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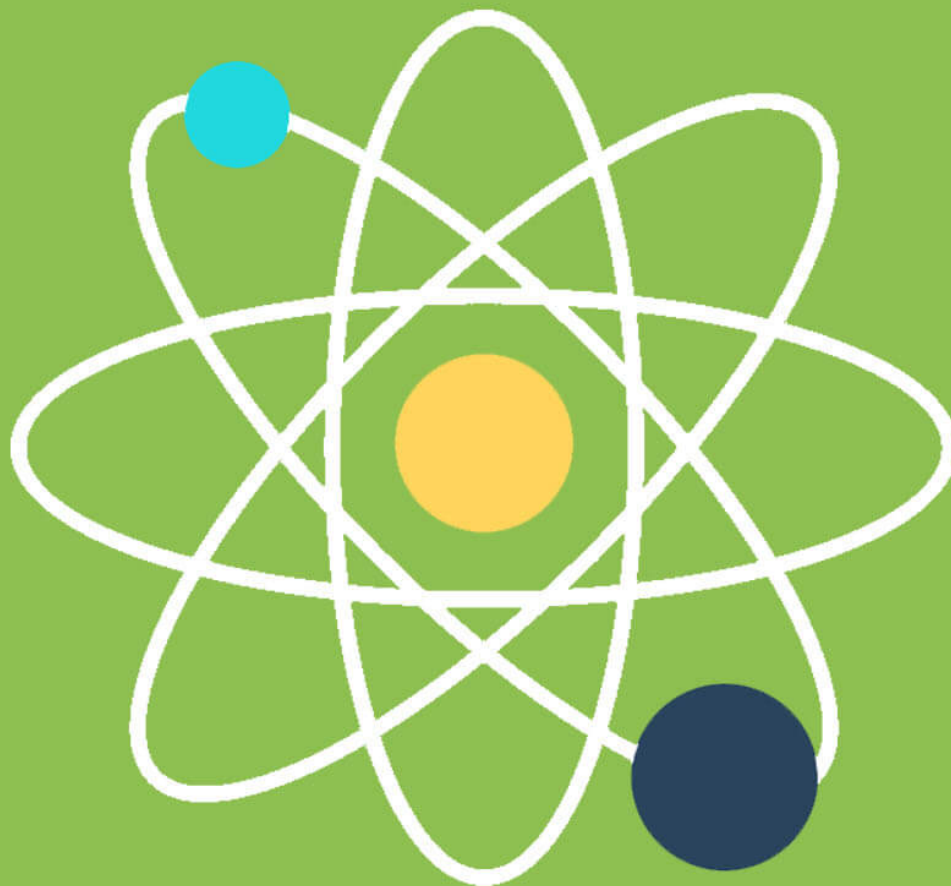
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10.2 Functional Group Chemistry



IB Chemistry - Revision Notes

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10.2.1 Alkanes – Combustion

Unreactive Alkanes

Strength of C-H bonds

- Alkanes consist of carbon and hydrogen atoms which are bonded together by **single bonds**
- Unless a lot of heat is supplied, it is difficult to break these **strong** C-C and C-H covalent bonds
- This decreases the reactivity of alkanes in chemical reactions

Lack of polarity

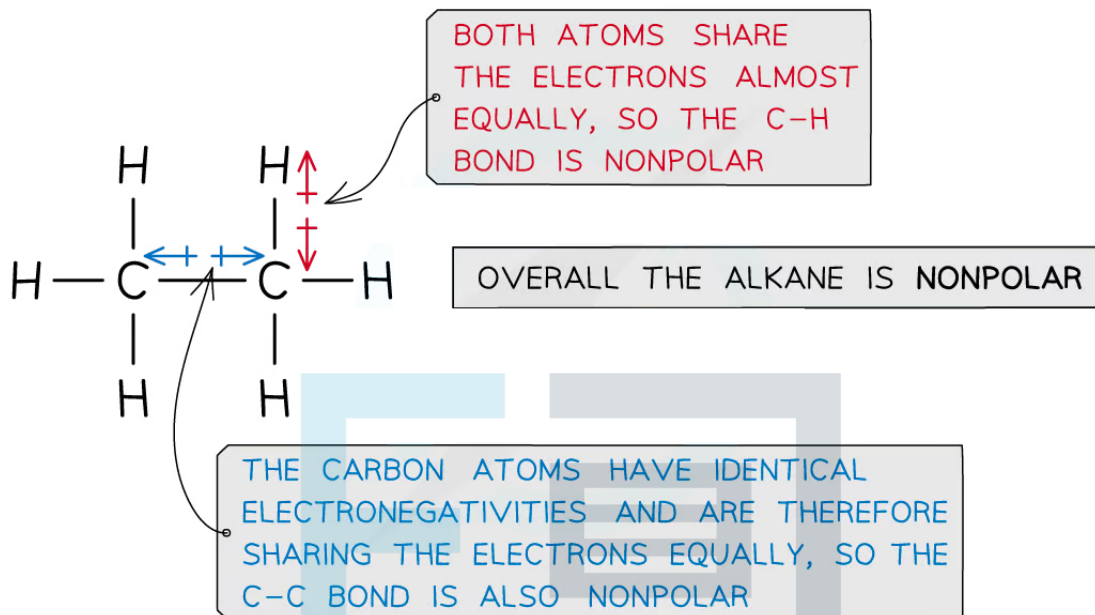
- The **electronegativities** of the carbon and hydrogen atoms in alkanes are almost the same
- This means that both atoms share the electrons in the covalent bond almost equally

PAULING ELECTRONEGATIVITY VALUES FOR THE ELEMENTS

H 2.1																		He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0		Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0		Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8		Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5		Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.1-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2		Rn –
Fr 0.7	Ra 0.9	Ac-No 1.1-1.7																

The Pauling Scale shows that the difference in electronegativity between carbon and hydrogen is only 0.4

- 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**



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

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- Due to the unreactivity of alkanes, they only react in combustion reactions and undergo substitution by halogens

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Exam Tip

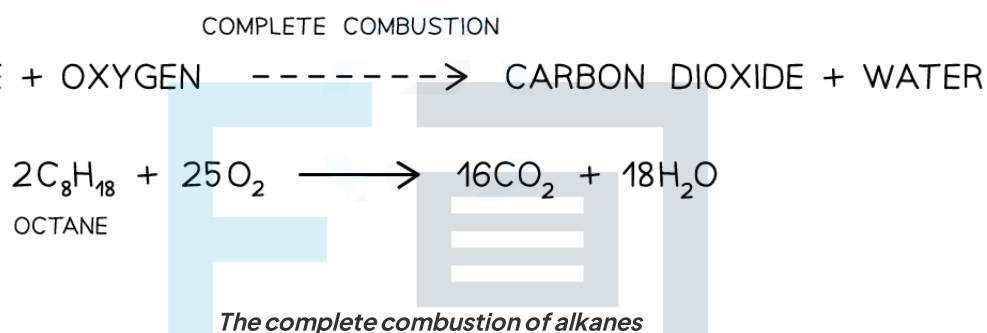
Remember: nucleophiles are negatively charged and are attracted to electron-deficient regions. Electrophiles are positively charged and attracted to electron-rich regions.

Combustion of Alkanes

- Alkanes are **combusted** (burnt) on a large scale for their use as fuels
- They also react in **free-radical substitution** reactions to form more reactive halogenoalkanes

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



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

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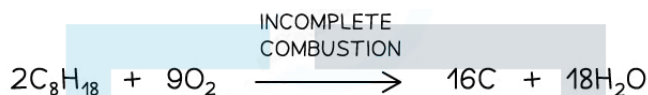
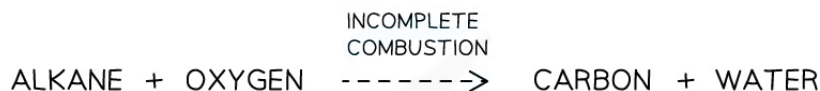


The incomplete combustion of alkanes

- Carbon monoxide is a **toxic** gas as it will bind to haemoglobin in blood which can then no longer bind **oxygen**



- As no oxygen can be transported around the body, victims will feel **dizzy, lose consciousness** and if not removed from the carbon monoxide, they can **die**
- Carbon monoxide is extremely dangerous as it is **odourless** (it doesn't smell) and will not be noticed
- 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:



The incomplete combustion of alkanes (2)

 **Exam Tip**

Incomplete combustion of alkanes never produces hydrogen as it is always preferentially oxidised in any available oxygen, rather than carbon



10.2.2 Alkanes – Halogenation

Halogenation of Alkanes

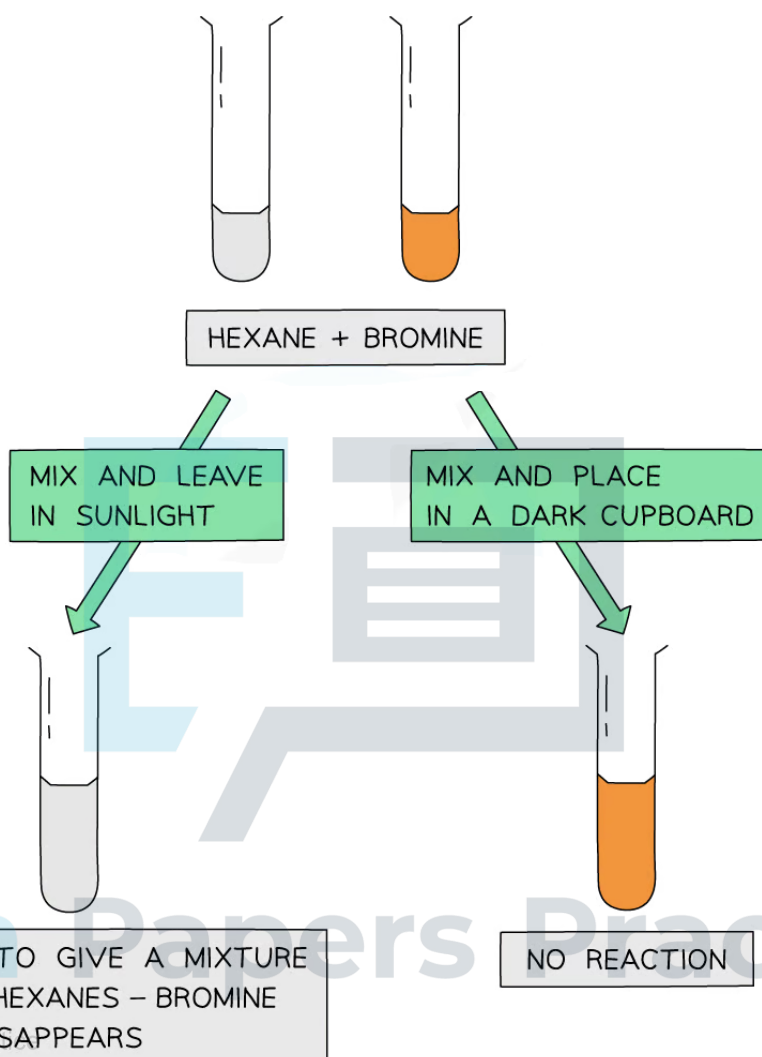
Free-radical substitution of alkanes

- 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 type reaction called the **propagation step**
 - The reaction is terminated when two radicals collide with each other in a **termination step**

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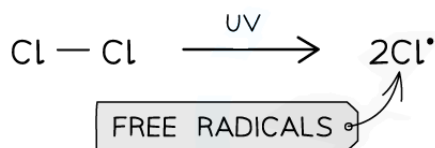
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The fact that the bromine colour has disappeared only when mixed with an alkane and placed in sunlight suggests that the ultraviolet light is essential for the free radical substitution reaction to take place

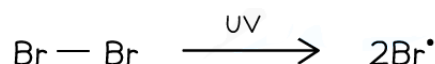
Initiation step

- 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



EACH ATOM TAKES ONE ELECTRON FROM THE COVALENT BOND, SO THIS IS A HOMOLYTIC FISSION REACTION

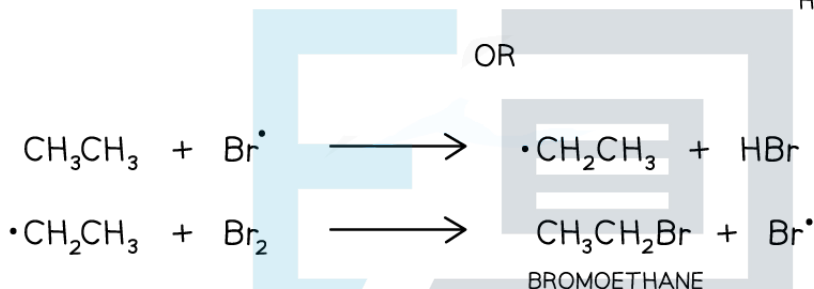
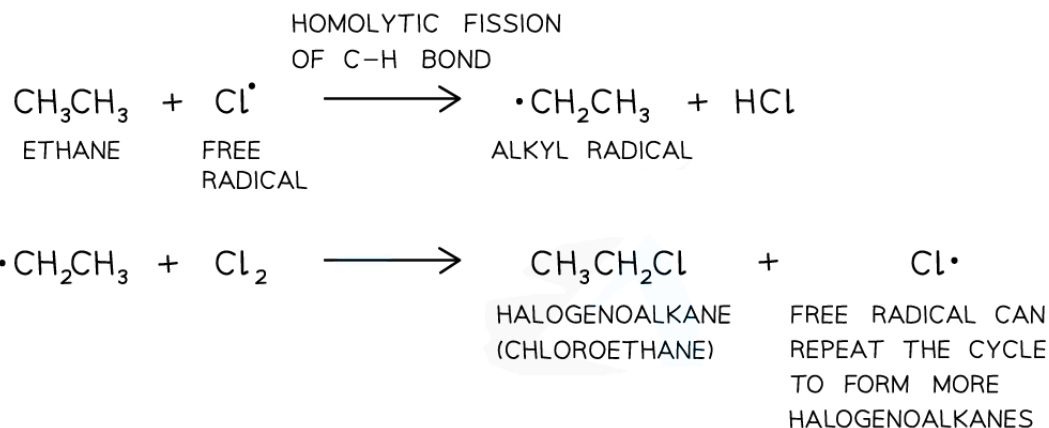
OR



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

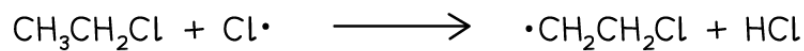
Propagation step

- The **propagation step** refers to the **progression** (growing) of the substitution reaction in a **chain type 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

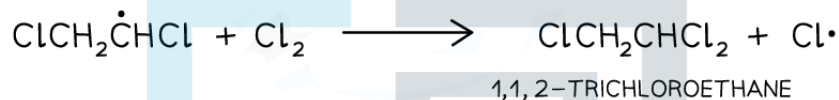
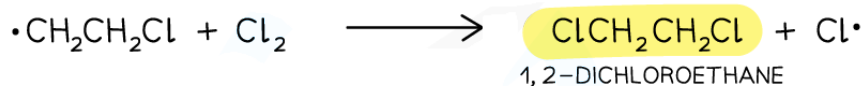


The second step of the free-radical substitution reaction is the propagation step in which the reaction grows in a chain type reaction

- 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

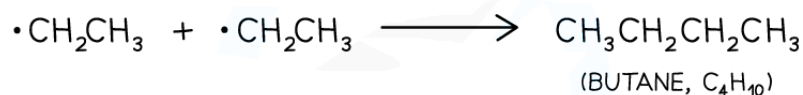
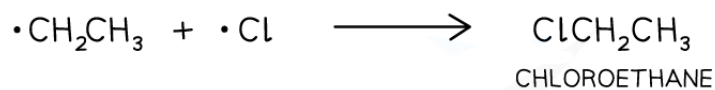
The free-radical substitution reaction gives a variety of products and not a pure halogenoalkane

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

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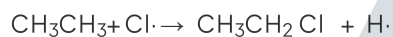


THE SAME PROCESS CAN TAKE PLACE WITH BROMINE INSTEAD OF CHLORINE

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

 **Exam Tip**

Make sure you practice and are able to write out these equations, especially the **propagation** steps which students frequently get wrong. It is quite common for students to incorrectly show a hydrogen radical produced in propagation, which does not happen:



Do not fall into this trap!

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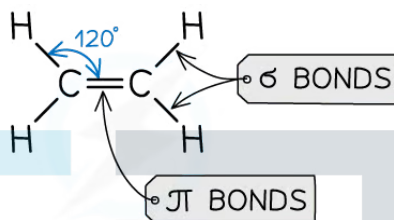
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10.2.3 Alkenes – Reactivity

Reactivity of Alkenes

- Alkenes are **hydrocarbons** containing a carbon-carbon double bond
- The atoms around the carbon-carbon double bond adopt a **planar arrangement** and the bond angle is 120°



The bonding arrangement around a carbon-carbon double bond

- The presence of the **C=C** bond gives **alkenes** a number of chemical properties that are not seen in **alkanes**
- Since the **alkene** contains **π-bonds**, it is possible to break the weaker **π-bond** and form stronger **σ-bonds** with other species without forcing any atoms on the molecule to break off
- As a result **alkenes** (unlike **alkanes**) are capable of undergoing **addition reactions**



Addition reactions in alkenes

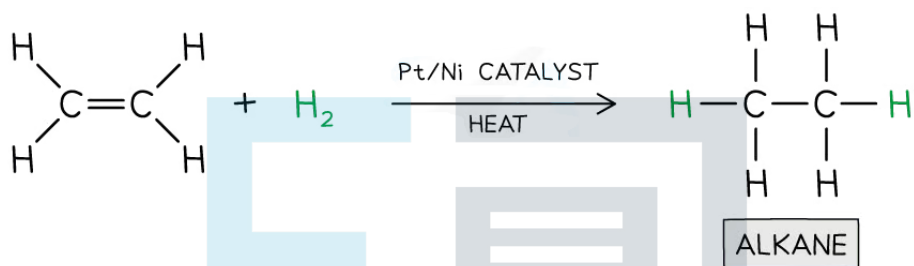
- Molecules which contain **π-bonds** and which can hence undergo **addition** are said to be **unsaturated**
- Molecules which do not contain **π-bonds** and which hence cannot undergo **addition** are said to be **saturated**.
- Alkenes** are **unsaturated** and can hence undergo **addition**
- Addition** is the combination of two or more molecules to form a single molecule
- Addition reactions** are generally faster than **substitution reactions** since only weak **π-bonds** are broken, rather than stronger **σ-bonds**
- The ability of **alkenes** to undergo **addition** means that they are much **more reactive** than **alkanes**



10.2.4 Alkenes – Hydrogenation

Hydrogenation 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
- 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

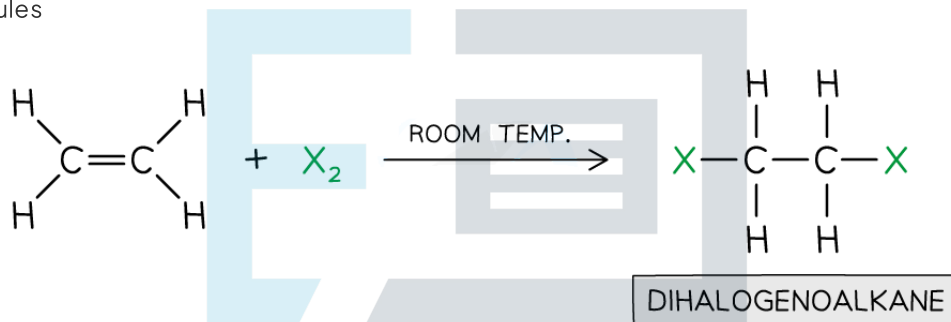
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10.2.5 Alkenes – Halogenation

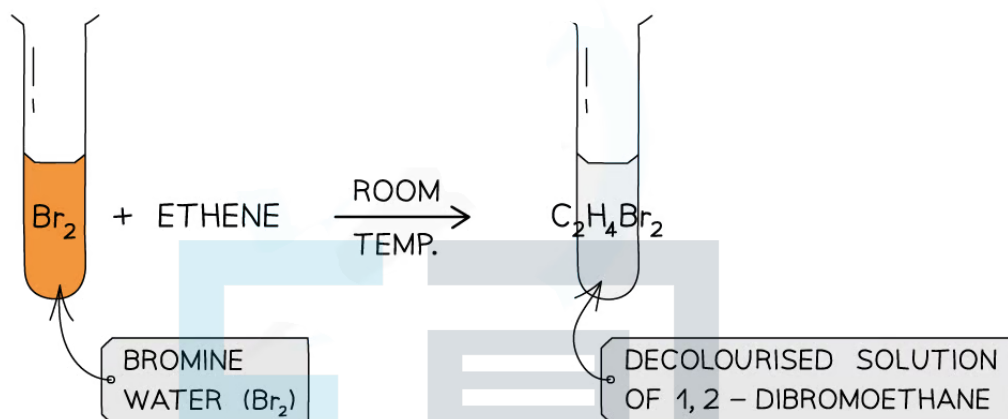
Halogenation of Alkenes

- 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

Exam Tip

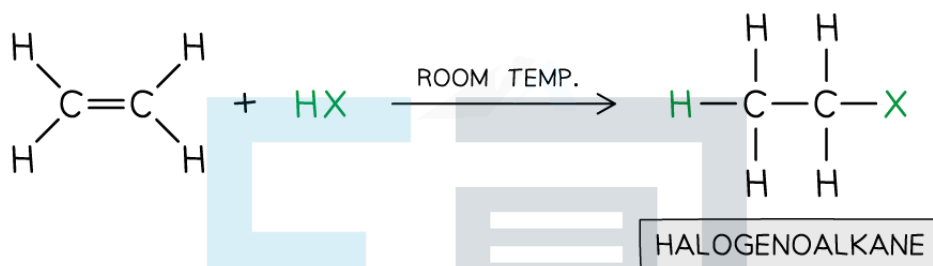
The mechanism of this reaction is part of Higher Level Chemistry and is covered in Section 20



10.2.6 Alkenes – Hydrohalogenation

Hydrohalogenation of Alkenes

- **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
- The mechanism of this reaction is part of Higher Level Chemistry and is covered in Section 20

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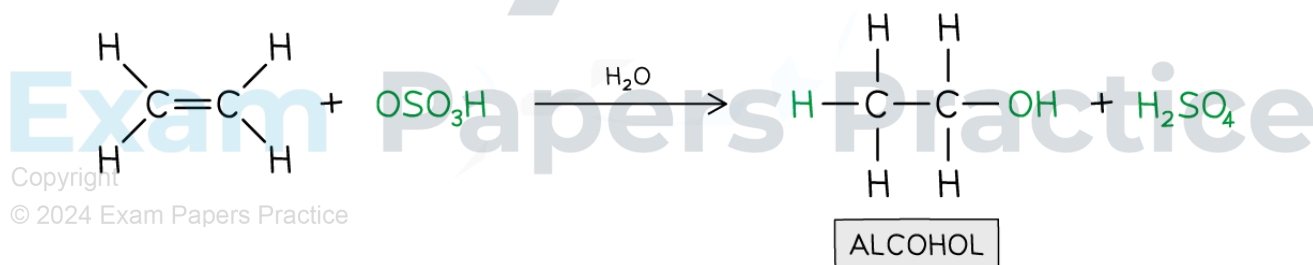
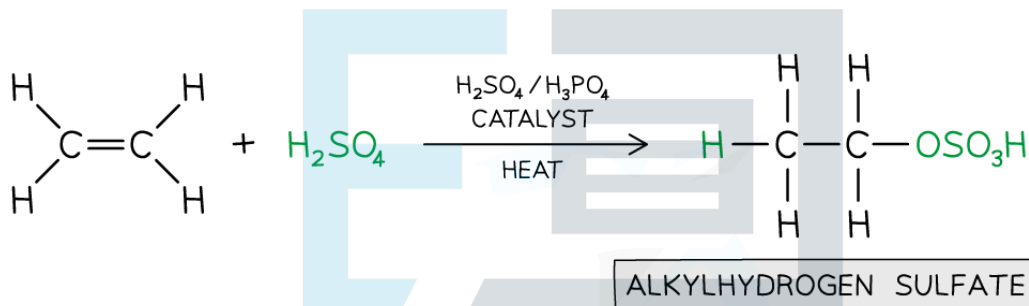
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10.2.7 Alkenes – Hydration

Hydration of Alkenes

- 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**

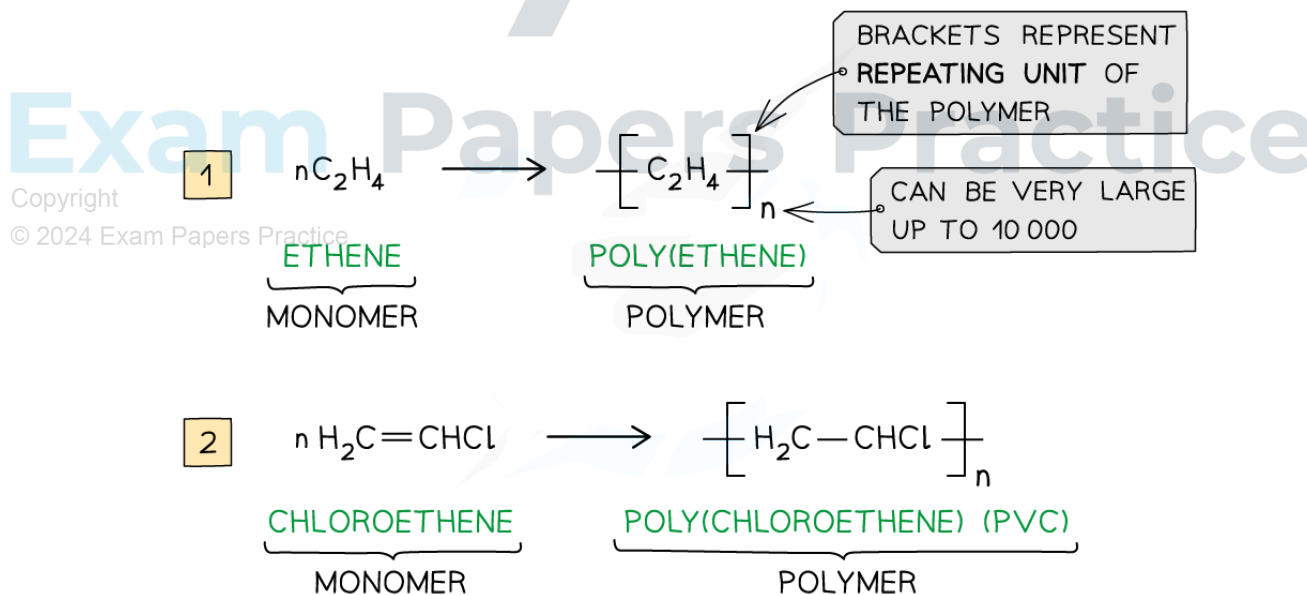
10.2.8 Addition Polymers

Polymers

Addition polymerisation

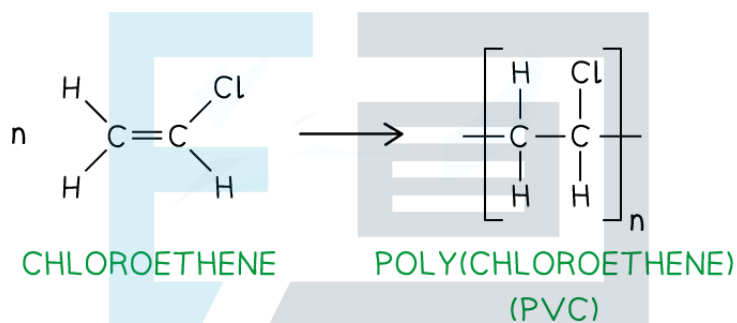
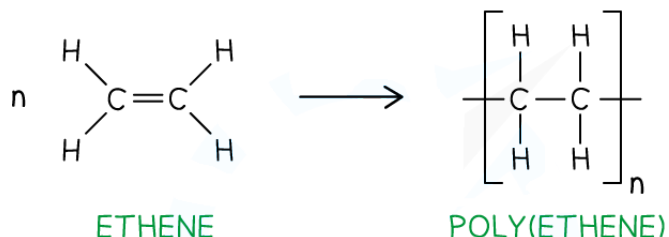
- **Addition polymerisation** is one of the most important addition reactions of alkenes which form the basis of the plastic industry
- Addition polymerisation is the reaction in which many **monomers** containing at least one C=C double bond form long chains of **polymers** as the only product
 - Just 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



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

DISPLAYED FORMULAE ADDITION POLYMERISATION



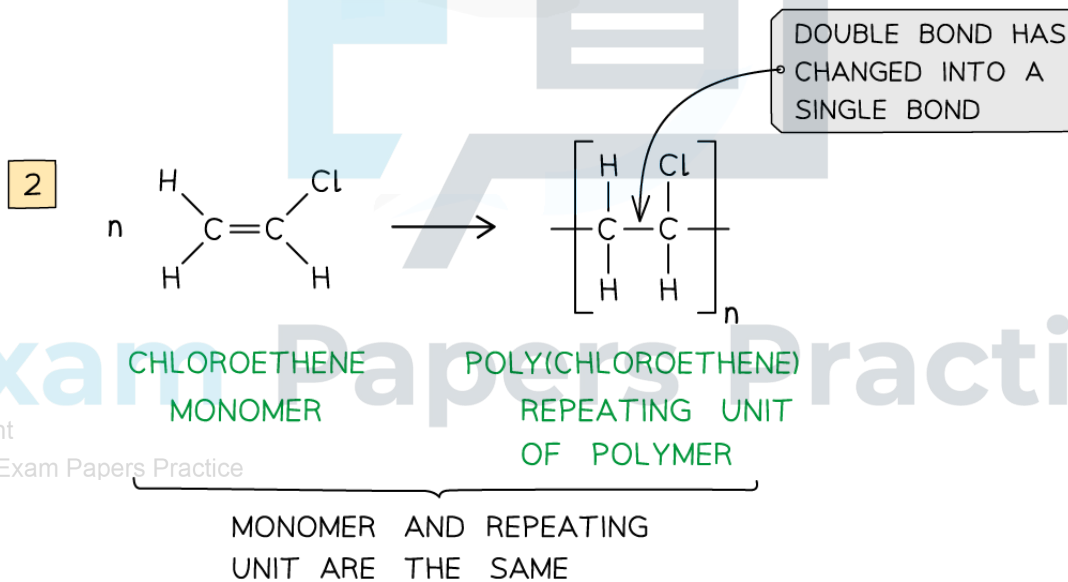
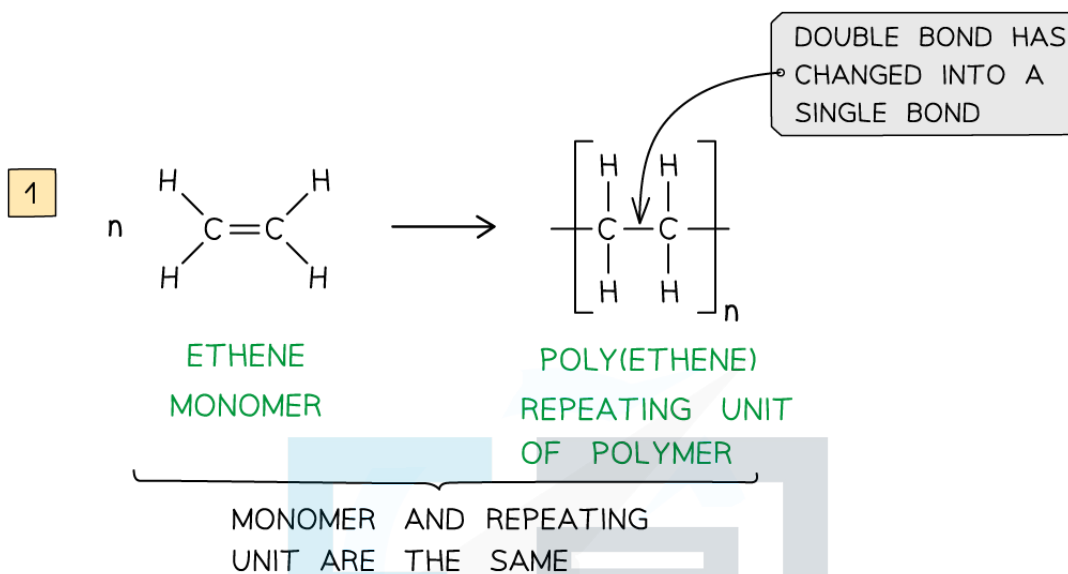
The addition polymerisation of ethene (1) and chloroethene (2)

- Just like any other **addition** reaction of alkenes, addition polymerisation gives only **one** product

Deducing repeat units

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 A **repeat unit** is the smallest group of atoms that when connected one after the other make up the polymer chain

- It is represented by **square brackets** in the displayed and general formula
- In **poly(alkenes)** (such as poly(ethene)) and **substituted poly(alkenes)** (such as PVC) made of **one type of monomer** the repeating unit is the same as the monomer except that the C=C double bond is changed to a C-C single bond



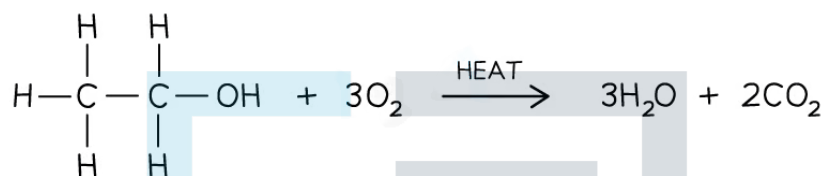
The repeating units of poly(ethene) and poly(chloroethene) are similar to their monomer except that the C=C bond has changed into a C-C bond

10.2.9 Alcohols – Combustion

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



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

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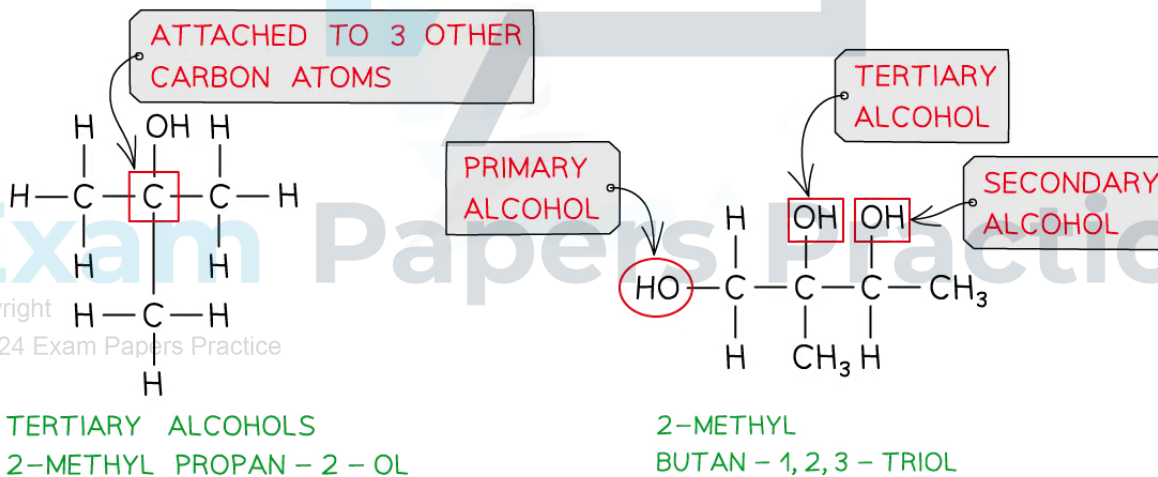
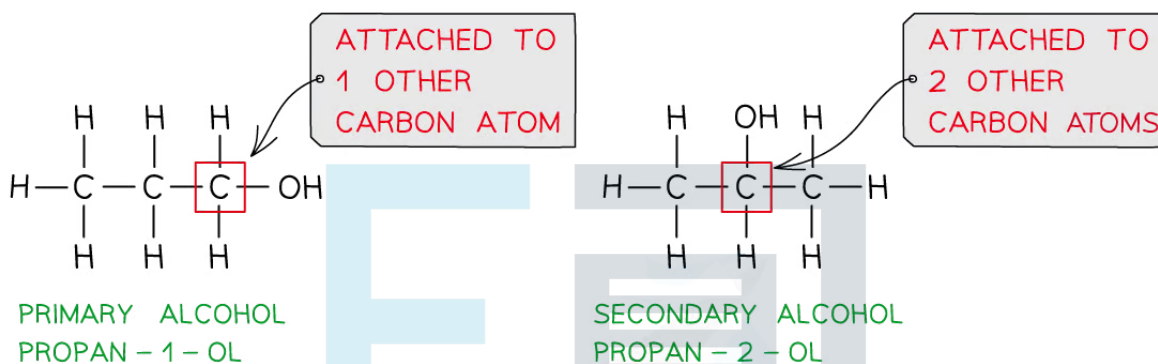
Exam Tip

Be careful when balancing equations for the combustion of alcohols as students often forget to count the oxygen in the alcohol

10.2.10 Alcohols – Oxidation

Oxidation of Primary Alcohols

- The products of oxidation of **alcohols** depends on the class of **alcohols**
- Here is a reminder of the three classes of alcohols:



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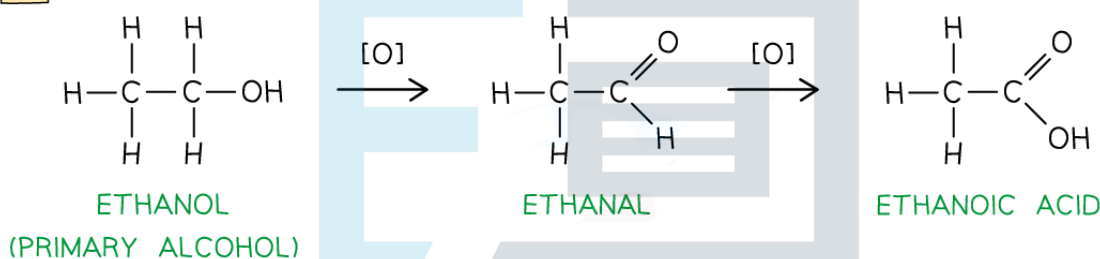
The three classes of alcohols

Primary alcohols

- **Primary alcohols** can be oxidised to form **aldehydes** which can undergo further oxidation to form **carboxylic acids**
- The oxidising agents of alcohols include **acidified $\text{K}_2\text{Cr}_2\text{O}_7$** or **acidified KMnO_4**
- **Acidified potassium dichromate(VI)**, $\text{K}_2\text{Cr}_2\text{O}_7$, is an orange oxidising agent

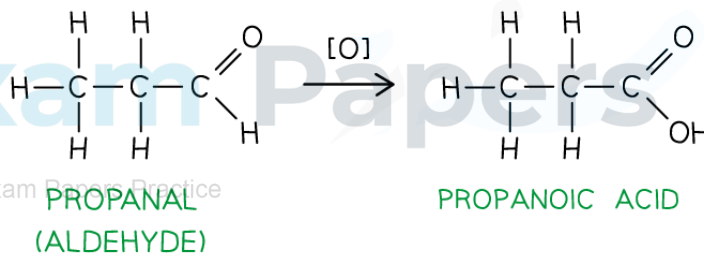
- Acidified means that the potassium dichromate(VI) is in a solution of **dilute acid** (such as dilute sulfuric acid)
- For potassium dichromate(VI) to act as an oxidising agent, it itself needs to be reduced
 - When alcohols are **oxidised** the orange dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) are reduced to green Cr^{3+} ions
- **Acidified potassium manganate(VII)**, KMnO_4 , is a purple oxidising agent
 - As with acidified KMnO_4 the potassium manganate(VII) is in an acidic medium to allow reduction of potassium manganate(VII) to take place
 - When alcohols are **oxidised**, the purple manganate ions (MnO_4^-) are reduced to colourless Mn^{2+} ions

1



[O] = ACIDIFIED $\text{K}_2\text{Cr}_2\text{O}_7$
OR
ACIDIFIED KMnO_4

2



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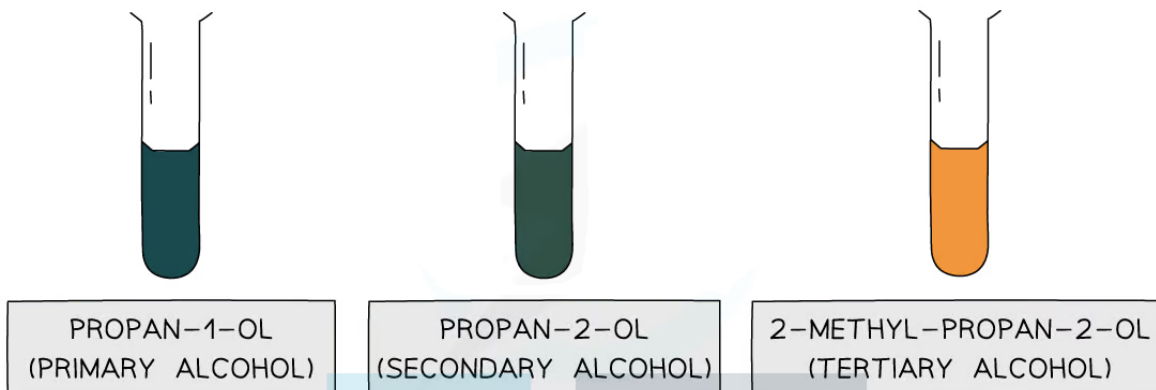
Further Oxidation

- If the **aldehyde** is not distilled off, further oxidation with **excess** oxidising agent will oxidise it to a **carboxylic acid**
- The reaction takes some time to complete and requires sustained heating

Test for alcohols

- The oxidation using **acidified dichromate** provides the basis for the test for **alcohols** as the reaction gives a strong colour change from **orange to green**

- Unfortunately, it does not work for tertiary alcohols, which cannot be oxidised



The test for primary and secondary alcohols

Oxidation of Secondary Alcohols

- Secondary alcohols** can be oxidised to form **ketones** only
- To get a good yield of the **ketone** the reaction requires some sustained heating



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 PROPAN-2-OL
 (SECONDARY ALCOHOL)

PROPANONE (KETONE)

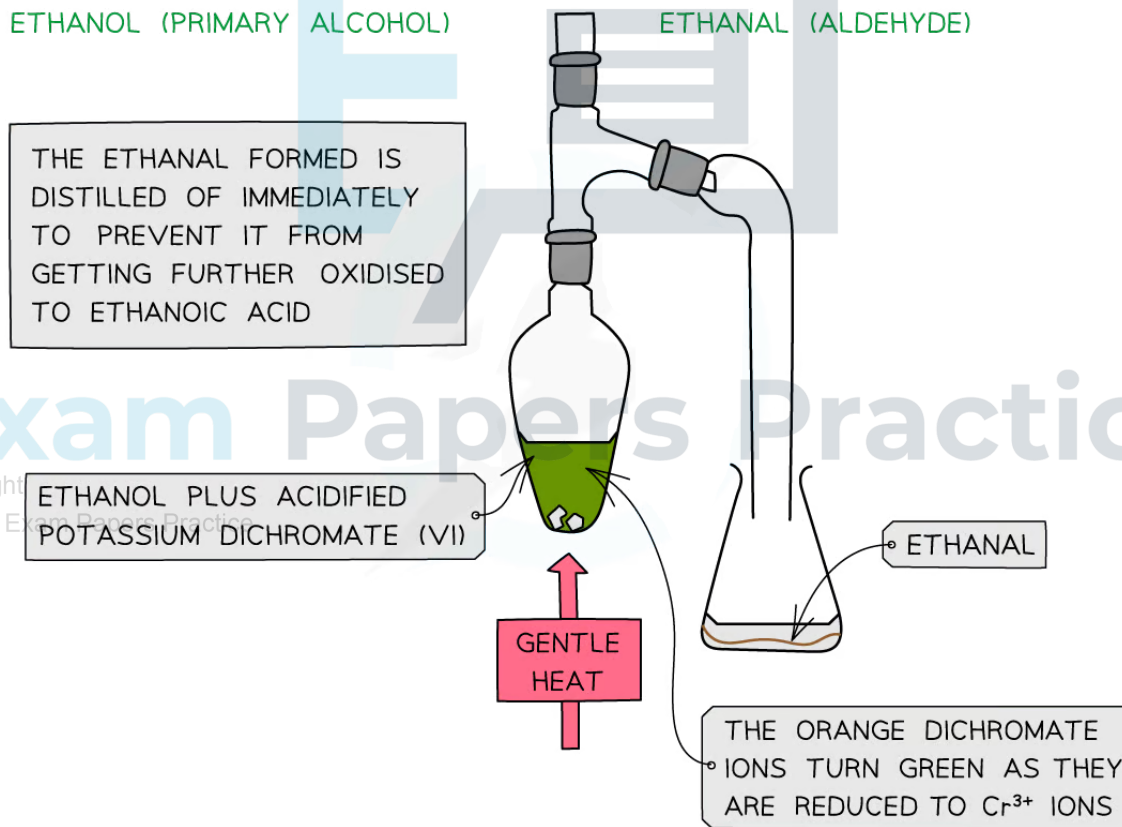
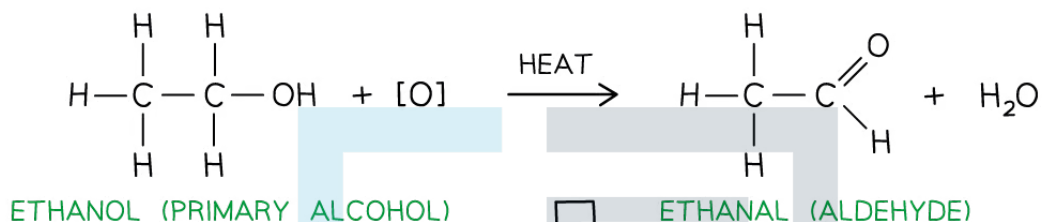
Oxidation of Secondary Alcohols

- Tertiary alcohols** do not undergo oxidation
 - This is because there must be a hydrogen on the functional group carbon, which breaks off to form water
 - There are only **C-C** bonds on the functional group carbon in a **tertiary alcohol**

Distillation & Reflux

The difference between using distillation and heating under reflux

- To produce an aldehyde from a primary alcohol the reaction mixture must be heated
- 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
- **Distillation** can be carried out using a simple side arm arrangement which acts as an air condenser or the vapours can be made to pass through a condenser

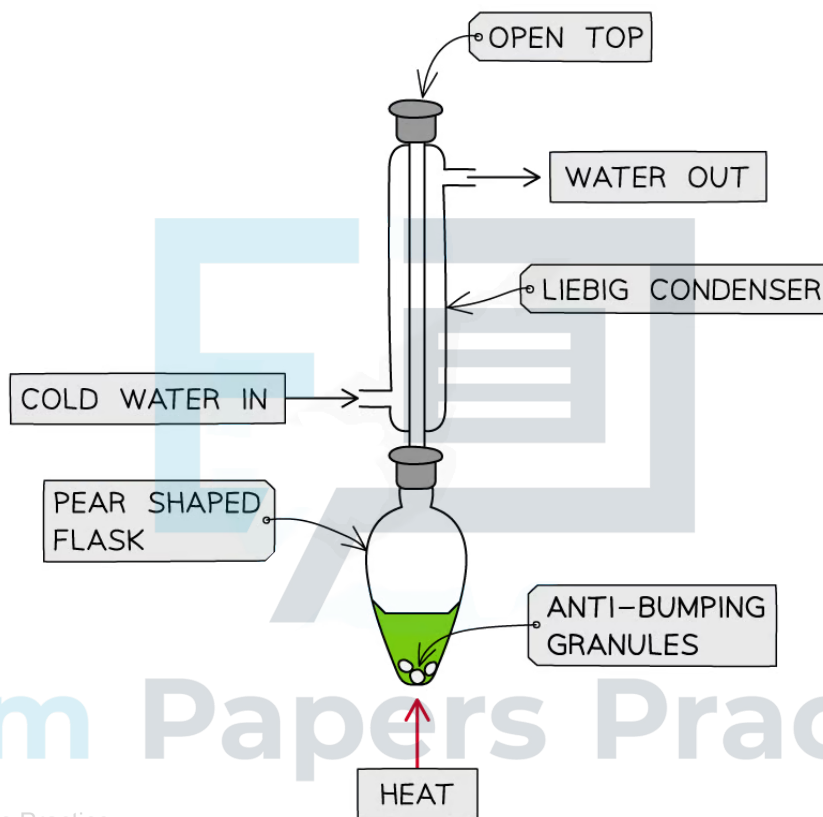


Oxidation of ethanol by acidified K₂Cr₂O₇ to form an aldehyde by distillation



Heating under reflux

- For reactions that require sustained heating the apparatus has to be modified
- To prevent loss of volatile reactants the apparatus includes a condenser in the vertical position which returns components back into the reaction flask
- This is known as **heating under reflux** (reflux means re-boiling)



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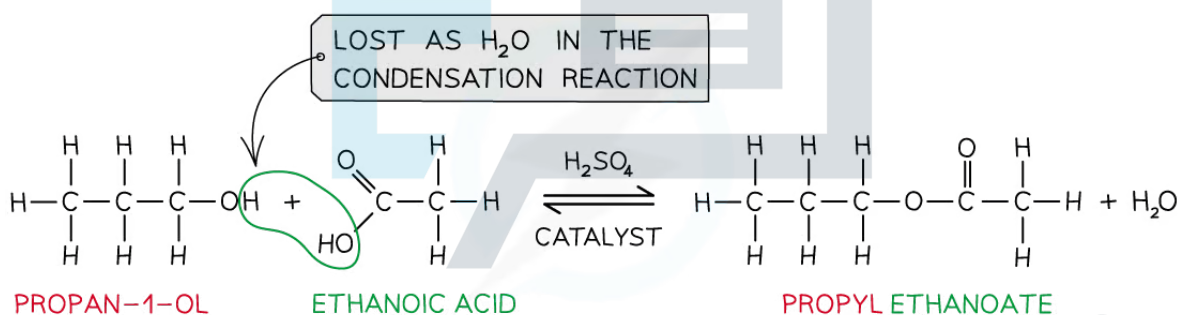
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Heating under Reflux Apparatus

10.2.11 Alcohols – Esterification

Esterification

- **Esters** are compounds with an -COOR functional group and are characterised by their **sweet** and **fruity** smells
- They are prepared from the **condensation** reaction between a **carboxylic acid** and **alcohol** with **concentrated H₂SO₄** as **catalyst**
 - This is also called **esterification**
- The first part of the ester's name comes from the alcohol and the second part of the name comes from the carboxylic acid
 - E.g. Propanol and ethanoic acid will give the ester propyl ethanoate



Esters are formed from the condensation reaction between carboxylic acids and alcohols

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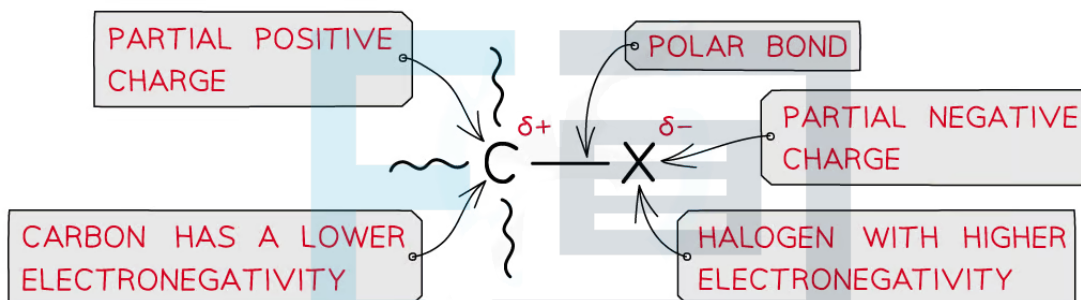
Exam Tip

The reaction is also classified as a **nucleophilic substitution** reaction

10.2.12 Halogenoalkanes

Reactions of Halogenoalkanes

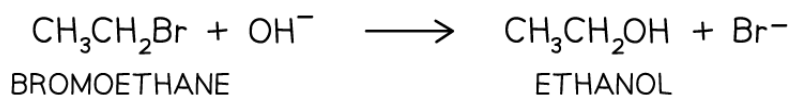
- **Halogenoalkanes** are much more reactive than alkanes due to the presence of the **electronegative** halogens
 - The halogen-carbon bond is polar causing the carbon to carry a partial positive and the halogen a partial negative charge
- A **nucleophilic substitution** reaction is one in which a **nucleophile** attacks a carbon atom which carries a **partial positive charge**
- An atom that has a **partial negative charge** is replaced by the nucleophile



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

Reaction with NaOH

- The reaction of a halogenoalkane with **aqueous alkali** results in the formation of an alcohol
- The halogen is **replaced** by the OH⁻
- The **aqueous hydroxide** (OH⁻ ion) behaves as a **nucleophile** by donating a pair of electrons to the carbon atom bonded to the halogen
- Hence, this reaction is a **nucleophilic substitution**
 - For example, bromoethane reacts with aqueous alkali when heated to form ethanol



The halogen is replaced by a nucleophile, OH⁻

- The reaction is slow at room temperature so to ensure a high yield it is **heated under reflux**
- Since haloalkanes are not usually soluble in water, a polar solvent such as ethanol is often used as it will dissolve haloalkanes as well as sodium hydroxide

10.2.13 Reactions of Benzene

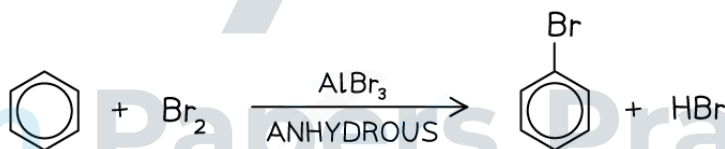
Reactions of Benzene

- **Arenes** are very stable compounds due to the **delocalisation of π electrons** in the ring
 - This is because the electron density is spread out over the molecule instead of being confined to a small area
- During chemical reactions such as **substitution reactions**, this delocalised ring is maintained
- **Addition reactions** however, **disrupt** the **aromatic stabilisation** so they are not favoured

Substitution

- **Halogenation** reactions are examples of **electrophilic substitution** reactions
- Arenes undergo **substitution** reactions with chlorine (Cl_2) and bromine (Br_2) in the presence of anhydrous AlCl_3 or AlBr_3 **catalyst** respectively to form **halogenoarenes (aryl halides)**
 - The chlorine or bromine act as an **electrophile** and replaces a hydrogen atom on the benzene ring
 - The catalyst is required for the reaction to take place, due to the stability of the benzene structure

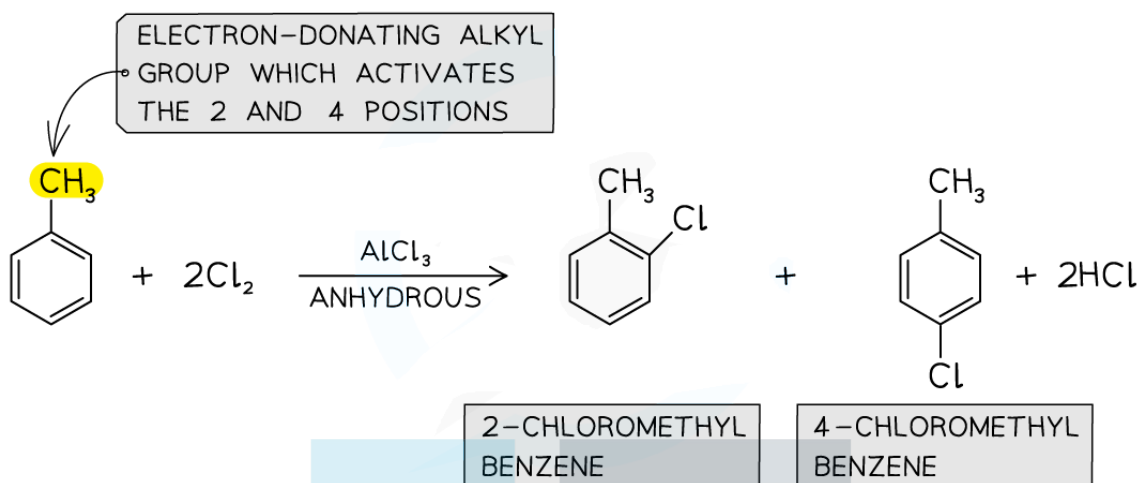
OVERALL REACTION



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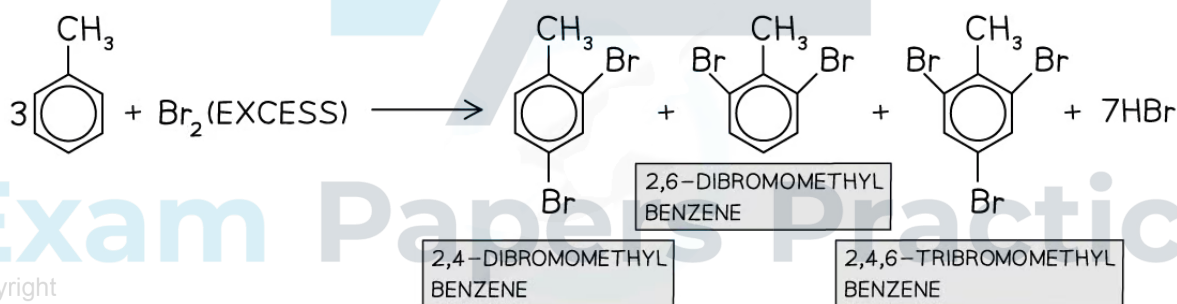
© 2024 Exam Papers Practice. **Arenes undergo substitution reactions with halogens to form aryl halides**

- **Alkylarenes** such as methylbenzene undergo halogenation on the 2 or 4 positions
- This is due to the **electron-donating** alkyl groups which activate these positions
- The halogenation of alkylarenes therefore result in the formation of **two products**



Alkylarenes are substituted on the 2 or 4 position

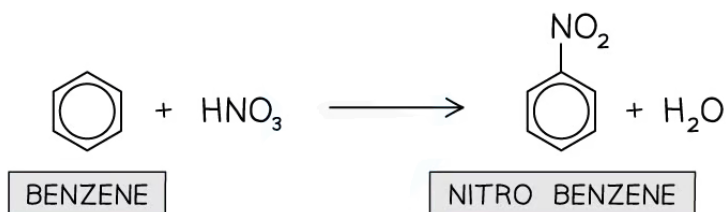
- Multiple substitutions occur when **excess** halogen is used



In the presence of excess halogen, multiple substitutions occur

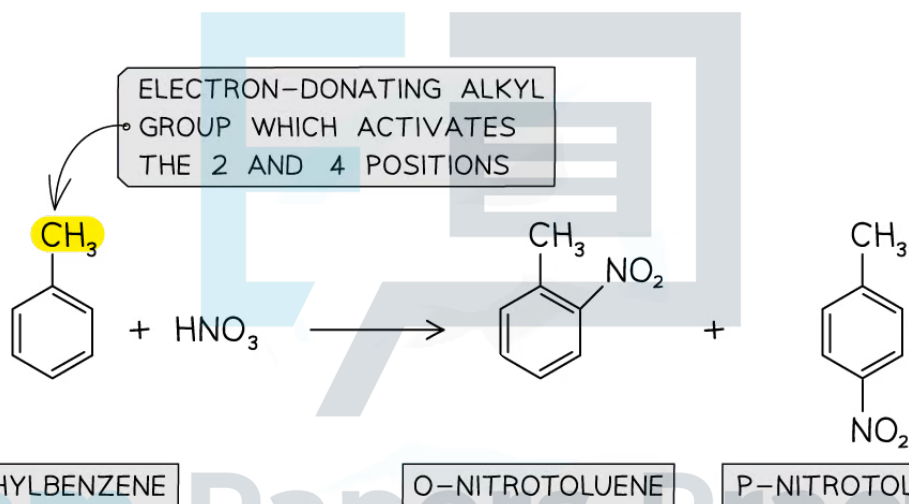
Nitration

- Another example of a substitution reaction is the **nitration** of arenes
- In these reactions, a nitro ($-\text{NO}_2$) group replaces a hydrogen atom on the arene
- The benzene is reacted with a mixture of concentrated nitric acid (HNO_3) and concentrated sulfuric acid (H_2SO_4) at a temperature between 25 and 60°C



Nitration of benzene

- Again, due to the **electron-donating** alkyl groups in alkylarenes, nitration of methylbenzene will occur on the 2 and 4 position



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Nitration of alkylarenes