

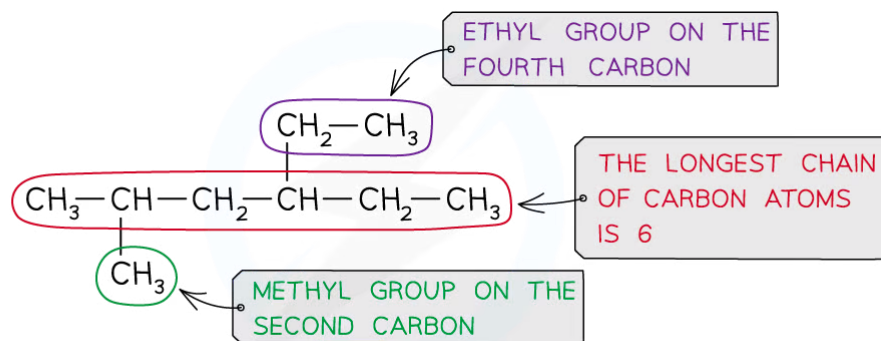


3, 3, 4 - TRIMETHYL HEXANE

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Naming Multiple Side Chains

- If there is more than one type of alkyl side-chain, they are listed in alphabetic order



4-ETHYL-2-METHYL HEXANE

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Naming Side Chains in Alphabetical Order



Exam Tip

An **aliphatic** compound is **straight** or **branched-chain** and also includes **cyclic** organic compounds that do not contain a **benzene** ring.

Functional Groups & their Nomenclature Table

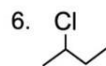
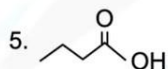
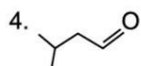
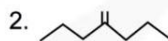
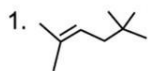
Functional Group	Nomenclature	Example	Name
Alkenes	-ene	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	Ethene
Halogenoalkane	chloro- fluoro- iodo- bromo-	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}- & \text{C}-\text{Cl} \\ & \\ \text{H} & \text{H} \end{array}$	Chloroethane
Alcohol	-ol	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}- & \text{C}-\text{OH} \\ & \\ \text{H} & \text{H} \end{array}$	Ethanol
Aldehyde	-al	$\begin{array}{c} \text{H} & & \text{O} \\ & & // \\ \text{H}-\text{C}- & \text{C} \\ & \backslash \\ \text{H} & \text{H} \end{array}$	Ethanal
Ketone	-one	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$	Propanone
Carboxylic Acid	-oic acid	$\begin{array}{c} \text{H} & & \text{O} \\ & & // \\ \text{H}-\text{C}- & \text{C} \\ & \backslash \\ \text{H} & \text{OH} \end{array}$	Ethanoic acid
Ester	alkyl -oate	$\begin{array}{c} \text{H} & \text{H} & \text{H} & & \text{O} & \text{H} \\ & & & & // & \\ \text{H}-\text{C}- & \text{C}- & \text{C}-\text{O}- & \text{C}- & \text{C}-\text{H} \\ & & & & \\ \text{H} & \text{H} & \text{H} & & \text{H} \end{array}$	Propyl Ethanoate
Amine	alkyl -amine	$\begin{array}{c} \text{H} & \text{H} \\ & \\ \text{H}-\text{C}- & \text{C}-\text{NH}_2 \\ & \\ \text{H} & \text{H} \end{array}$	Ethylamine
Nitrile	-nitrile	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{C}=\text{N} \\ \\ \text{H} \end{array}$	Ethane nitrile

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Worked Example

Naming organic molecules

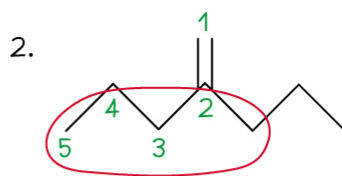
Name the following molecules using correct systematic nomenclature:



Answer



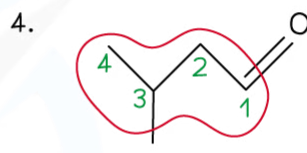
2, 5, 5 - TRIMETHYLHEX-2-ENE



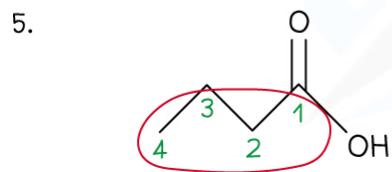
2-PROPYLPENT-1-ENE



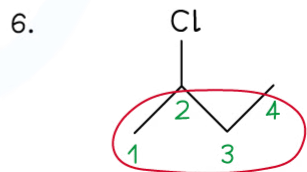
PROPANAL



3-METHYLBUTANAL



BUTANOIC ACID



2-CHLOROBUTANE

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Chemical Formulae

- The **general formula** is a formula that represents a **homologous series** of compounds using letters and numbers
 - E.g. the general formula of alkanes is C_nH_{2n+2}
 - A homologous series is a group of organic compounds that have the same functional group, the same general formula and the same chemical properties
- The **structural formula** is a formula that shows how the atoms are bonded to each carbon atom in a molecule
- The **displayed formula** is a 2D representation of an organic molecule showing **all** its atoms (by their **symbols**) and their bonds (by single, double or triple bonds)
- The **skeletal formula** is a simplified displayed formula with all the carbon and hydrogen atoms removed, with the exception of hydrogens that are part of a functional groups, e.g. OH

Overview of the Formulae of Organic Compounds Table

Homologous Series	General Formula	Structural Formula	Displayed Formula	Skeletal Formula	Name
Alkene	C_nH_{2n}				propene
Halogenoalkane	$C_nH_{2n+1}X$	$R-X$			halogenopropane
Alcohol	$C_nH_{2n+1}OH$	$R-OH$			propan-1-ol
Aldehydes	$C_nH_{2n+1}CHO$				propanal
Ketone	$C_nH_{2n}O$				propanone
Carboxylic Acid	$C_nH_{2n+1}COOH$				propanoic acid
Ester	$C_nH_{2n}O_2$				methyl propanoate
Amine	$C_nH_{2n+1}NH_2$	$R-NH_2$			propylamine
Nitrile	$C_nH_{2n+1}CN$	$R-C\equiv N$			propanitrile

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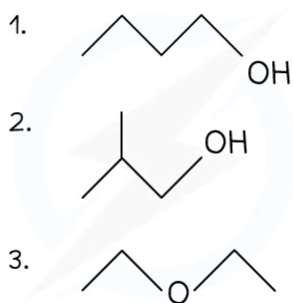
Worked Example

Drawing skeletal formulae of molecules

Draw the skeletal formula of the following molecules:

1. $\text{CH}_3(\text{CH}_2)_3\text{OH}$
2. $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$
3. $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

Answer:

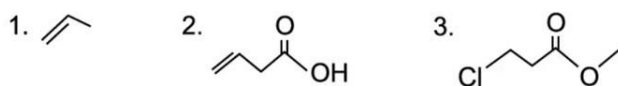


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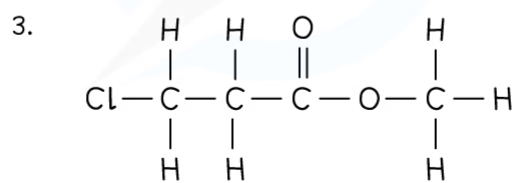
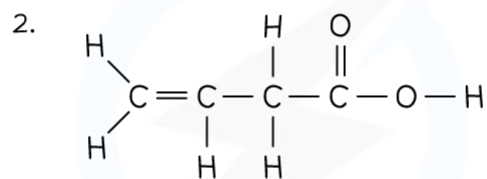
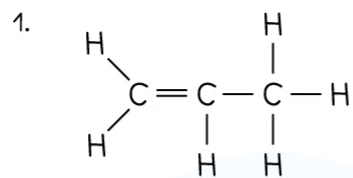
Worked Example

Drawing displayed formulae of molecules

Draw the displayed formula of the following molecules:



Answer



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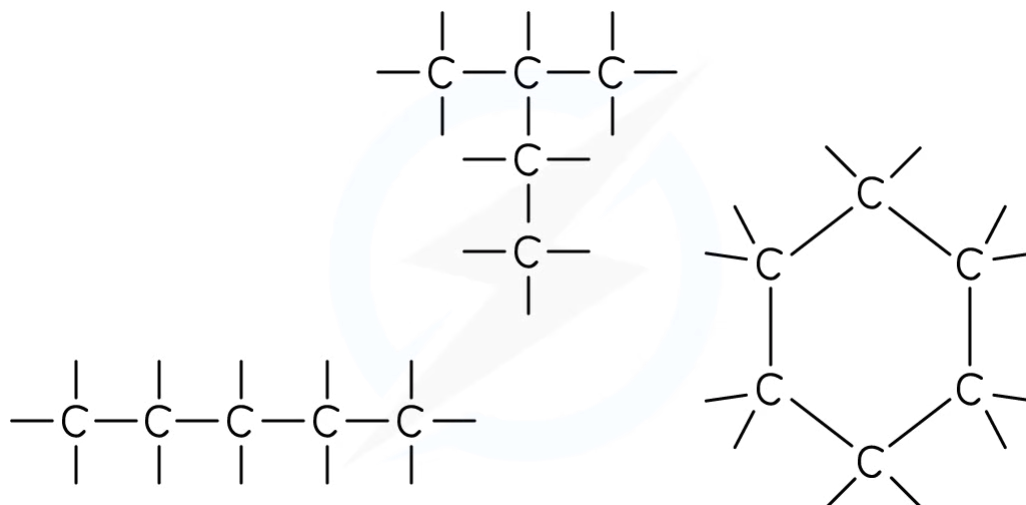
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4.1.2 Functional Groups

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Homologous Series

- **Organic chemistry** is the chemistry of carbon compounds
- Carbon forms a vast number of compounds because it can form strong covalent bonds with itself
- This enables it to form long chains of carbon atoms, and hence an almost infinite variety of carbon compounds are known

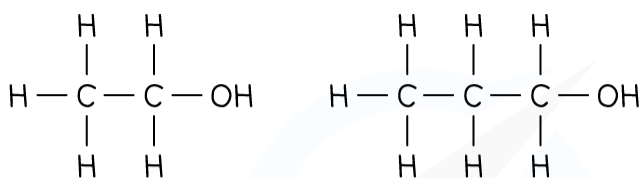


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An almost infinite variety of chains, branches and rings is possible

Homologous series

- A homologous series is a group of organic compounds that have the same functional group, but each successive member differs by CH_2



ETHANOL
 $\text{C}_2\text{H}_5\text{OH}$

PROPANOL
 $\text{C}_3\text{H}_7\text{OH}$

- BOTH HAVE AN ALCOHOL FUNCTIONAL GROUP ($-\text{OH}$)
- BOTH HAVE THE SAME GENERAL FORMULA ($\text{C}_n\text{H}_{2n+1}\text{OH}$)
- BOTH HAVE SIMILAR CHEMICAL REACTIVITY

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Ethanol and propanol belong to the same homologous series

Homologous Series of Alkanes

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Name of alkane	Number of carbons	Chemical formula	Boiling point in °C	State at room temperature	Melting point in °C
Methane	1	CH ₄	-162	gas	-182
Ethane	2	C ₂ H ₆	-89	gas	-183
Propane	3	C ₃ H ₈	-42	gas	-188
Butane	4	C ₄ H ₁₀	-1	gas	-138
Pentane	5	C ₅ H ₁₂	36	liquid	-130

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- ♦ Things we can say about a **homologous series**:
 - Each member has the same **functional group**
 - Each member has the same **general formula**
 - Each member has **similar** chemical properties
 - Each successive member differs by -CH₂ -
 - Members have gradually changing physical properties, for example, boiling point, melting point and density
- ♦ As a homologous series is ascended, the size of the molecule increases
- ♦ This has an effect on the physical properties, such as boiling point and density

Describing Chemicals

- A functional group is a group of atoms that are responsible for the characteristic reactions of a compound
 - They determine the physical and chemical properties of molecules
- Organic compounds can be classified into one of three categories:
 1. Aliphatic – a compound containing carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings
 2. Alicyclic – this is an aliphatic compound arranged in non-aromatic rings with or without side chains
 3. Aromatic – a compound containing a benzene ring
- The table below shows a summary of common functional groups found in compounds
- R is any other atom or group of atoms (except for hydrogen)

Functional Groups found in Compounds Table

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Family	Functional Group						
Alkene	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{R} - \text{C} = \text{C} - \text{R} \end{array}$						
Halogenoalkane	$\text{R} - \text{X}$ <p>Where X = F, Cl, Br and I</p>						
Alcohol	<table style="width: 100%; text-align: center;"> <tr> <td> $\begin{array}{c} \text{H} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{H} \end{array}$ </td> <td> $\begin{array}{c} \text{R} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{H} \end{array}$ </td> <td> $\begin{array}{c} \text{R} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{R} \end{array}$ </td> </tr> <tr> <td>Primary alcohol</td> <td>Secondary alcohol</td> <td>Tertiary alcohol</td> </tr> </table>	$\begin{array}{c} \text{H} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{R} \end{array}$	Primary alcohol	Secondary alcohol	Tertiary alcohol
$\begin{array}{c} \text{H} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R} - \text{C} - \text{OH} \\ \\ \text{R} \end{array}$					
Primary alcohol	Secondary alcohol	Tertiary alcohol					
Aldehydes	$\begin{array}{c} \text{O} \\ // \\ \text{R} - \text{C} \\ \backslash \\ \text{H} \end{array}$						
Ketone	$\begin{array}{c} \text{R} \\ \backslash \\ \text{C} = \text{O} \\ / \\ \text{R} \end{array}$						
Carboxylic Acid	$\begin{array}{c} \text{O} \\ // \\ \text{R} - \text{C} \\ \backslash \\ \text{OH} \end{array}$						
Ester	$\begin{array}{c} \text{O} \\ \\ \text{R} - \text{C} - \text{O} - \text{R} \end{array}$						
Primary Amine	$\text{R} - \text{NH}_2$						
Nitrile	$\text{R} - \text{C} \equiv \text{N}$						

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Exam Tip

Remember: Organic compounds can also be described as:

- Saturated - containing single carbon-carbon bonds only
- Unsaturated - containing a minimum of one carbon-carbon bond that is **not** single, e.g. C=C or C≡C

Converting Names to Formulae

- As previously discussed, a homologous series is a group of organic compounds that have the same functional group, but each successive member differs by CH_2
 - The homologous series of hydrocarbons called the alkanes has the general formula $\text{C}_n\text{H}_{2n+2}$
 - The homologous series of hydrocarbons called the alkenes has the general formula C_nH_{2n}
- These general formulae can be used to predict the chemical formula of any member of the same homologous series

Worked Example

Use the descriptions to deduce the formula of the following chemicals:

- Eicosane – an alkane containing a 20 carbon backbone
- n*-nonapentacontane – a long chain alkane isolated in 1997 containing 59 carbons
- Oct-3-ene – an 8 carbon alkene with one $\text{C}=\text{C}$ bond on carbon-3

Answers

Answer 1: Eicosane is an alkane so has the general formula $\text{C}_n\text{H}_{2n+2}$

There are 20 carbons so n is 20, which means that there are $2n+2$ hydrogens or $(2 \times 20) + 2 = 42$

Therefore, the formula of eicosane is $\text{C}_{20}\text{H}_{42}$

Answer 2: *n*-nonapentacontane is an alkane so has the general formula $\text{C}_n\text{H}_{2n+2}$

There are 59 carbons so n is 59, which means that there are $2n+2$ hydrogens or $(2 \times 59) + 2 = 120$

Therefore, the formula of *n*-nonapentacontane is $\text{C}_{59}\text{H}_{120}$

Answer 3: Oct-3-ene is an alkene so has the general formula C_nH_{2n}

There are 8 carbons in oct-3-ene so n is 8, which means that there are $2n$ hydrogens or $(2 \times 8) = 16$

Therefore, the formula of oct-3-ene is C_8H_{16}

- The process shown in the worked examples can be applied to any homologous series **providing** that the general formula and the number of at least one of the component elements are known

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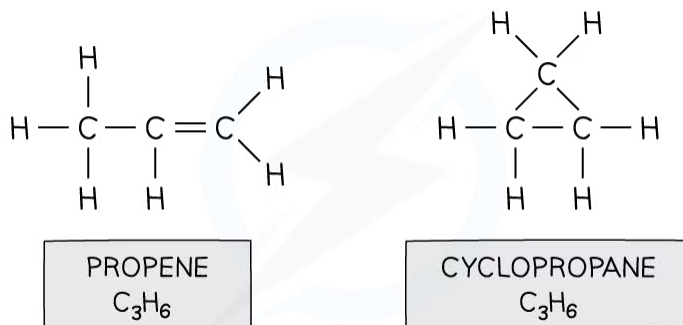
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4.1.3 Structural Isomerism

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Types of Structural Isomerism

- **Structural isomers** are compounds that have the same **molecular** formula but different **structural** formulae
 - E.g. propene and cyclopropane

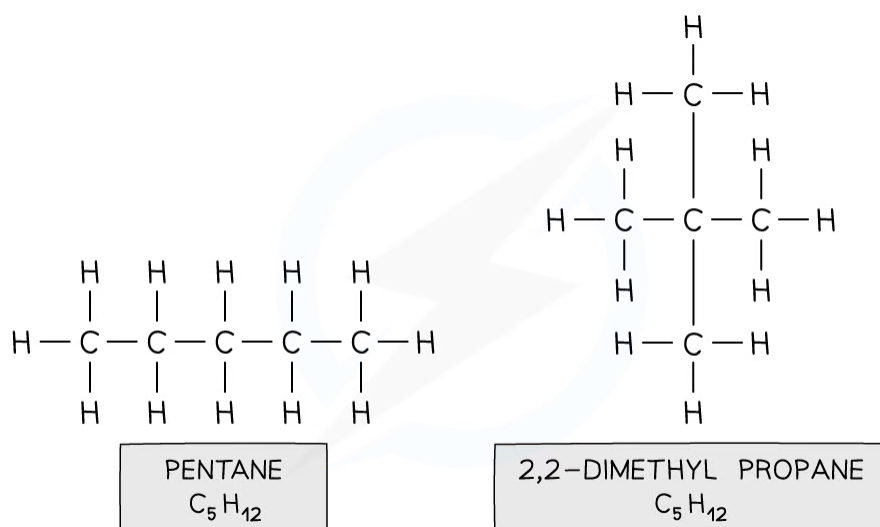


Both propene and cyclopropane are made up of 3 carbon and 6 hydrogen atoms but the structure of the two molecules differs

- There are three different types of structural isomerism:
 - **Chain** isomerism
 - **Positional** isomerism
 - **Functional** group isomerism

Chain isomerism

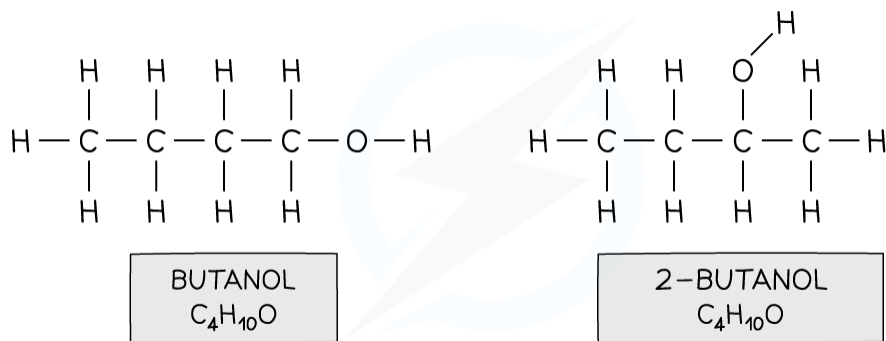
- **Chain isomerism** is when compounds have the same molecular formula, but their longest hydrocarbon chain is not the same
- This is caused by branching
 - E.g. pentane and 2,2-dimethylpropane



Both compounds are made up of the same atoms, however the longest carbon chain in pentane is 5 and in 2,2-dimethylpropane it is 3 (with two methyl branches)

Positional isomerism

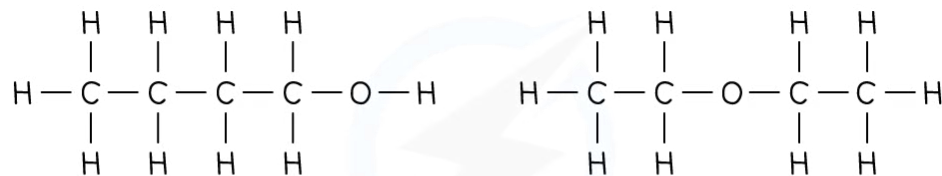
- **Positional isomers** arise from differences in the position of a functional group in each isomer
 - The functional group can be located on different carbons
 - For example, butan-1-ol (or butanol) and butan-2-ol (or 2-butanol)



Both compounds have an alcohol group and are made up of 4 carbons, 10 hydrogens and one oxygen, however in butanol the functional group is located on the first carbon and in 2-butanol on the second carbon

Functional group isomerism

- When different functional groups result in the same molecular formula, **functional group isomers** arise
- The isomers have very different chemical properties as they have different functional groups
 - For example, butanol and ethoxyethane



BUTANOL
 $C_4H_{10}O$

ETHOXYETHANE
 $C_4H_{10}O$

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Both compounds have the same molecular formula however butanol contains an alcohol functional group and ethoxyethane an ether functional group

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Determining Isomers

- You should be able to deduce all possible isomers for organic compounds knowing their molecular formula

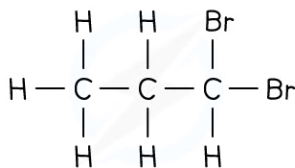
Worked Example

Isomers of dibromopropane

How many isomers are there of dibromopropane, $C_3H_6Br_2$?

Answer

Step 1: Draw the structural formula of the compound

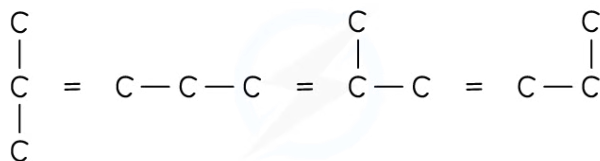


Step 2: Determine whether it is a stereo or structural isomer

- There is no restricted bond rotation around the C–C bond, so it is structural isomerism

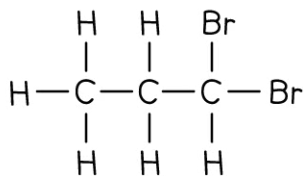
Step 3: Determine whether it is a functional group, chain or positional isomerism

- Functional group? No, as Br is the only functional group possible
- Chain? No, as the longest chain can only be 3
- Positional? Yes, as the two bromine atoms can be bonded to different carbon atoms

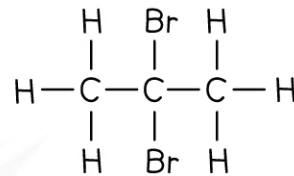


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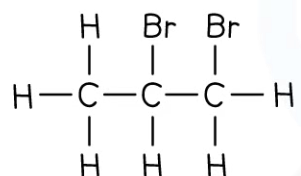


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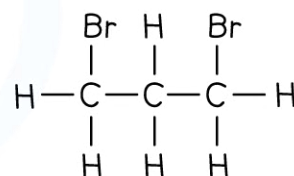


1,1-DIBROMOPROPANE

2,2-DIBROMOPROPANE



AND



1,2-DIBROMOPROPANE

1,3-DIBROMOPROPANE

$\text{C}_3\text{H}_6\text{Br}_2$ THEREFORE HAS 4 STRUCTURAL ISOMERS

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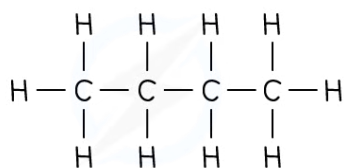
Worked Example

Deducing isomers of C_4H_{10}

How many isomers are there of the compound with molecular formula C_4H_{10} ?

Answer

Step 1: Draw the structural formula of the compound



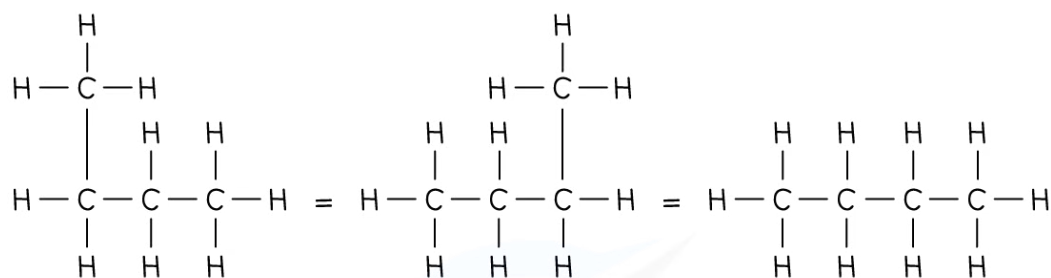
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Step 2: Determine whether it is a stereo or structural isomer.

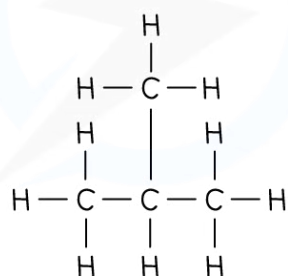
- There is no restricted bond rotation around the C-C bond so it is structural isomerism

Step 3: Determine whether it is a functional group, chain or positional isomerism

- Functional group? No, as there are no functional groups
- Positional? No, as there are no functional groups which can be positioned on different carbon atoms
- Chain? Yes!



BUTANE



2-METHYLPROPANE

C_4H_{10} THEREFORE HAS 2 STRUCTURAL ISOMERS

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Exam Tip

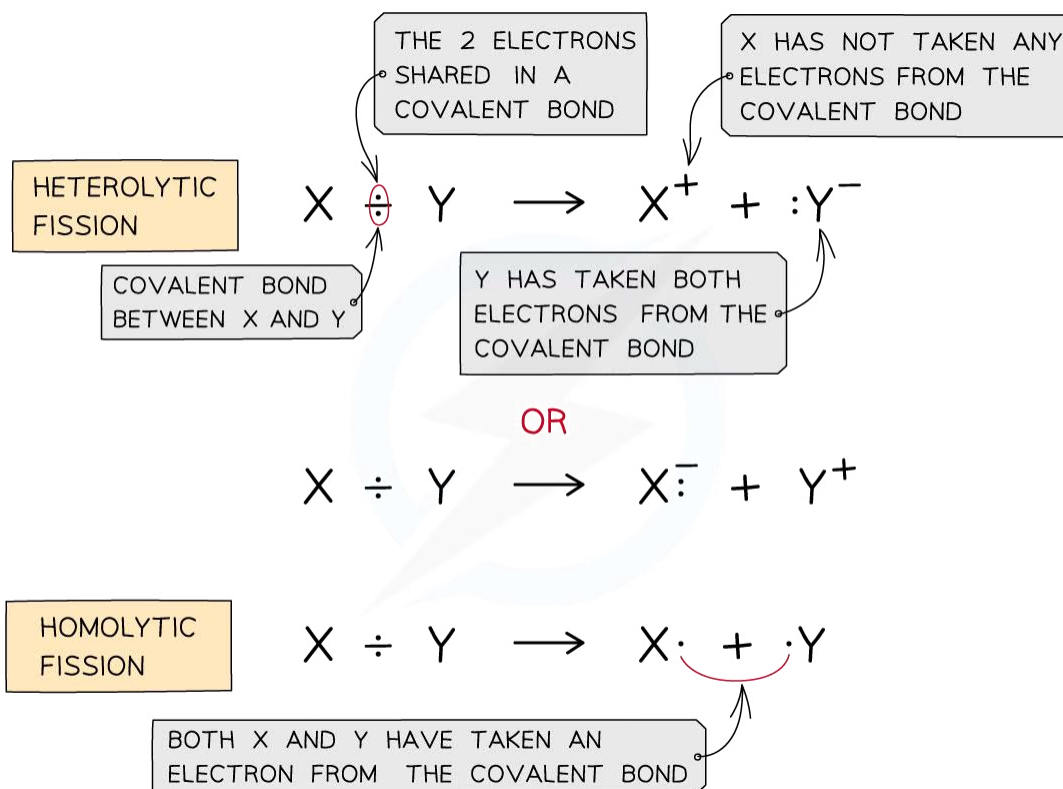
Use a pencil when deducing isomers as it makes it easier to remove sections of your molecule

Careful: Always check your structures as it can be very easy to draw 2 identical "isomers" without realising that they are simply the same molecule viewed from the other side of your sheet of paper. You can always try naming your isomers to help

Bond fission

Homolytic & Heterolytic fission

- **Homolytic fission** is breaking a covalent bond in such a way that each atom takes an electron from the bond to form two **radicals**
 - A radical is a reactive chemical species with an unpaired electron
- **Heterolytic fission** is breaking a covalent bond in such a way that the more electronegative atom takes both the electrons from the bond to form a **negative ion** and leaving behind a **positive ion**



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The diagram shows heterolytic fission in which the most electronegative atom takes both electrons in the covalent bond and homolytic fission in which each atom takes one electron from the covalent bond

Curly Arrows

- Reaction equations tell you about the amount of reactants and products, including their stoichiometry, in a reaction
- Reaction mechanisms tell you about how the reaction actually takes place
- In a reaction mechanism, curly arrows show the movement of electrons
 - Curly arrows can be single headed, sometimes called fish-hook arrows or half curly arrows, to show the movement of one electron which can occur when:
 - A covalent bond undergoes **homolytic fission** to form two radicals
 - Two radicals **terminate** forming a covalent bond in the process
 - A radical and a covalent compound **propagate** as part of a reaction, as shown:



During this propagation step, the unpaired electron from chlorine and one of the electrons from the C-H bond react together to form a new covalent bond and the other electron from the C-H bond moves to form a methyl radical

Exam Tip

The use of single headed arrows is not required knowledge
Their main use is in free radical reactions which are usually represented using written equations rather than outlined mechanisms

- Curly arrows can be double headed to show the movement of a pair of electrons, which can occur when:
 - A covalent bond undergoes fission to form a positive and a negative ion
 - A lone pair of electrons attacks a positive or δ^+ centre and forms a new covalent bond, as shown:



During this step of an addition reaction, the lone pair from the bromide ion reacts with the positive carbocation to form a new covalent bond

- Curly arrows are a feature of three main types of reaction:
 1. **Addition** reactions – where two reactants combine to form one product, e.g. ethene and bromine undergoing addition to form 1,2-dibromoethane
 2. **Substitution** reactions – where an atom or group of atoms in a compounds is replaced by another atom or group of atoms, e.g. bromoethane reacting with the hydroxide ion to form ethanol and the bromide ion
 3. **Elimination** reactions – where a small molecule is removed from a larger molecule, e.g. ethanol reacting with an acid catalyst to form ethene alongside a small molecule of water which is eliminated

4.2 Alkanes

YOUR NOTES

4.2.1 Introduction to Alkanes

Bonding in Alkanes

- ♦ Alkanes are a homologous series made up of **saturated hydrocarbons** (containing only hydrogen and carbon) which are joined by sigma (σ) bonds
- ♦ They have a general formula of C_nH_{2n+2}
- ♦ The electronegativities of carbon and hydrogen are very similar so the C–H sigma (σ) bonds are **non-polar**
- ♦ As a result of this, alkanes are **nonpolar** molecules and have no partial positive or negative charges (δ^+ and δ^- respectively)
 - Alkanes therefore do not react with **polar reagents**
 - They have no electron-deficient areas to attract **nucleophiles**
 - And also lack electron-rich areas to attract **electrophiles**
- ♦ Given that each carbon has four valence electrons, each carbon atom forms four covalent bonds
- ♦ This results in a tetrahedral bonding arrangement with a bond angle of 109.5°
- ♦ Alkanes are non-polar and therefore only exhibit weak temporary induced dipole-dipole forces between the molecules
- ♦ As the bond length of the alkane molecule increases the boiling point also increases

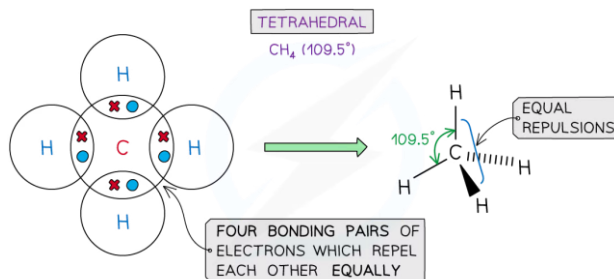
Homologous Series of Alkanes

Name of alkane	Number of carbons	Chemical formula	Boiling point in $^\circ\text{C}$	State at room temperature	Melting point in $^\circ\text{C}$
Methane	1	CH_4	-162	gas	-182
Ethane	2	C_2H_6	-89	gas	-183
Propane	3	C_3H_8	-42	gas	-188
Butane	4	C_4H_{10}	-1	gas	-138
Pentane	5	C_5H_{12}	36	liquid	-130

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Shape of Alkanes

- ♦ Each carbon atom has four valence electrons and will form four sigma bonds in an alkane
 - Therefore there are no lone pairs present
 - The shape will be tetrahedral around each carbon atom



Tetrahedral shape of methane

- ♦ Remember different types of electron pairs have different repulsive forces
 - Lone pairs of electrons have **stronger repulsive forces** than bonding pairs
 - The order of repulsion is therefore: lone pair – lone pair > lone pair – bond pair > bond pair – bond pair
- ♦ As alkanes only have bonding pairs of electrons there is equal repulsion between all four bonding electron pairs

Boiling Points of Alkanes

The boiling point of alkanes varies with two factors

- ♦ Chain length
- ♦ Branching

Chain length

- ♦ Temporary induced dipole–dipole forces will be very small for an alkane such as methane but will increase as the size of the molecules increase
- ♦ Therefore, the boiling points of the alkanes increases with the molecular size, due to the increased temporary induced dipole–dipole forces

Branching

- ♦ Branched alkanes normally exhibit lower boiling points than unbranched alkanes containing the same number of carbon atoms
- ♦ The more branched the chain, the lower the boiling point tends to be
- ♦ Temporary induced dipole–dipole forces can only operate over very short distances between one molecule and its neighbouring molecules
- ♦ It is more difficult for short, bulky molecules to lie close together (compact) compared with long, thin molecules
- ♦ The unbranched alkanes have greater van der Waals' forces of attraction because of their greater surface areas

Reactivity of Alkanes

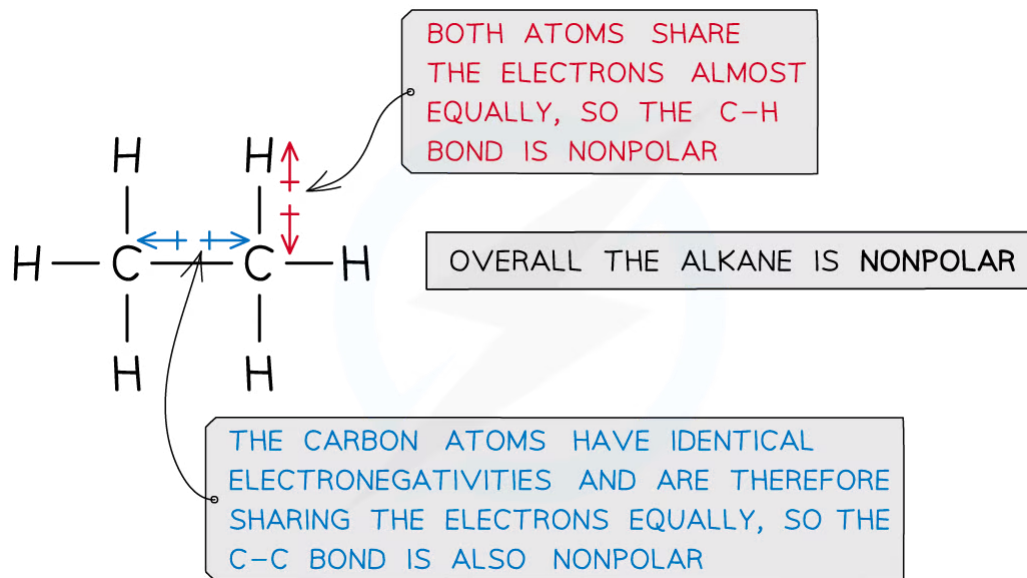
- The **unreactive** nature of alkanes can be explained by two factors
 - The **high bond enthalpies** of the C–C and C–H bonds
 - The very **low polarity** of the sigma (σ) bonds present

Bond enthalpy

- The C–C bond has a bond enthalpy of 346 kJ mol^{-1} and the C–H bond has a bond enthalpy of 411 kJ mol^{-1}
- The C–H bond is stronger as the bond length is less than the C–C bond
 - This is because the hydrogen atom only consists of one shell, so the distance between the nuclei is shorter
 - Creating greater force of attraction to the nuclei and the pair of electrons between them

Polarity

- The electronegativities of carbon and hydrogen are very similar, therefore the bonds will have very low polarity



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Ethane is an example of an alkane that lacks polarity due to almost similar electronegativities of the carbon and hydrogen atoms

Complete & Incomplete Combustion

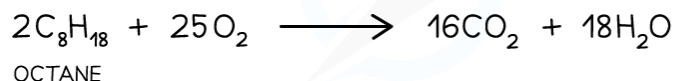
Alkanes are **combusted** (burnt) on a large scale for their use as fuels

Complete combustion

- When alkanes are burnt in **excess** (plenty of) oxygen, **complete combustion** will take place and all carbon and hydrogen will be oxidised to **carbon dioxide** and **water** respectively
 - For example, the complete combustion of octane to carbon dioxide and water

COMPLETE COMBUSTION

ALKANE + OXYGEN -----> CARBON DIOXIDE + WATER



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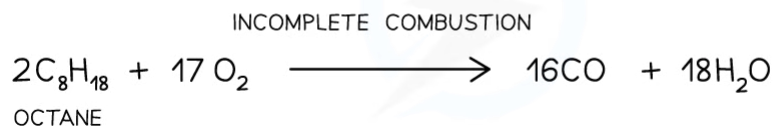
The complete combustion of alkanes

Incomplete combustion

- When alkanes are burnt in only a **limited supply** of oxygen, **incomplete combustion** will take place and not all the carbon is fully oxidised
- Some carbon is only **partially** oxidised to form **carbon monoxide**
 - For example, the incomplete combustion of octane to form carbon monoxide

INCOMPLETE COMBUSTION

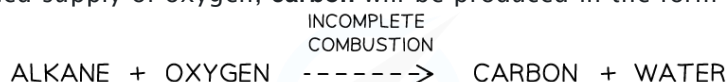
ALKANE + OXYGEN -----> CARBON MONOXIDE + WATER



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The incomplete combustion of alkanes

- Incomplete combustion often takes place inside a **car engine** due to a limited amount of oxygen present
- With a reduced supply of oxygen, **carbon** will be produced in the form of soot:



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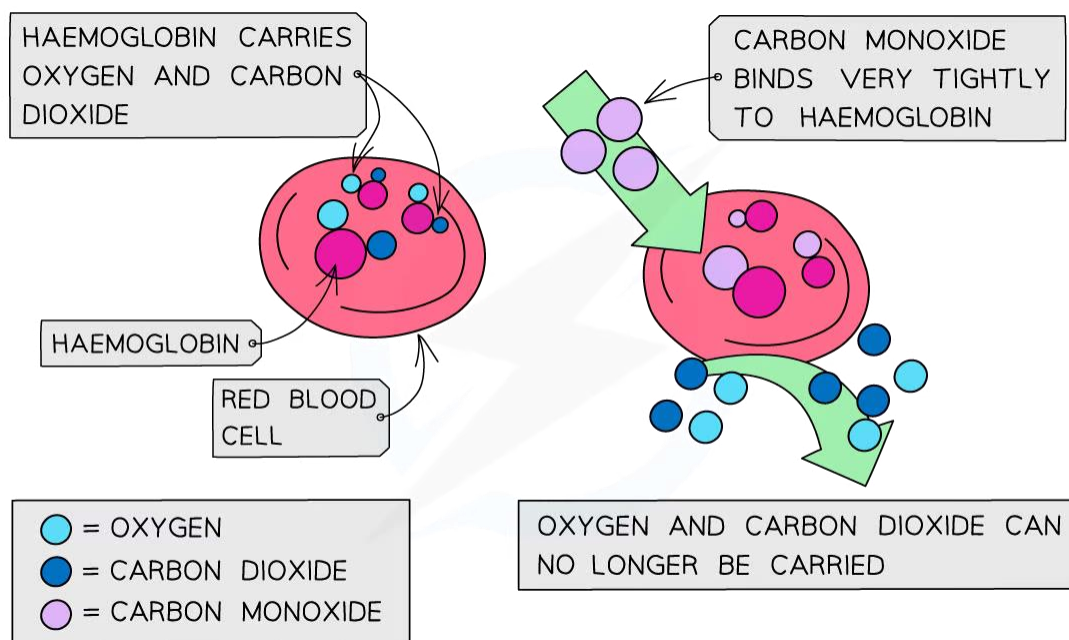
- Car **exhaust fumes** include toxic gases such as **carbon monoxide** (CO), **oxides of nitrogen** (NO/NO₂) and **volatile organic compounds** (VOCs)

- When released into the atmosphere, these pollutants have serious environmental consequences damaging nature and health

YOUR NOTES

Carbon monoxide

- CO is a toxic and odourless gas which can cause dizziness, loss of consciousness and eventually death
 - The CO binds well to haemoglobin which therefore cannot bind oxygen and carbon dioxide
 - Oxygen is transported to organs
 - Carbon dioxide is removed as waste material from organs



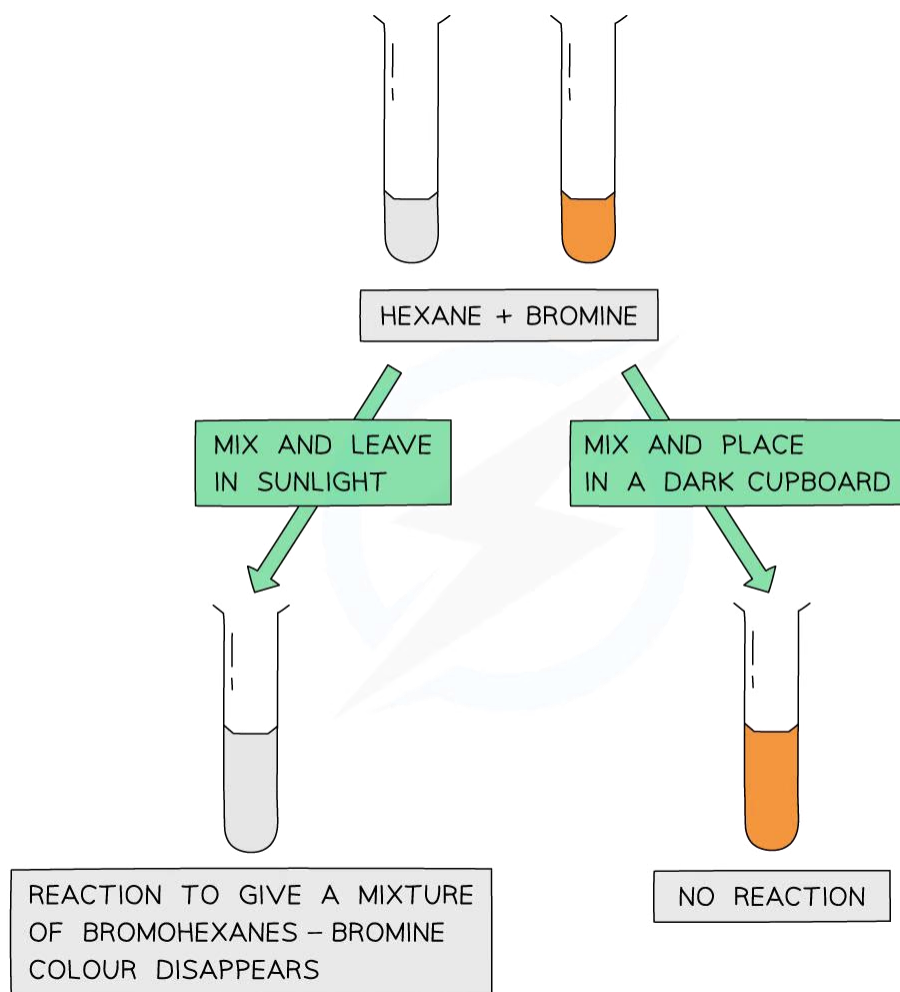
The high affinity of CO to haemoglobin prevents it from binding to O₂ and CO₂

4.2.3 Free Radical Substitution of Alkanes

YOUR NOTES

Free Radical Substitution of Alkanes

- Alkanes can undergo **free-radical substitution** in which a hydrogen atom gets **substituted** by a halogen (chlorine / bromine)
- Since alkanes are very unreactive, **ultraviolet light (sunlight)** is needed for this substitution reaction to occur
- The free-radical substitution reaction consists of three steps:
 - In the **initiation step**, the halogen bond (Cl-Cl or Br-Br) is broken by UV energy to form two radicals
 - These radicals create further radicals in a chain reaction called the **propagation step**
 - The reaction is terminated when two radicals collide with each other in a **termination step**
- Alkanes can undergo **free-radical substitution** in which a hydrogen atom gets **substituted** by a halogen (chlorine/bromine)
 - Ultraviolet light (sunlight)** is needed for this substitution reaction to occur



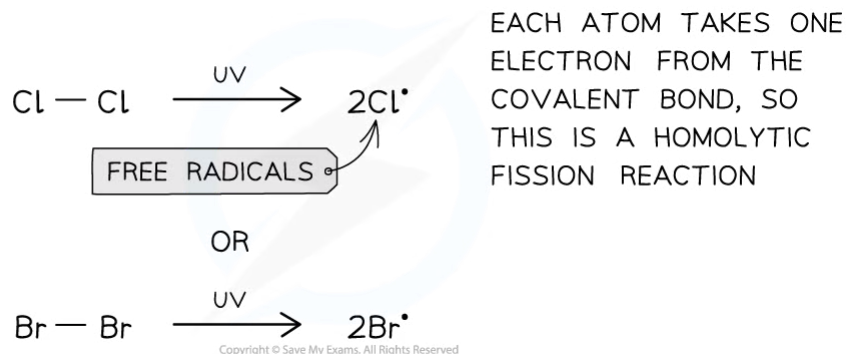
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The fact that the bromine colour has disappeared only when mixed with an alkane and placed in sunlight suggests that the ultraviolet light is essential for the free radical substitution reaction to take place

- The free-radical substitution reaction consists of three steps:

Initiation step

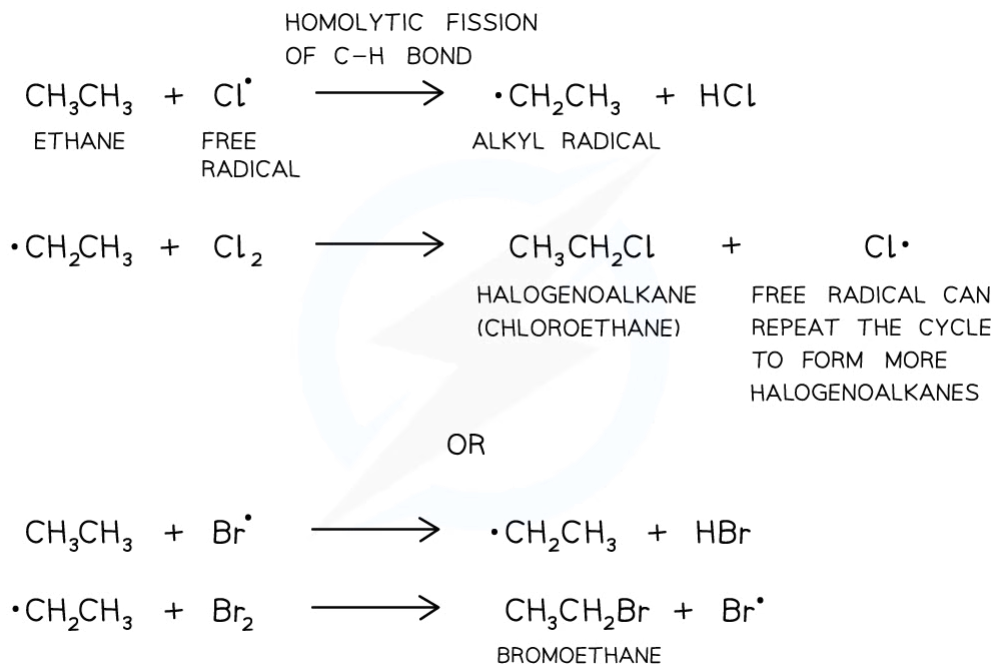
- In the **initiation step** the Cl-Cl or Br-Br is broken by energy from the UV light
- This produces two radicals in a **homolytic fission** reaction



The first step of the free-radical substitution reaction is the initiation step in which two free radicals are formed by sunlight

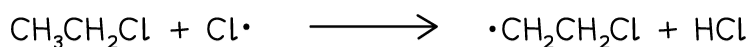
Propagation step

- The **propagation step** refers to the **progression** (growing) of the substitution reaction in a **chain reaction**
 - **Free radicals** are very reactive and will attack the unreactive alkanes
 - A C-H bond breaks **homolytically** (each atom gets an electron from the covalent bond)
 - An **alkyl** free radical is produced
 - This can attack another chlorine/bromine molecule to form the **halogenoalkane** and **regenerate** the chlorine/bromine free radical
 - This free radical can then **repeat** the cycle

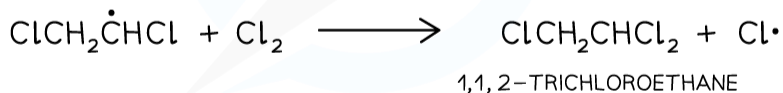
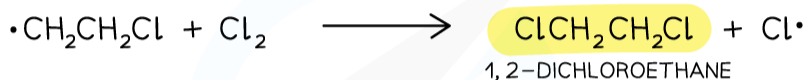


The second step of the free-radical substitution reaction is the propagation step in which the reaction grows in a chain reaction

- This reaction is not very suitable for preparing specific halogenoalkanes as a **mixture** of substitution products are formed
- If there is enough chlorine/bromine present, all the hydrogens in the alkane will eventually get substituted (eg. ethane will become $\text{C}_2\text{Cl}_6/\text{C}_2\text{Br}_6$)



THIS CAN BE FOLLOWED BY:



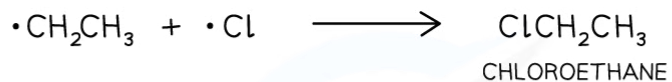
THE SAME PROCESS CAN TAKE PLACE WITH BROMINE INSTEAD OF CHLORINE. THE REACTION WILL CARRY ON TO EVENTUALLY FORM C_2Cl_6

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The free-radical substitution reaction gives a variety of products and not a pure halogenoalkane

Termination step

- The **termination step** is when the chain reaction **terminates** (stops) due to two free radicals reacting together and forming a single unreactive molecule
 - Multiple products are possible



THE SAME PROCESS CAN TAKE PLACE WITH BROMINE INSTEAD OF CHLORINE

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The final step in the substitution reaction to form a single unreactive molecule

Limitations of Free Radical Substitution

YOUR NOTES

Impurities

- ♦ In the termination step there are a number of possibilities
- ♦ Remember that termination involves any free radical bonding with another free radical
- ♦ If we have two $\cdot\text{CH}_3$ radicals they can bond to form ethane, CH_3CH_3
 - $\cdot\text{CH}_3 + \cdot\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_3$
 - If we are trying to form a chloroalkane, then ethane is an impurity

Further substitution

- ♦ Excess chlorine present when reacted with methane in the presence of UV light will promote further substitution and could produce CH_2Cl_2 , CHCl_3 , CCl_4
- ♦ Further substitution can occur as follows
 - $\text{CH}_3\text{Cl} + \cdot\text{Cl} \rightarrow \text{HCl} + \cdot\text{CH}_2\text{Cl}$
 - $\cdot\text{CH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \cdot\text{Cl}$
- ♦ These reactions could occur
 - $\text{CH}_3\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{HCl}$
 - $\text{CH}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow \text{CHCl}_3 + \text{HCl}$
 - $\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$

Substitution of different carbon atoms

- ♦ If we have an alkane with a middle carbon such as propane, substitution can occur here
- ♦ Propagation steps for substitution of propane with excess bromine in the presence of UV light on the middle carbon are as follows
 - $\text{CH}_3\text{CH}_2\text{CH}_3 + \cdot\cdot\text{Br} \rightarrow \text{CH}_3\cdot\text{CHCH}_3 + \text{HBr}$
 - $\text{CH}_3\cdot\text{CHCH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}(\text{Br})\text{CH}_3 + \text{HBr}$
- ♦ If the question asks for the halogen to be substituted onto a middle carbon you must show the radical dot in the correct place, so on the electron deficient carbon

Exam Tip

Ultraviolet (UV) light is the main condition required for free radical substitution but a high temperature of 400°C is also needed. This is not stated on the specification, but be aware that this could come up in a question or during a description of a reaction.

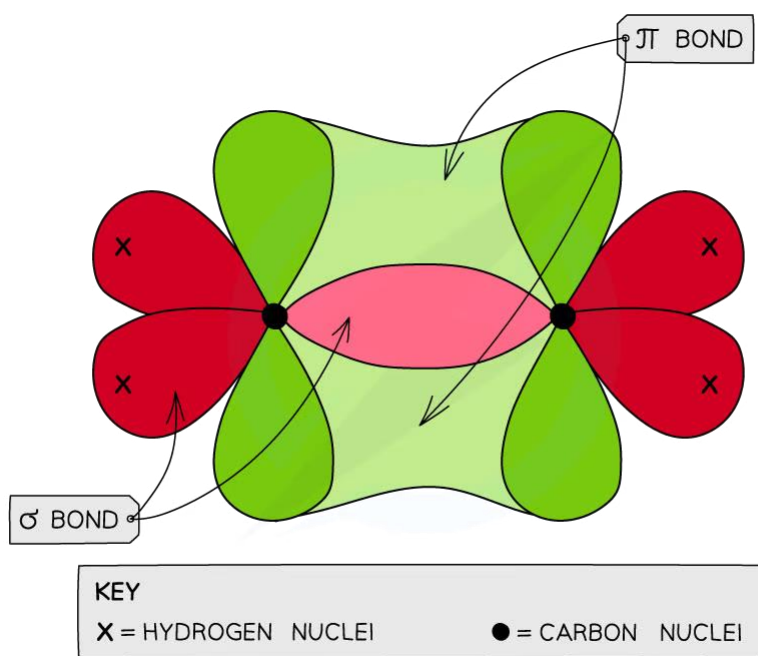
4.3 Alkenes

YOUR NOTES

4.3.1 Introduction to Alkenes

Bonding in Alkenes

- Each carbon atom has four electrons in its outer shell (**electronic configuration:** $1s^2 2s^2 2p^2$)
- Carbon atoms share these four electrons in four covalent bonds with other atoms to achieve a **full outer shell configuration**
- These electrons are found in orbitals within the respective atoms
- When forming a covalent bond, the orbitals overlap in such a way to form two types of bonds
 - Sigma bonds (σ)
 - Pi bonds (π)
- When carbon atoms use only three of their electron pairs to form a σ bond, each carbon atom will have a p orbital which contains **one** spare electron
- When the p orbitals of two carbon atoms overlap with each other, a π bond is formed (the π bond contains two electrons)
- The two orbitals that form the π bond lie above and below the plane of the two carbon atoms to maximise bond overlap



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Each carbon atom in ethene forms two sigma bonds with hydrogen atoms and one σ bond with another carbon atom. The fourth electron is used to form a π bond between the two carbon atoms

Exam Tip

A **double bond** is a combination of a σ and π bond and a **triple bond** is a combination of one σ and two π bonds.

The strength of the bonds increases as follows: **single < double < triple bond**

This is due to the increased electron density around the carbon-carbon bond, making the bond stronger and more difficult to break.

You must be able to draw and explain these diagrams for the exam.

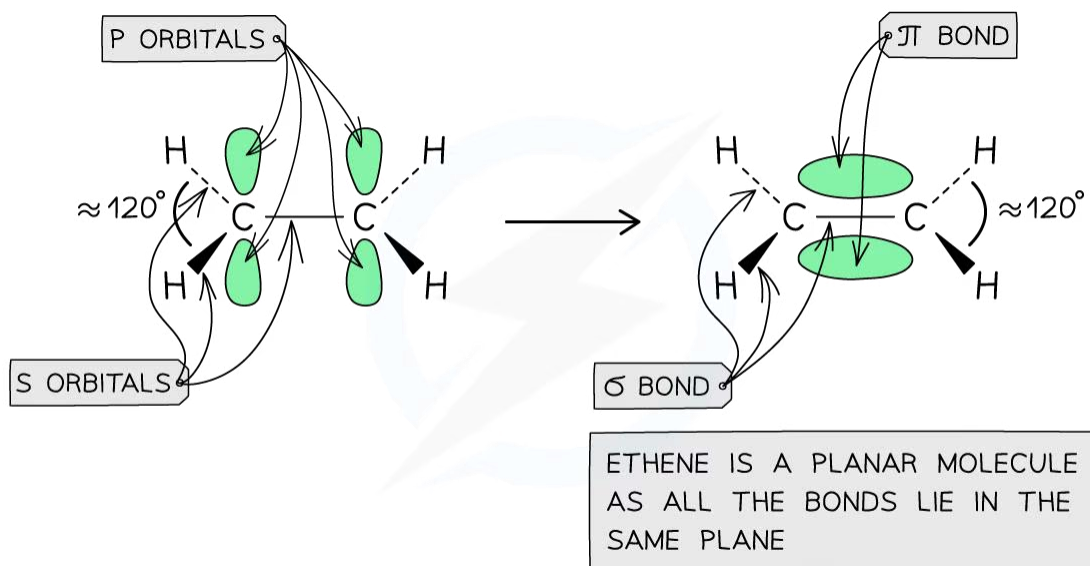
YOUR NOTES

Shape of Alkenes

- The carbon of an alkene double bond has three σ bonding pairs of electrons
 - Two pairs forming σ bonds with other atoms
 - One pair forming σ bonds with the other carbon atom of the double bond
- The three bonding pair of electrons are in the plane of the molecule and repel each other
- This means that the molecule adopts a **planar** arrangement with bond angles of **120°**
- The fourth π bonding pair forms the double bond in combination with the carbon-carbon σ bond

Ethene

- Each carbon atom uses **three** of its **four** electrons to form σ bonds
- Two σ bonds are formed with the hydrogen atoms
- One σ bond is formed with the other carbon atom
- The fourth electron from each carbon atom occupies a p orbital which overlaps **sideways** with another p orbital on the other carbon atom to form a π bond
- This means that the C-C is a **double bond**: one σ and one π bond



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The overlap of the two p orbitals results in the formation of a π bond in ethene in which the bonding pair of electrons repel each other to force the molecule into a planar configuration with bond angles of 120°

4.3.2 Stereoisomerism in Alkenes

YOUR NOTES

Types of Stereoisomerism

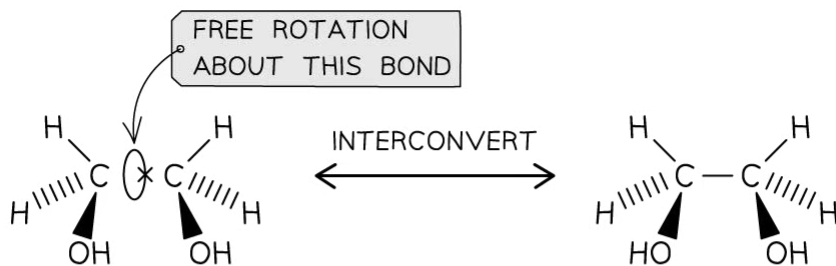
- One of the features of alkenes is their stereoisomerism or geometric isomerism, which can be classed as ***E/Z*** or ***cis / trans***
 - *E / Z* isomerism is an example of stereoisomerism where different atoms or groups of atoms are attached to each carbon atom of the C=C bond
 - *Cis / trans* isomerism is a special case of *E / Z* isomerism where two of the atoms or groups of atoms attached to each carbon atom of the C=C bond are the same

Cis / trans isomers

- In saturated compounds, the atoms / functional groups attached to the single, σ -bonded carbons are not fixed in their position due to the free rotation about the C-C σ -bond
- In unsaturated compounds, the groups attached to the C=C carbons remain fixed in their position
 - This is because free rotation of the bonds about the C=C bond is not possible due to the presence of a π bond
- *Cis / trans* nomenclature can be used to distinguish between the isomers
 - *Cis* isomers have two functional groups on the same side of the double bond / carbon ring, i.e. both above the C=C bond or both below the C=C bond
 - *Trans* isomers have two functional groups on opposite sides of the double bond / carbon ring, i.e. one above and one below the C=C bond

1, 2 - ETHANEDIOL

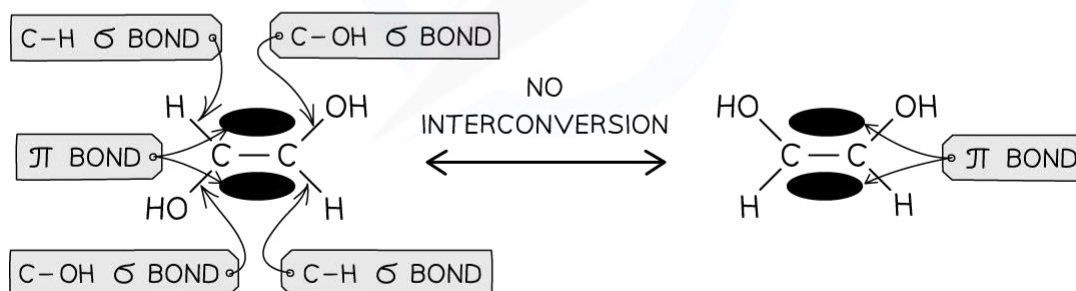
1, 2 - ETHANEDIOL



ROTATION ABOUT C-C BOND IS POSSIBLE SO THE TWO MOLECULES CAN CHANGE FROM ONE CONFORMATION INTO THE OTHER: THE 2 MOLECULES ARE IDENTICAL

TRANS-1, 2-ETHENEDIOL

CIS-1, 2-ETHENEDIOL



NO ROTATION AROUND C=C POSSIBLE SO THE 2 MOLECULES CAN'T CHANGE FROM ONE CONFORMATION INTO THE OTHER: EACH ISOMER HAS DIFFERENT CHEMICAL AND PHYSICAL PROPERTIES

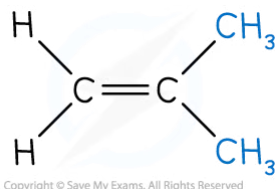
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The presence of a π bond in unsaturated compounds restricts rotation about the C=C bond forcing the groups to remain fixed in their position and giving rise to the formation of certain configurational isomers

Deducing E / Z Isomers

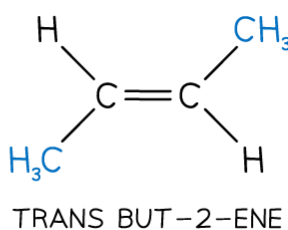
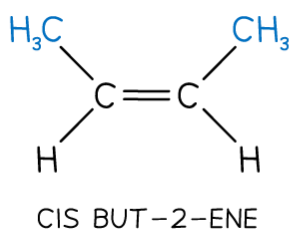
Naming cis / trans isomers

- For cis / trans isomers to exist, we need two different atoms or groups of atoms on either side of the C=C bond
 - This means that 2-methylpropene cannot have cis / trans isomers as the methyl groups are both on the same side of the C=C bond:



2-methylpropene molecules do not have cis / trans isomers

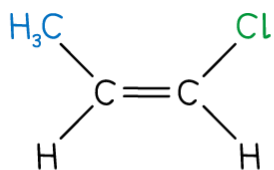
- However, moving one of the methyl groups to the other side of the C=C bond causes cis / trans isomerism:



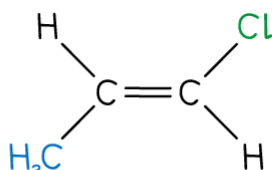
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But-2-ene does have cis / trans isomers

- The atoms or groups of atoms on either side of the C=C bond do not have to be the same for cis / trans isomers:



CIS 1-CHLOROPROP-1-ENE



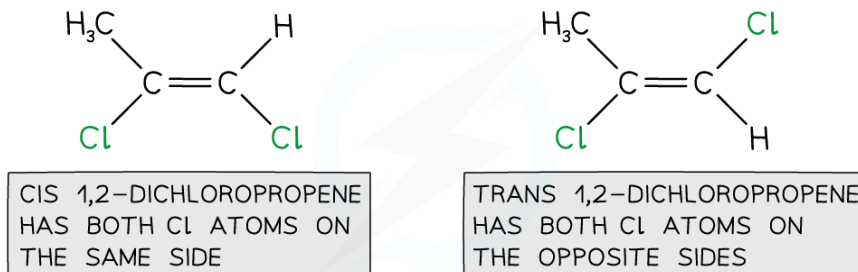
TRANS 1-CHLOROPROP-1-ENE

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1-chloroprop-1-ene also shows cis / trans isomerism

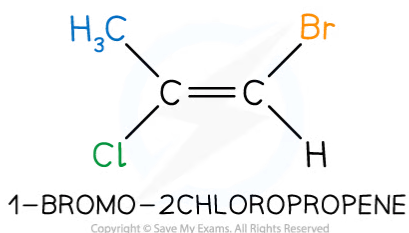
- However, the cis / trans naming system starts to fail once we have more than one atom or group of atoms on either side of the C=C bond
 - The cis / trans naming system can still be used with three atoms / groups of atoms but only if:
 - Two of the three atoms or groups of atoms are the same

- These two atoms or groups of atoms are on opposite sides of the double bond



1,2-dichloropropene can be named using cis / trans

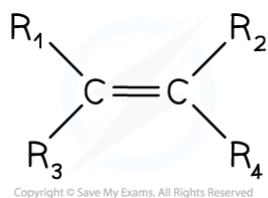
- The cis / trans naming system cannot be used with three atoms / groups of atoms when they are all different
 - This requires the use of the *E* / *Z* naming system



1-bromo-2-chloropropene cannot be named using cis / trans

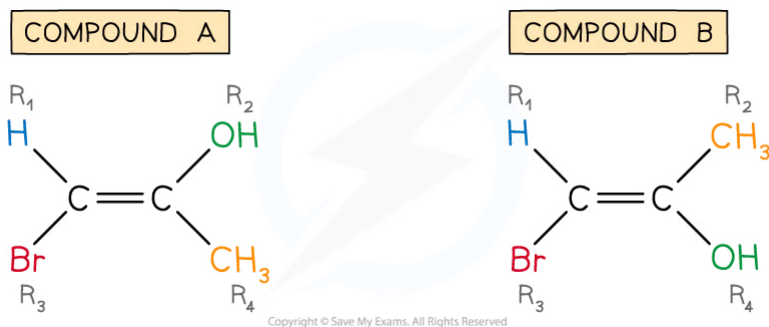
***E* / *Z* isomers**

- ♦ To discuss *E* / *Z* isomers, we will use an alkene of the general formula C_2R_4 :



The general alkene, C_2R_4

- ♦ When the groups R_1 , R_2 , R_3 and R_4 are all different (i.e. $R_1 \neq R_2 \neq R_3 \neq R_4$), we have to use the *E* / *Z* naming system
 - This is based on Cahn-Ingold-Prelog (CIP) priority rules
- ♦ To do this, we look at the **atomic number** of the first atom attached to the carbon in question
 - The higher the atomic number; the higher the priority
- ♦ For example, 2-bromo-1-propen-1-ol has four different atoms or groups of atoms attached to the $C=C$ bond
 - This means that it can have two different displayed formulae:



2-Bromo-1-propen-1-ol (compounds A and B)

Compound A

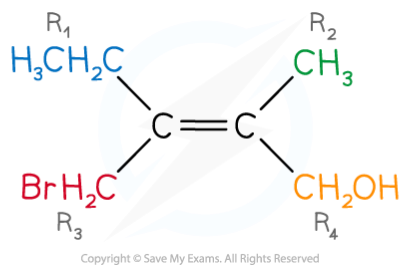
- ♦ **Step 1: Apply the CIP priority rules**
 - Look at R₁ and R₃:
 - Bromine has a higher atomic number than hydrogen so bromine has priority
 - Look at R₂ and R₄:
 - Oxygen has a higher atomic number than carbon so oxygen has priority
- ♦ **Step 2: Deduce E or Z**
 - E isomers have the highest priority groups on opposite sides of the C=C bond, i.e. one above and one below
 - The E comes from the German word "entgegen" meaning opposite
 - Z isomers have the highest priority groups on the same side of the C=C bond, i.e. both above or both below
 - The Z comes from the German word "zusammen" meaning together
 - In compound A, the two highest priority groups are on opposite sides (above and below) the C=C bond
 - Therefore, compound A is E-2-bromo-1-propen-1-ol

Compound B

- ♦ **Step 1: Apply the CIP priority rules**
 - Look at R₁ and R₃:
 - Bromine has a higher atomic number than hydrogen so bromine has priority
 - Look at R₂ and R₄:
 - Oxygen has a higher atomic number than carbon so oxygen has priority
- ♦ **Step 2: Deduce E or Z**
 - In compound B, the two highest priority groups are on the same side (both below) the C=C bond
 - Therefore, compound B is Z-2-bromo-1-propen-1-ol

More complicated E / Z isomers

- Compound X exhibits *E* / *Z* isomerism:



Compound X

- **Step 1: Apply the CIP priority rules**

- Look at R_1 and R_3 :
 - Carbon is the first atom attached to the $C=C$ bond, on the left hand side
- Look at R_2 and R_4 :
 - Carbon is the first atom attached to the $C=C$ bond, on the right hand side
- This means that we cannot deduce if compound X is an *E* or *Z* isomer by applying the CIP priority rules to the first atom attached to the $C=C$ bond
 - Therefore, we now have to look at the second atoms attached
- Look again at R_1 and R_3 :
 - The second atoms attached to R_1 are hydrogens and another carbon
 - The second atoms attached to R_3 are hydrogens and bromine
 - We can ignore the hydrogens as both R groups have hydrogens
 - Bromine has a higher atomic number than carbon, so bromine is the higher priority
 - Therefore, the CH_2Br group has priority over the CH_3CH_2 group
- Look again at R_2 and R_4 :
 - The second atoms attached to R_2 are hydrogens
 - The second atoms attached to R_4 are hydrogens and an oxygen
 - Oxygen has a higher atomic number than hydrogen, so oxygen is the higher priority
 - Therefore, the CH_2OH group has priority over the CH_3 group

- **Step 2: Deduce *E* or *Z***

- In compound X, the two highest priority groups are on the same side (both below) the $C=C$ bond
 - Therefore, compound X is the *Z* isomer

YOUR NOTES

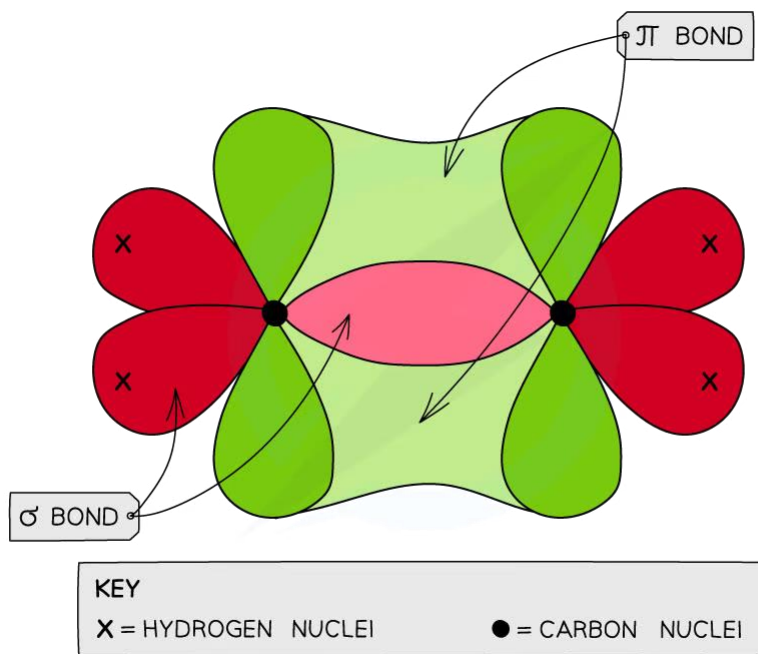
□

4.3.3 Addition Reactions of Alkenes

YOUR NOTES

Reactivity of Alkenes

- ♦ Alkenes are more reactive than alkanes
 - This is due to the presence of the C=C bond or more specifically the π bond



The σ bond between the two carbon atoms is in the centre of the C=C bond with the π bond concentrated above and below the plane of the σ bond, therefore, exposing the π electrons

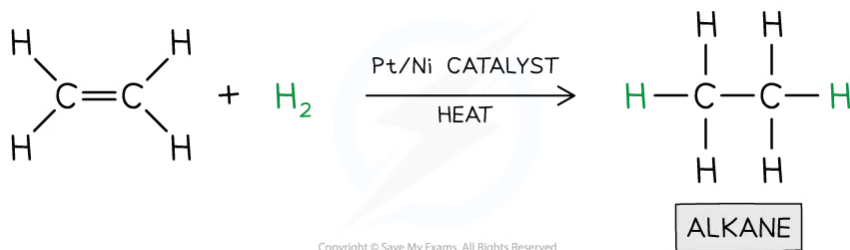
- ♦ A C-C single bond has a bond enthalpy value of 347 kJ mol^{-1}
 - This is equivalent to the σ bond portion of a C=C bond
- ♦ A C=C double bond has a bond enthalpy value of 612 kJ mol^{-1}
 - This value represents the bond enthalpy of the σ and π bond
- ♦ Using these values, we can estimate the value of the π bond alone
 - $612 - 347 = 265 \text{ kJ mol}^{-1}$
- ♦ This calculation shows that the π bond of the C=C double bond is weaker than a C-C single bond and explains why alkenes are more reactive
 - The π bond of the C=C bond requires less energy to break than a C-C single bond and consequently reacts more readily

Addition Reactions of Alkenes

- **Alkenes** are very useful compounds as they can undergo many types of reactions
- They can therefore be used as starting molecules when making new compounds

Hydrogenation

- The reaction between an **alkene** and hydrogen is known as **hydrogenation** or **reduction**
- As well as a **nickel catalyst**, this requires a temperature of 200 °C and a pressure of 1000 kPa



Catalytic hydrogenation converts alkenes into useful alkanes

- One important application of this reaction is in the production of margarine from vegetable oils
- Vegetable oils are **unsaturated** and may be **hydrogenated** to make margarine, which has a higher melting point due to stronger **London Dispersion Forces**
- By controlling the conditions it is possible to restrict how many of the C=C bonds are broken and produce **partially hydrogenated vegetable oils** which have which have the desired properties and textures for margarine manufacture

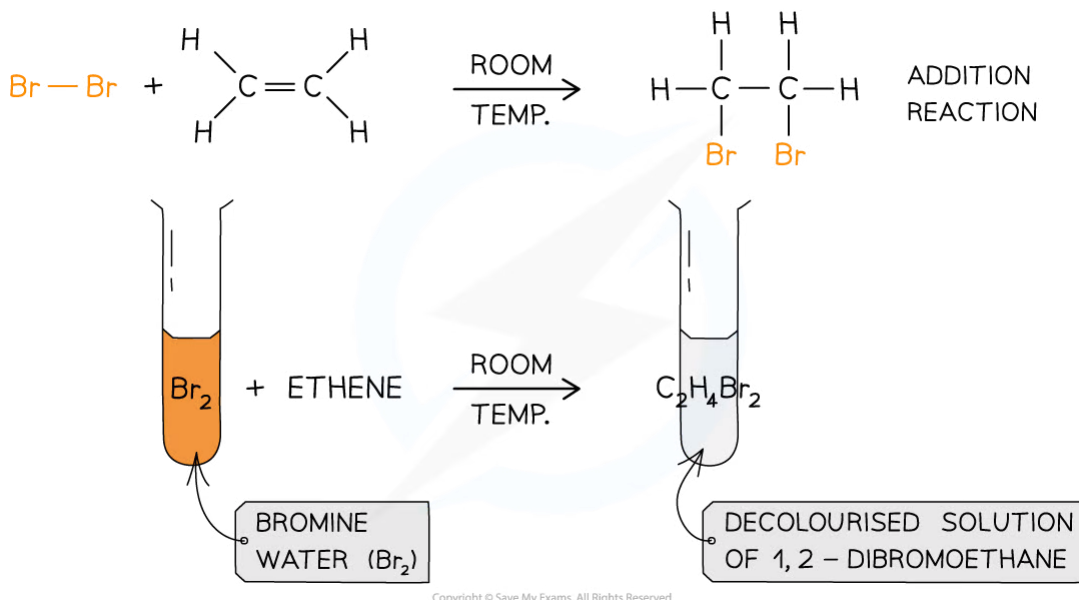
Halogenation

- The reaction between **alkenes** and halogens is known as **halogenation**
- It is an example of an **electrophilic addition** where an electrophile ('electron seeker') joins onto to a double bond
- The C=C double bond is broken, and a new single bond is formed from each of the two carbon atoms
- The result of this reaction is a **dihaloalkane**
- The reaction occurs readily at room temperature and is the basis for the test for **unsaturation** in molecules



Halogenation in alkenes

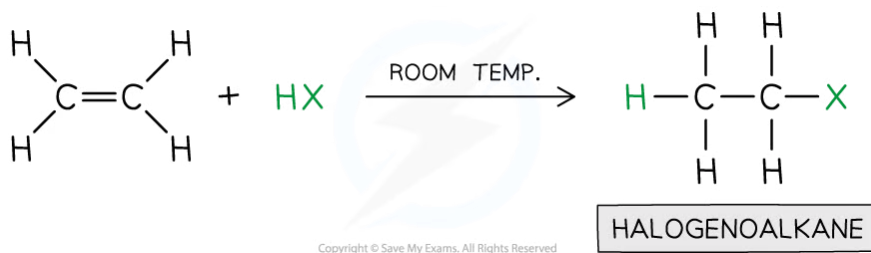
- Halogens can be used to test if a molecule is **unsaturated** (i.e. contain a double bond)
- Br₂ is an orange or yellow solution, called **bromine water**
- The unknown compound is **shaken** with the bromine water
- If the compound is unsaturated, an addition reaction will take place and the coloured solution will decolourise



The bromine water test is the standard test for unsaturation in alkenes

Hydrohalogenation

- **Alkenes** will react readily with **hydrogen halides** such as HCl and HBr to produce **halogenoalkanes**
- This reaction is known as **hydrohalogenation**
- It is also an **electrophilic addition** reaction that occurs quickly at room temperature

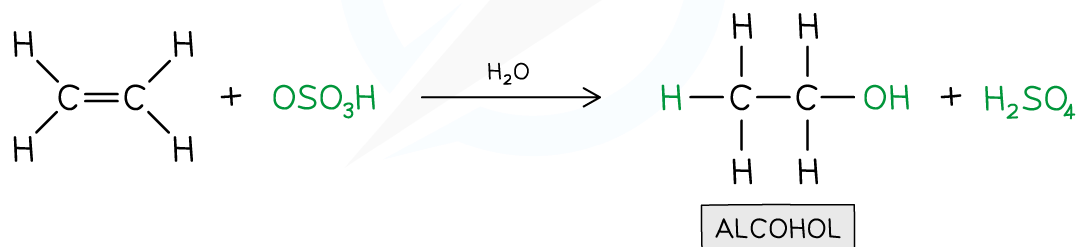
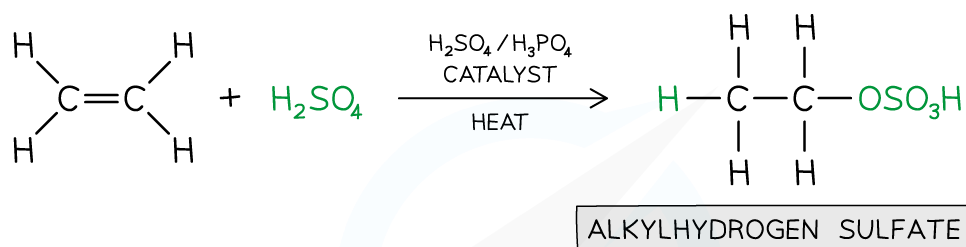


Hydrohalogenation reactions in alkenes

- All the **hydrogen halides** react in this way, but the **fastest reaction** occurs in the order **HI > HBr > HCl** due to the increasing bond strength of the hydrogen-halogen bond, so the weakest bond reacts most easily

Hydration

- When alkenes are treated with steam at **300 °C**, a pressure of **60 atmospheres** and **sulfuric acid (H₂SO₄)** or **phosphoric acid (H₃PO₄)** catalyst, the water is added across the double bond in a reaction known as **hydration**
- An **alkene** is converted into an **alcohol**
- The reaction processes via an intermediate in which H⁺ and HSO₄⁻ ions are added across the **double bond**
- The intermediate is quickly hydrolysed by water, reforming the sulfuric acid



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Hydration in Alkenes

- This is a very important industrial reaction for producing large quantities of ethanol, a widely used solvent and fuel
- The process is much faster and higher yielding than producing ethanol by **fermentation**

4.3.4 Electrophilic Addition

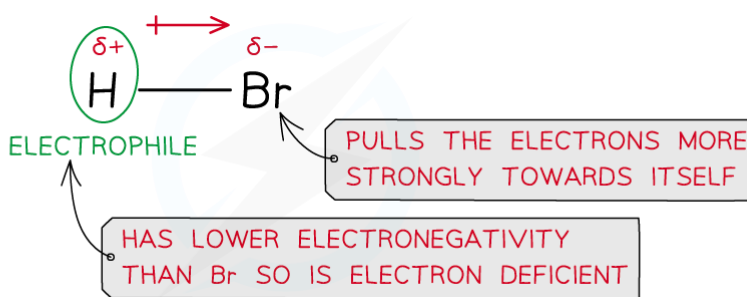
YOUR NOTES

Electrophilic Addition

- **Electrophilic addition** is the addition of an electrophile to an alkene double bond, C=C
- The alkene double bond, C=C, is an area of high electron density which makes it susceptible to attack by electrophiles
- The C=C bond breaks forming a single C-C bond and 2 new bonds from each of the two carbon atoms

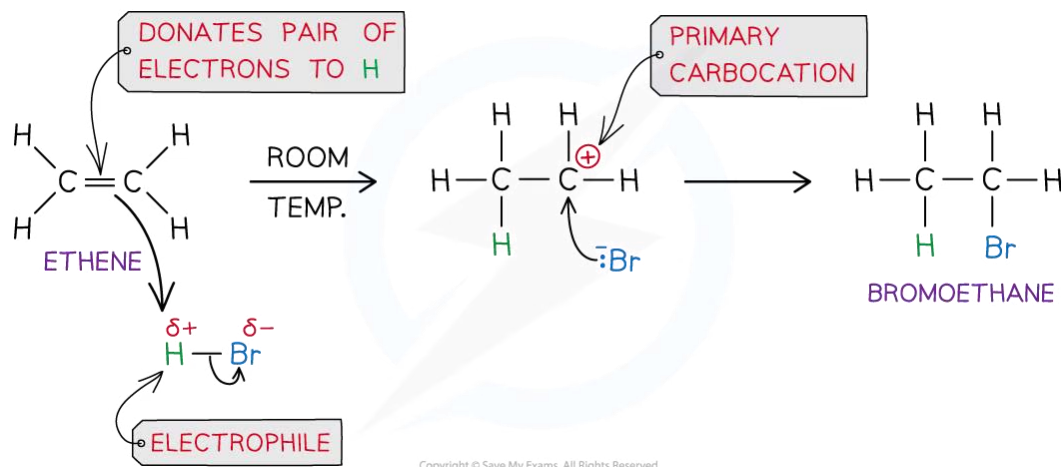
Electrophilic addition of hydrogen halides

- A hydrogen halide molecule is polar as the hydrogen and halogen atoms have different electronegativities
 - For example, in a molecule of hydrogen bromide, HBr, the bromine atom has a stronger pull on the electrons in the H-Br bond
 - As a result of this, the Br atom has a partial negative and the H atom a partial positive charge



Due to differences in electronegativities of the hydrogen and bromine atom, HBr is a polar molecule

- In electrophilic addition reactions with hydrogen halides, the H atom acts as an electrophile by accepting a pair of electrons from the C=C bond in the alkene
 - The H-Br bond breaks heterolytically, forming a Br⁻ ion
- This results in the formation of a highly reactive carbocation intermediate which reacts with the bromide ion, Br⁻
- For example, the mechanism for the electrophilic addition of hydrogen bromide and ethene is:



Electrophilic addition reaction of HBr and ethene to form bromoethane

Exam Tip

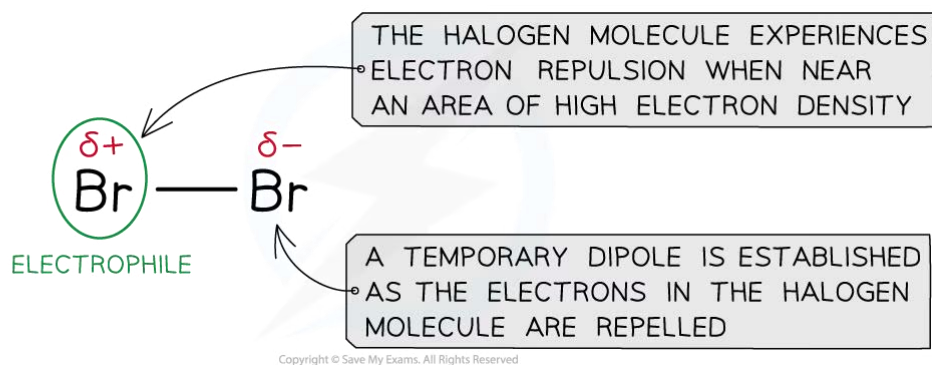
For electrophilic addition mechanisms, the curly arrows must:

- Be double-headed to show the movement of a pair of electrons
- Start from a lone pair of electrons or an area of high electron density, e.g. the C=C bond
- Move towards a $\delta+$ electrophile or the positive charge of a carbocation

Examiners often comment about the poor and incorrect use of curly arrows in organic mechanisms

Electrophilic addition of halogens

- The mechanism for the electrophilic addition of halogens (and hydrogen) is the same as the electrophilic addition of hydrogen halides with one key exception:
 - Hydrogen halide molecules have a **permanent dipole** (as shown above)
 - Halogen molecules have a **temporary (or induced) dipole** caused by the repulsion of the halogens electrons by the high electron density C=C bond



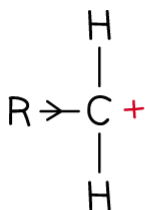
The temporary (or induced) dipole in a halogen molecule

Markownikoff Addition

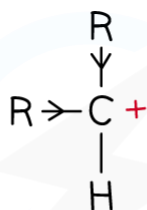
- **Carbocations** are positively charged carbon atoms with only three covalent bonds instead of four
- There are three types of carbocations: primary, secondary and tertiary

Inductive effect

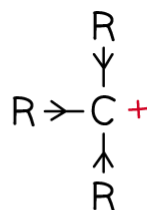
- The alkyl groups attached to the positively charged carbon atoms are 'electron donating groups'
 - This is also known as the inductive effect of alkyl groups
- The inductive effect is illustrated by the use of arrowheads on the bonds to show the alkyl groups pushing electrons towards the positively charged carbon
 - This causes the carbocation to become less positively charged
- As a result of this, the charge is spread around the carbocation which makes it energetically more stable
- This means that tertiary carbocations are the most stable as they have three electron-donating alkyl groups which energetically stabilise the carbocation
- Due to the positive charge on the carbon atom, carbocations are electrophiles



PRIMARY CARBOCATION
(LEAST STABLE)



SECONDARY
CARBOCATION



TERTIARY CARBOCATION
(MOST STABLE)

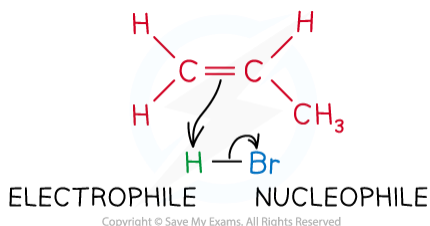
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Alkyl groups push electron density towards the carbocation making it energetically more stable; the more alkyl groups the carbocation is bonded to, the more stabilised it is

Markownikoff's rule

- Markownikoff's rule predicts the outcome of electrophilic addition reactions and states that:
 - In an electrophilic addition reaction of a hydrogen halide (HX) to an alkene, the halogen ends up bonded to the most substituted carbon atom
 - In an electrophilic addition reaction of an interhalogen to an alkene, the most electronegative halogen ends up bonded to the most substituted carbon atom
- Markownikoff addition applies to electrophilic addition reactions with unsymmetrical alkenes, e.g. propene and but-1-ene
 - Markownikoff addition favours the formation of the major product
 - Anti-Markownikoff addition favours the formation of the minor product

- In electrophilic addition reactions, an electrophile reacts with the double bond of alkenes (as previously discussed)
- The mechanism for electrophilic addition reactions with unsymmetrical alkenes is slightly different, e.g. propene + hydrogen bromide



The electrophile reacts with the electron-rich C-C double bond

- The electrophile can attach in two possible ways:
 1. Breaking the C=C bond and attaching to the the least substituted carbon
 - This will give the **most** stable carbocation as an intermediate that will form the **major** product
 2. Breaking the C=C bond and attaching to the the most substituted carbon
 - This will give the **least** stable carbocation as an intermediate that will form the **minor** product



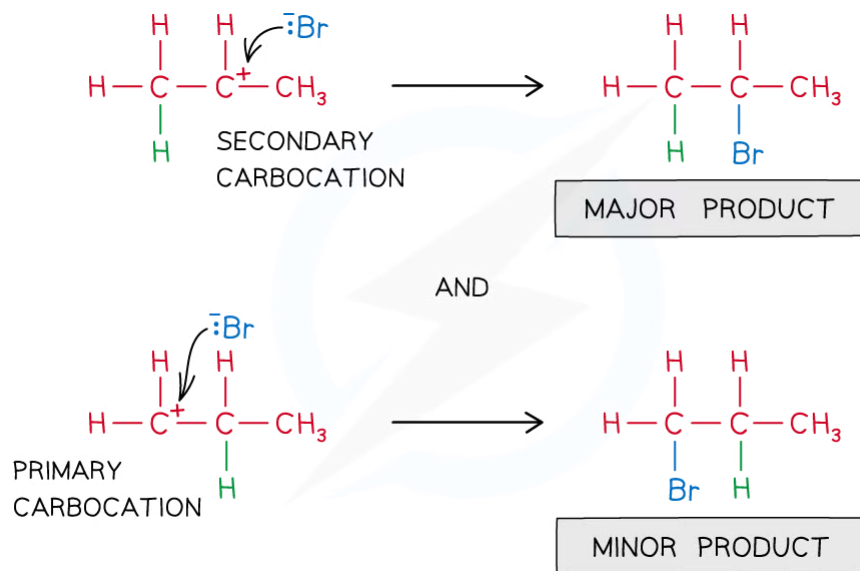
MORE STABLE SECONDARY
CARBOCATION INTERMEDIATE

LESS STABLE PRIMARY
CARBOCATION INTERMEDIATE

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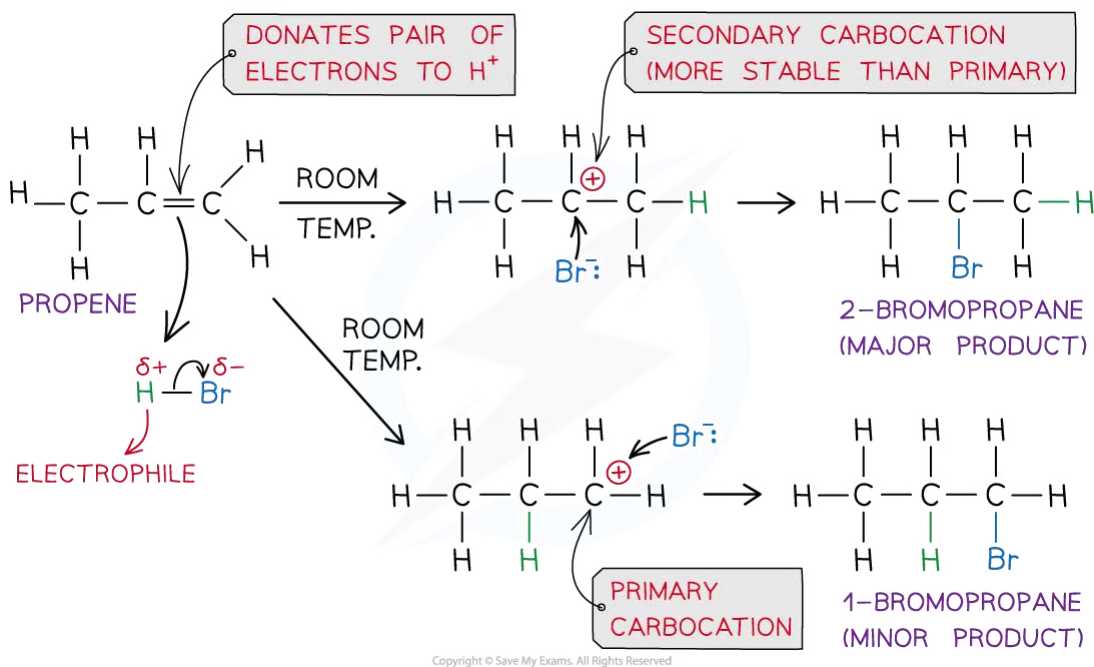
The major and minor carbocation intermediates formed during the reaction of propene and hydrogen bromide

- The nucleophile will bond to the positive carbon atom of the carbocation
 - The more stable carbocation produces the major product
 - The less stable carbocation produces the minor product



Formation of the major and minor products of the reaction of propene with hydrogen bromide

- The mechanism for the electrophilic addition of hydrogen bromide to propene, showing the formation of the major and minor products can be shown as:



The electrophilic addition reaction mechanism of HBr and propene to form 1-bromopropane and 2-bromopropane



Exam Tip

The stability of the carbocation intermediate is as follows:

tertiary > secondary > primary

When more than one carbocation can be formed, the major product of the reaction will be the one that results from the nucleophilic attack of the most stable carbocation.

YOUR NOTES

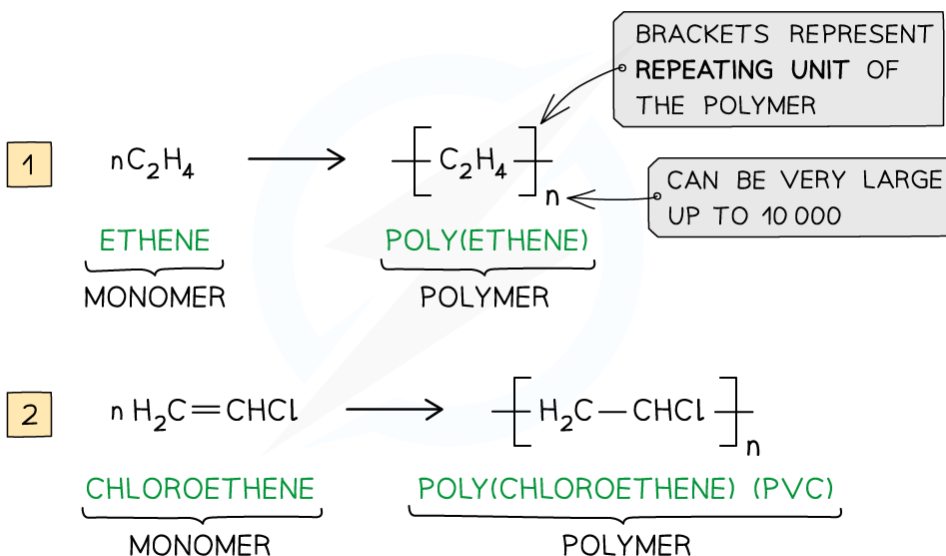


4.3.5 Polymers from Alkenes

Addition Polymerisation

- **Addition polymerisation** is one of the most important addition reactions of alkenes which form the basis of the plastic industry
- Addition polymerisation is the reaction in which many **monomers** containing at least one C=C double bond form long chains of **polymers** as the only product
 - Just like in other addition reactions of alkenes, the π -bond in each C=C bond breaks and then the monomers link together to form new C-C single bonds
- A **polymer** is a long-chain molecule that is made up of many repeating units
- The small, reactive molecules that react together to form the polymer are called **monomers**
- A polymerisation reaction can be represented by a **general formula** or by using **displayed formulae**
 - E.g. poly(ethene) and poly(chloroethene) (also known as **PVC**) are polymers made up of the ethene and chloroethene monomers respectively and are commonly used in making plastics

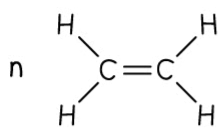
GENERAL FORMULA ADDITION POLYMERISATION



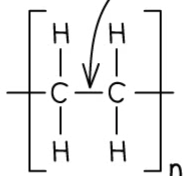
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The general formulae of the addition polymerisation of ethene (1) and chloroethene (2)

1



ETHENE
MONOMER

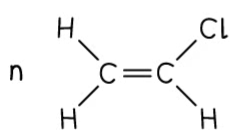


POLY(ETHENE)
REPEATING UNIT
OF POLYMER

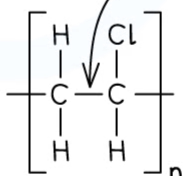
DOUBLE BOND HAS
CHANGED INTO A
SINGLE BOND

MONOMER AND REPEATING
UNIT ARE THE SAME

2



CHLOROETHENE
MONOMER



POLY(CHLOROETHENE)
REPEATING UNIT
OF POLYMER

DOUBLE BOND HAS
CHANGED INTO A
SINGLE BOND

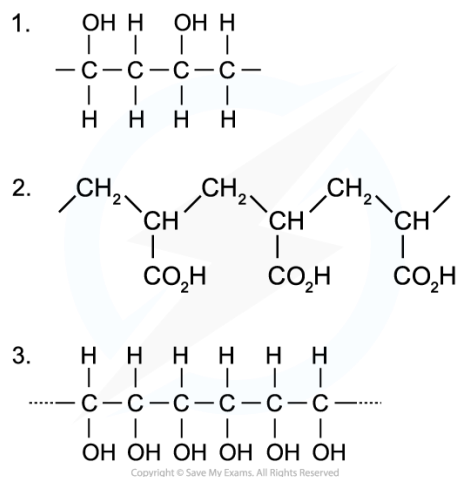
MONOMER AND REPEATING
UNIT ARE THE SAME

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The repeating units of poly(ethene) and poly(chloroethene) are similar to their monomer except that the C=C bond has changed into a C-C bond

Worked Example

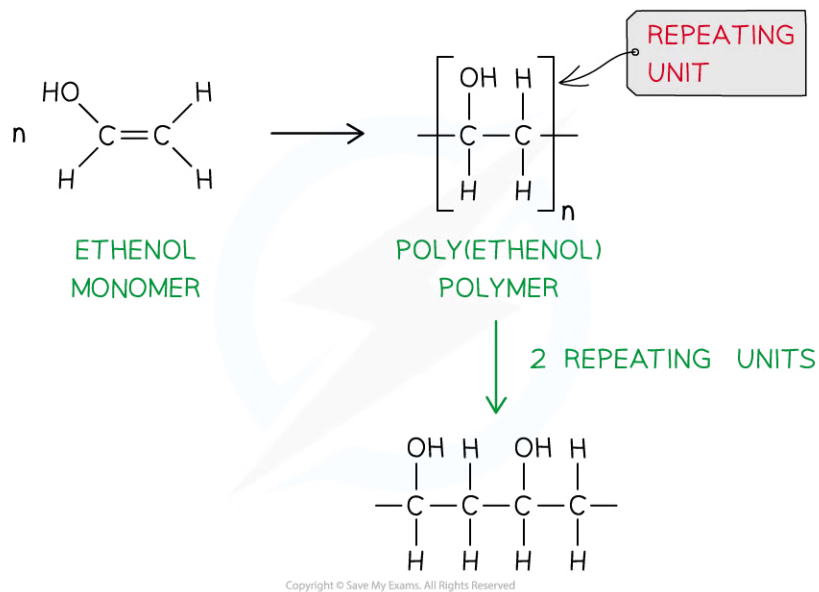
Identify the monomers present in the given sections of addition polymer molecules:



Answers

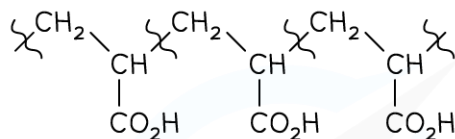
Answer 1:

When ethenol ($\text{CH}(\text{OH})=\text{CH}_2$) is polymerised, the C-C double bond opens to produce a repeating unit of $\text{CH}(\text{OH})-\text{CH}_2$. This gives the polymer poly(ethenol)

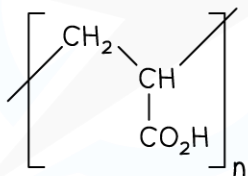


Answer 2:

- To find the monomer, first the repeating unit should be deduced. Repeating units have only 2 carbons in the polymer main chain



ONE REPEATING UNIT

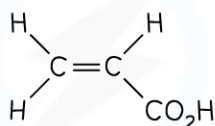


POLY(PROP-2-ENOIC ACID)

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- Since the repeating unit is now found, it can be concluded that the monomer is prop-2-enoic acid

MONOMER

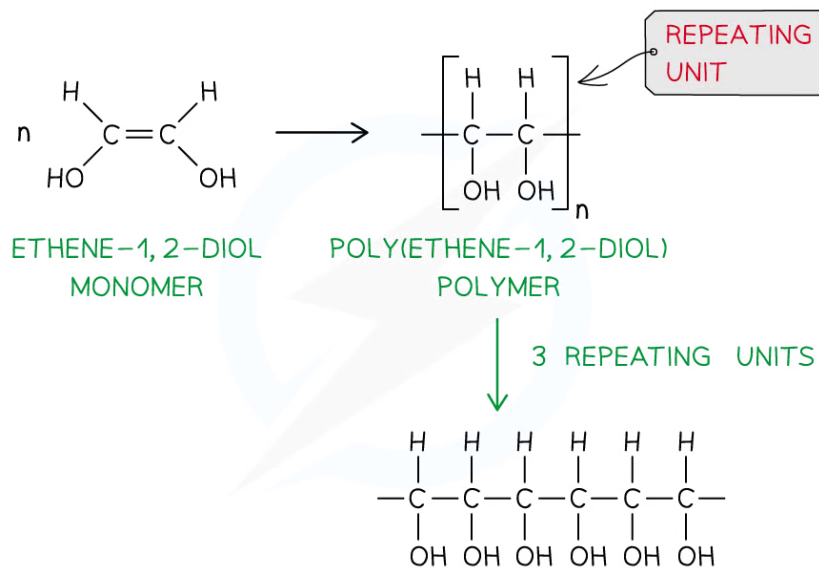


PROP-2-ENOIC ACID

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Answer 3:

- Again, the repeating unit only has 2 carbons in the polymer chain which in this case are two carbon atoms that each contain one OH group
- Thus, when ethene-1,2-diol (CH(OH)=CH(OH)) is polymerised, the C=C double bond opens to produce a repeating unit of CH(OH)-CH(OH) which gives the polymer poly(ethene-1,2-diol)



YOUR NOTES

□

□ **Exam Tip**

The section of the polymer chain shown inside the square brackets by the structural or displayed formula is the **repeat unit** and **not** the monomer

The monomer is the same as the repeat unit except for that it has C=C bonds instead of C-C bonds

Waste polymers & Alternatives

- Polymers provide a readily available, cheap alternative to many metal, glass, paper and cardboard materials in everyday use
- The **low reactivity** of many polymers makes them ideal for certain uses, e.g. food packaging, but at the same time creates problems with their disposal as a lot of polymers are **non-biodegradable**
 - There are many published articles about the **environmental problems** of waste plastic killing marine animals
- One method of polymer disposal continues to be the use of landfill sites
 - This is not ideal and various initiatives are being introduced aiming to reduce this method of waste disposal in general as well as with specific regard to polymers

Recycling

- Polymer **recycling** reduces the amount of waste that is going to **landfill** sites
 - Newer landfill sites can have a recycling point where the new waste is brought before going into the actual landfill – this is in an effort to reduce the amount of polymers (and other recyclable materials) unnecessarily going into the waste site
- The recycling of polymers can also reduce the use of **finite resources**
 - Lots of polymers are made from the products of cracking crude oil and its fractions
- Recycling polymers is a **time-consuming** process as they have to be sorted into the different categories
 - These categories are usually shown somewhere on the plastic / polymer product with the recycling symbol and numbers or abbreviations for the different polymers, e.g.:



The recycling symbol for the polyethylene terephthalate polymer

- After sorting, the polymers are chopped, washed, dried, melted and then cast into pellets ready for use
 - However, mixed polymers can mean that this process is wasted as it produces an unusable mix of polymers
- Certain polymers can cause problems when recycling due to their chemical composition, e.g. PVC contains a large amount of toxic chlorine which can be released

- Modern techniques are overcoming this PVC problem by dissolving the polymer and precipitating out the recycled material

Combustion

- ♦ Some petroleum / natural gas derived polymers are still difficult to recycle
- ♦ Since they have a large amount of energy stored within the polymer chains, these polymers can be incinerated
 - This process can then be used to boil water and use the water vapour to turn turbines inside a power station, in a similar fashion to coal-fired power stations
- ♦ This process still causes environmental pollution as the carbon within the polymer can be released as carbon dioxide contributing to global warming
 - Other toxic waste products include hydrogen chloride from the combustion of PVC

Feedstock recycling

- ♦ **Feedstock recycling** is where waste polymers are broken down, by chemical and thermal processes, into monomers, gases and oils
- ♦ These products are then used as the raw materials in the production of new polymers and other organic chemicals
- ♦ The major benefit of feedstock recycling, compared to other methods of polymer disposal, is that it works with unsorted and unwashed polymers

Bioplastics

- ♦ **Bioplastics** are polymers that are made from plant starch / cellulose, plant oils and plant proteins
 - They provide a renewable and sustainable alternative to the current polymers which are predominantly based on finite resources such as crude oil

Biodegradable polymers

- ♦ Biodegradable polymers can be broken down over time by microorganisms
 - Common products from this process include carbon dioxide, water and other organic compounds
- ♦ The **polyester** and **polyamide** condensation polymers are considered to be biodegradable as they can be broken down using **hydrolysis** reactions
 - This is a major advantage over the polymers produced using alkene monomers (polyalkenes)
 - When polyesters and polyamides are taken to landfill sites, they can be broken down easily and their products used for other applications

Compostable polymers

- ♦ Compostable polymers are commonly plant based
 - Plant starch is being used in the production of biodegradable bin liners
 - Sugar cane fibres are replacing polystyrene in the production of disposable plates and cups
- ♦ Compostable polymers degrade naturally leaving no harmful residues

Photodegradable polymers

- Photodegradable polymers contain bonds that are weakened by absorbing light / visible radiation
 - This starts the breakdown of the polymer
- A lot of photodegradable polymers are oil-based
 - In certain cases, an additive that absorbs light is mixed into the polymer to promote degradation

YOUR NOTES

□

4.4 Alcohols

YOUR NOTES

4.4.1 Properties of Alcohols

Properties of Alcohols

Intermolecular Forces

- ♦ **Alcohols** are compounds that contain at least one **hydroxy** (-OH) group
- ♦ The general formula of alcohols is $C_nH_{2n+1}OH$
- ♦ Alcohols can be prepared by a wide range of chemical reactions

Hydrogen bonding

- ♦ Hydrogen bonding occurs between molecules where you have a hydrogen atom attached to one of the very electronegative elements – fluorine, **oxygen** or nitrogen
- ♦ In an alcohol, there are **O-H bonds** present in the structure
- ♦ Therefore hydrogen bonds set up between the slightly positive hydrogen atoms ($\delta^+ H$) and lone pairs on oxygens in other molecules
- ♦ The hydrogen atoms are slightly positive because the bonding electrons are pulled away from them towards the very electronegative oxygen atoms
- ♦ In **alkanes**, the only intermolecular forces are **temporary induced dipole-dipole forces**
- ♦ Hydrogen bonds are much stronger than these and therefore it takes more energy to separate alcohol molecules than it does to separate alkane molecules
- ♦ Therefore, the boiling point of alkanes is lower than the boiling point of the respective alcohols
 - For example, the boiling point of propane is $-42\text{ }^\circ\text{C}$ and the boiling point of propanol is $97\text{ }^\circ\text{C}$

Temporary induced dipole-dipole forces

- ♦ As with all molecules, there are also temporary induced dipole-dipole forces between alcohols
- ♦ The boiling points increase as the number of carbon atoms in the chains increases. It takes more energy to overcome the temporary induced dipole-dipole forces and so the boiling points rise
- ♦ This is because the dipole is caused by the changing position of the electron cloud, so the more electrons there are, the larger the temporary induced dipole-dipole forces will be

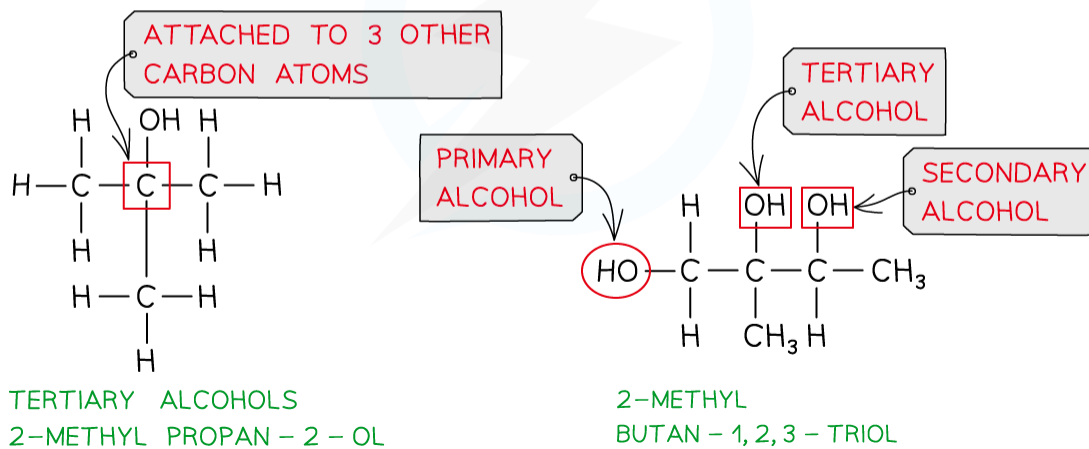
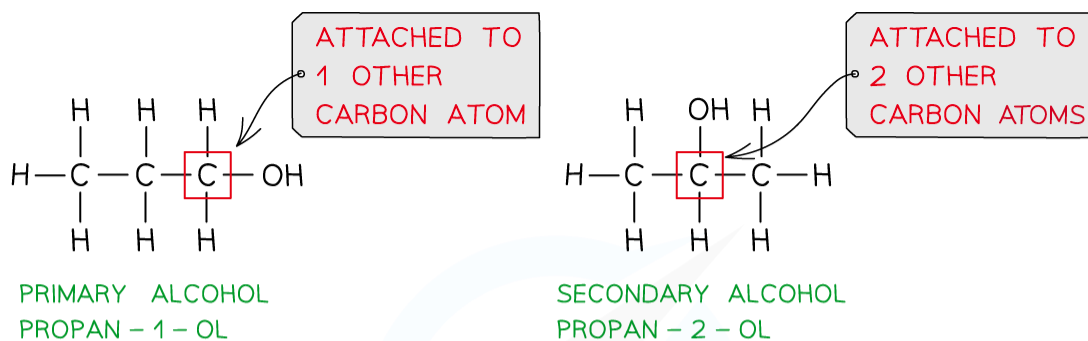
Solubility

- ♦ The small alcohols are completely soluble in water
- ♦ If they are mixed with water, there will be one solution
- ♦ However, solubility falls as the length of the hydrocarbon chain in the alcohol increases
- ♦ The hydrocarbon chains are forcing their way between water molecules and so breaking hydrogen bonds between those water molecules

- The -OH end of the alcohol molecules can form new hydrogen bonds with water molecules, but the hydrocarbon can not form hydrogen bonds

Classification of Alcohols

- **Primary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **one** other carbon atom (or alkyl group).
- **Secondary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **two** other carbon atoms (or alkyl groups)
- **Tertiary alcohols** are alcohols in which the carbon atom bonded to the -OH group is attached to **three** other carbon atoms (or alkyl groups)



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Classifying primary, secondary and tertiary alcohols and alcohols with more than one alcohol group

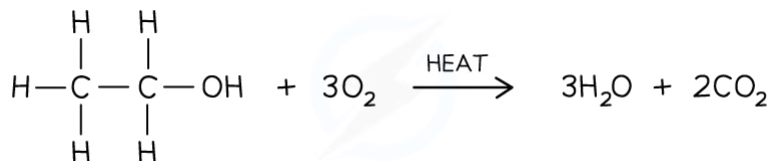
4.4.2 Reactions of Alcohols

YOUR NOTES

Combustion of Alcohols

- Alcohols react with oxygen in the air when ignited and undergo **complete combustion** to form carbon dioxide and water

alcohol + oxygen → carbon dioxide + water



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Complete combustion of alcohols to produce carbon dioxide and water

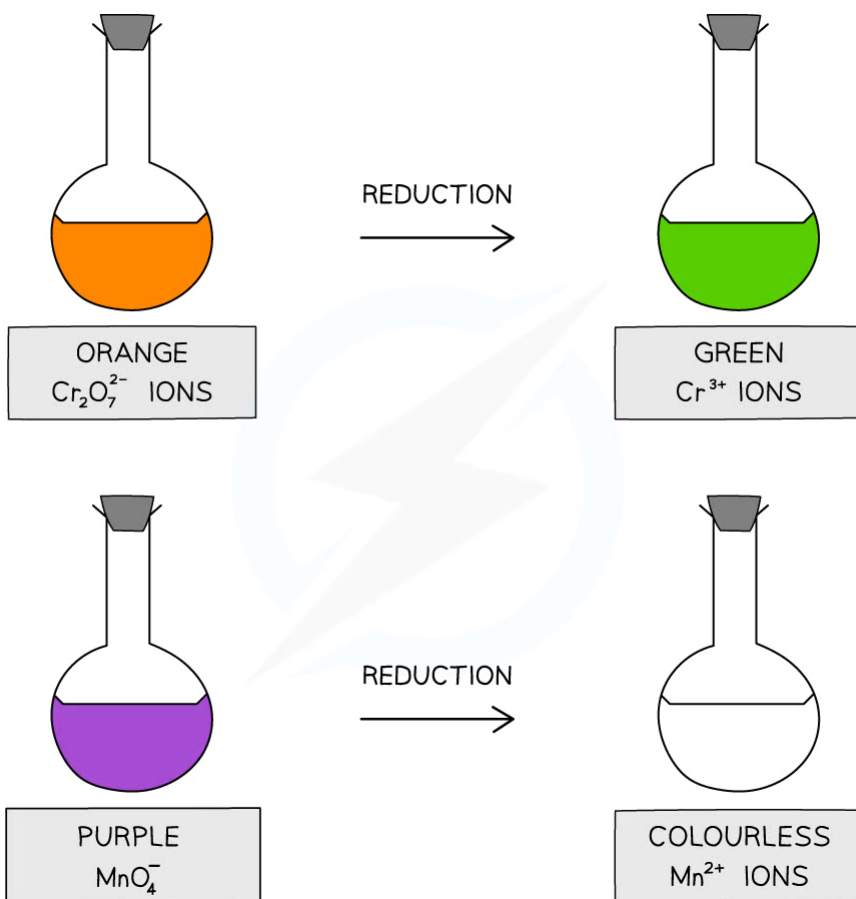
- Lower alcohols burn with an almost invisible flame and make good fuels
- Ethanol** can be produced sustainably as a fuel by the **fermentation** of sugars
- However, the **energy density** (the amount of energy in kJ per kg of fuel) is lower than gasoline so cars that run on ethanol must either have a larger fuel tank or fill up more often
- Blending **ethanol** with gasoline or diesel increases the **energy density** and makes it safer in case of fires as it is easier to see the flames compared to pure **ethanol** burning
- However, there are socio-economic concerns about using large quantities of farm land to produce crops for fermentation, which could be better used for food production

Oxidation of Alcohols

- Primary alcohols can be oxidised to form **aldehydes** which can undergo further oxidation to form **carboxylic acids**
- Secondary alcohols can be oxidised to form **ketones** only
- Tertiary alcohols do not undergo oxidation
- The oxidising agents of alcohols include **acidified $K_2Cr_2O_7$** or **acidified $KMnO_4$**

Oxidising agents

- The oxidising agents used to prepare aldehydes and ketones from alcohols include **acidified potassium dichromate** ($K_2Cr_2O_7$) and **acidified potassium manganate** ($KMnO_4$)
 - The acidified **potassium dichromate(VI)**, $K_2Cr_2O_7$, is an orange oxidising agent
 - When the alcohols are **oxidised** the orange dichromate ions ($Cr_2O_7^{2-}$) are reduced to green Cr^{3+} ions
 - The acidified **potassium manganate(VII)**, $KMnO_4$ is a purple oxidising agent
 - When the alcohols are **oxidised** the purple manganate ions (MnO_4^-) are reduced to colourless Mn^{2+} ions



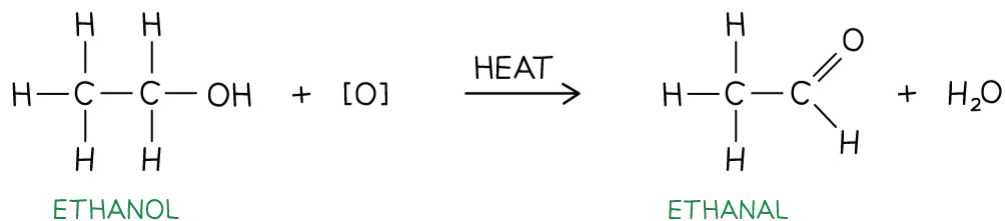
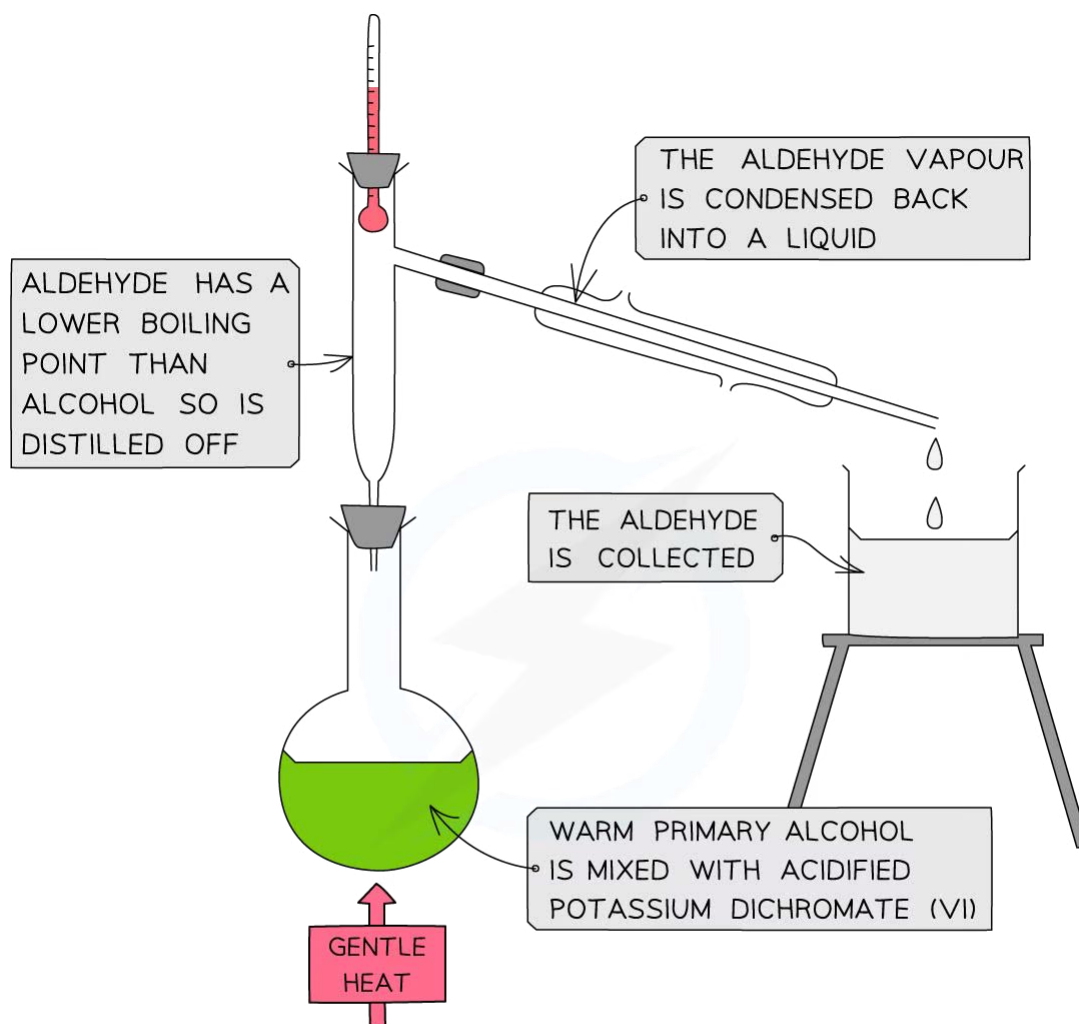
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The oxidising agents change colour when they oxidise an alcohol and get reduced themselves

Forming aldehydes and carboxylic acids

- For aldehydes, a primary alcohol is added to the oxidising agent and warmed
- The aldehyde product has a lower boiling point than the alcohol reactant so it can be **distilled off** as soon as it forms

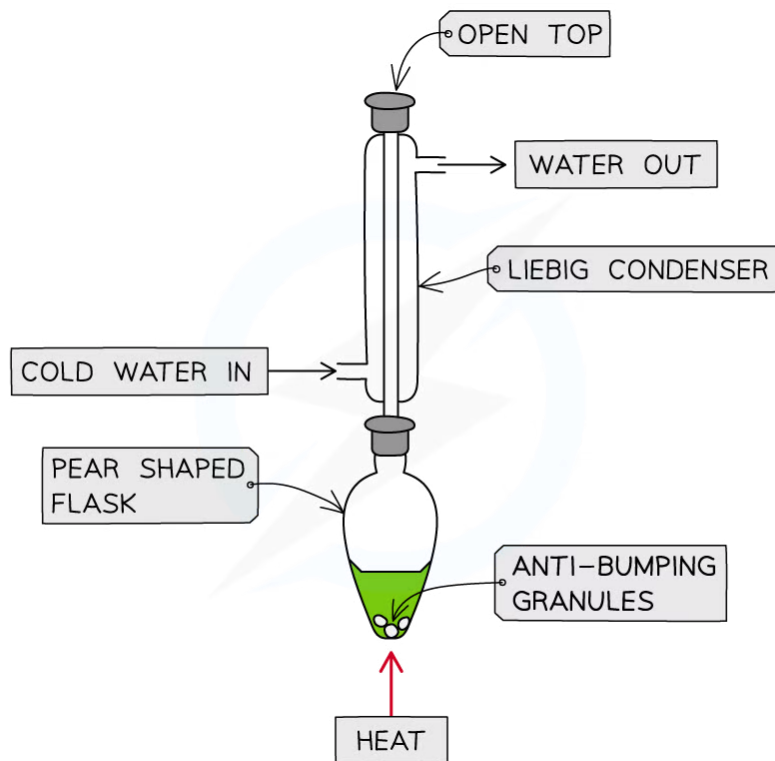


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Oxidation of ethanol by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to form an aldehyde by distillation

- If the aldehyde is not distilled off, further **refluxing** with excess oxidising agent will oxidise it to a carboxylic acid

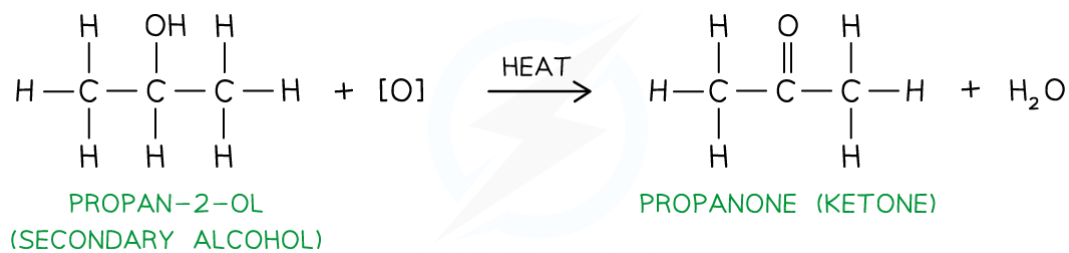
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Further oxidation of the aldehyde via reflux can be done to produce a carboxylic acid

Forming ketones



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Oxidation of propan-2-ol by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ to form a ketone

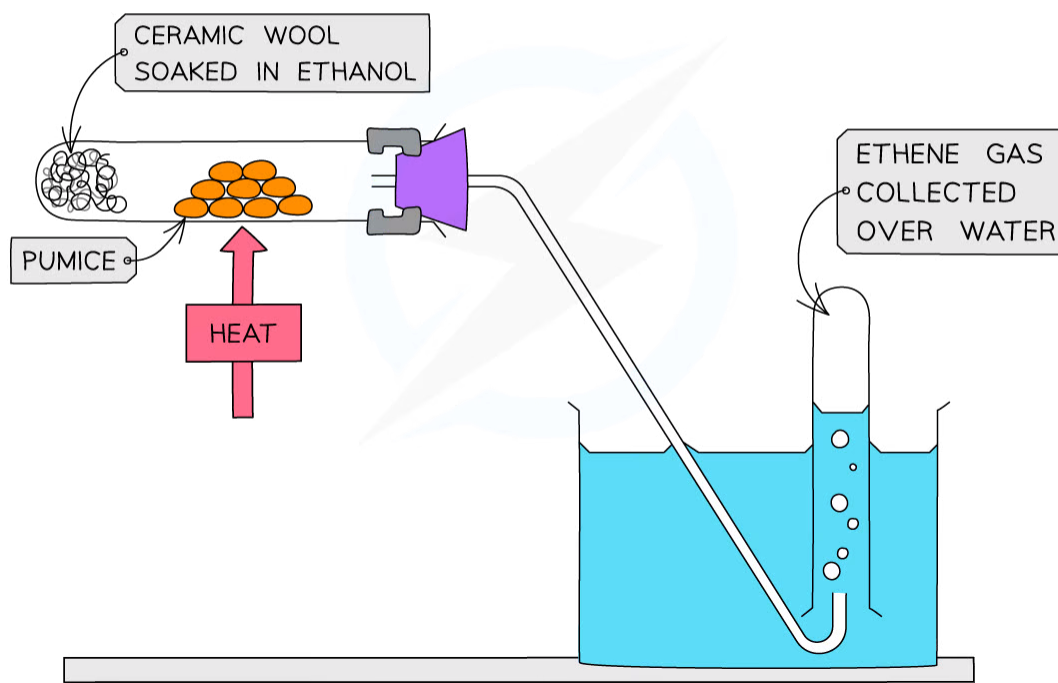
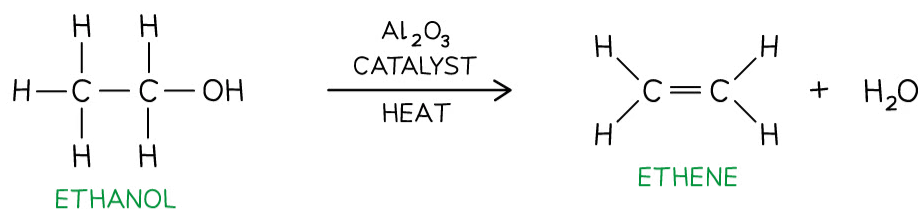
- Since ketones cannot be further oxidised, the ketone product does not need to be **distilled off** straight away after it has been formed

Elimination & Substitution Reactions of Alcohols

YOUR NOTES

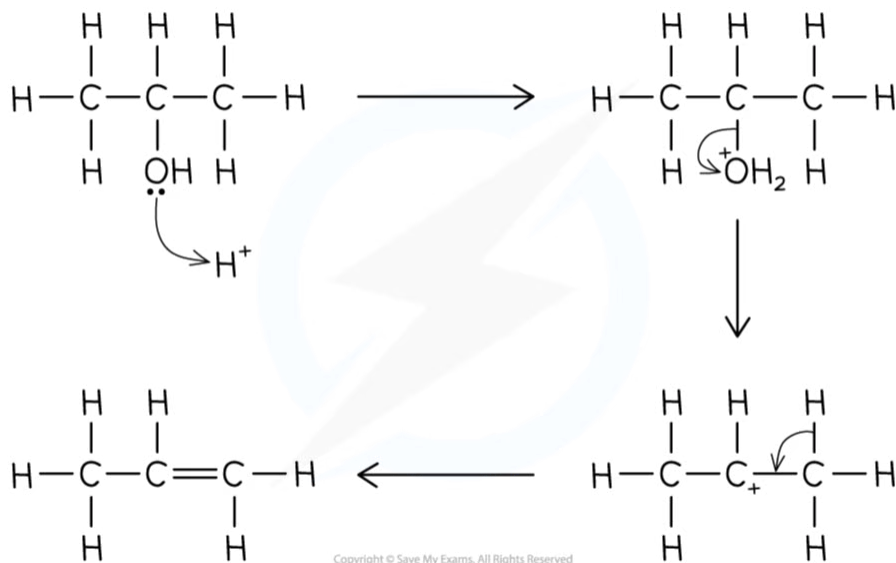
Elimination Reaction of Alcohols

- ♦ Alcohols can also undergo **dehydration** to form alkenes
 - This is an example of an elimination reaction
 - Elimination reactions involve a small molecule leaving the parent molecule as a byproduct
 - In this case, the small molecule is a water molecule
 - The water molecule is formed from the -OH group and a hydrogen atom from the adjacent carbon atom
- ♦ Alcohol vapour is passed over a **hot catalyst** of aluminium oxide (Al_2O_3) powder or pieces of porous pot
 - Excess hot, concentrated sulfuric acid or phosphoric acid is used as a catalyst



Dehydration of ethanol using aluminium oxide as a catalyst forms ethene gas, which can be collected over water

- ♦ The reaction and mechanism for the dehydration of propan-2-ol is shown below



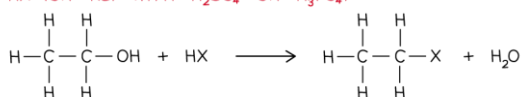
Dehydration of propan-2-ol mechanism

Substitution Reactions of Alcohols

- In the **substitution** of alcohols, a hydroxy group (-OH) is replaced by a halogen to form an **haloalkane**
- The substitution of the alcohol group for a halogen can be achieved by reacting the alcohol with:
 - HX (rather than using HBr, KBr is reacted with H₂SO₄ or H₃PO₄ to make HBr that will then react with the alcohol)

SUBSTITUTION OF ALCOHOLS

• HX (OR KBr WITH H₂SO₄ OR H₃PO₄)



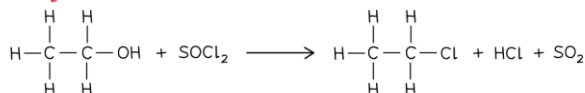
• PCl₃ + HEAT



• PCl₅



• SOCl₂

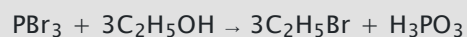


Substitution of alcohols to produce haloalkanes

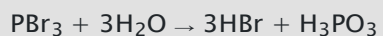
Exam Tip

An alternative method to produce the bromoalkane by reacting the alcohol with sodium or potassium bromide and concentrated sulfuric acid generating HBr is to use **phosphorus tribromide, PBr₃**.

To form bromoethane from ethanol, PBr₃ can be added **drop wise** to ethanol (this reaction is very vigorous).



The water removes excess PBr₃ by the hydrolysis reaction



YOUR NOTES

4.5 Haloalkanes

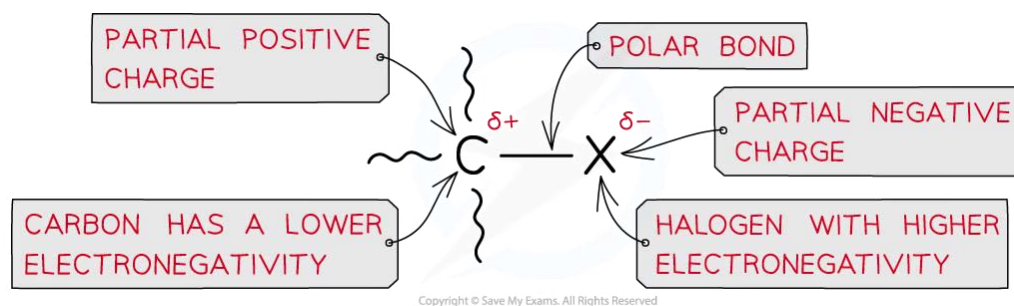
YOUR NOTES

4.5.1 Reactions of Haloalkanes

Substitution Reactions of Haloalkanes

Reactivity of Haloalkanes

- **Haloalkanes** are much more reactive than alkanes due to the presence of the **electronegative** halogens
- The carbon-halogen bond is polar causing the carbon to carry a partial positive and the halogen a partial negative charge

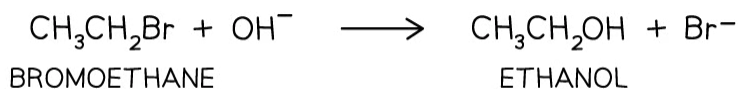


Due to the large difference in electronegativity between the carbon and halogen atom, the C-X bond is polar

- Because of this, haloalkanes will undergo two key types of reaction
- **Nucleophilic substitution** reactions
 - A halogen is substituted for another atom or group of atoms
 - The products formed when haloalkanes undergo this type of reaction are alcohols, amines and nitriles
- **Elimination** reactions
 - A hydrogen halide is eliminated during the reaction
 - The key product formed from this type of reaction is an alkene

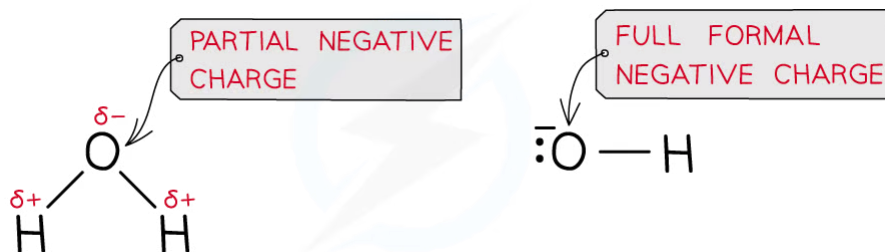
Formation of alcohols

- The nucleophile in this reaction is the hydroxide, OH⁻ ion
- An **aqueous** solution of **sodium hydroxide** (NaOH) or **potassium hydroxide** (KOH) with **ethanol** is used
- This reaction is very slow at room temperature, so the reaction mixture is warmed
- This is an example of a **hydrolysis reaction** and the product is an alcohol
 - The rate of this reaction depends on the type of halogen in the haloalkanes
 - The stronger the C-X bond, the slower the rate of the reaction
 - In terms of bond enthalpy, C-F > C-Cl > C-Br > C-I
 - Fluoroalkanes do not react at all, but iodoalkanes have a very fast rate of reaction



The halogen is replaced by the nucleophile, OH⁻

- ♦ This reaction could also be done with water as the nucleophile, but it is very slow
 - The hydroxide ion is a better nucleophile than water as it carries a full negative charge
 - In water, the oxygen atom only carries a partial charge



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A hydroxide ion is a better nucleophile as it has a full formal negative charge whereas the oxygen atom in water only carries a partial negative charge; this causes the nucleophilic substitution reaction with water to be much slower than the aqueous alkali

Measuring the rate of hydrolysis

- ♦ Acidified silver nitrate can be used to measure the rate of hydrolysis of halogenoalkanes
- ♦ Set up three test tubes in a 50 °C water bath, with a mixture of ethanol and acidified silver nitrate
- ♦ Add a few drops of a chloroalkane, bromoalkane and an iodoalkane to each test tube and start a stop watch
- ♦ Time how long it takes for the precipitates to form
- ♦ The precipitate will form as the reaction progresses and the halide ions are formed
- ♦ A white precipitate will form from the chloroalkane, a cream precipitate will form from the bromoalkane and a yellow precipitate will form from the iodoalkane
 - The yellow precipitate will form the fastest
 - This is because the C-I bond has the lowest bond enthalpy, so it is the easiest to break and will cause the I⁻ ions to form the fastest
 - The white precipitate will form the slowest
 - This is because the C-Cl bond has the highest bond enthalpy, so it is the hardest to break and will cause the Cl⁻ ions to form the slowest

YOUR NOTES

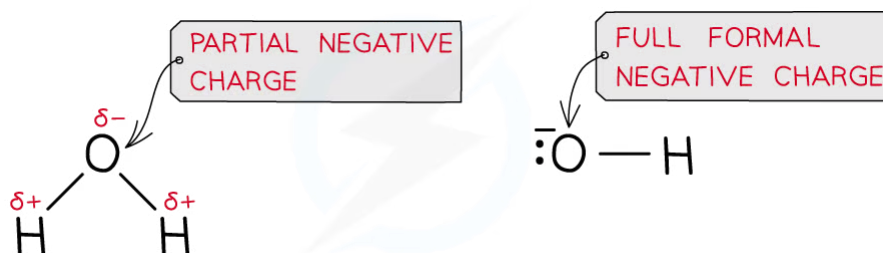
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4.5.2 Nucleophilic Substitution of Haloalkanes

Nucleophilic Substitution of Haloalkanes

Nucleophiles

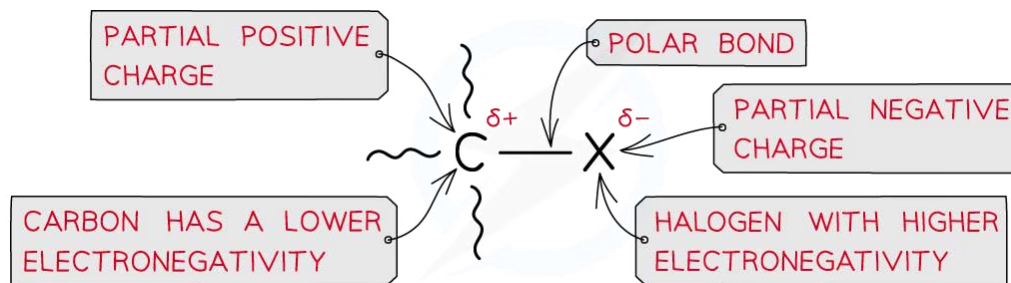
- A **nucleophile** is an electron-rich species that can **donate** a pair of electrons
 - 'Nucleophile' means 'nucleus/positive charge loving' as nucleophiles are attracted to positively charged species
 - **Nucleophilic** refers to reactions that involve a nucleophile
- There are various different species which can behave as nucleophiles, and some make better nucleophiles than others



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A hydroxide ion is a better nucleophile as it has a full formal negative charge whereas the oxygen atom in water only carries a partial negative charge

- A **nucleophilic substitution** reaction is one in which a **nucleophile** attacks a carbon atom which carries a **partial positive charge**
- An atom that has a **partial negative charge** is replaced by the nucleophile
- Haloalkanes will undergo nucleophilic substitution reactions due to the polar C-X bond (where X is a halogen)



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Due to large differences in electronegativity between the carbon and halogen atom, the C-X bond is polar

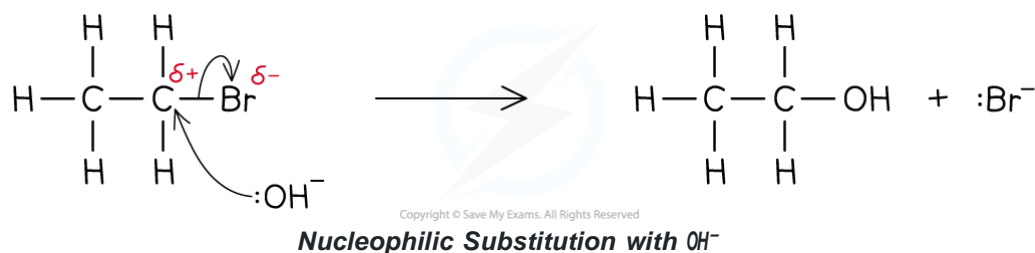


General Mechanism for Nucleophilic Substitution

Hydrolysis of Haloalkanes

- The nucleophile in this reaction is the hydroxide, OH⁻ ion
- An **aqueous** solution of **sodium hydroxide** (NaOH) or **potassium hydroxide** (KOH) with **ethanol** is used
- This reaction is very slow at room temperature, so the reaction mixture is warmed
- This is an example of a **hydrolysis reaction** and the product is an alcohol
- The rate of this reaction depends on the type of halogen in the haloalkane
- The stronger the C-X bond, the slower the rate of the reaction
- In terms of bond enthalpy, C-F > C-Cl > C-Br > C-I
- Fluoroalkanes do not react at all, but iodoalkanes have a very fast rate of reaction

The nucleophilic substitution mechanisms for the above reactions are as follows:



4.5.3 Hydrolysis of Primary Haloalkanes

YOUR NOTES

Hydrolysis of Primary Haloalkanes

Bond Enthalpy

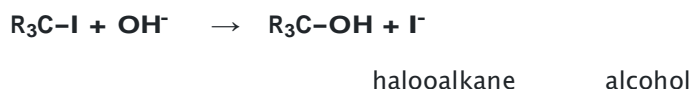
- The halogenoalkanes have different **rates** of **substitution reactions**
- Since substitution reactions involve **breaking** the **carbon-halogen bond** the **bond energies** can be used to explain their different reactivities

Haloalkane Bond Energy Table

Bond	Bond Energy (kJ mol ⁻¹)
C-F	467 (strongest bond)
C-Cl	346
C-Br	290
C-I	228 (weakest bond)

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- The table above shows that the C-I bond requires the least energy to break, and is therefore the **weakest** carbon-halogen bond
- During substitution reactions the C-I bond will therefore **heterolytically** break as follows:



- The C-F bond, on the other hand, requires the most energy to break and is, therefore, the **strongest** carbon-halogen bond
- Fluoroalkanes will therefore be less likely to undergo substitution reactions

Exam Tip

- Bond energy / enthalpy values can vary in published literature despite theoretically being completed under the same conditions
- Another reason for variation in bond energy / enthalpy values is due to the published values being the mean average of the specific bond from different substances
- The key point is that you are able to use the data given to you and apply it in your answers

Aqueous silver nitrate

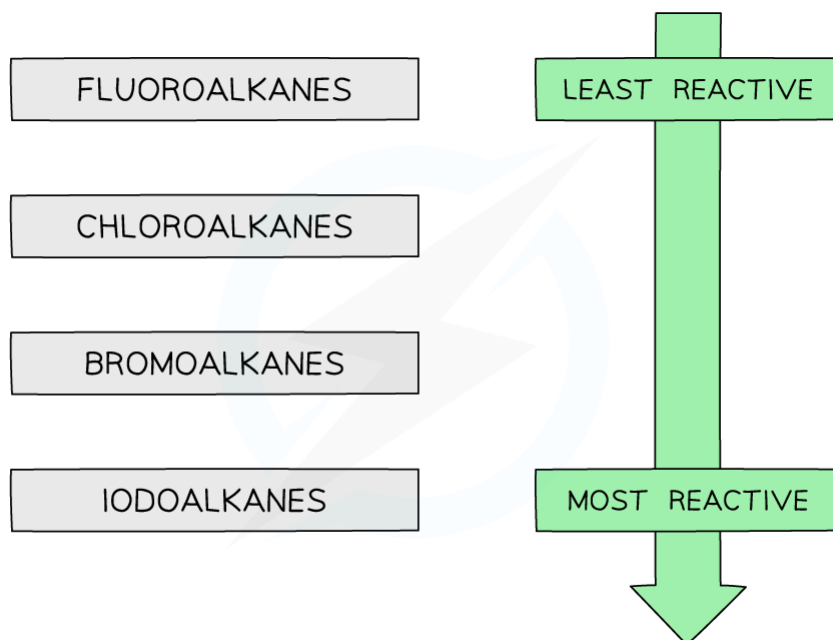
- Reacting haloalkanes with **aqueous silver nitrate solution** will result in the formation of a **precipitate**
- The **rate of formation** of these precipitates can also be used to determine the reactivity of the haloalkane

Haloalkane Precipitates Table

Halogenoalkane	Precipitate
Chlorides	White (silver chloride)
Bromides	Cream (silver bromide)
Iodides	Pale yellow (silver iodide)

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- The formation of the pale yellow silver iodide is the fastest (fastest **nucleophilic substitution** reaction) whereas the formation of the silver fluoride is the slowest (slowest **nucleophilic substitution** reaction)
- This confirms that fluoroalkanes are the least reactive and iodoalkanes are the most reactive haloalkanes



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The trend in reactivity of haloalkanes

4.5.4 Environmental Concerns of Organohalogen Use

YOUR NOTES

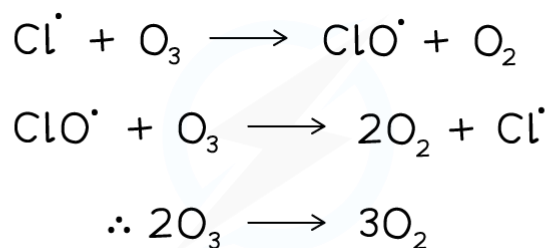
Breakdown of the Ozone Layer

Fluorohalogenoalkanes

- The most common **halogenoalkanes** are **chlorofluorocarbons** (CFCs)
- These compounds contain carbon atoms with chlorine and fluorine atoms attached to them
 - E.g. CCl_3F and CCl_2F_2
- CFCs have many uses due to their **chemical inertness** as they are **non-flammable** and **non-toxic**
 - They are used as refrigerators
 - Propellants for aerosols
 - As solvents for dry cleaning

Hydrofluorocarbons

- **Hydrofluorocarbons** (HFCs) are compounds that contain a carbon attached to hydrogen and fluorine atoms only
 - E.g. $\text{CH}_2\text{F}-\text{CF}_3$
- As with CFCs, HFCs are chemically inert and are therefore used for a wide range of purposes
- Though **chlorofluorocarbons** (CFCs) have many beneficial uses, they also have devastating effects on the ozone layer:
 - CFCs absorb a lot of UV radiation in the upper atmosphere
 - The CFCs are then broken down by the UV light causing the formation of chlorine radicals
 - These radicals react with ozone and break down the ozone layer as shown:



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Chlorine radicals and the ozone layer

- This is why **hydrofluorocarbons** (HFCs) are often used as an alternative to CFCs
- As these compounds don't contain any chlorine atoms, they will not have adverse effects on the **ozone layer**

Exam Tip

- There is another set of accepted propagation steps for the breakdown of ozone by chlorine radicals:
 - Propagation 1: $\text{Cl}^\cdot + \text{O}_3 \rightarrow \text{Cl}^\cdot + \text{O}_2$
 - Propagation 2: $\text{ClO}^\cdot + \text{O} \rightarrow \text{Cl}^\cdot + \text{O}_2$
- The difference is actually in the second propagation step where this version reacts with a lone oxygen atom rather than another ozone molecule

Other radicals

- CFCs are not the only radicals that catalyse the breakdown of the ozone
- One of the other sets of radicals linked to ozone breakdown are the nitrogen oxide radicals which can be formed:
 - Naturally during lightning strikes
 - As a result of air travel in the stratosphere
- Nitrogen monoxide is formed by the direct combination of nitrogen and oxygen at high temperatures inside a combustion engine
 - The nitrogen monoxide formed is a free radical as it has an odd number of electrons / unpaired electron
- The nitrogen monoxide radical reacts with one molecule of ozone to form the nitrogen dioxide molecule
 - $\text{NO}^\cdot + \text{O}_3 \rightarrow \text{NO}_2^\cdot + \text{O}_2$
- The nitrogen monoxide radical is then reformed
 - $\text{NO}_2^\cdot + \text{O} \rightarrow \text{NO}^\cdot + \text{O}_2$
- Overall, the breakdown equation is $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$

4.6 Organic Synthesis

4.6.1 Techniques

YOUR NOTES

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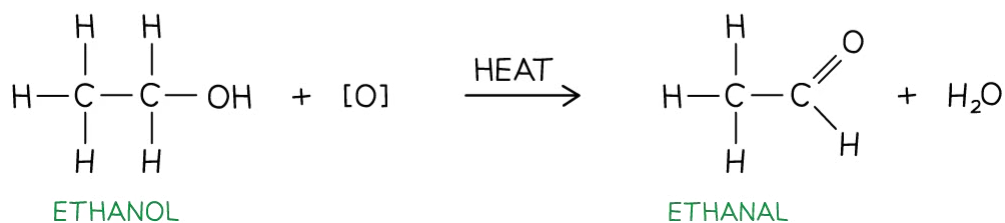
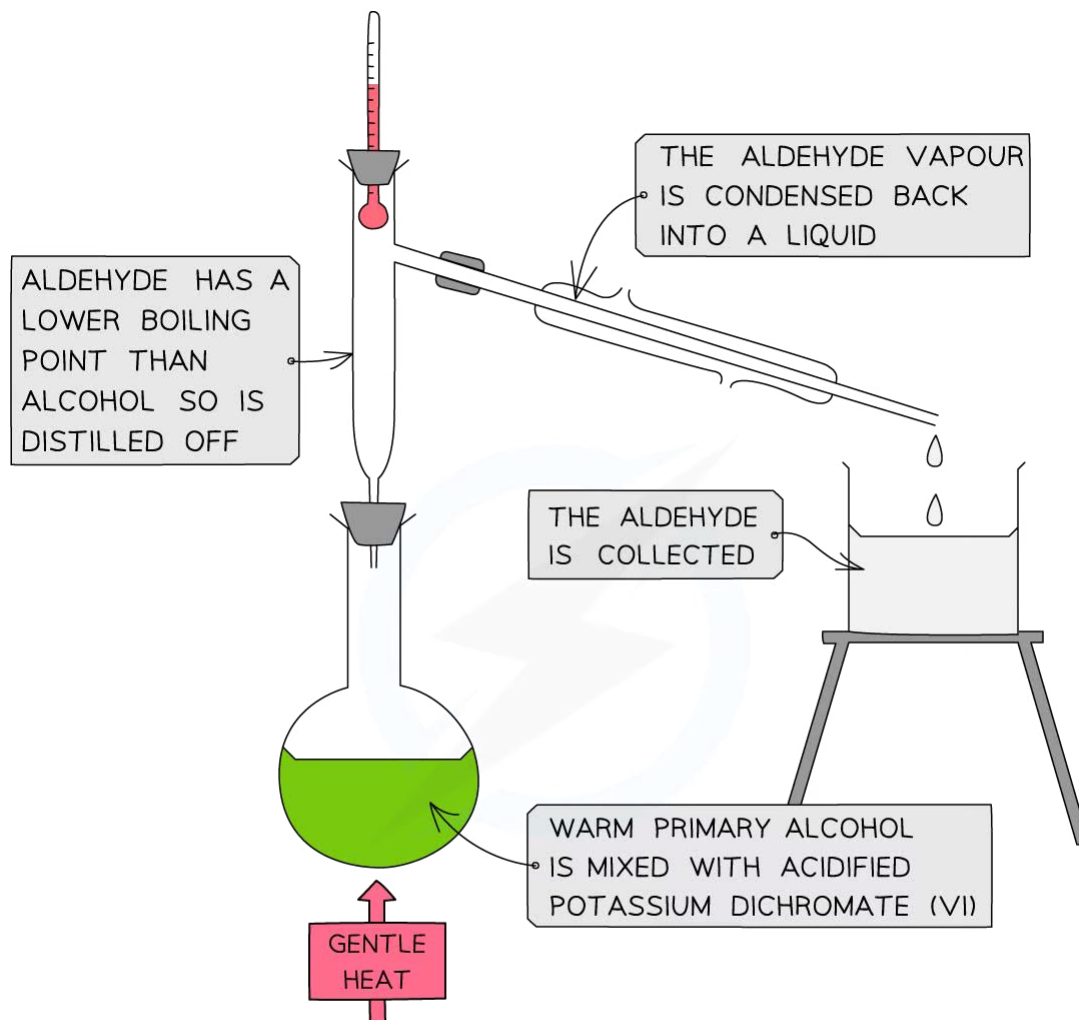
Distillation & Reflux

Distillation

- Distillation is a common practical completed in organic chemistry
- Distillation is used as there are times that a reaction does not go to completion or there are other chemicals produced as well as the desired product
- Distillation allows you to separate compounds by their boiling point
 - Chemicals with the lowest boiling point will distill first
- One of the most common distillation practicals is the oxidation of primary and secondary alcohol to aldehydes and ketones

The Distillation Process:

- To produce an aldehyde from a primary alcohol, a reaction mixture containing the primary alcohol and acidified potassium dichromate solution is placed into a pear-shaped or round bottomed flask
- Anti-bumping granules are added to promote smooth boiling
- Quickfit apparatus is then set up, including a still head and condenser connected to the side
 - The joints of the Quickfit apparatus are often have a thin layer of silicon grease smeared over them to give a better seal as well as to make it easier to disassemble the equipment afterwards
- A Quickfit thermometer can be used, with the thermometer bulb sitting where the vapours will pass into the condenser
- A steady and constant stream of water passes through the condenser in a 'water jacket' – it enters at the bottom of the condenser and the drainage pipe removes the water from the top of the condenser



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Heating under Distillation Apparatus

- ♦ The reaction mixture is heated until it boils using a heating mantle
 - Electric heating mantles are used for this because the temperature can be controlled, and because you are using chemicals which are flammable
- ♦ The distillate which forms in the condenser drips directly into a receiving vessel
 - The distillate which should be collected, is that which is given off at $\pm 2^\circ\text{C}$ of the boiling point of the desired product
 - Some distillate may be given off below this temperature – this needs to be discarded and a clean vessel used to collect the desired product

- Stop collecting the distillate if the temperature rises above $\pm 2^{\circ}\text{C}$ of the boiling point of the desired product
- ♦ The **aldehyde** product has a lower boiling point than the **alcohol** (since it has lost the **H-bonding**) so it can be **distilled off** as soon as it forms

Heating under reflux

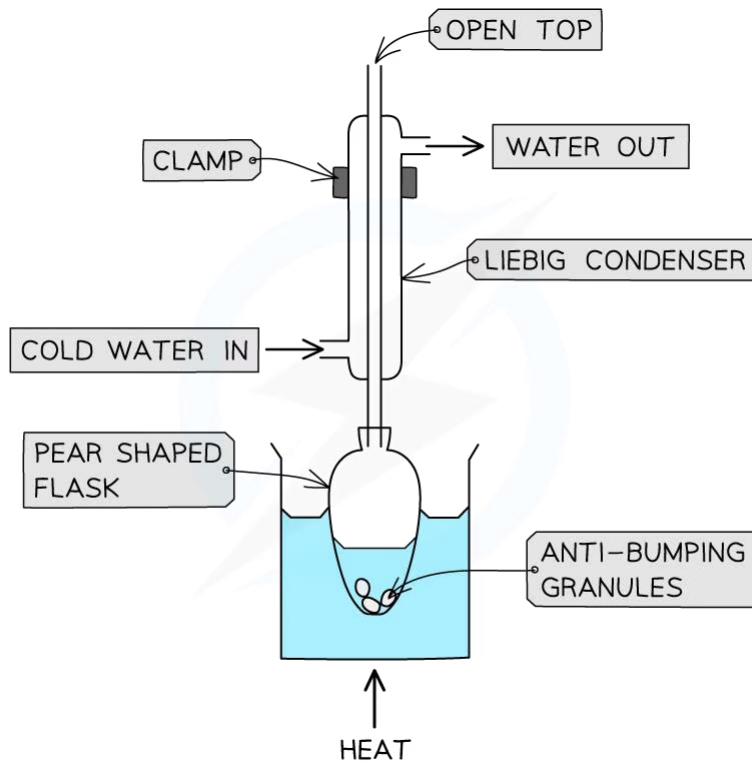
- ♦ Organic reactions often occur slowly at room temperature
- ♦ Therefore, organic reactions can be completed by heating under reflux to produce an **organic liquid**
- ♦ This allows the mixture to react as fully as possible without the loss of any reactants, products or solvent
 - In distillation, you are trying to separate a chemical or product from a mixture
 - When heating under reflux, you aim to keep all the chemicals inside the reaction vessel

The Heating under Reflux Process:

- ♦ Example reactions where heating under reflux could be used include:
 - The production of a carboxylic acid from a primary alcohol using acidified potassium dichromate
 - The production of an ester from an alcohol and acid in the presence of an acid catalyst
- ♦ The reaction mixture is placed into a pear-shaped or round bottomed flask
- ♦ Anti-bumping granules are, again, added to promote smooth boiling
- ♦ The flask is placed in a heating mantle or it can be immersed in a water bath for heating
- ♦ Quickfit apparatus is then set up with the condenser clamped vertically in place
 - The joints of the Quickfit apparatus are commonly greased as with distillation
- ♦ A steady and constant stream of water passes through the condenser in a 'water jacket' – it enters at the bottom of the condenser and the drainage pipe removes the water from the top of the condenser
- ♦ The water is heated and the reaction mixture allowed to boil
- ♦ The heated is stopped and the mixture allowed to cool back to room temperature

YOUR NOTES

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The preparation of ethyl ethanoate involves heating under reflux for about 15 minutes

Exam Tip

- ◆ These practicals give you the opportunity to discuss:
 - The use of an electric heating mantles and water baths rather than a Bunsen burner
 - The choice and setup of laboratory apparatus
 - Health and safety considerations including the careful handling of different liquids, including those which are corrosive, irritant, flammable and toxic

Preparation & Purification of an Organic Liquid

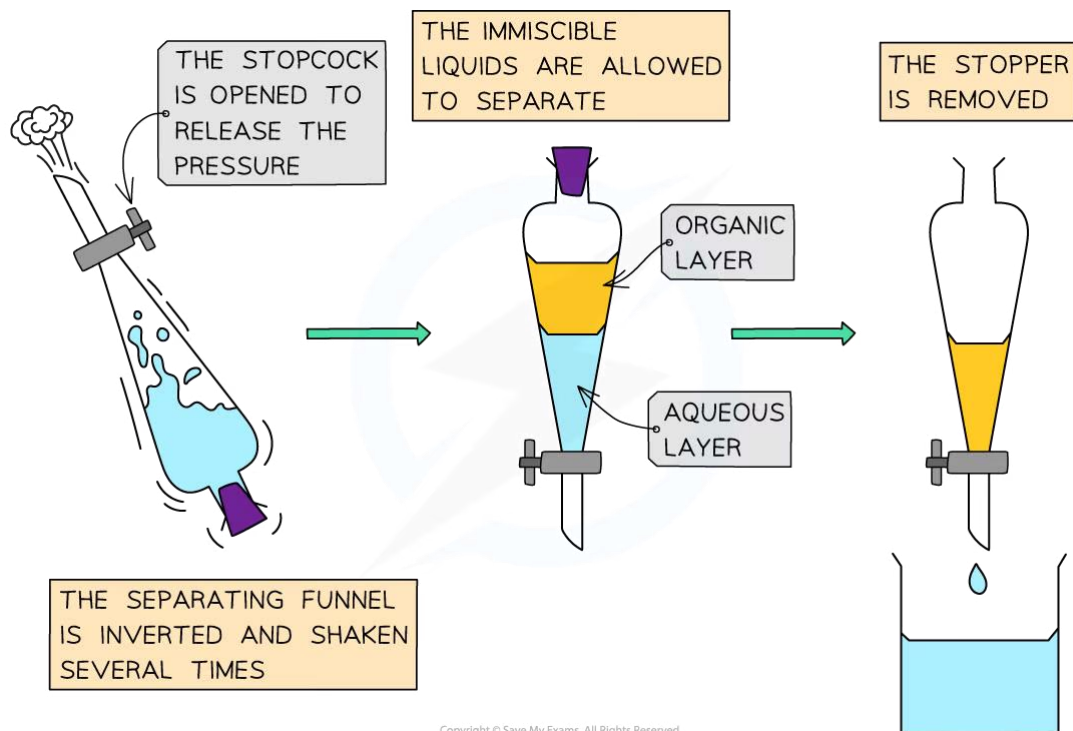
- There are different methods to purify organic liquids, including:
 - Use of a separating funnel
 - Use of drying agents
 - Redistillation

Use of a Separating Funnel

- When organic liquids are being prepared, water can often be obtained along with the organic product
- The water will usually form an aqueous layer with the product in the organic layer
 - It can sometimes be hard to identify which layer is the organic layer – this can be achieved by simply adding water and seeing which layer increases in volume
- Other organic reactions may need to be neutralised before being purified, this can be achieved by adding sodium carbonate solution to the reaction vessel or separating funnel
- The contents of the reaction vessel are transferred to a separating funnel and a stopper added
- The separating funnel is inverted and the stopcock opened to release the pressure – this is repeated 15–20 times
 - If neutralisation has occurred then the stopcock is opened slowly to avoid losing any product
- The two layers are allowed to separate
 - In the following example, the aqueous layer is the bottom layer inside the separating funnel
- The stop cock is opened so that the aqueous layer drains away and the organic layer can be drained into a clean beaker

YOUR NOTES

▮



A separating funnel allows the product to be cleaned and isolated

Exam Tip

- You cannot assume that the organic layer will always be the top layer
- The position of the organic layer depends on its density
 - If the organic layer is denser than the aqueous layer, then it will be the bottom layer
 - If the organic layer is less dense than the aqueous layer, then it will be the top layer
- If you need to know the position of the layers, then the examiners will either make this clear or provide you with the information you require to deduce the position of the layers

Use of drying agents

- Drying agents can be used to remove traces of water from an organic product
- Drying agents are usually anhydrous inorganic salts that readily hydrate in the presence of water
 - Anhydrous calcium chloride is commonly used to dry hydrocarbons
 - Anhydrous calcium or magnesium sulfate are used more general purpose drying agents
- A spatula of drying agent is added into the organic product and swirled
 - If the organic product has a low boiling point, a lid / stopped can be added to reduce the potential evaporation of any product
- If the drying agent clumps together, then there is still water in the organic liquid

YOUR NOTES

- More drying agent is added until some remains dispersed in the organic liquid as a fine powder
- The dry organic liquid can then be decanted or filtered
 - If the organic liquid is dry then it should appear clear

Redistillation

- Sometimes when an organic liquid is obtained via distillation there can be traces of other liquids
 - This is particularly the case if any liquids in the reaction vessel or other by-products have a similar boiling point to the desired organic liquid
- In this situation, the distillation apparatus is cleaned, dried and set up for a second distillation
- The aim of the second distillation is to obtain just the desired organic liquid
- This can be done by aiming for a narrower boiling point range in the distillate
 - The narrower the boiling point range, the more pure the organic liquid is

YOUR NOTES

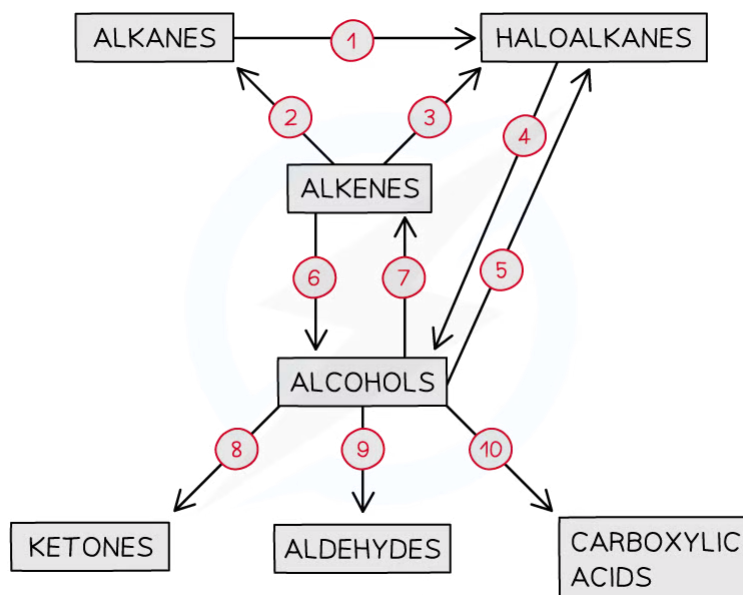
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Two-Stage Organic Synthetic Routes

- It is possible to make a large number of organic products from a few starting compounds and the necessary reagents and conditions
- Knowing how organic functional groups are related to each other is key to the synthesis of a given molecule
- The main functional groups you need to know are
 - Alkanes
 - Alkenes
 - Haloalkanes
 - Alcohols
 - Carbonyls (aldehydes & ketones)
 - Carboxylic acids

Aliphatic Reaction Pathways

- The key functional groups and their interconversions are summarised here:



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The main reaction pathways at AS level

Reaction	Reagent	Condition	Mechanism	Reaction Type
1	Halogen	UV light	Free Radical	Substitution
2	Hydrogen + Ni catalyst	150°C	Electrophilic	Addition/ Hydrogenation
3	Hydrogen halide	Room temperature	Electrophilic	Addition
4	NaOH (aq)	Heat under reflux	Nucleophilic	Substitution
5	NaX + H ₂ SO ₄	Heat under reflux	Nucleophilic	Substitution
6	Steam + H ₂ SO ₄	Heat	–	Hydration
7	Al ₂ O ₃ or conc. acid	Heat	Elimination	Dehydration/ Elimination
8	K ₂ Cr ₂ O ₇ / H ₂ SO ₄	Heat under reflux	–	Oxidation
9	K ₂ Cr ₂ O ₇ / H ₂ SO ₄	Distillation	–	Oxidation
10	K ₂ Cr ₂ O ₇ / H ₂ SO ₄	Heat under reflux	–	Oxidation

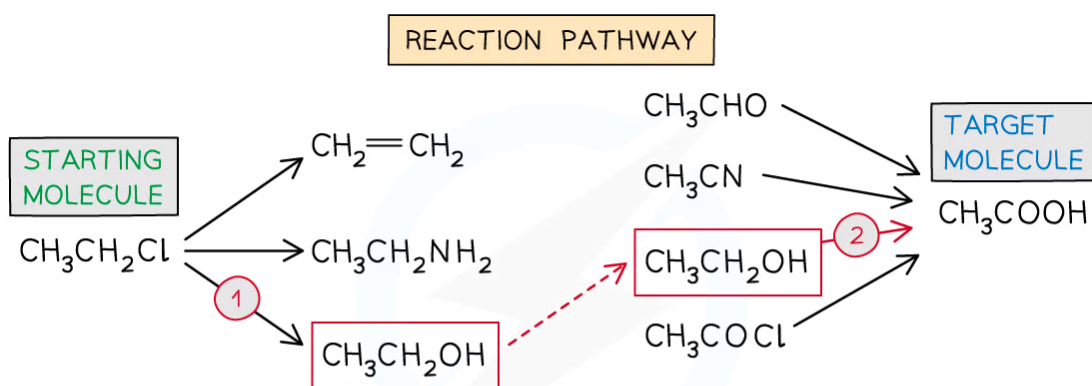
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Designing a Reaction Pathway

- The given molecule is usually called the **target molecule** and chemists try to design a synthesis as efficiently as possible
- Designing a reaction pathway starts by drawing the structures of the **target molecule** and the **starting molecule**
- Determine if they have the **same number** of carbon atoms
 - If you need to lengthen the carbon chain you will need to put on a **nitrile group** by nucleophilic substitution
- Work out all the compounds that can be made from the starting molecule and all the molecules that can be made into the target molecule
 - Match the groups they have in common and work out the reagents and conditions needed

Worked Example
 Suggest how the following synthesis could be carried out:
 Chloroethane to ethanoic acid

Answer



1 REACT WITH NaOH(aq) + HEAT UNDER REFLUX

2 OXIDISE WITH $\text{K}_2\text{Cr}_2\text{O}_7$ + H_2SO_4 + HEAT UNDER REFLUX

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 Exam Tip

At AS level, you will only be required to design a synthesis with two steps, i.e. reactant → intermediate → product

However, sound knowledge of all of the different reactions will be beneficial in the long run – especially as the A-level course simply states that you should be able to design a multistage synthesis

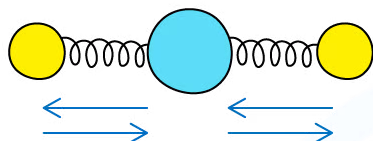
4.7 Analytical Techniques

4.7.1 Infrared Spectroscopy

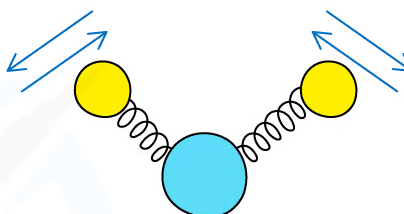
Introduction to Infrared Spectroscopy

- All **covalent bonds** act rather like springs, as opposed to rigid bars
- Like springs, the bonds can vibrate in a number of different ways
- The frequency of vibration occurs in the **infra-red region** of the **electromagnetic spectrum**
- If an organic molecule is irradiated with **infra-red energy** that matches the **natural vibration frequency** of its bonds, it absorbs some of that energy and the amplitude of vibration increases
- This is known as **resonance**

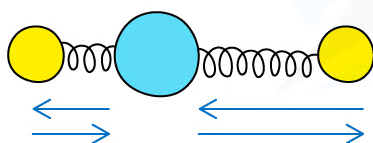
SYMMETRIC STRETCHING



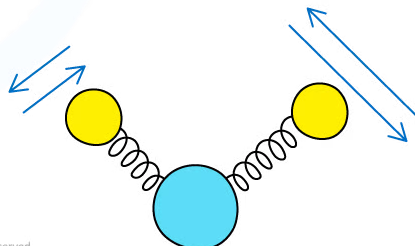
SYMMETRIC BENDING



ASYMMETRIC STRETCHING



ASYMMETRIC BENDING



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Different modes of vibration in molecules. Each mode has a characteristic frequency of vibration

Infrared (IR) spectroscopy

- **Infrared (IR) spectroscopy** is a technique used to identify compounds based on changes in **vibrations** of atoms when they **absorb** IR of certain **frequencies**
- A **spectrophotometer** irradiates the sample with IR radiation and then detects the **intensity** of **IR radiation** absorbed by the molecule
- **IR energy** is absorbed only if a molecule has a **permanent dipole** that changes as it vibrates
 - Symmetrical molecules such as O₂ or H₂, are therefore **IR inactive**
- The **resonance frequency** is the specific frequency at which the bonds will vibrate

- Rather than displaying frequency, an **IR spectrum** shows a unit called **wavenumber**
 - **Wavenumber** is the reciprocal of the **wavelength** and has units of cm^{-1}
- Characteristic absorptions can be matched to specific bonds in molecules
 - This enables chemists to determine the **functional groups** present

Absorption Range of Bonds

Bond	Functional Groups containing the bond	Characteristic infrared absorption range in wavenumbers / cm^{-1}
C–C	Alkanes and alkyl chains	750–1100
C–X	Haloalkanes (X=C, Br, I)	500–800
C–F	Fluoroalkanes	1000–1350
C–O	Alcohols, esters and carboxylic acids	1000–1300
C=C	Alkenes	1620–1680
C=O	Aldehydes, ketones, carboxylic acids, esters, amides, acyl chlorides and acid anhydrides	1630–1820
Aromatic C=C	Arenes	Several peaks in the range 1450–1650
C≡N	Nitriles	2200–2260
C–H	Alkyl groups, alkenes and arenes	2850–3100
O–H	Carboxylic acids	2500–3300 (broad)
N–H	Amines and amides	3300–3500
O–H	Alcohols and phenols	3200–3600

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- Due to some absorption bands overlapping each other, other analytical techniques such as **mass spectroscopy** should be used alongside **IR spectroscopy** to identify an unknown compound

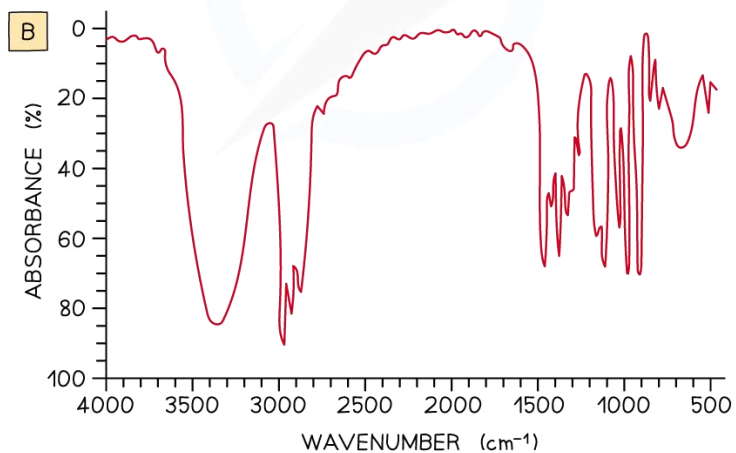
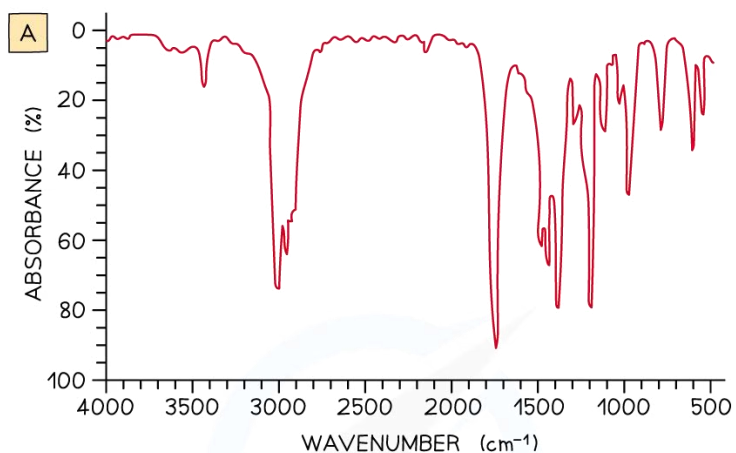
Interpreting & Predicting Infrared Spectra

YOUR NOTES

- ♦ The best way to understand how to interpret an **IR spectrum** is by looking at examples and becoming familiar with the characteristic features of an **IR spectrum**

Worked Example

Examine the two spectra shown and determine which one belongs to propan-2-ol and which one belongs to propanone



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Answer:

- IR spectrum **A** is **propanone**
 - In IR spectrum **A** the presence of a strong, sharp absorption around 1710 cm^{-1} corresponds to the characteristic $\text{C}=\text{O}$, carbonyl, group in a ketone.
- IR spectrum **B** is **propan-2-ol**.
 - In spectrum **B** the presence of a strong, broad absorption around $3200\text{--}3600 \text{ cm}^{-1}$ suggests that there is an alcohol group present, which corresponds to the -OH group in propan-2-ol.



Exam Tip

You can be asked to interpret or predict infrared spectra of both familiar and unfamiliar substances

Three of the key peaks to be aware of are:

1. The narrow scoop caused by the O-H bond of an alcohol at between 3200 and 3600 cm^{-1}
2. The sharp spike caused by the carbonyl C=O bond that belongs to many compounds as listed in the data booklet and table above
3. The broad scoop caused by the O-H bond of a carboxylic acid between 2500 and 3300 cm^{-1} , this right hand side of this peak is often distorted by the peaks from C-H bonds

YOUR NOTES



Uses of Infrared Spectroscopy

- ♦ Infrared spectroscopy is used to identify pollutants in vehicle emissions in the air
 - Sensors detect and measure the amount of pollutants such as carbon monoxide, carbon dioxide and unburnt hydrocarbons
 - This commonly occurs on motorways and in busy town centres to monitor localised pollution
- ♦ Infrared spectroscopy can be used to measure alcohol levels using roadside breathalysers
 - A ray of infrared radiation is passed through the breath that is exhaled into the breathalyser chamber
 - The characteristic bonds of ethanol are detected and measured – the higher the absorbance of infrared radiation, the more ethanol in the person's breath

Fingerprint Region

- ♦ The region below about 1500 cm^{-1} is called the **fingerprint region** and is unique to every molecule
- ♦ It has many peaks that can be difficult to assign
- ♦ These peaks represent the complex vibrational interactions that occur between different bonds within a molecule
- ♦ The value of the **fingerprint region** is in being able to compare the **IR spectrum** to a known compound from a database and coming up with an exact match
- ♦ This is particularly useful, for example, in identifying a specific member of a **homologous series**
 - All members of the series will show the same type of bonds present, but no two molecules will have the same fingerprint region
- ♦ Infrared spectroscopy is one of a number of techniques used to determine the structure of organic molecules
 - It is most commonly used in combination with other analytical techniques such as:
 - Elemental analysis – to determine the empirical formula
 - Mass spectrometry – to determine the molecular mass and fragment ions from the whole molecule
 - (NMR spectroscopy is also included in the techniques but this is not covered as part of the AS course)

YOUR NOTES

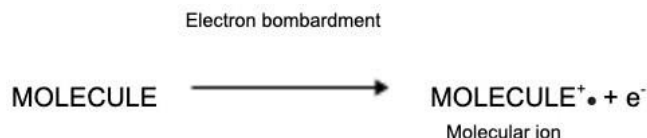
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4.7.2 Mass Spectrometry

YOUR NOTES

Interpreting Mass Spectra

- When a compound is analysed in a mass spectrometer, vaporised molecules are bombarded with a beam of high-speed electrons
- These knock off an electron from some of the molecules, creating **molecular ions**:



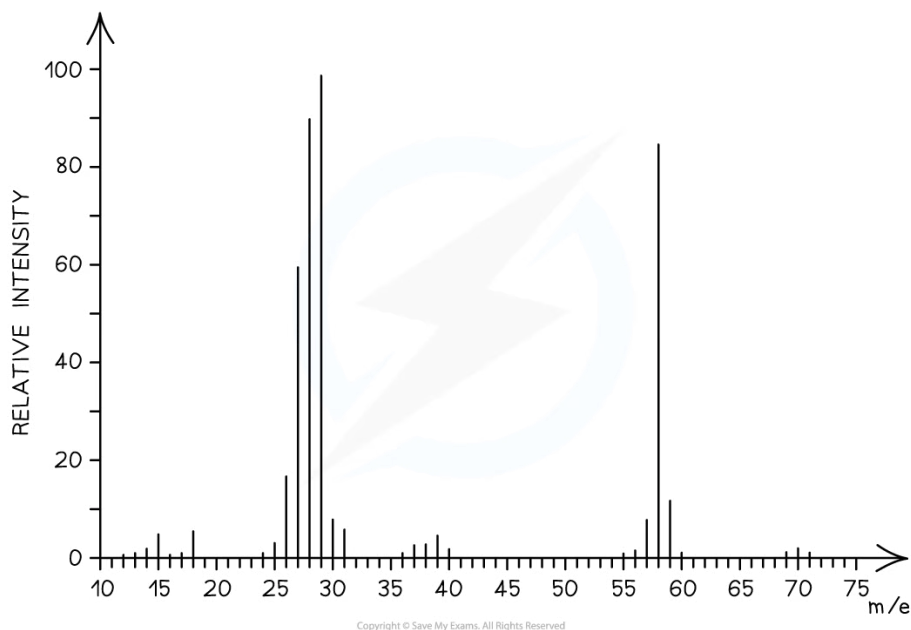
- The relative abundances of the detected ions form a **mass spectrum**: a kind of molecular fingerprint that can be identified by computer using a spectral database
- The peak with the highest ***m/z*** value is the molecular ion (***M*⁺**) peak which gives information about the **molecular mass** of the compound
- This value of *m/z* is equal to the **relative molecular mass** of the compound

The ***M*+1** peak

- The ***[M+1]*** peak is a smaller peak which is due to the natural abundance of the isotope **carbon-13**
- The height of the ***[M+1]*** peak for a particular ion depends on how many carbon atoms are present in that molecule; The more carbon atoms, the larger the ***[M+1]*** peak is
 - For example, the height of the ***[M+1]*** peak for an hexane (containing six carbon atoms) ion will be greater than the height of the ***[M+1]*** peak of an ethane (containing two carbon atoms) ion

Worked Example

Determine whether the following mass spectrum belongs to propanal or butanal



Answer:

- The mass spectrum corresponds to **propanal** as the molecular ion peak is at $m/z = 58$
- Propanal arises from the $\text{CH}_3\text{CH}_2\text{CHO}^+$ ion which has a molecular mass of 58
- Butanal arises from the $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}^+$ ion which has a molecular mass of 72

Fragmentation Peaks in Mass Spectra

- The molecular ion peak can be used to identify the **molecular mass** of a compound
- However, different compounds may have the same molecular mass
- To further determine the structure of the unknown compound, **fragmentation analysis** is used
- Fragments may appear due to the formation of **characteristic fragments** or the **loss of small molecules**
 - For example, a peak at 29 is due to the characteristic fragment $C_2H_5^+$
 - Loss of small molecules gives rise to differences between peaks of, for example, 18 (H_2O), 28 (CO), and 44 (CO_2)
 - An alcohol can typically dehydrate in a MS, so one peak to look for is $M-18$

Alkanes

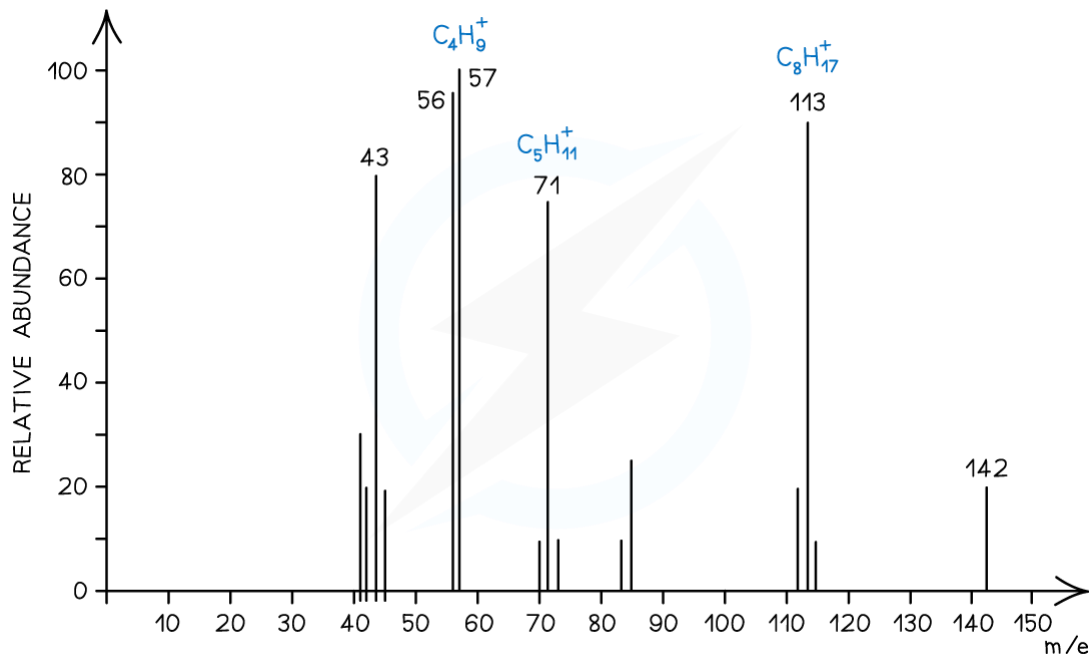
- Simple alkanes are fragmented in mass spectroscopy by breaking the C-C bonds
- ***M/z*** values of some of the common alkane fragments are given in the table below

***m/z* values of Fragments Table**

Fragment	<i>m/e</i>
CH_3^+	15
$C_2H_5^+$	29
$C_3H_7^+$	43
$C_4H_9^+$	57
$C_5H_{11}^+$	71
$C_6H_{13}^+$	85

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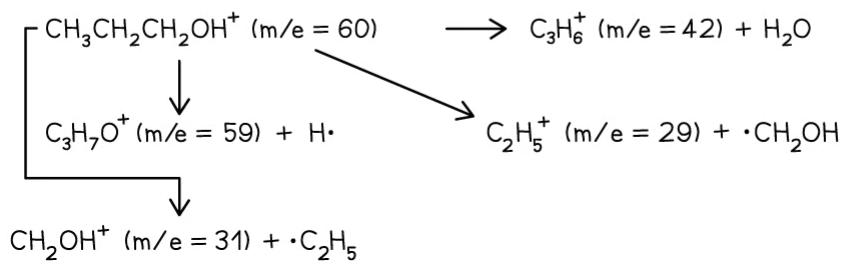
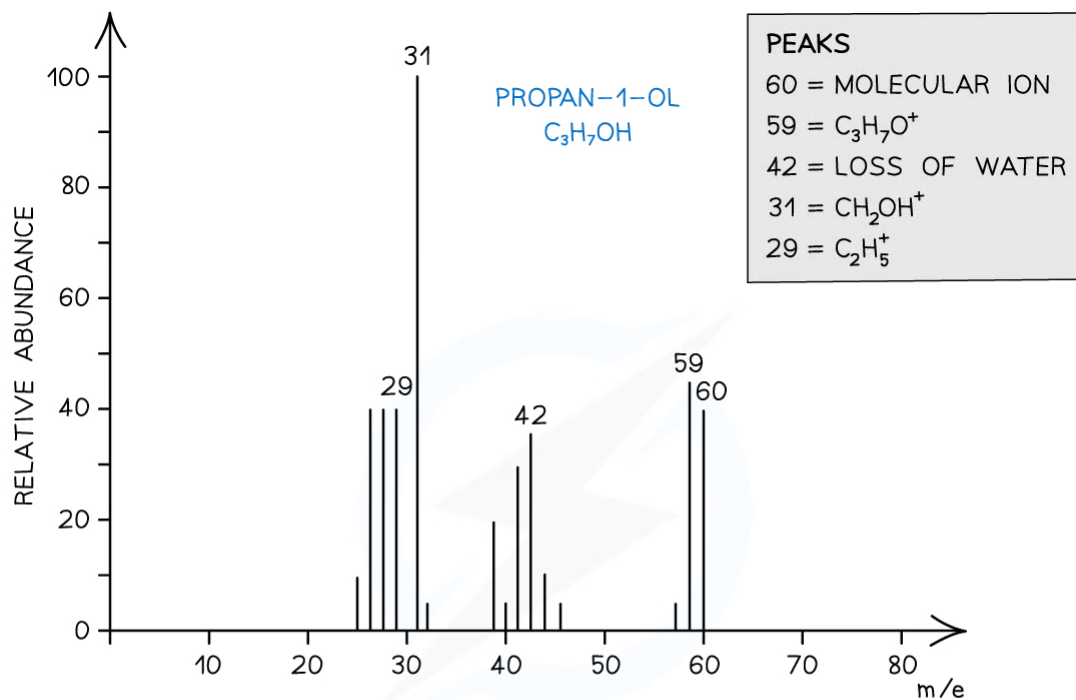
YOUR NOTES



Mass spectrum showing fragmentation of alkanes

Alcohols

- Alcohols often tend to lose a **water molecule** giving rise to a peak at **18 below the molecular ion**
- Another common peak is found at m/e value 31 which corresponds to the CH_2OH^+ fragment
- For example, the mass spectrum of propan-1-ol shows that the compound has fragmented in four different ways:
 - Loss of H^\cdot to form a $\text{C}_3\text{H}_7\text{O}^+$ fragment with $m/e = 59$
 - Loss of a water molecule to form a C_3H_6^+ fragment with $m/e = 42$
 - Loss of a $\cdot\text{C}_2\text{H}_5$ to form a CH_2OH^+ fragment with $m/e = 31$
 - And the loss of $\cdot\text{CH}_2\text{OH}$ to form a C_2H_5^+ fragment with $m/e = 29$



Mass spectrum showing the fragmentation patterns in propan-1-ol (alcohol)

Worked Example
Alcohol fragmentation

Which alcohol is not likely to have a fragment ion at m/z at 43 in its mass spectrum?

- A. $(CH_3)_2CHCH_2OH$
- B. $CH_3CH(OH)CH_2CH_2CH_3$
- C. $CH_3CH_2CH_2CH_2OH$
- D. $CH_3CH_2CH(OH)CH_3$

Answer

The correct answer is option **D**

- Because a line at $m/z = 43$ corresponds to an ion with a mass of 43 for example:
 - $[\text{CH}_3\text{CH}_2\text{CH}_2]^+$
 - $[(\text{CH}_3)_2\text{CH}]^+$
- 2-butanol is not likely to have a fragment at $m/z = 43$ as it does not have either of these fragments in its structure.

YOUR NOTES

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4.7.3 Combined Techniques

YOUR NOTES

Deducing Organic Structures

- Organic chemists often use a number of techniques in combination to determine the structure of a compound

Worked Example

10.00 g of an organic compound, A, was analysed and found to contain 6.21 g of carbon, 1.03 g of hydrogen and 2.76 g of oxygen. The relative molecular mass of the compound was 58.0

Determine the molecular formula of compound A.

Answer:

	Carbon	Hydrogen	Oxygen
Mass	6.21	1.03	2.76
Relative atomic mass	12.0	1.0	16.0
$\frac{\text{mass}}{A_r}$	$\frac{6.21}{12.0} = 0.5175$	$\frac{1.03}{1.0} = 1.03$	$\frac{2.76}{16.0} = 0.1725$
Ratio (divide by the smallest value)	$\frac{0.5175}{0.1725} = 3$	$\frac{1.03}{0.1725} = 5.97$	$\frac{0.1725}{0.1725} = 1$

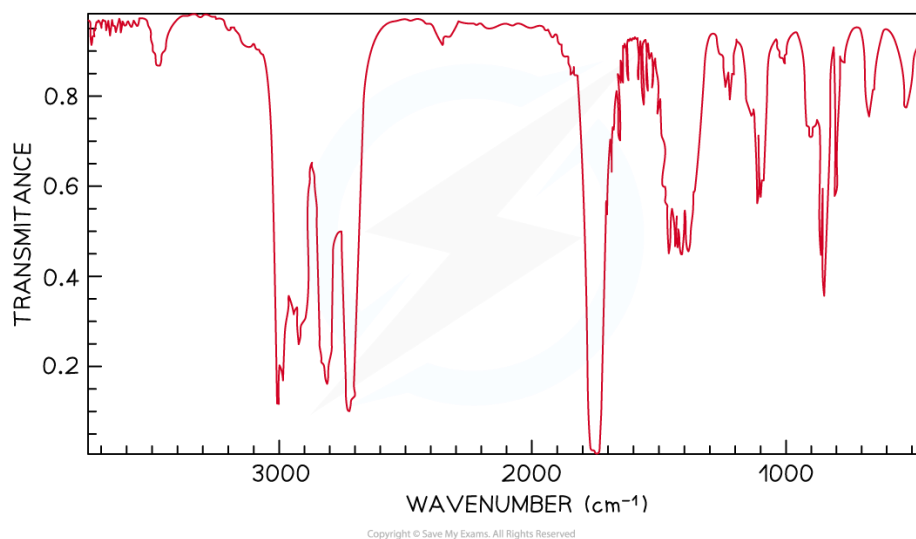
Therefore, the empirical formula of compound A is C₃H₆O

The empirical mass is $(12.0 \times 3) + (1.0 \times 6) + 16.0 = 58.0$

Therefore, the molecular formula of compound A is also C₃H₆O

Worked Example

The infrared spectrum of compound A is shown below:



Identify the peaks on the infrared spectrum

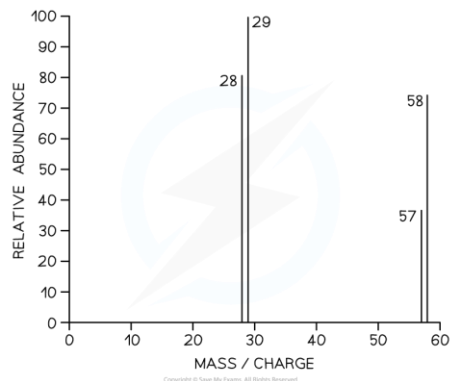
Use your molecular formula and the infrared data to suggest two possible structures for compound A

Answer

- The peaks at around 2850 cm^{-1} correspond to C–H bonds
 - This matches with the idea that compound A is a hydrocarbon derivative
- The peak at around 1750 cm^{-1} corresponds to a carbonyl / C=O group
 - Couple with a molecular formula of $\text{C}_5\text{H}_{10}\text{O}$, this suggests that compound A could be an aldehyde or a ketone
- As you are told that compound A has a straight chain structure, you can deduce that the possible structures are:
 1. Propanal
 2. Propanone

Worked Example

The mass spectrum of compound A is shown below:



Use the data from the mass spectrum to deduce the structure for compound A from your suggestions

Answer

- There are characteristic m/z peaks for a carbon chain:
 - $m/z = 29$ could represent $C_2H_5^+$ or CHO^+
- Therefore, compound A is propanal
 - Also, propanone would give a clear signal at $m/z = 15$ as it could fragment on either side of the carbonyl group

Exam Tip

You can be expected to work with any empirical and molecular formula combined with infrared and mass spectral data to identify unknown compounds

