

## 10.2 Functional Group Chemistry

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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

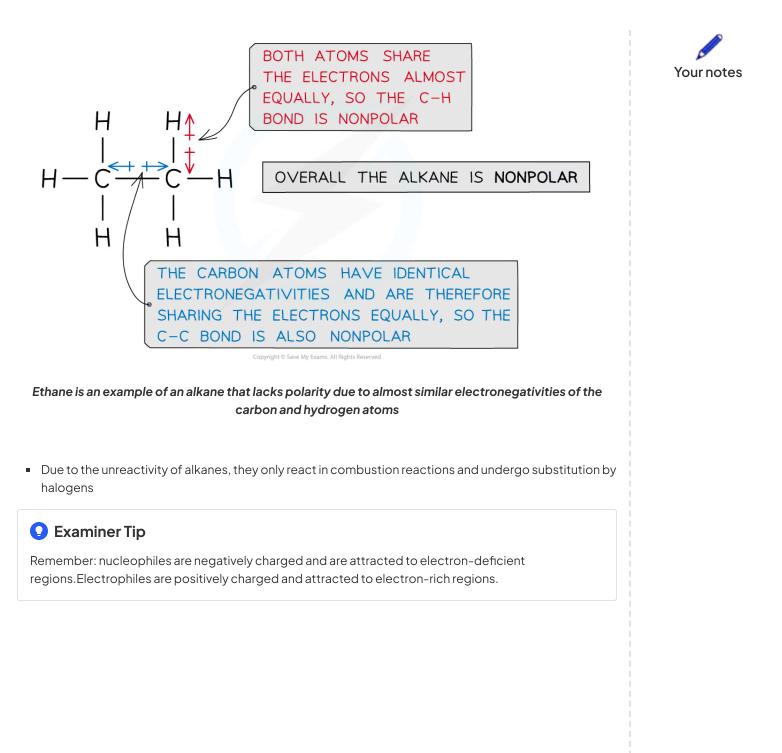
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|-----------|-----------|------------------|-----------|-------------------|-----------|-----------|-----------|-----------|---------------|--------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|
| H<br>2.1  |           |                  |           |                   |           |           |           |           |               |              |             |           |           |           |           |           | He<br>_   |
| Li<br>1.0 | Be<br>1.5 |                  |           |                   |           |           |           |           |               |              |             | В<br>2.0  | C<br>2.5  | N<br>3.0  | 0<br>3.5  | F<br>4.0  | Ne<br>-   |
| Na<br>0.9 | Mg<br>1.2 |                  |           |                   |           |           |           |           |               |              |             | Al<br>1.5 | Si<br>1.8 | P<br>2.2  | S<br>2.5  | Cl<br>3.0 | Ar<br>-   |
| К<br>0.8  | Ca<br>1.0 | Sc<br>1.3        | Ti<br>1.5 | ∨<br>1.6          | Cr<br>1.6 | Mn<br>1.5 | Fe<br>1.8 | Co<br>1.8 | Ni<br>1.8     | Cu<br>1.9    | Zn<br>1.6   | Ga<br>1.6 | Ge<br>1.8 | As<br>2.0 | Se<br>2.4 | Br<br>2.8 | Kr<br>3.0 |
| Rb<br>0.8 | Sr<br>1.0 | Y<br>1.2         | Zr<br>1.4 | NЬ<br>1.6         | Mo<br>1.8 | Tc<br>1.9 | Ru<br>2.2 | Rh<br>2.2 | Pd<br>2.2     | Ag<br>1.9    | Cd<br>1.7   | ln<br>1.7 | Sn<br>1.8 | Sb<br>1.9 | Te<br>2.1 | ا<br>2.5  | Xe<br>2.6 |
| Cs<br>0.7 | Ba<br>0.9 | La-Lu<br>1.1-1.2 | Hf<br>1.3 | Ta<br>1.5         | W<br>1.7  | Re<br>1.9 | Os<br>2.2 | lr<br>2.2 | Pt<br>2.2     | Au<br>2.4    | Hg<br>1.9   | Ti<br>1.8 | РЬ<br>1.8 | Bi<br>1.9 | Po<br>2.0 | At<br>2.2 | Rn<br>–   |
| Fr<br>0.7 | Ra<br>0.9 | Ac-No<br>1.1-1.7 |           |                   |           | 1         | Copyright | Save My E | ams. All Rigi | hts Reserved |             |           |           |           |           |           |           |

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<sup>+</sup> and δ<sup>-</sup> 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**

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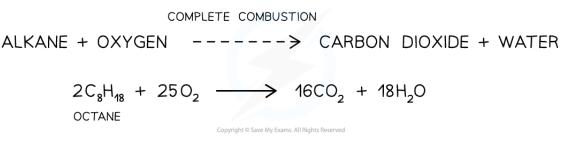


## **Combustion of Alkanes**

- 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



#### 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

INCOMPLETE COMBUSTION

2C<sub>8</sub>H<sub>18</sub> + 17 O<sub>2</sub> -Octane

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→ 16CO + 18H<sub>2</sub>O

#### 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

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- 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:

ALKANE + OXYGEN  $2C_8H_{18} + 9O_2$  Copyright © Save My Exams. All Rights Reserved INCOMPLETE COMBUSTION  $16C + 18H_2O$ 

#### The incomplete combustion of alkanes (2)

### **O** Examiner Tip

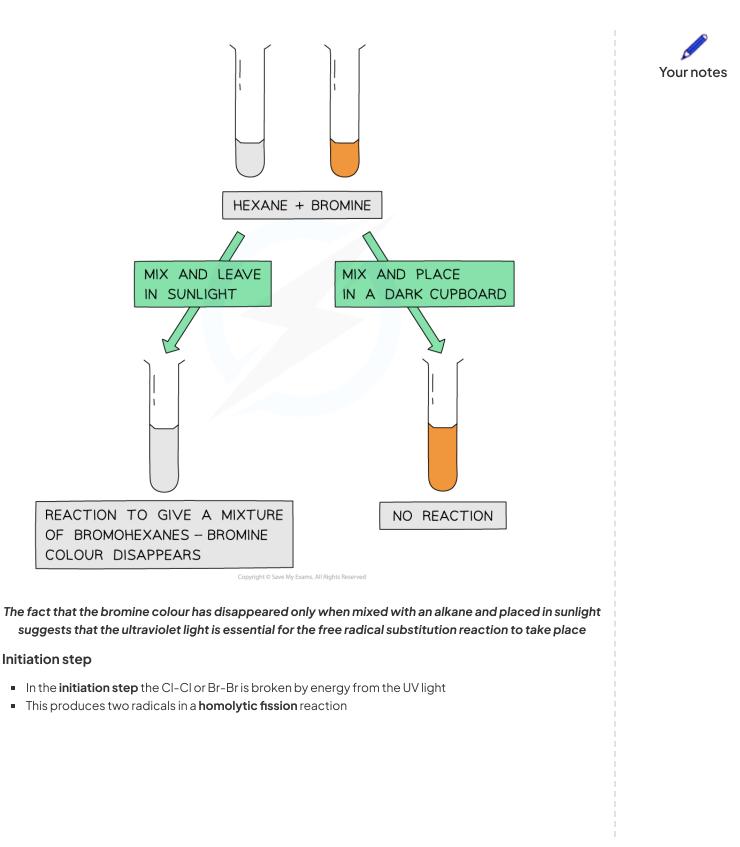
Incomplete combustion of alkanes never produces hydrogen as it is always preferentially oxidised in any available oxygen, rather than carbon

## 10.2.2 Alkanes - Halogenation

### Halogenation of Alkanes

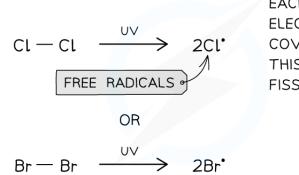
#### Free-radical substitution of alkanes

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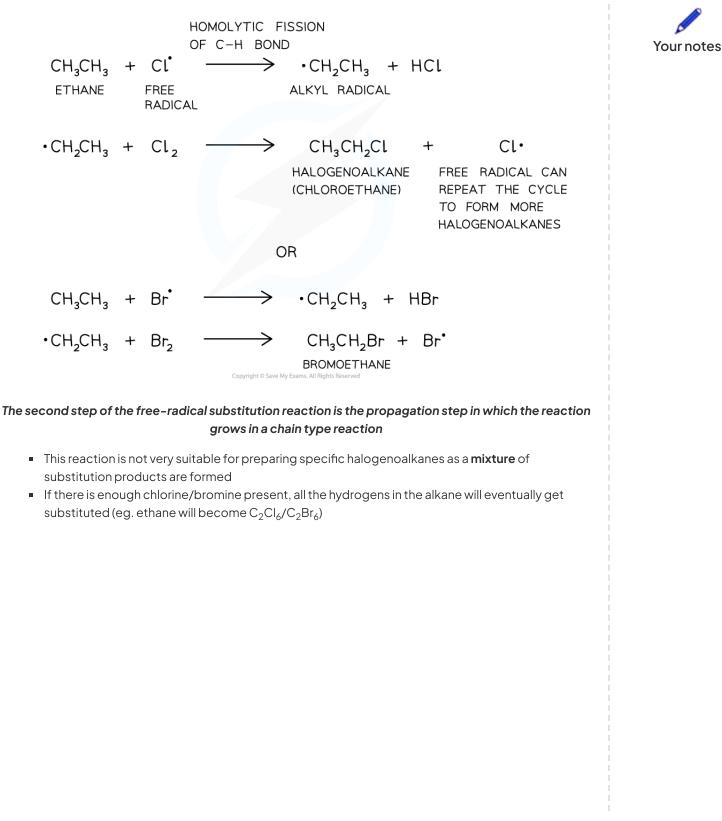
EACH ATOM TAKES ONE ELECTRON FROM THE COVALENT BOND, SO THIS IS A HOMOLYTIC FISSION REACTION



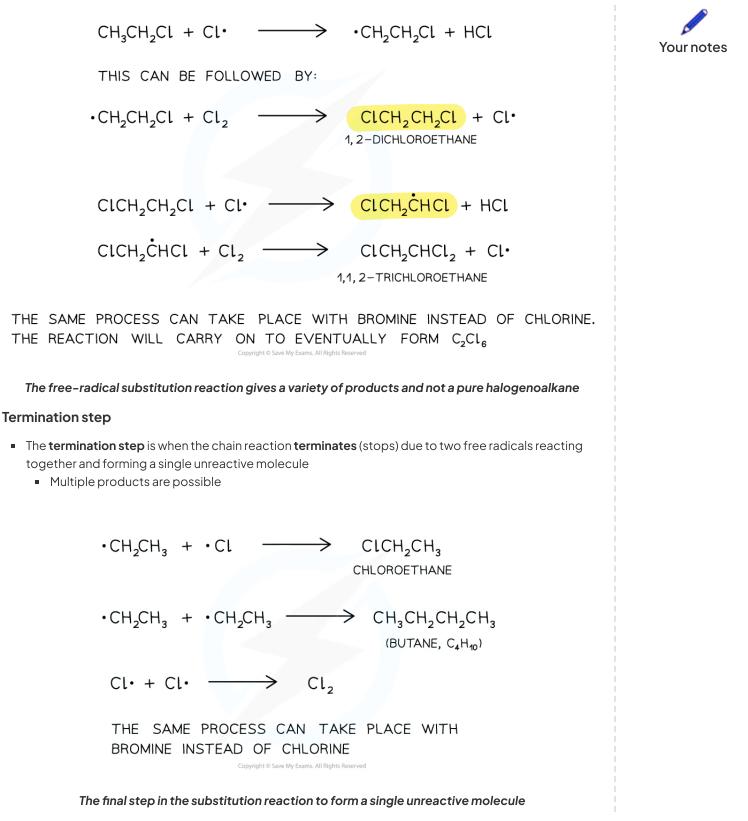
## The first step of the free-radical substitution reaction is the initiation step in which two free radicals are formed by sunlight

#### **Propagation step**

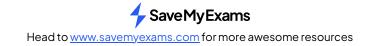
- The propagation step refers to the progression (growing) of the substitution reaction in a chain type reaction
  - Free radicals are very reactive and will attack the unreactive alkanes
  - A C-H bond breaks **homolytically** (each atom gets an electron from the covalent bond)
  - An **alkyl** free 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



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## Examiner 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:

 $CH_{3}CH_{3}+CI \rightarrow CH_{3}CH_{2}CI + H \cdot$ 

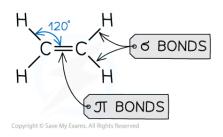
Do not fall into this trap!



## 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 σbonds 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  $\pi$ -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**

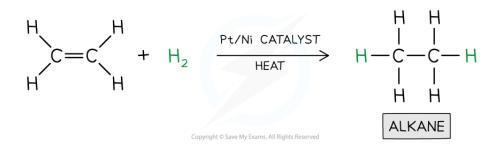


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## 10.2.4 Alkenes - Hydrogenation

### 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



## 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 dihalogenoalkane
- The reaction occurs readily at room temperature and is the basis for the test for **unsaturation** in molecules

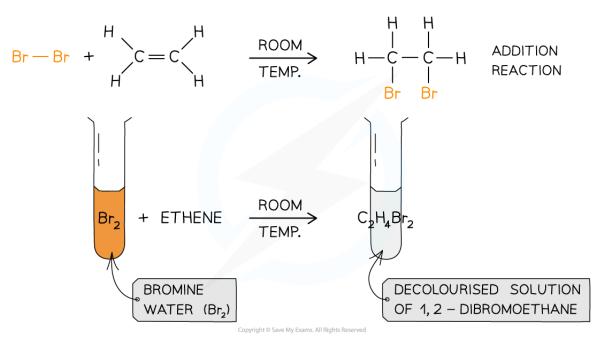


#### Halogenation in alkenes

- Halogens can be used to test if a molecule is **unsaturated** (i.e. contain a double bond)
- Br<sub>2</sub> 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



**Your notes** 



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

## Examiner Tip

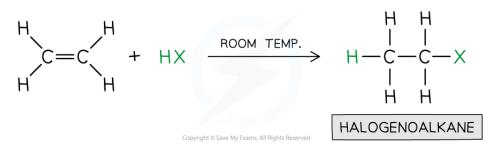
The mechanism of this reaction is part of Higher Level Chemistry and is covered in Section 20

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## 10.2.6 Alkenes - Hydrohalogenation

## Hydrohalogenation of Alkenes

- Alkenes will react readily with hydrogen halides such as HCI 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

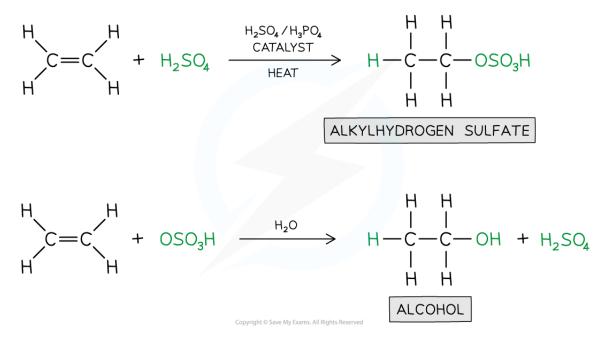
- All the hydrogen halides react in this way, but the fastest reaction occurs in the order HI > HBr > HCI due to the increasing bond strength of the hydrogen-halogen bond, so the weakest bond reacts most easily
- The mechanism of this reaction is part of Higher Level Chemistry and is covered in Section 20



## 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 (H<sub>2</sub>SO<sub>4</sub>) or phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) 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<sup>+</sup> and HSO<sub>4</sub><sup>-</sup> ions are added across the **double** bond
- The intermediate is quickly hydrolysed by water, reforming the sulfuric acid



#### 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 that producing ethanol by fermentation



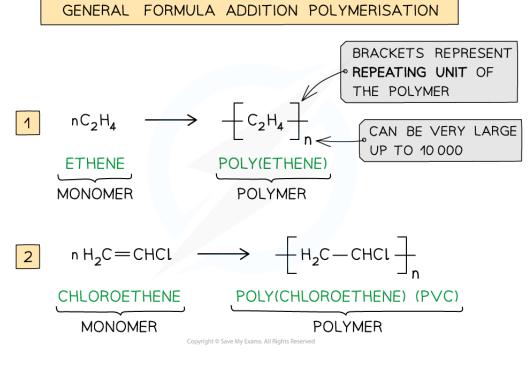
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## 10.2.8 Addition Polymers

### Polymers

#### Addition polymerisation

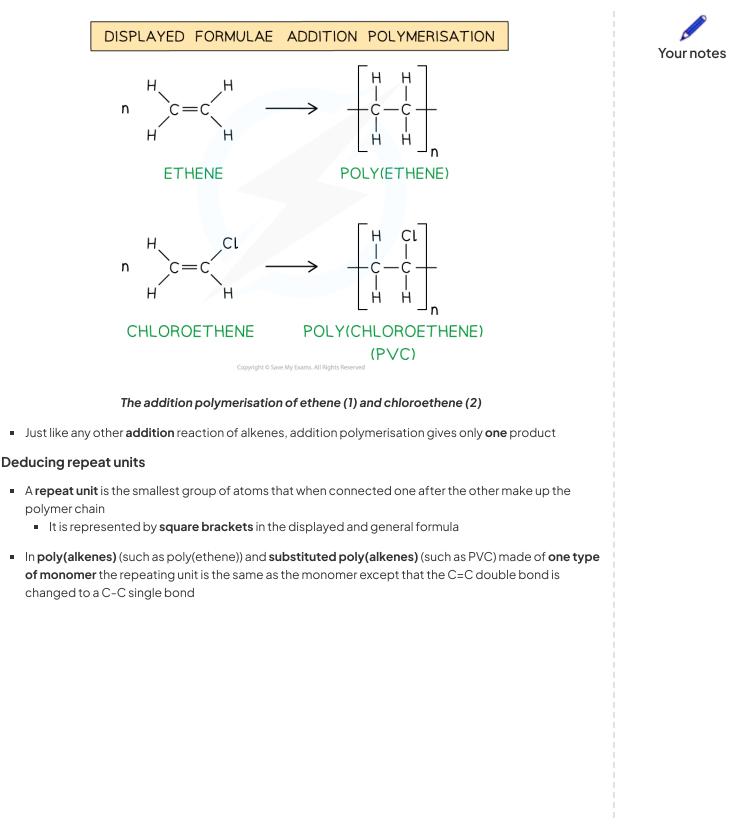
- Addition polymerisation is one of the most important addition reactions of alkenes which form the basis of the plastic industry
- Addition polymerisation is the reaction in which many monomers containing at least one C=C double bond form long chains of polymers as the only product
  - Just like in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



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

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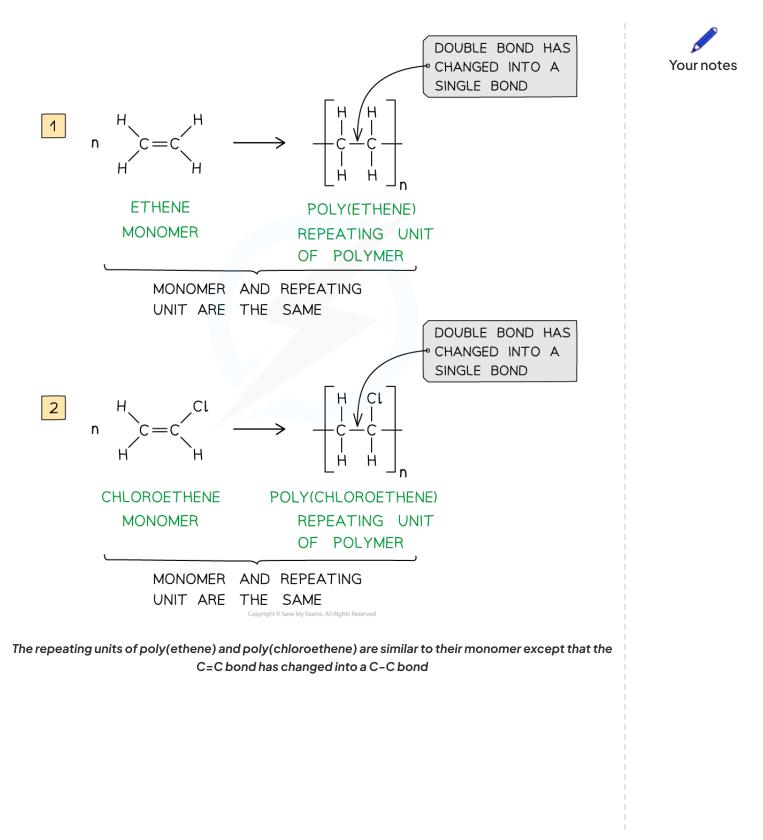




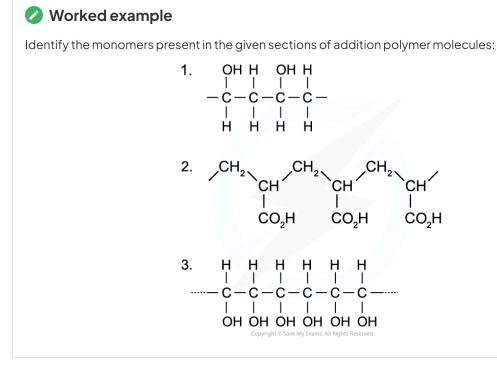
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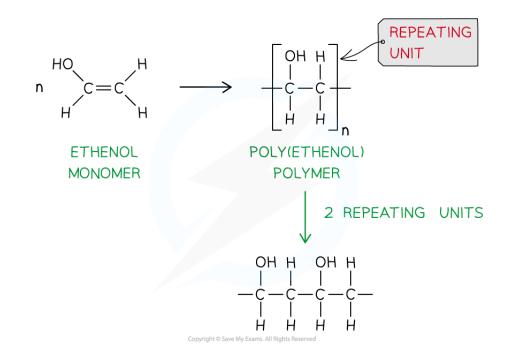
#### Answers:

#### Answer 1:

When ethenol (CH(OH)=CH<sub>2</sub>) is polymerised, the C-C double bond opens to produce a repeating unit of CH(OH)-CH<sub>2</sub>. This gives the polymer poly(ethenol)

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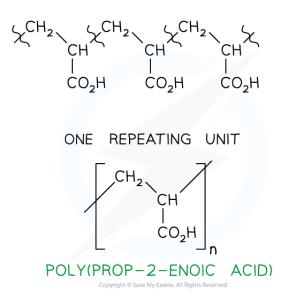
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# Your notes

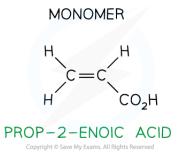
#### Answer 2:

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



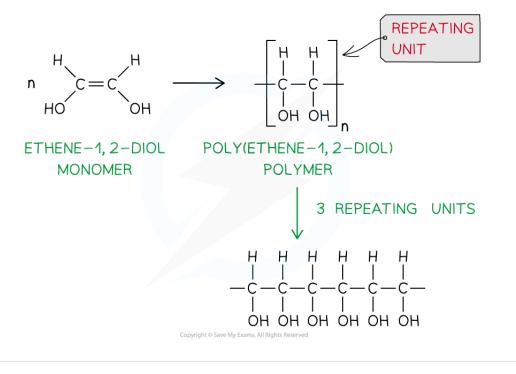
• Since the repeating unit is now found, it can be concluded that the monomer is prop-2-enoic acid

Your notes



#### 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)



### 💽 Examiner 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 monomerThe monomer is the same as the repeat unit except for that it has C=C bonds instead of C-C bonds

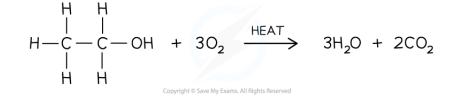
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## 10.2.9 Alcohols - Combustion

## **Combustion of Alcohols**

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

#### Alcohol + oxygen $\rightarrow$ 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, the are socio-economic concerns about using large quantities of farm land to produce crops for fermentation, which could be better used for food production

## 😧 Examiner Tip

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

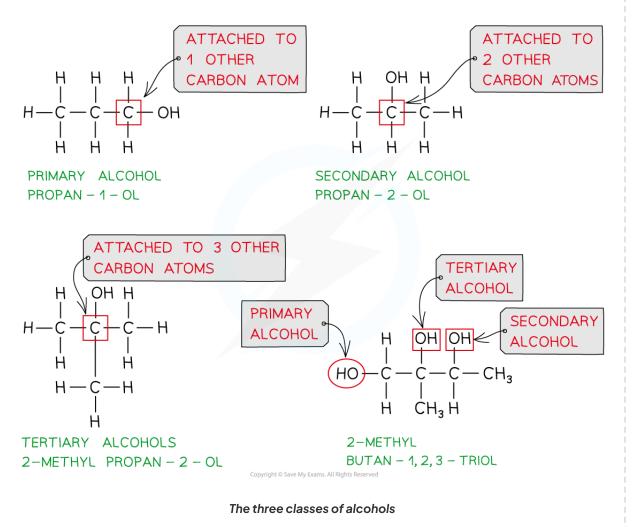


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## 10.2.10 Alcohols – Oxidation

## **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:



#### **Primary alcohols**

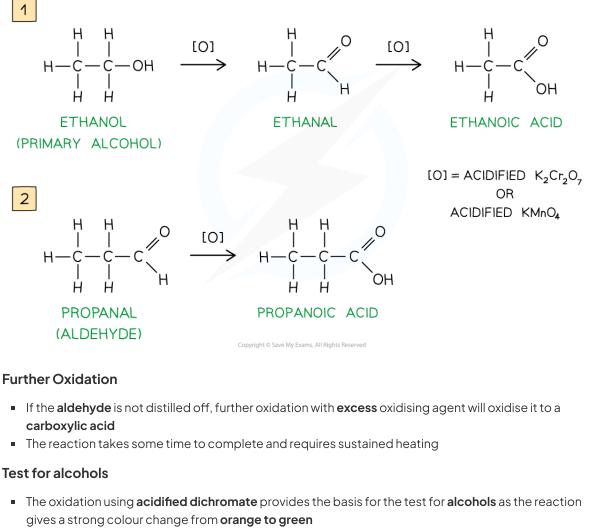
- Primary alcohols can be oxidised to form aldehydes which can undergo further oxidation to form carboxylic acids
- The oxidising agents of alcohols include acidified K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> or acidified KMnO<sub>4</sub>
- Acidified potassium dichromate(VI), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, is an orange oxidising agent
  - Acidified means that the potassium dichromate(VI) is in a solution of dilute acid (such as dilute sulfuric acid)

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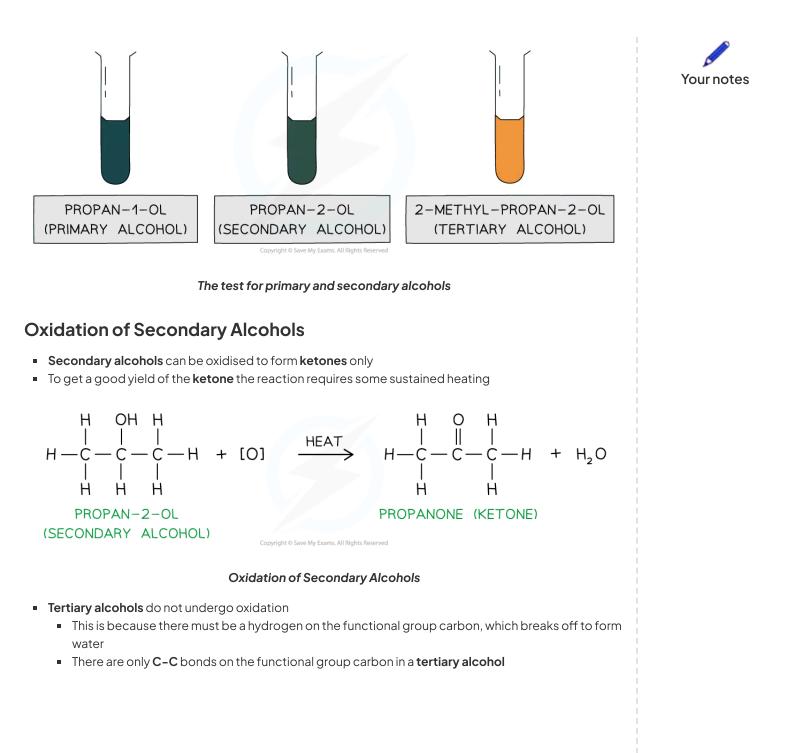
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- For potassium dichromate(VI) to act as an oxidising agent, it itself needs to be reduced
  - When alcohols are **oxidised** the orange dichromate ions (Cr<sub>2</sub>O<sub>7<sup>2-</sup></sub>) are reduced to green Cr<sup>3+</sup> ions
- Acidified potassium manganate(VII), KMnO<sub>4</sub>, is a purple oxidising agent
  - As with acidified KMnO<sub>4</sub> 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<sub>4</sub><sup>-</sup>) are reduced to colourless Mn<sup>2+</sup> ions



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

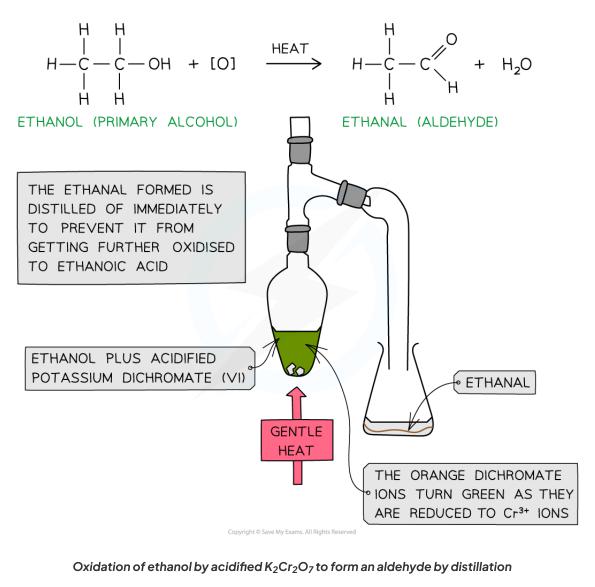




## **Distillation & Reflux**

#### 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



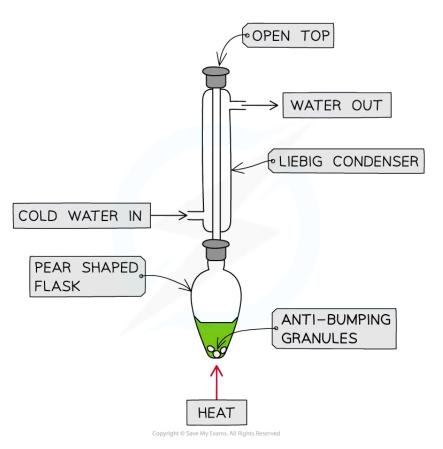
#### Heating under reflux

• For reactions that require sustained heating the apparatus has to be modified

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- 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)



Heating under Reflux Apparatus

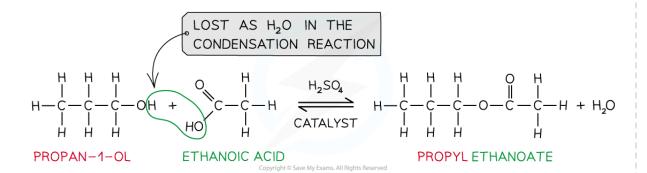


**Your notes** 

## 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 H<sub>2</sub>SO<sub>4</sub> 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

### Examiner Tip

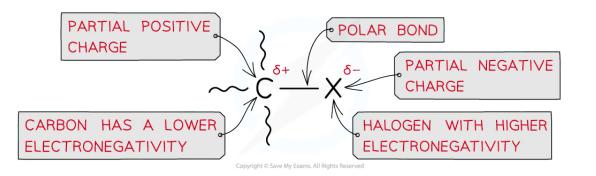
The reaction is also classified as a nucleophilic substitution reaction

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## 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

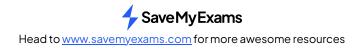
- The reaction of a halogenoalkane with **aqueous alkali** results in the formation of an alcohol
- The halogen is **replaced** by the OH<sup>-</sup>
- The **aqueous hydroxide** (OH<sup>-</sup> ion) behaves as a **nucleophile** by donating a pair of electrons to the carbon atom bonded to the halogen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

 $CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$ BROMOETHANE ETHANOL

The halogen is replaced by a nucleophile,  $OH^-$ 

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- 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



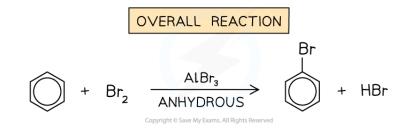
## 10.2.13 Reactions of Benzene

### **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

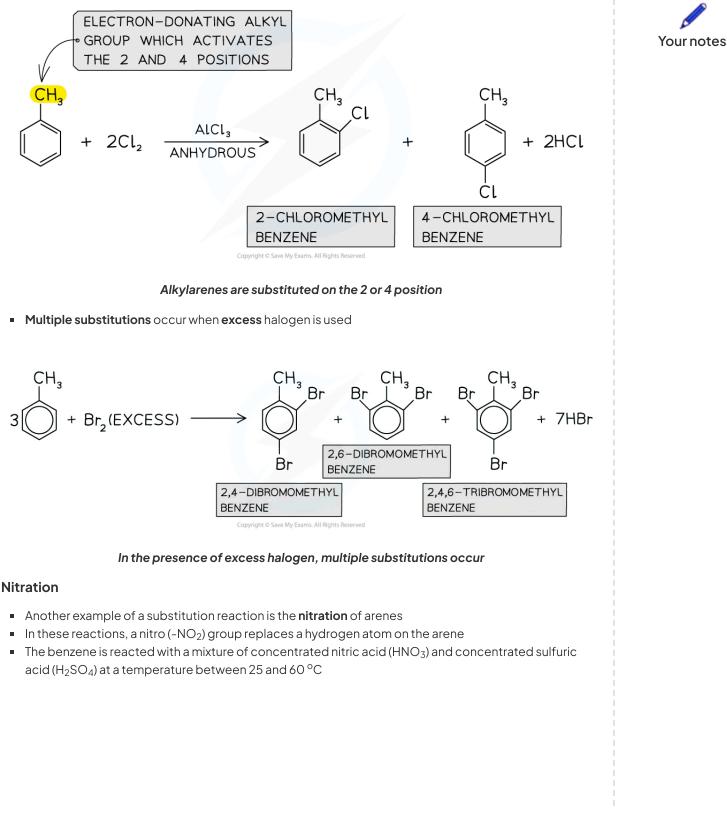
- Halogenation reactions are examples of electrophilic substitution reactions
- Arenes undergo substitution reactions with chlorine (Cl<sub>2</sub>) and bromine (Br<sub>2</sub>) in the presence of anhydrous AICl<sub>3</sub> or AIBr<sub>3</sub> catalyst respectively to form halogenoarenes (aryl halides)
  - 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



#### 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**





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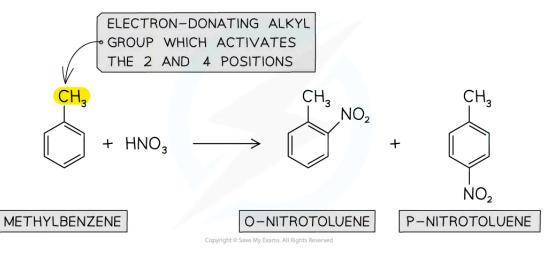
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#### Nitration of benzene

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



Nitration of alkylarenes