

Cambridge (CIE) A Level Chemistry



Your notes

Alkenes

Contents

- * Producing Alkenes
- * Reactions of Alkenes
- * Test for Unsaturation
- * Electrophilic Addition of Alkenes
- * Markovnikov's Rule



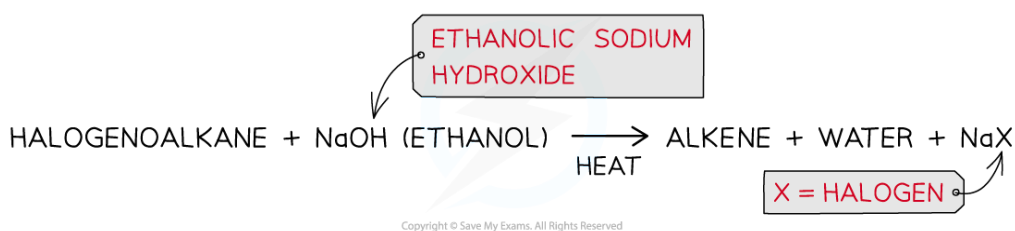
Production of Alkenes: Elimination, Dehydration & Cracking

- Alkenes can be made by a series of reactions including **elimination reactions** and **cracking**

Elimination reaction

- Alkenes can be produced from the elimination reaction of a **halogenoalkane**
- An **elimination reaction** is one in which a **small molecule** is lost
 - In the case of halogenoalkanes, the small molecule that is eliminated is a hydrogen halide, HX, where X is the halogen
- The halogenoalkane is heated with **ethanolic sodium hydroxide**

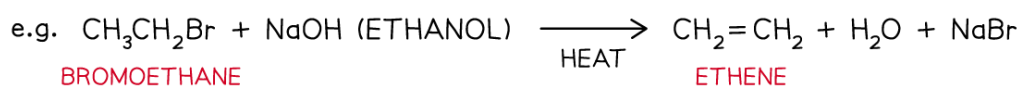
Making alkenes from halogenoalkanes



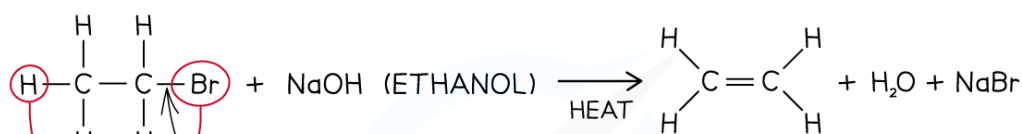
Production of an alkene from a halogenoalkane by reacting it with ethanolic sodium hydroxide and heating it

- The eliminated H^+ in HBr reacts with the ethanolic OH^- to form water
- The eliminated Br^- in HBr reacts with Na^+ to form NaBr

Overview of halogenoalkane elimination



Your notes

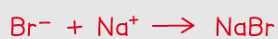
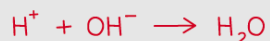


HETEROLYTIC BOND BREAKING OF THE C-Br BOND
 • THE Br TAKES BOTH ELECTRONS FROM THE COVALENT BOND FORMING Br^-

BROMOETHANE LOSES AN H AND Br ATOM

• THE ETHANOLIC OH^- ACTS AS A BASE AND ACCEPTS THE H^+ TO FORM H_2O
 • THE Br^- COMBINES WITH THE Na^+ TO FORM NaBr

• HBr IS ELIMINATED



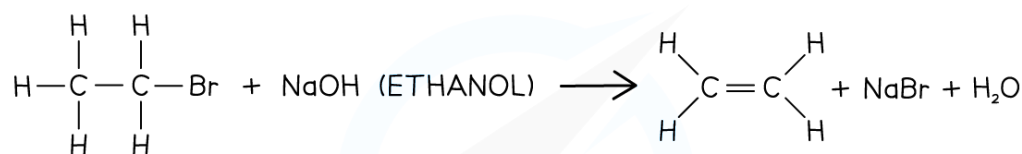
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The eliminated HBr reacts with ethanolic OH^- and Na^+ to form water and sodium bromide

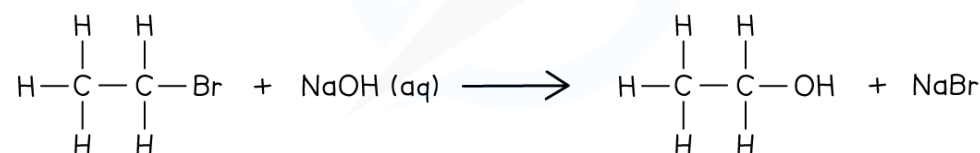
- Note that the reaction conditions should be stated correctly as different reaction conditions will result in different types of organic reactions
- NaOH (ethanol): an **elimination** reaction occurs to form an **alkene**
- NaOH (aq): a **nucleophilic substitution** reaction occurs, and an **alcohol** is one of the products

Comparing reaction conditions

ELIMINATION REACTION



SUBSTITUTION REACTION



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Different reaction conditions will give different products

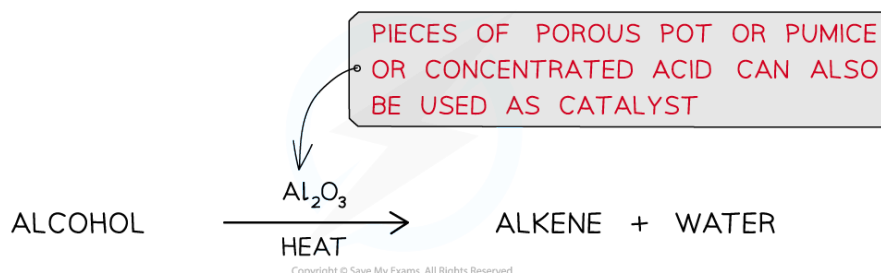
Dehydration reaction



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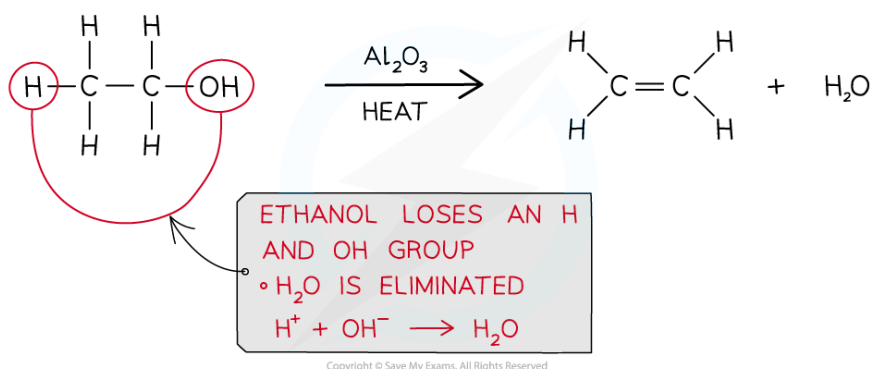
- Alkenes can also be produced from the elimination reaction of alcohols in which a water molecule is lost
 - This is also called a **dehydration** reaction
- Alcohol vapour is passed over a hot catalyst of **aluminium oxide powder** (Al_2O_3)
 - Concentrated acid, pieces of porous pot or pumice** can also be used as catalysts

Making alkenes from alcohols



Production of an alkene from an alcohol by using a hot aluminium oxide powder catalyst

Overview of alcohol elimination



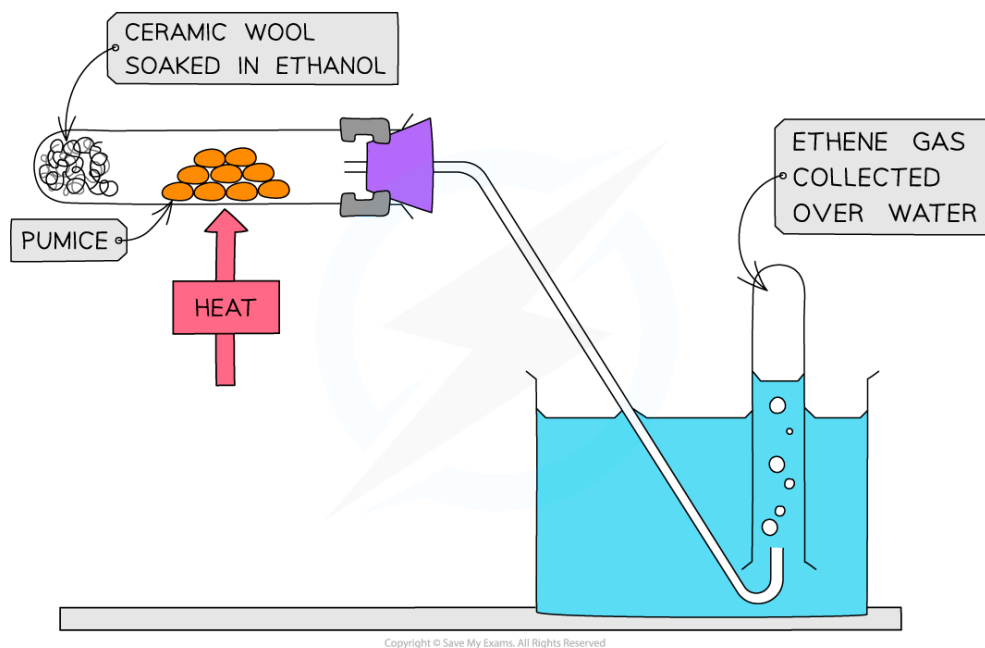
The formation of ethene from ethanol is an example of a dehydration reaction of alcohol

- The smaller alkenes (such as ethene, propene and butene) are all **gases** at room temperature and can be **collected** over **water**

Practical set-up to form alkenes from alcohol



Your notes

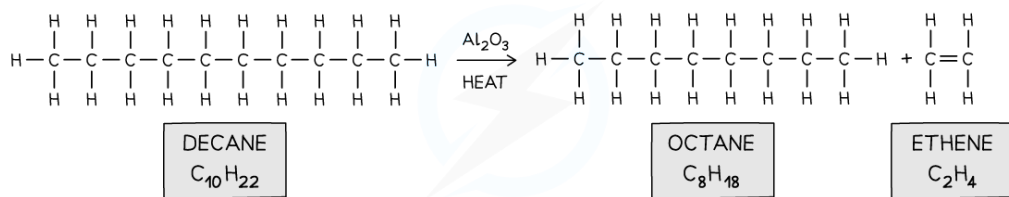


The smaller alkenes are gases at room temperature and collected over water

Cracking

- Alkenes can also be produced from the **cracking** of long hydrocarbon molecules in crude oil
- An **aluminium oxide** (Al_2O_3) catalyst and high temperatures are used to speed up this reaction.
- It is important to ensure that the crude oil doesn't come into contact with **oxygen** as this can cause the **combustion** of the hydrocarbons to produce **water** and **carbon dioxide**
- The cracking of crude oil produces **smaller alkane** and **alkene** molecules

Cracking hydrocarbons



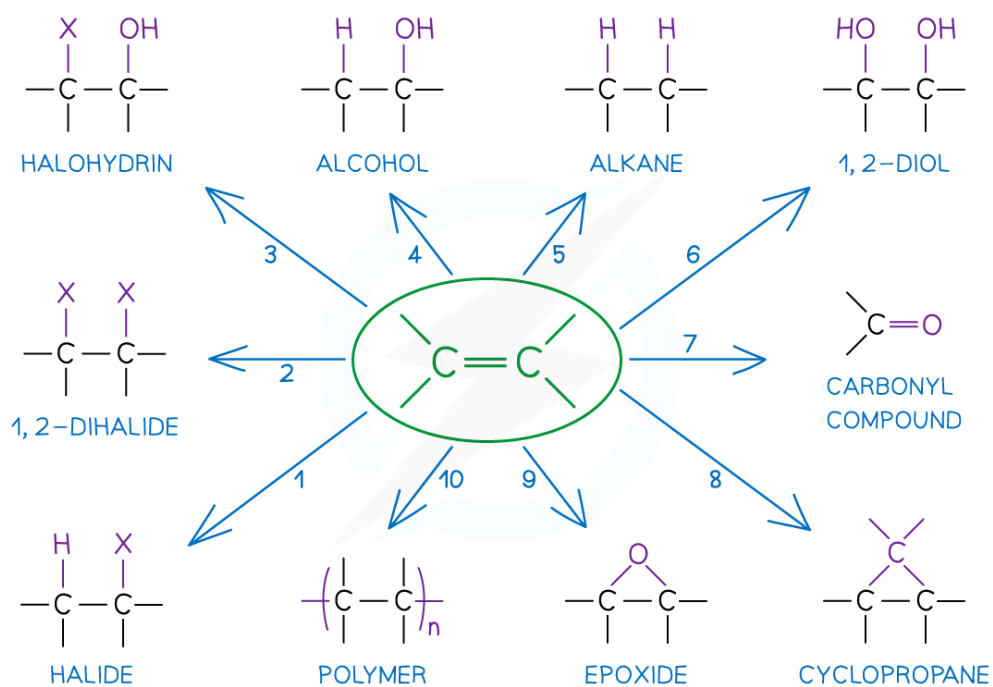
Long hydrocarbon fraction is cracked into two smaller ones

- The **low-molecular mass alkenes** are more reactive than alkanes as they have an electron-rich double bond
- They can therefore be used as **feedstock** for making new products

Possible compounds formed from alkenes



Your notes



Alkenes are reactive molecules and can undergo many different types of reactions making them useful as starting compounds



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

Electrophilic addition

- **Electrophilic addition** is the addition of an electrophile 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
- Electrophilic addition reactions include the addition of:
 - Hydrogen (also known as **hydrogenation reaction**)
 - Steam (H_2O (g))
 - Hydrogen halide (HX)
 - Halogen

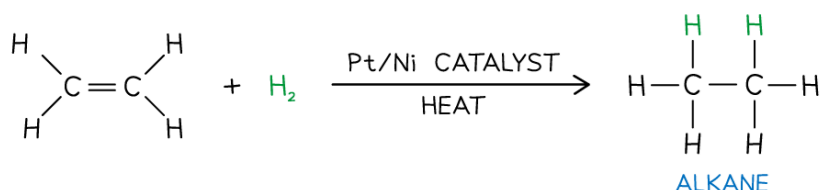
Electrophilic addition reactions of alkenes

ELECTROPHILIC ADDITION

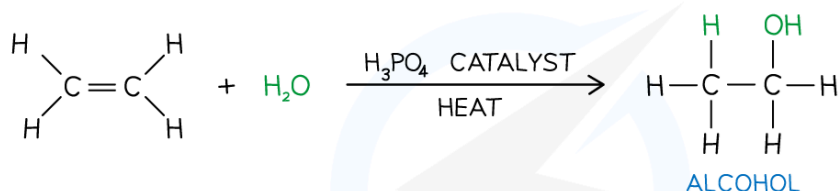


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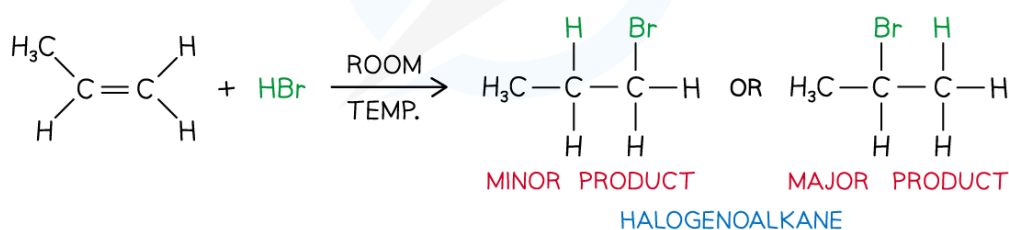
HYDROGENATION



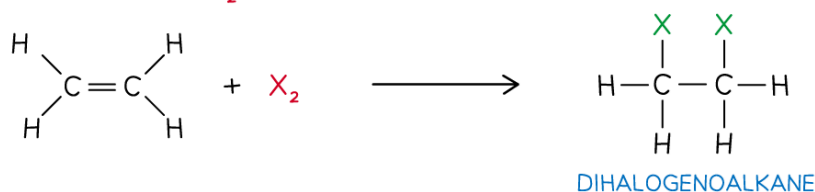
STEAM



HYDROGEN HALIDES (HX)



HALOGENS (X₂)



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Oxidation

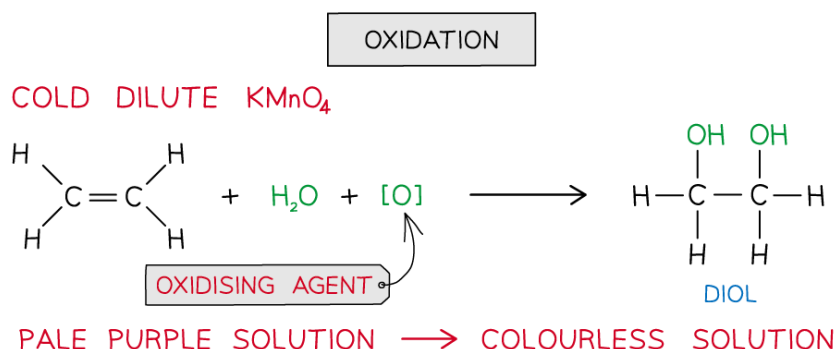
- Alkenes can also be **oxidised** by **acidified potassium manganate(VII)** (KMnO₄) which is a very powerful **oxidising agent**
- Alkenes can be oxidised by both **hot** and **cold** KMnO₄ which will result in different products being formed
 - When shaken with **cold dilute KMnO₄** the **pale purple** solution turns **colourless** and the product is a **diol**
 - When alkenes are reacted with **hot concentrated KMnO₄** the conditions are harsher causing the C-C double bond to completely break
 - The O-H groups in the diol formed are further oxidised to **ketones**, **aldehydes**, **carboxylic acids** or **carbon dioxide gas**

- The actual products formed depend on what is bonded to the carbon atoms in the alkene

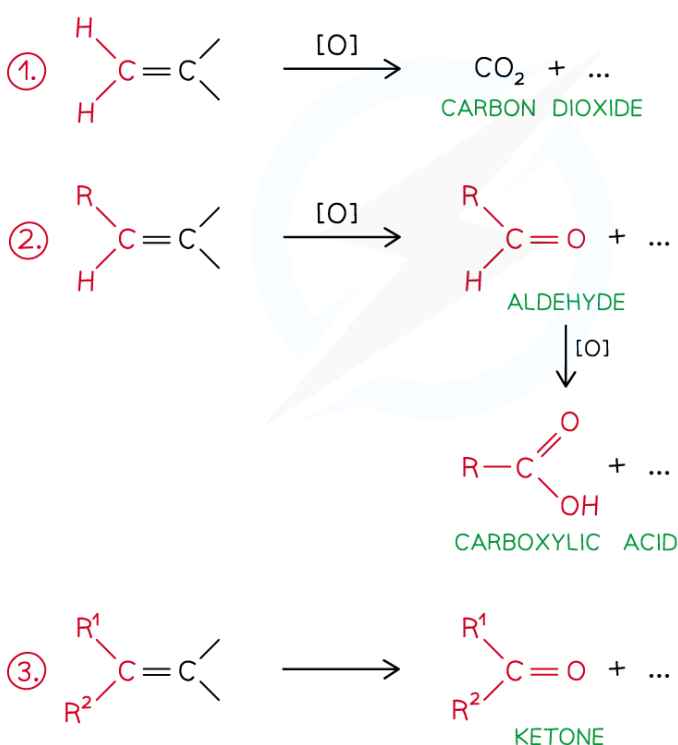
Oxidising alkenes using KMnO_4



Your notes



HOT CONCENTRATE KMnO_4



Alkenes can be oxidised by cold dilute and hot concentrated KMnO_4 to give different products

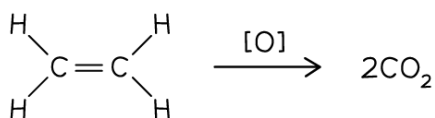
- The reactions of alkenes with hot concentrated KMnO_4 can be used to determine the position of the double bond in larger alkenes

Predicting the position of double bonds formed

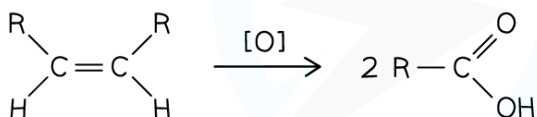


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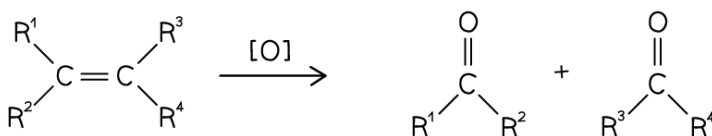
IF C-ATOM IS BONDED TO 2 H-ATOMS, OXIDATION TO CO_2 TAKES PLACE



IF C-ATOM IS BONDED TO ONE H-ATOM AND ONE ALKYL GROUP, OXIDATION TO $-\text{COOH}$ (CARBOXYLIC ACID) TAKES PLACE



IF A C-ATOM IS BONDED TO TWO ALKYL GROUPS, OXIDATION TO $\text{C}=\text{O}$ (KETONE) TAKES PLACE



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The above reactions can be used to predict where the double bond in a larger molecule is

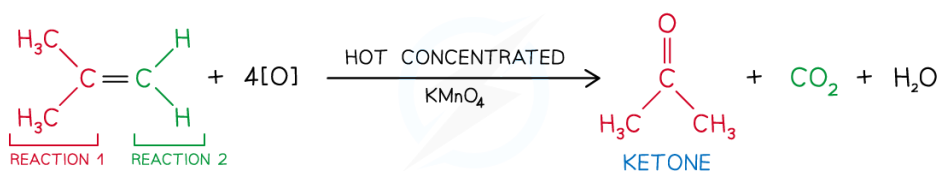


Worked Example

What are the products of the oxidation of 2-methylprop-1-ene with hot, concentrated acidified KMnO_4 (aq)?

Answer:

The products are propanone (a ketone), carbon dioxide and water



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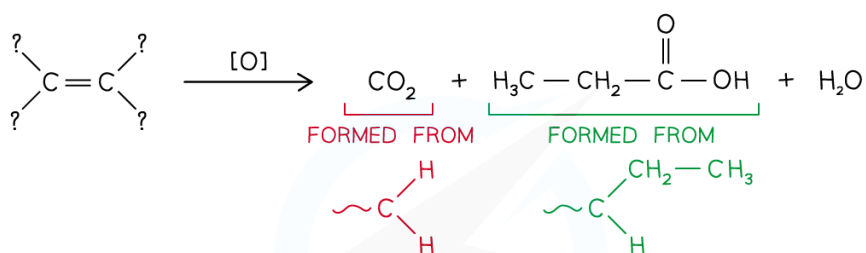


Worked Example

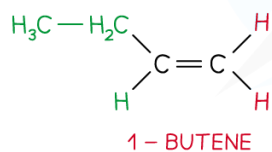
The oxidation of an alkane produces carbon dioxide gas, water and propanoic acid. Identify the alkene.

Answer:

The alkene is 1-butene



THE ALKENE IS THEREFORE



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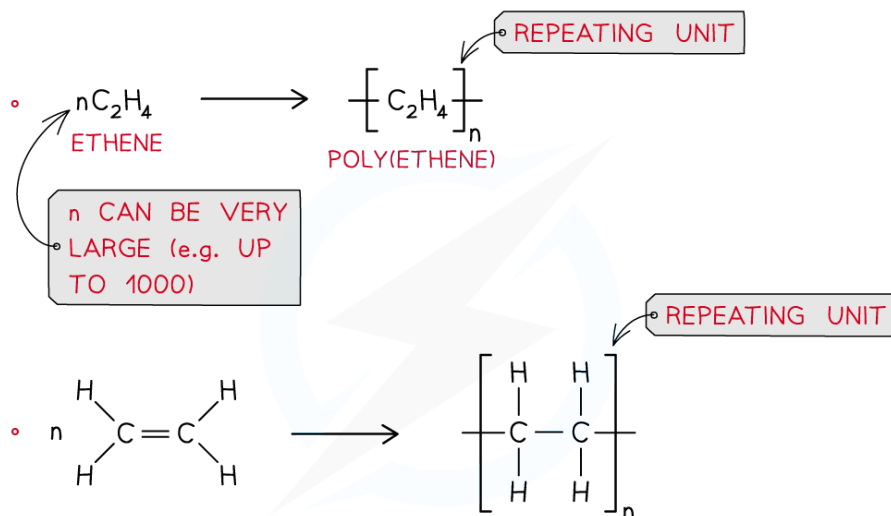
Addition polymerisation

- **Addition polymerisation** is the reaction of many monomers containing at least one double C-C bond to form the long-chain polymers as the only product
 - **Monomers** are small, reactive molecules that react together to make the polymer
 - A **polymer** is a long-chain molecule made up of many **repeating units** (monomers)
- In an addition polymerisation reaction, the C-C double bond is broken to link together the monomers and form a polymer
- This is a common method of making **plastics**

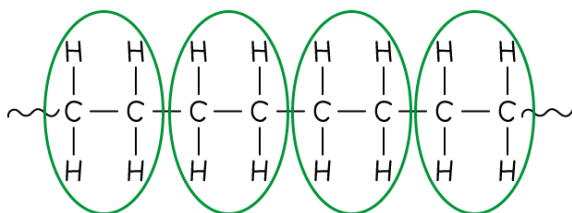
The polymerisation of ethene



e.g. POLYMERISATION OF ETHENE



SECTION OF THE POLYMER MADE UP OF 4 MONOMERS



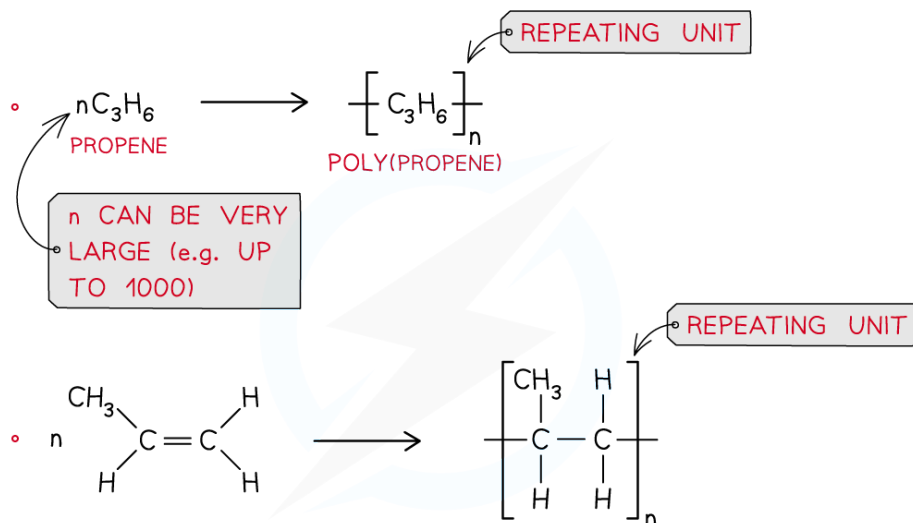
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The polymer backbone consists of a carbon chain with monomers that contain 2 carbon atoms

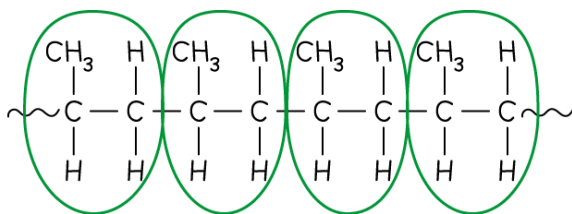
The polymerisation of propene



e.g. POLYMERISATION OF PROPENE



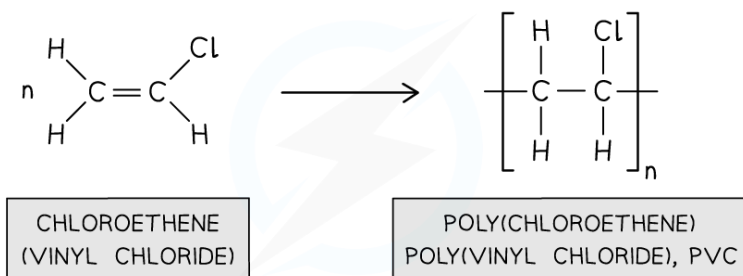
SECTION OF THE POLYMER MADE UP OF 4 MONOMERS



The polymer backbone consists of a carbon chain with monomers that contain 2 carbon atoms with the methyl group, from the propane monomer, as a side chain

- Other alkenes and **substituted** alkenes can also polymerise to make polymers with different **properties**
 - E.g. poly(chloroethene), also known as PVC is the most versatile plastic used

The polymerisation of chloroethene



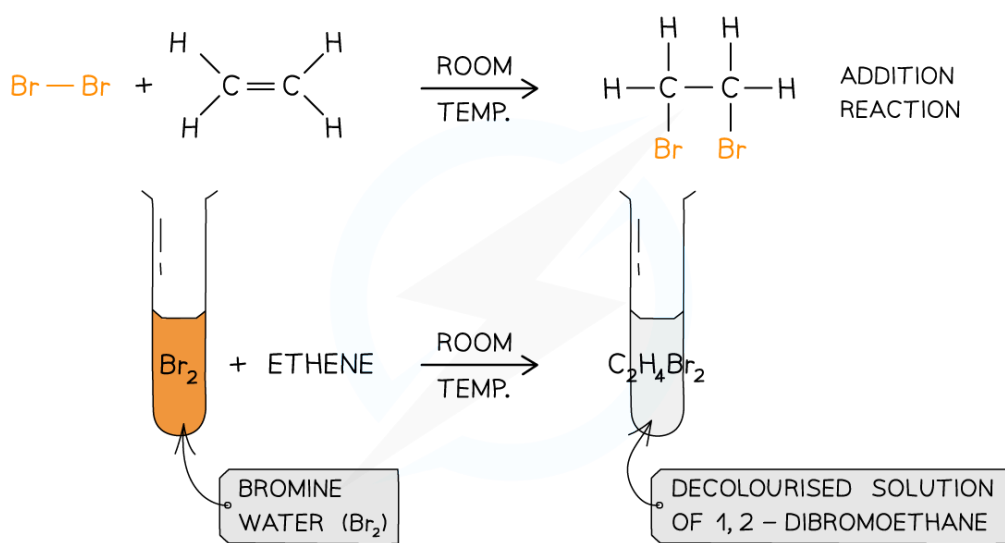
Poly(chloroethene) is used as plastic



Test for Unsaturation

- Halogens can be used to test if a molecule is **unsaturated** (i.e. contains a double bond)
- $\text{Br}_2(\text{aq})$ is an orange or yellow solution, called **bromine water** and this is the halogen most commonly used
- 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 unsaturation test



The decolourisation of bromine water by an unsaturated compound as a result of an addition reaction



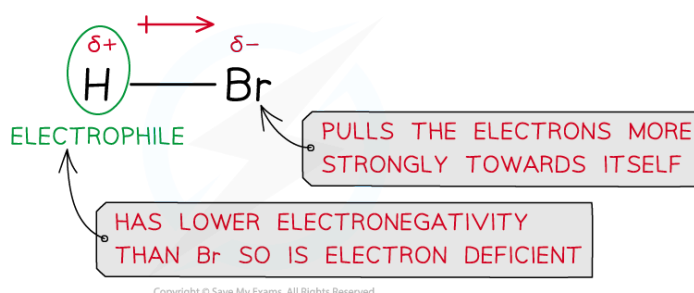
Electrophilic Addition of Alkenes

- The double bond in alkenes is an area of high electron density (there are four electrons found in this double bond)
- This makes the double bond susceptible to attack by electrophiles (electron-loving species)
- An **electrophilic addition** is the addition of an **electrophile** to a double bond

Electrophilic addition of hydrogen bromide

- A molecule of hydrogen bromide (HBr) is polar as the hydrogen and bromine atoms have different electronegativities
- 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

Explaining the polarity of a HBr molecule



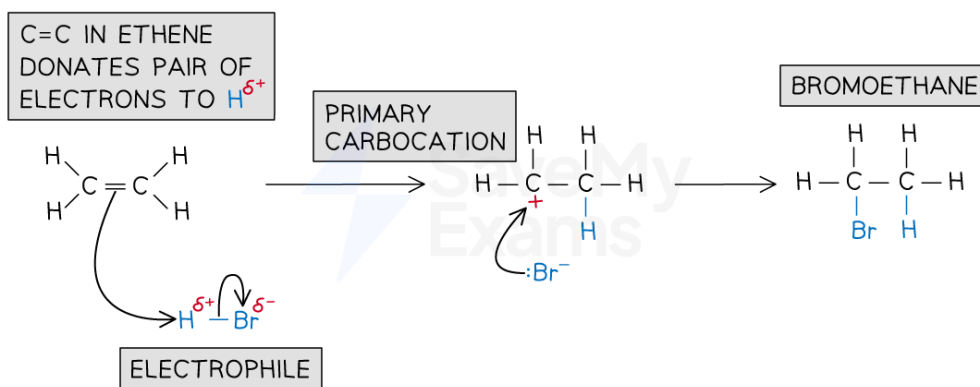
Due to differences in electronegativities of the hydrogen and bromine atoms, HBr is a polar molecule

- In an addition reaction, the H atom acts as an electrophile and accepts 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 of HBr mechanism



Your notes



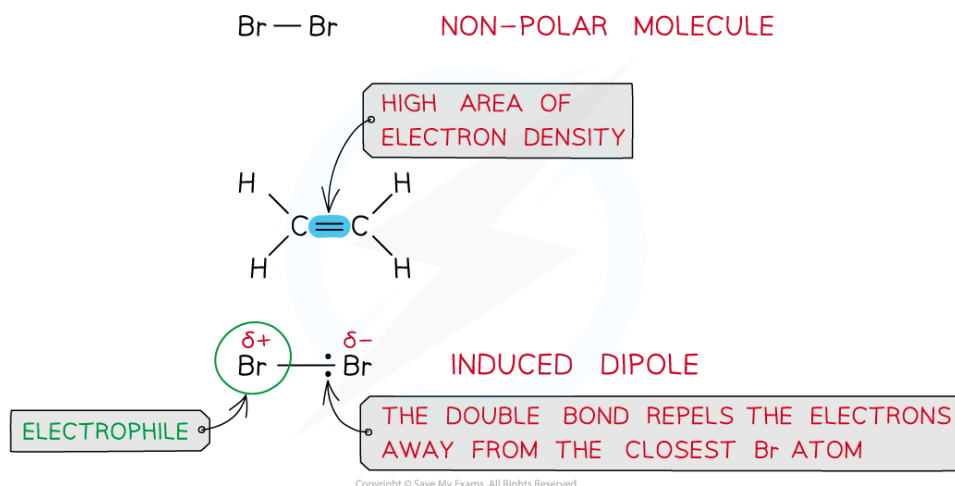
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Electrophilic addition reaction of HBr and ethene to form bromoethane

Electrophilic addition of bromine

- Bromine (Br_2) is a non-polar molecule as both atoms have similar electronegativities and therefore equally share the electrons in the covalent bond
- However, when a bromine molecule gets closer to the double bond of an alkene, the high electron density in the double bond repels the electron pair in $\text{Br}-\text{Br}$ away from the closest Br atom
- As a result of this, the closest Br atom to the double bond is slightly positive and the further Br atom is slightly negatively charged

The polarity of a Br_2 molecule



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Bromine is a non-polar molecule however when placed close to an area of high electron density it can get polarised

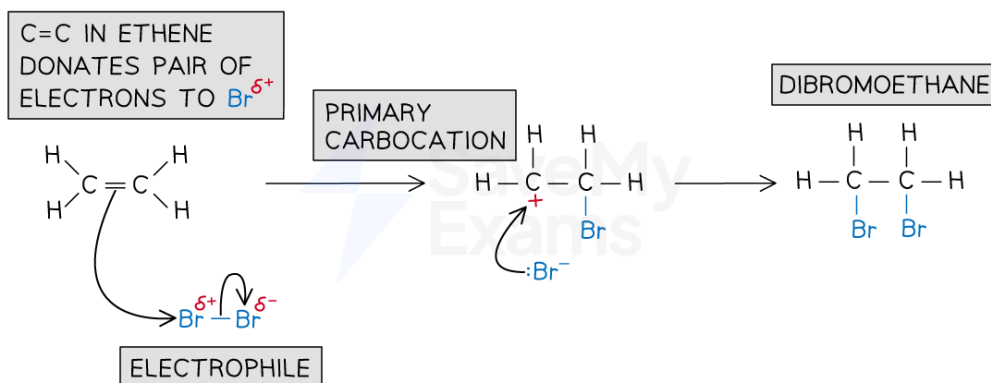
- In an addition reaction, the closest Br atom acts as an electrophile and accepts a pair of electrons from the C-C bond in the alkene
 - The $\text{Br}-\text{Br}$ bond breaks heterolytically, forming a Br^- ion

- This results in the formation of a highly reactive carbocation intermediate which reacts with the Br^- (nucleophile)

Electrophilic addition of Br_2 mechanism



Your notes



Example of an electrophilic addition reaction of bromine and ethene to form dibromoethane



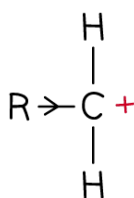
Alkenes: Stability of Cations & Markovnikov's Rule

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

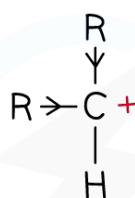
Inductive effect

- 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**

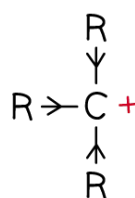
Primary, secondary and tertiary carbocations



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

Markovnikov's rule

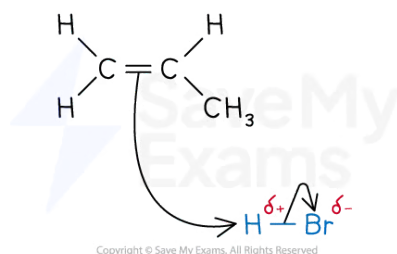
- Markovnikov's rule predicts the outcome of electrophilic addition reactions and states that:



Your notes

- 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
- Markovnikov addition applies to electrophilic addition reactions with unsymmetrical alkenes, e.g. propene and but-1-ene
 - Markovnikov addition favours the formation of the **major** product
 - Anti-Markovnikov 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

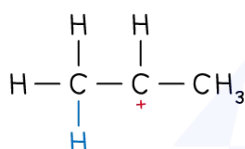
Step 1 in the electrophilic addition mechanism



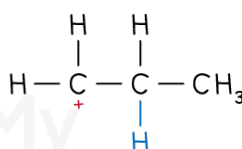
The electrophile reacts with the electron-rich C-C double bond

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

Relative stabilities of primary and secondary carbocations



MORE STABLE SECONDARY
CARBOCATION INTERMEDIATE



LESS STABLE PRIMARY
CARBOCATION INTERMEDIATE

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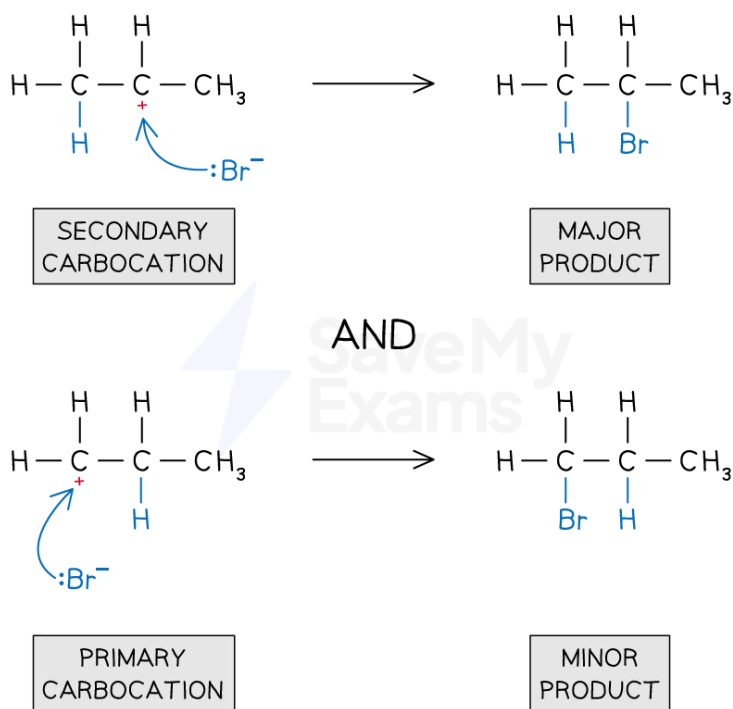
The major and minor carbocation intermediates formed during the reaction of propene and hydrogen bromide



Your notes

- 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 major and minor products



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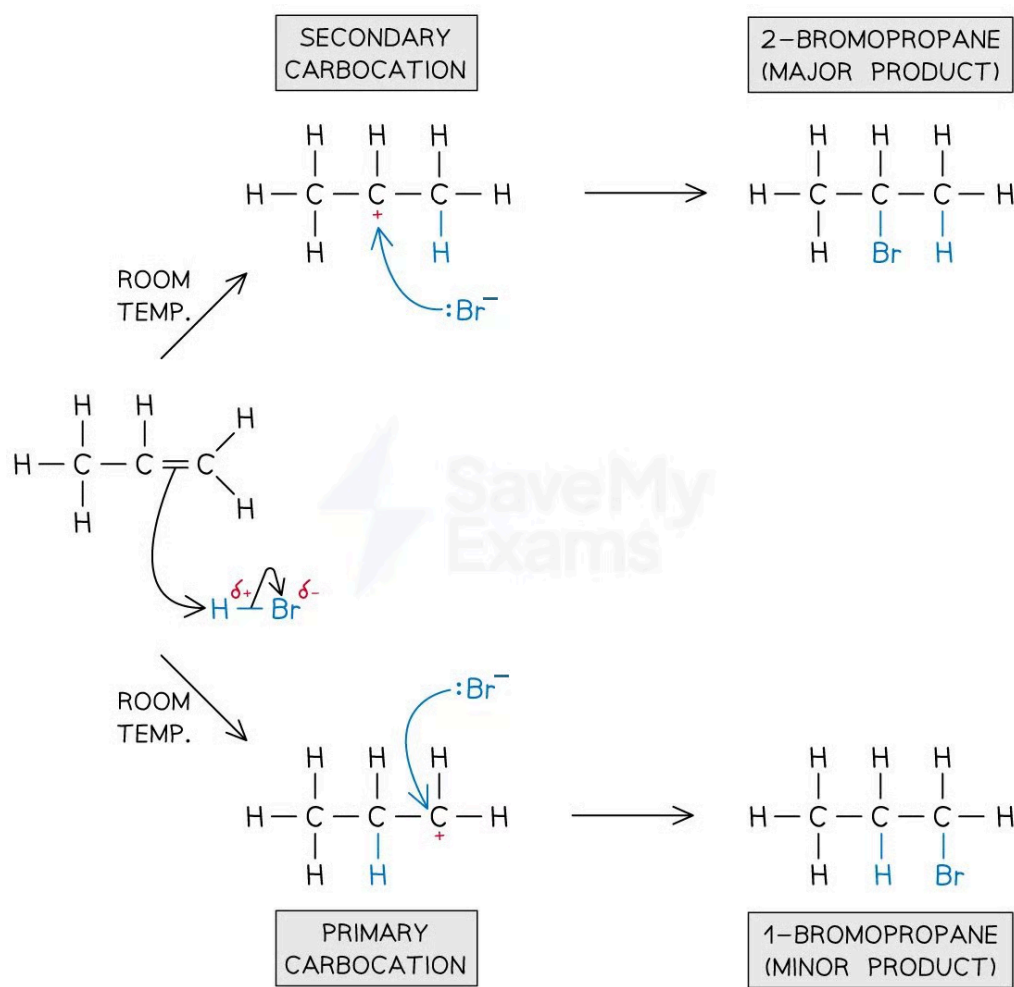
Formation of the major and minor products of the reaction of propene with hydrogen bromide

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

Electrophilic addition mechanism showing the formation of the major and minor products



Your notes



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



Examiner Tips and Tricks

- 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.