



Cambridge (CIE) A Level Chemistry



Alkenes

Contents

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



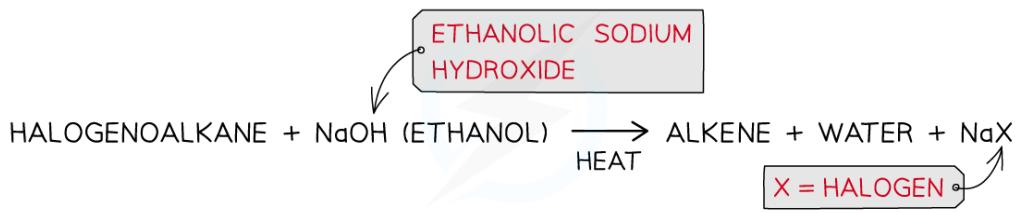
Production of Alkenes: Elimination, Dehydration & Cracking

- Alkenes can be made by a series of reactions including **elimination**, **dehydration** 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**

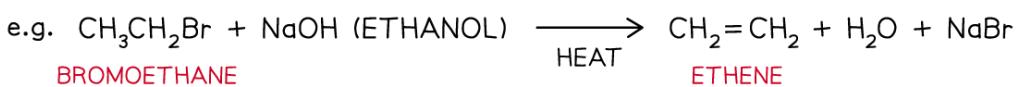
Making alkenes from halogenoalkanes



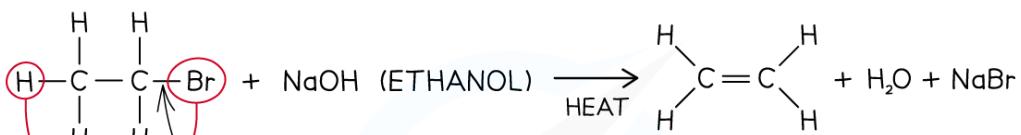
Production of an alkene from a halogenoalkane by reacting it with ethanolic sodium hydroxide and heating it

- 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



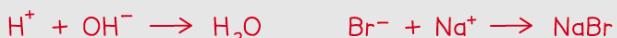
HETEROLYtic BOND BREAKING OF THE C–Br BOND

- 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 H₂O
 - THE Br⁻ COMBINES WITH THE Na⁺ TO FORM NaBr

◦ HBr IS ELIMINATED

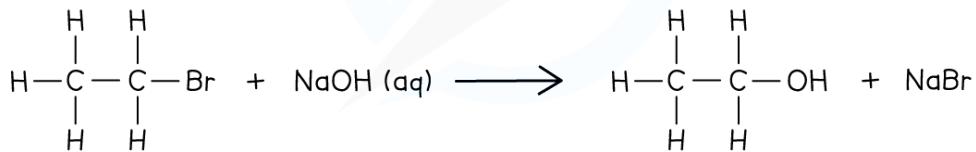
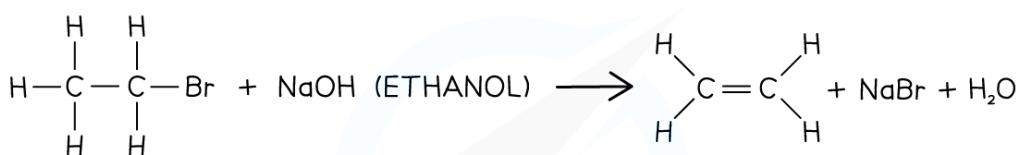


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The eliminated HBr reacts with ethanolic OH⁻ and Na⁺ to form water and sodium bromide.

- 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



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Different reaction conditions will give different products

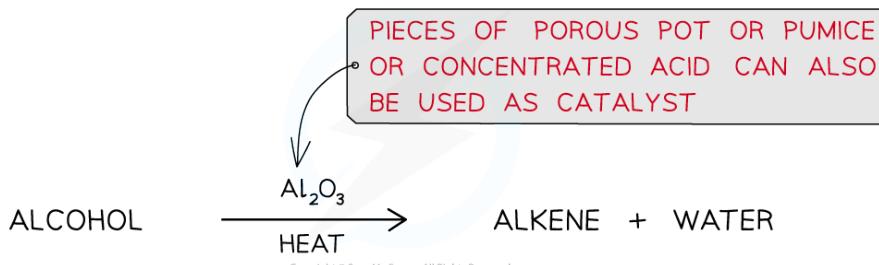
Dehydration reaction



Your notes

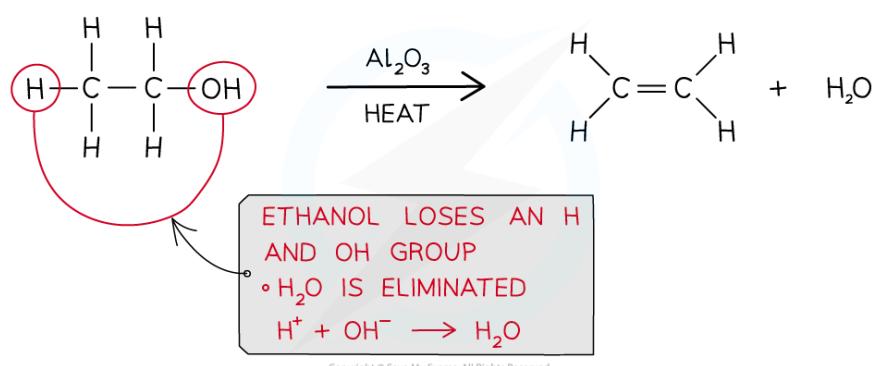
- Alkenes can also be produced from the elimination reaction of alcohols in which a water molecule is lost
 - This is also called a **dehydration** reaction
- Alcohol vapour is passed over a hot catalyst of **aluminium oxide powder** (Al_2O_3)
 - Concentrated acid, pieces of porous pot or pumice** can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

Making alkenes from alcohols



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

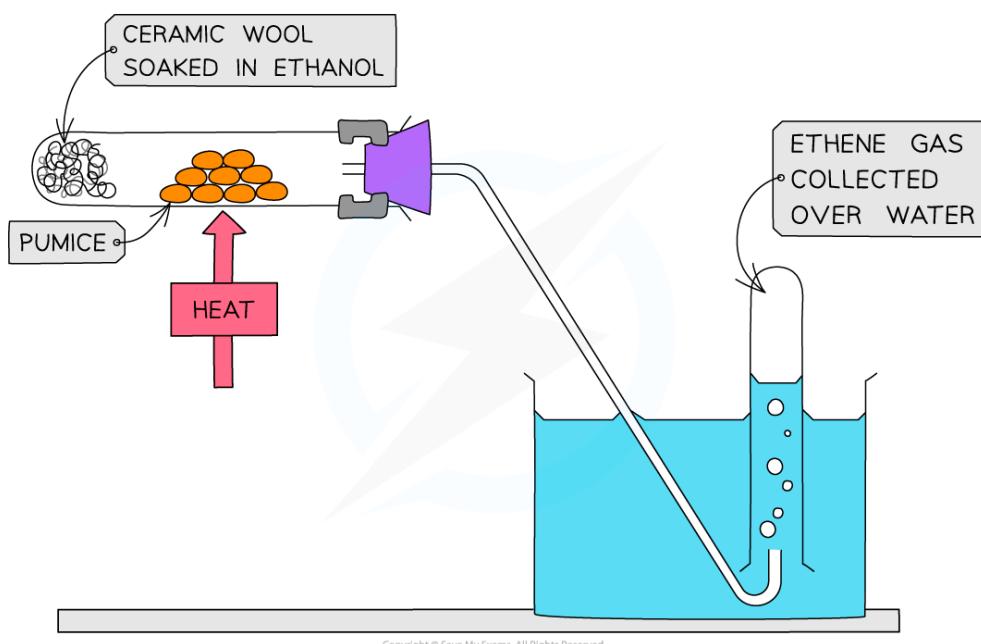
Overview of alcohol elimination



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

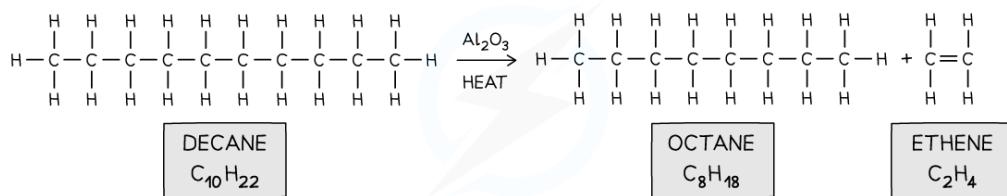


The smaller alkenes are gases at room temperature and collected over water

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



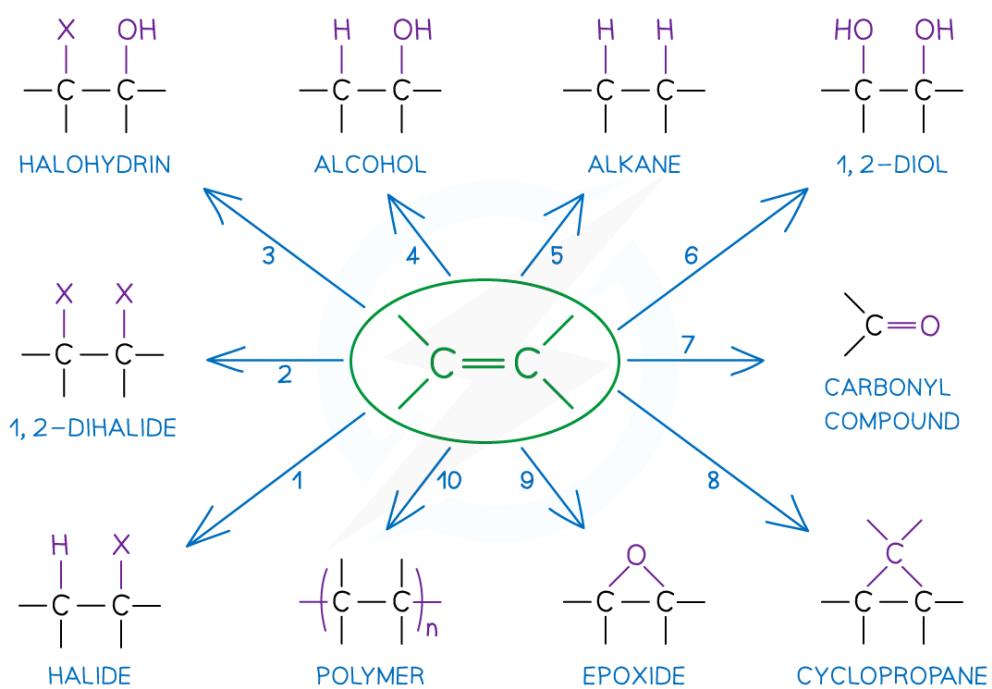
Long hydrocarbon fraction is cracked into two smaller ones

- 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



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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

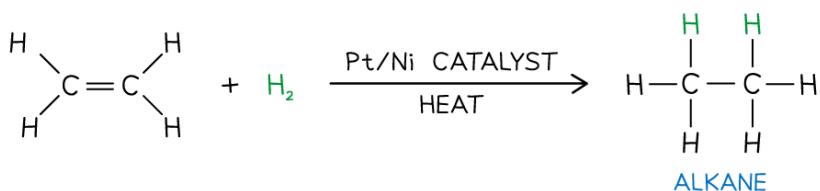
- **Electrophilic addition** is the addition of an electrophile to a double bond
- The C-C double bond is broken, and a new single bond is formed from each of the two carbon atoms
- Electrophilic addition reactions include the addition of:
 - Hydrogen (also known as **hydrogenation reaction**)
 - Steam ($H_2O(g)$)
 - Hydrogen halide (HX)
 - Halogen

Electrophilic addition reactions of alkenes

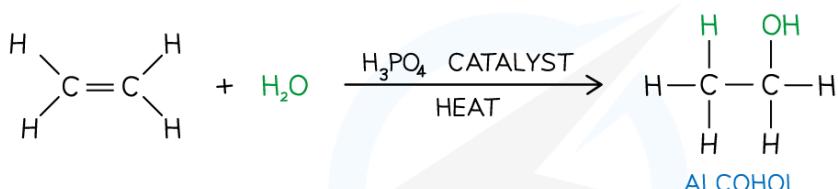


Your notes

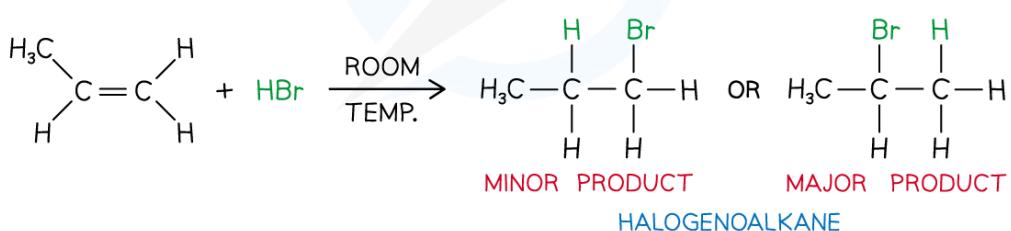
HYDROGENATION



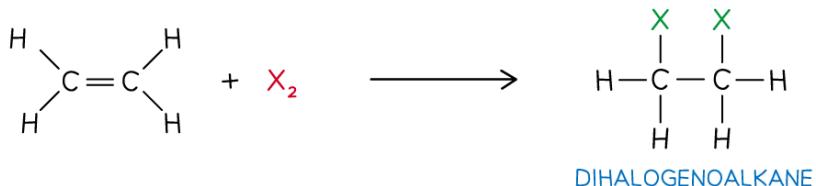
STEAM



HYDROGEN HALIDES (HX)



HALOGENS (X_2)



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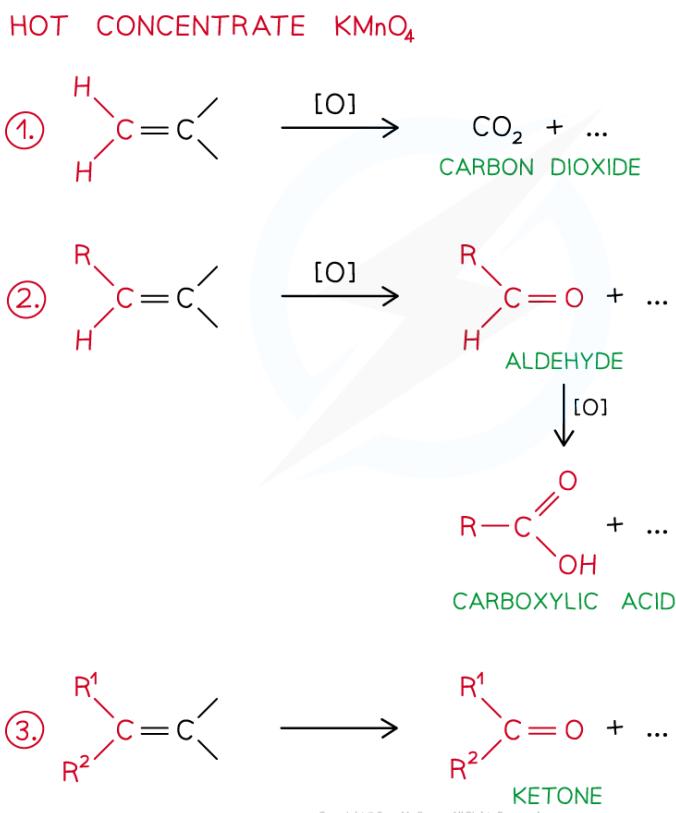
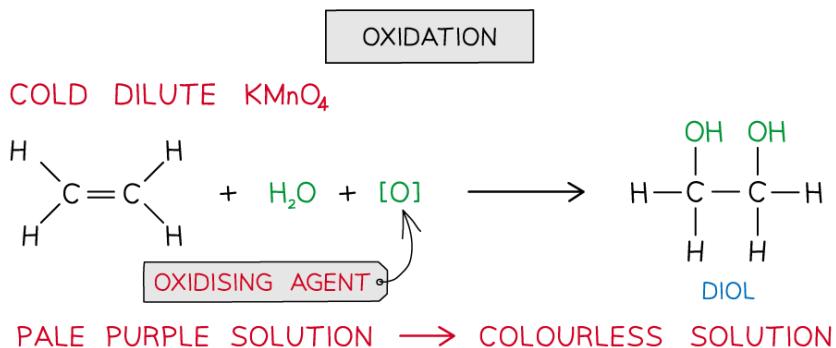
Oxidation

- Alkenes can also be **oxidised** by **acidified potassium manganate(VII)** (KMnO_4) which is a very powerful **oxidising agent**
- Alkenes can be oxidised by both **hot** and **cold** KMnO_4 which will result in different products being formed
 - When shaken with **cold dilute KMnO_4** the **pale purple** solution turns **colourless** and the product is a **diol**
 - When alkenes are reacted with **hot concentrated KMnO_4** 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



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

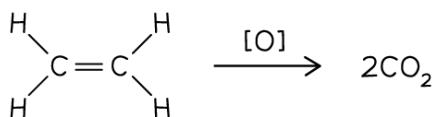
- The reactions of alkenes with hot concentrated KMnO_4 can be used to determine the position of the double bond in larger alkenes

Predicting the position of double bonds formed



Your notes

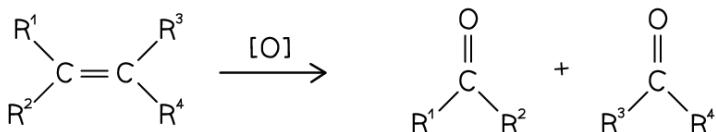
IF C-ATOM IS BONDED TO 2 H-ATOMS, OXIDATION TO CO₂ TAKES PLACE



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



IF A C-ATOM IS BONDED TO TWO ALKYL GROUPS, OXIDATION TO C=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

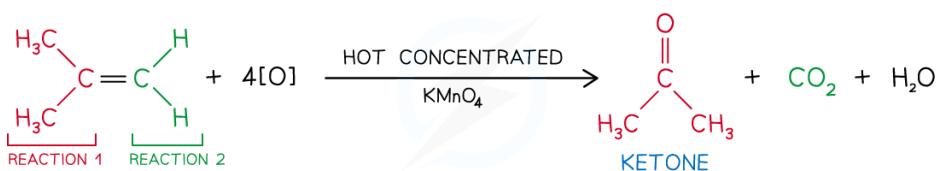


Worked Example

What are the products of the oxidation of 2-methylprop-1-ene with hot, concentrated acidified KMnO₄ (aq)?

Answer:

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



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Worked Example

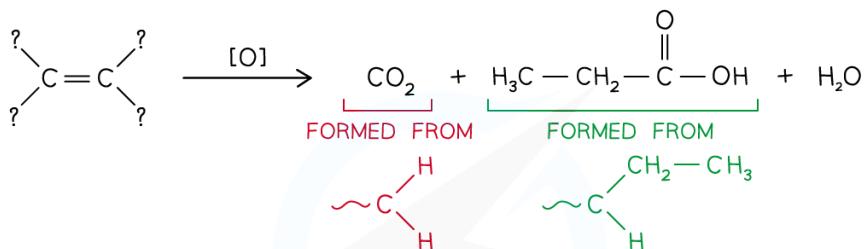
The oxidation of an alkane produces carbon dioxide gas, water and propanoic acid.
Identify the alkene.



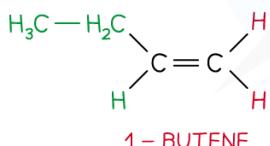
Your notes

Answer:

The alkene is 1-butene



THE ALKENE IS THEREFORE



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Addition polymerisation

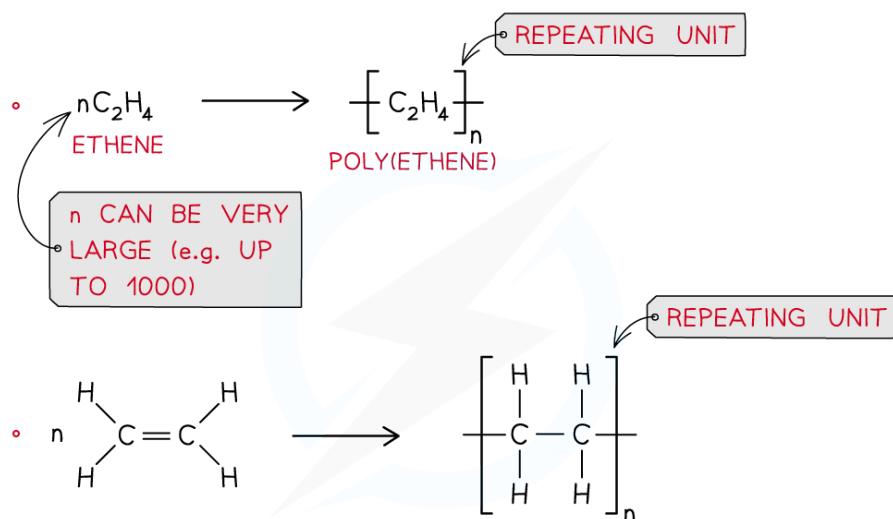
- **Addition polymerisation** is the reaction of many monomers containing at least one double C-C bond to form the long-chain polymers as the only product
 - **Monomers** are small, reactive molecules that react together to make the polymer
 - A **polymer** is a long-chain molecule made up of many **repeating 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

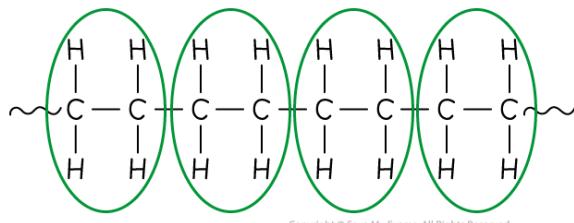


POLYMERISATION REACTION

e.g. POLYMERISATION OF ETHENE



• SECTION OF THE POLYMER MADE UP OF 4 MONOMERS

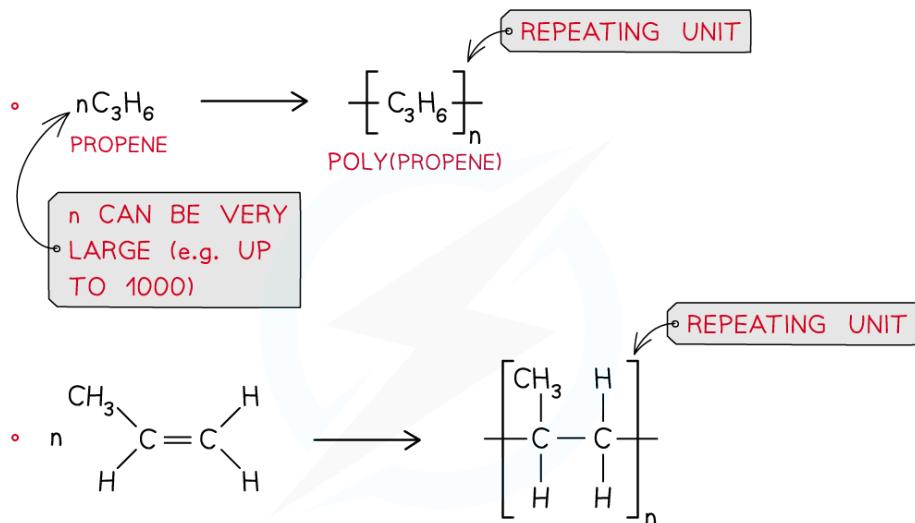
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The polymer backbone consists of a carbon chain with monomers that contain 2 carbon atoms

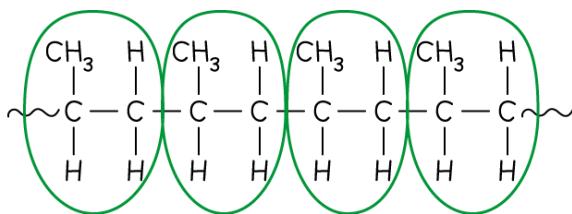
The polymerisation of propene



e.g. POLYMERISATION OF PROPENE



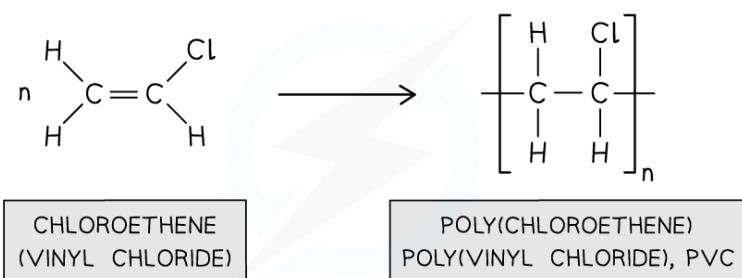
• SECTION OF THE POLYMER MADE UP OF 4 MONOMERS



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



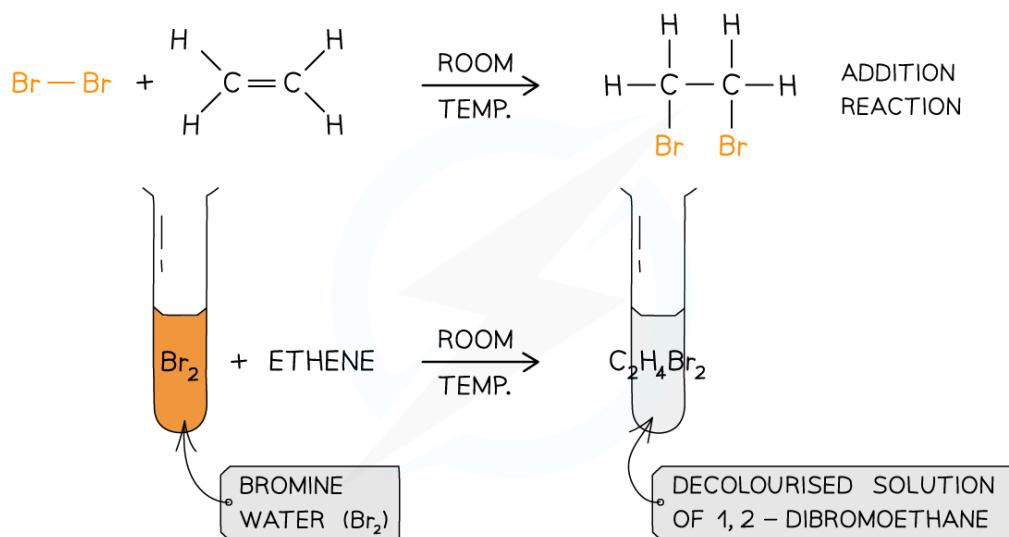
Poly(chloroethene) is used as plastic



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



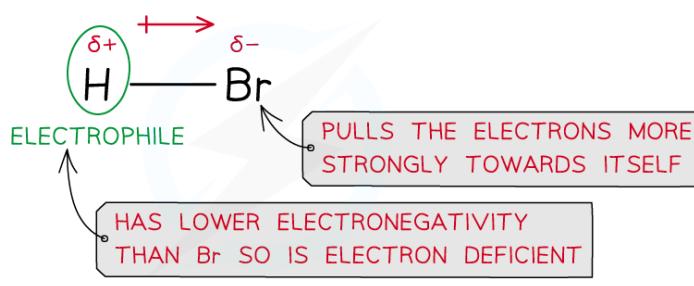
Electrophilic Addition of Alkenes

- 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



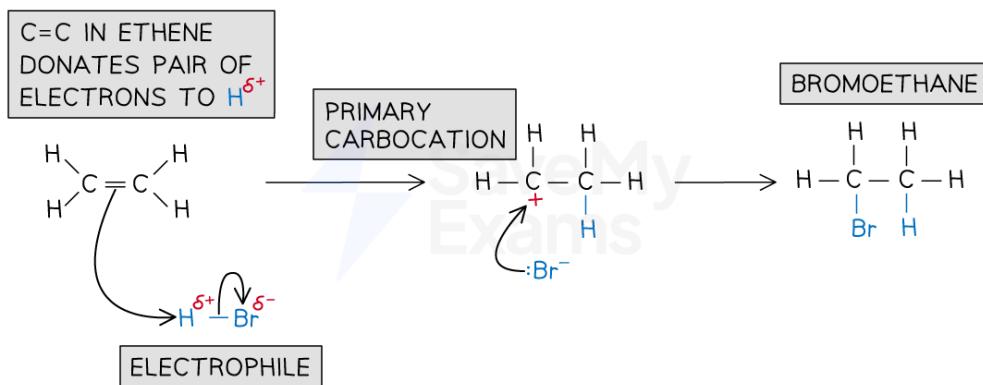
Due to differences in electronegativities of the hydrogen and bromine atoms, HBr is a polar molecule

- 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

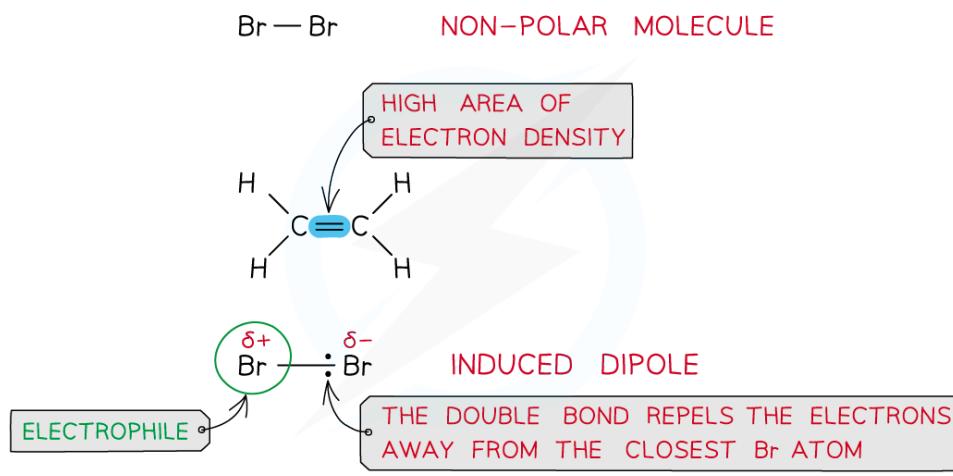


Electrophilic addition reaction of HBr and ethene to form bromoethane

Electrophilic addition of bromine

- Bromine (Br₂) 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 Br-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 Br₂ molecule



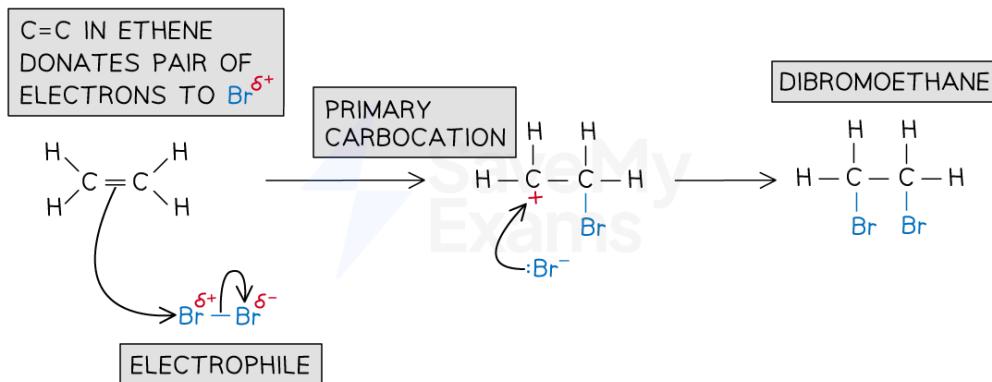
Bromine is a non-polar molecule however when placed close to an area of high electron density it can get polarised

- 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 Br-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



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



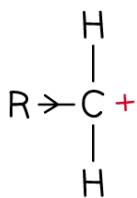
Alkenes: Stability of Cations & Markovnikov's Rule

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

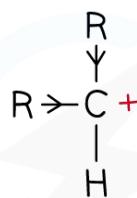
Inductive effect

- 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**

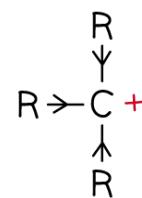
Primary, secondary and tertiary carbocations



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

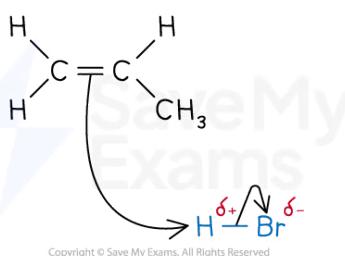
- Markovnikov's rule predicts the outcome of electrophilic addition reactions and states that:



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 alkanes, 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

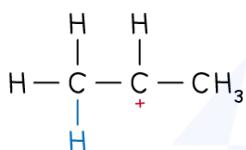
Step 1 in the electrophilic addition mechanism



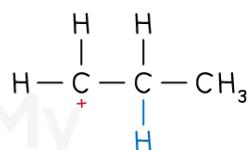
The electrophile reacts with the electron-rich C-C double bond

- 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



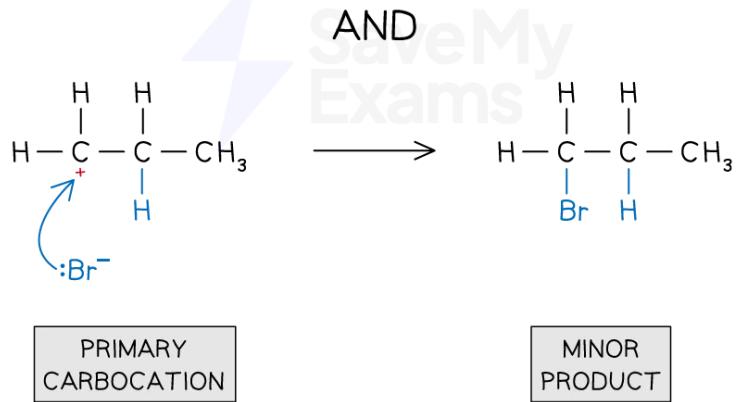
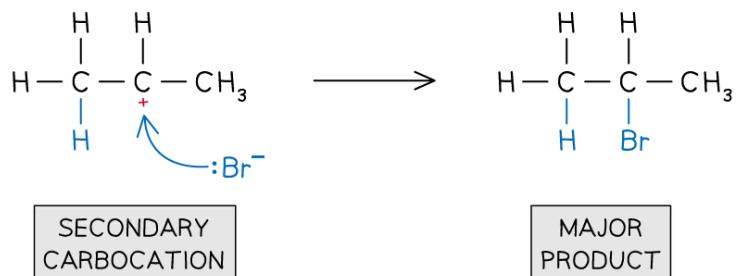
LESS STABLE PRIMARY CARBOCATION INTERMEDIATE

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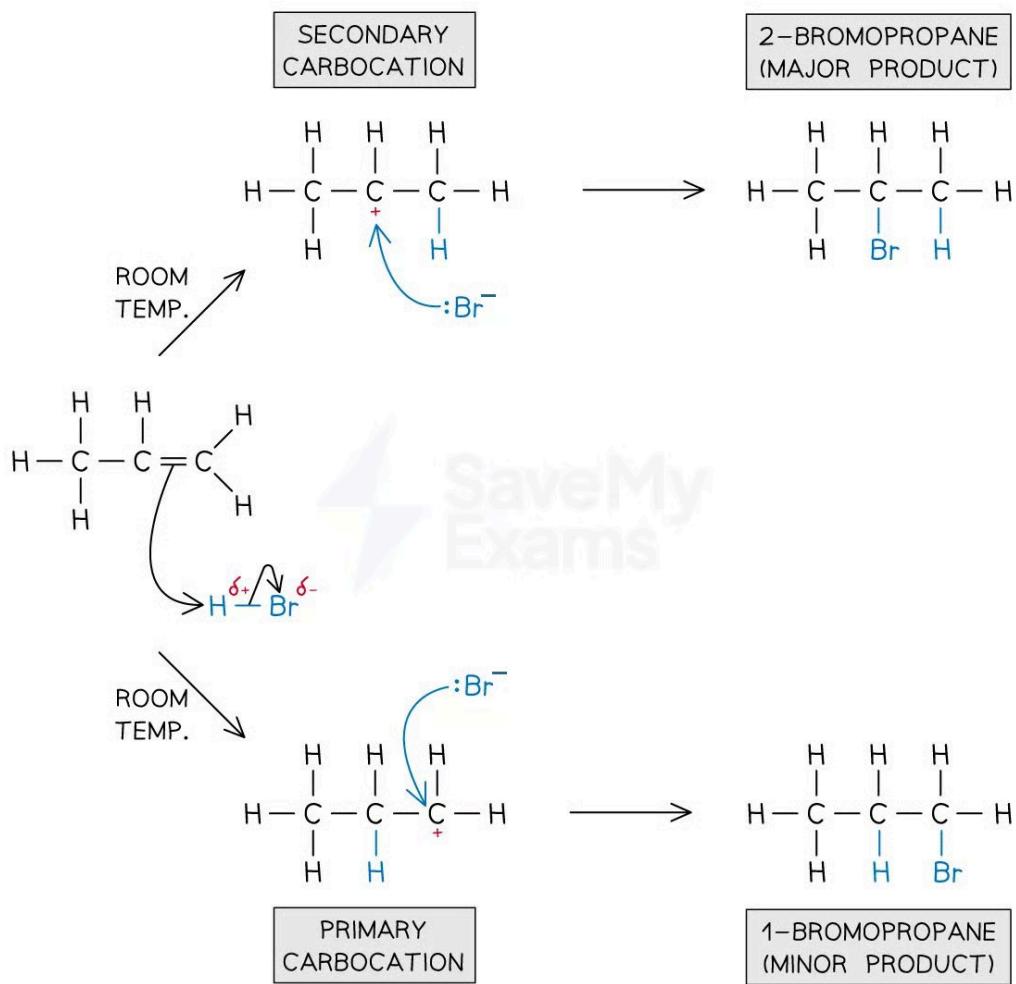
Formation of the major and minor products of the reaction of propene with hydrogen bromide

- 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.