Edexcel International AS Chemistry

Your notes

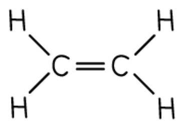
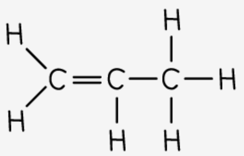
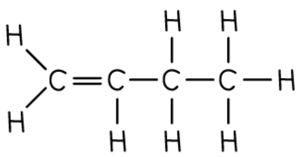
Alkenes

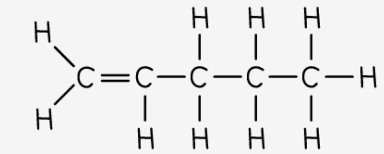
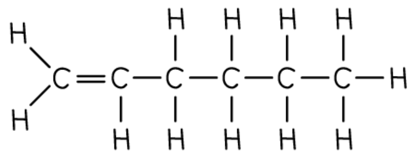
Contents

Alkenes – Introduction

- All alkenes contain a **double carbon bond**, which is shown as two lines between two of the carbon atoms i.e. C=C
- All alkenes contain a double carbon bond, which is the functional group and is what allows alkenes to react in ways that alkanes cannot
- **Alkenes** have the general molecular formula $\mathbf{C_nH_{2n}}$
- They are said to be **unsaturated hydrocarbons**
  - They contain carbon-carbon double bonds
  - They are made up of hydrogen and carbon atoms only
- Alkenes are named using the nomenclature rule **alk + ene**
- In molecules with a straight chain of 4 or more carbon atoms, the position of the C=C double bond must be specified
- The carbon atoms on the straight chain must be numbered, starting with the end closest to the double bond
- The lowest-numbered carbon atom participating in the double bond is indicated just before the -ene:

The First Five Members of the Alkene Family

Structural Formula	Name	Molecular Formula
	ethene	C_2H_4
	propene	C_3H_6
	but-1-ene	C_4H_8

	pent-1-ene	C_5H_{10}
	hex-1-ene	C_6H_{12}

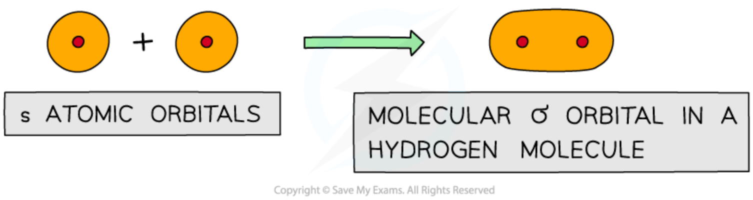
Your notes

Bonding in Alkenes

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

σ bonds

- **Sigma** (σ) bonds are formed from the **end to end overlap** of atomic orbitals
- s orbitals overlap this way as well as p orbitals

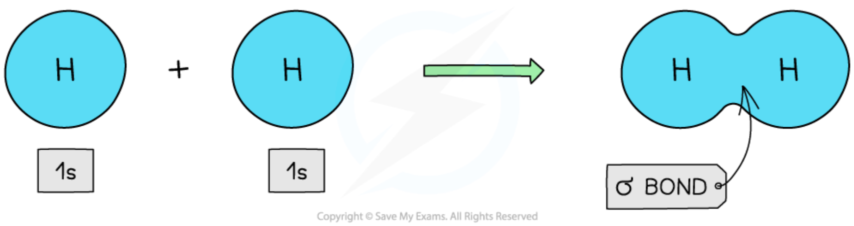


Sigma orbitals can be formed from the end to end overlap of s orbitals

- The electron density in a σ bond is symmetrical about a line joining the nuclei of the atoms forming the bond
- The pair of electrons is found between the nuclei of the two atoms
- The electrostatic attraction between the electrons and nuclei bonds the atoms to each other

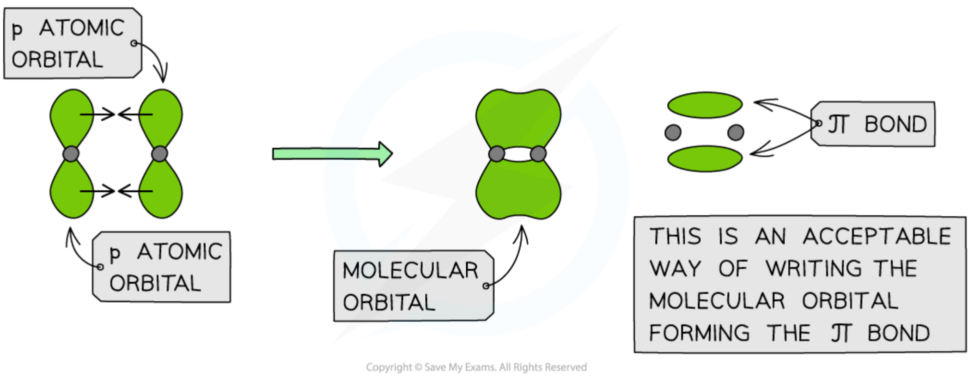
Hydrogen

- The hydrogen atom has only one s orbital
- The s orbitals of the two hydrogen atoms will overlap to form a σ bond



π bonds

- **Pi** (π) bonds are formed from the **sideways overlap** of **adjacent** p orbitals
- The two lobes that make up the π bond lie **above and below the plane** of the σ bond
- This maximises overlap of the p orbitals
- A single π bond is drawn as **two-electron clouds,** one arising from each lobe of the p orbitals
- The two clouds of electrons in a π bond represent **one** bond containing **two electrons**



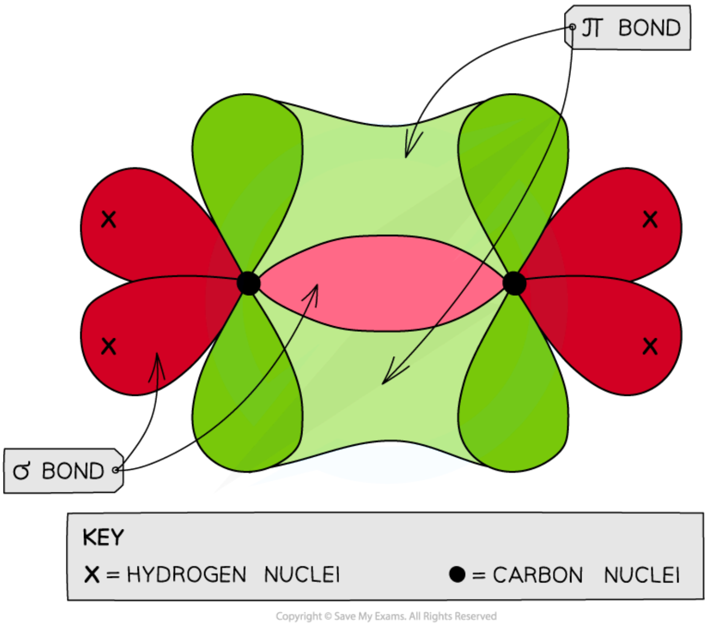
π orbitals can be formed from the sideways overlap of p orbitals

Ethene

- Each carbon atom uses **three** of its **four** electrons to form σ bonds

Your notes

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



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

Your notes

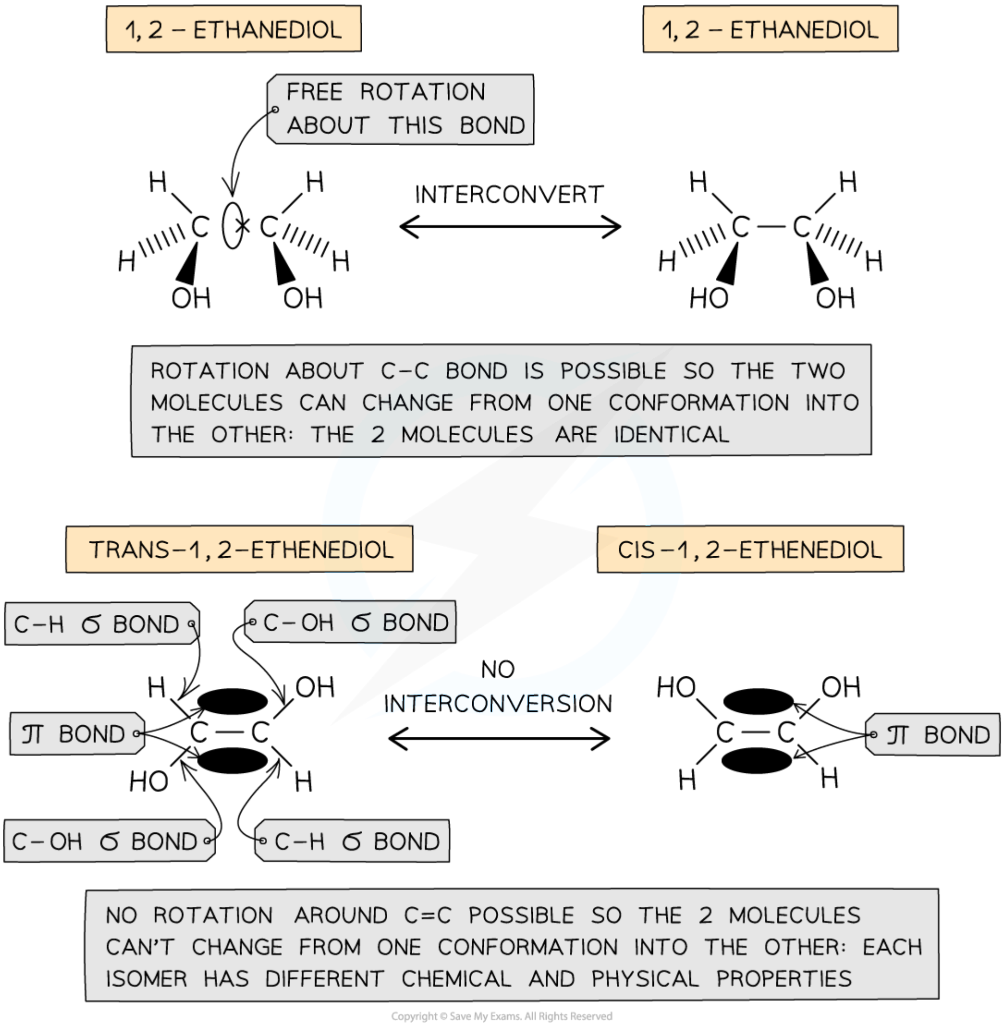
Your notes

Isomers – Geometric

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

Cis / trans isomers

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

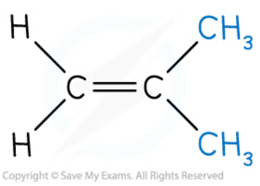


The presence of a π bond in unsaturated compounds restricts rotation about the C=C bond forcing the groups to remain fixed in their position and giving rise to the formation of certain configurational isomers

Deducing E / Z Isomers

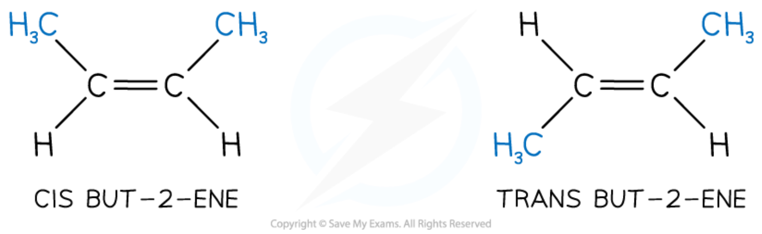
Naming cis / trans isomers

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



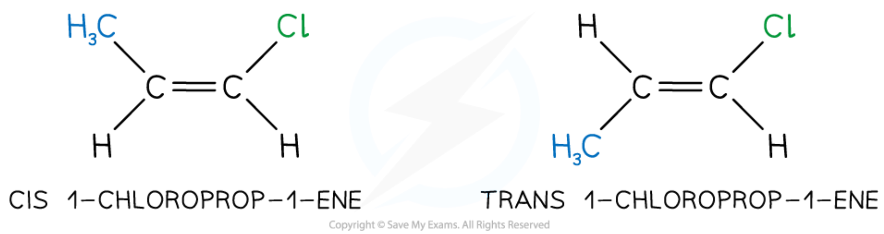
2-methylpropene molecules do not have cis / trans isomers

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



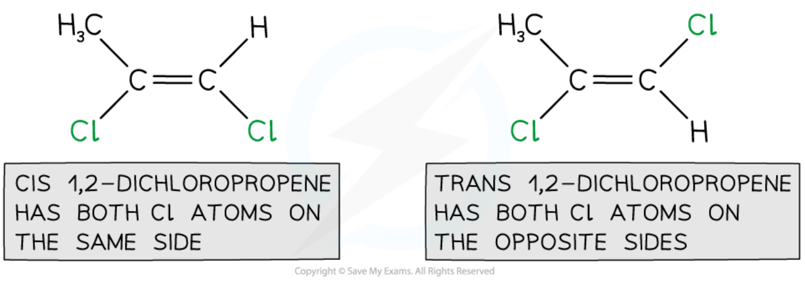
But-2-ene does have cis / trans isomers

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



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

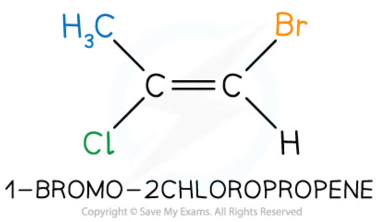
- However, the cis / trans naming system starts to fail once we have more than one atom or group of atoms on either side of the C=C bond
  - The cis / trans naming system can still be used with three atoms / groups of atoms but only if:
    - Two of the three atoms or groups of atoms are the same
  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



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

- The cis / trans naming system cannot be used with three atoms / groups of atoms when they are all different

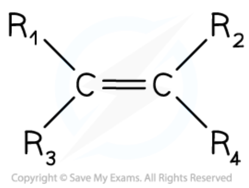
- This requires the use of the *E / Z* naming system



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

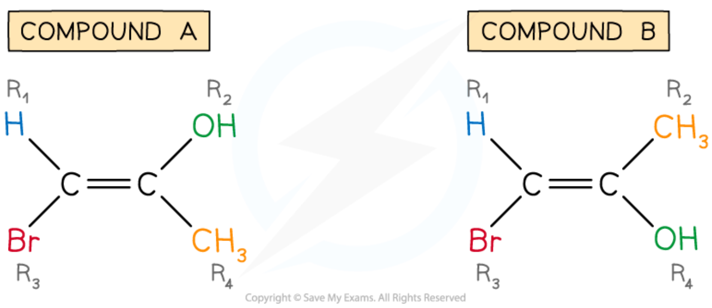
E / Z isomers

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



The general alkene, C_2R_4

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



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

Compound A

Your notes

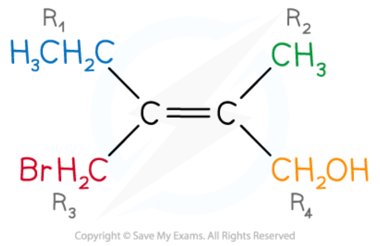
- **Step 1: Apply the CIP priority rules**
  - Look at R_1 and R_3:
    - Bromine has a higher atomic number than hydrogen so bromine has priority
  - Look at R_2 and R_4:
    - Oxygen has a higher atomic number than carbon so oxygen has priority
- **Step 2: Deduce *E* or *Z***
  - *E* isomers have the highest priority groups on opposite sides of the C=C bond, i.e. one above and one below
    - The *E* comes from the German word "entgegen" meaning opposite
  - *Z* isomers have the highest priority groups on the same side of the C=C bond, i.e. both above or both below
    - The *Z* comes from the German word "zusammen" meaning together
  - In compound A, the two highest priority groups are on opposite sides (above and below) the C=C bond
    - Therefore, compound A is *E*-1–bromo-1–propen-2–ol

Compound B

- **Step 1: Apply the CIP priority rules**
  - Look at R_1 and R_3:
    - Bromine has a higher atomic number than hydrogen so bromine has priority
  - Look at R_2 and R_4:
    - Oxygen has a higher atomic number than carbon so oxygen has priority
- **Step 2: Deduce *E* or *Z***
  - In compound B, the two highest priority groups are on the same side (both below) the C=C bond
    - Therefore, compound B is *Z*-1–bromo-1–propen-2–ol

More complicated E / Z isomers

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



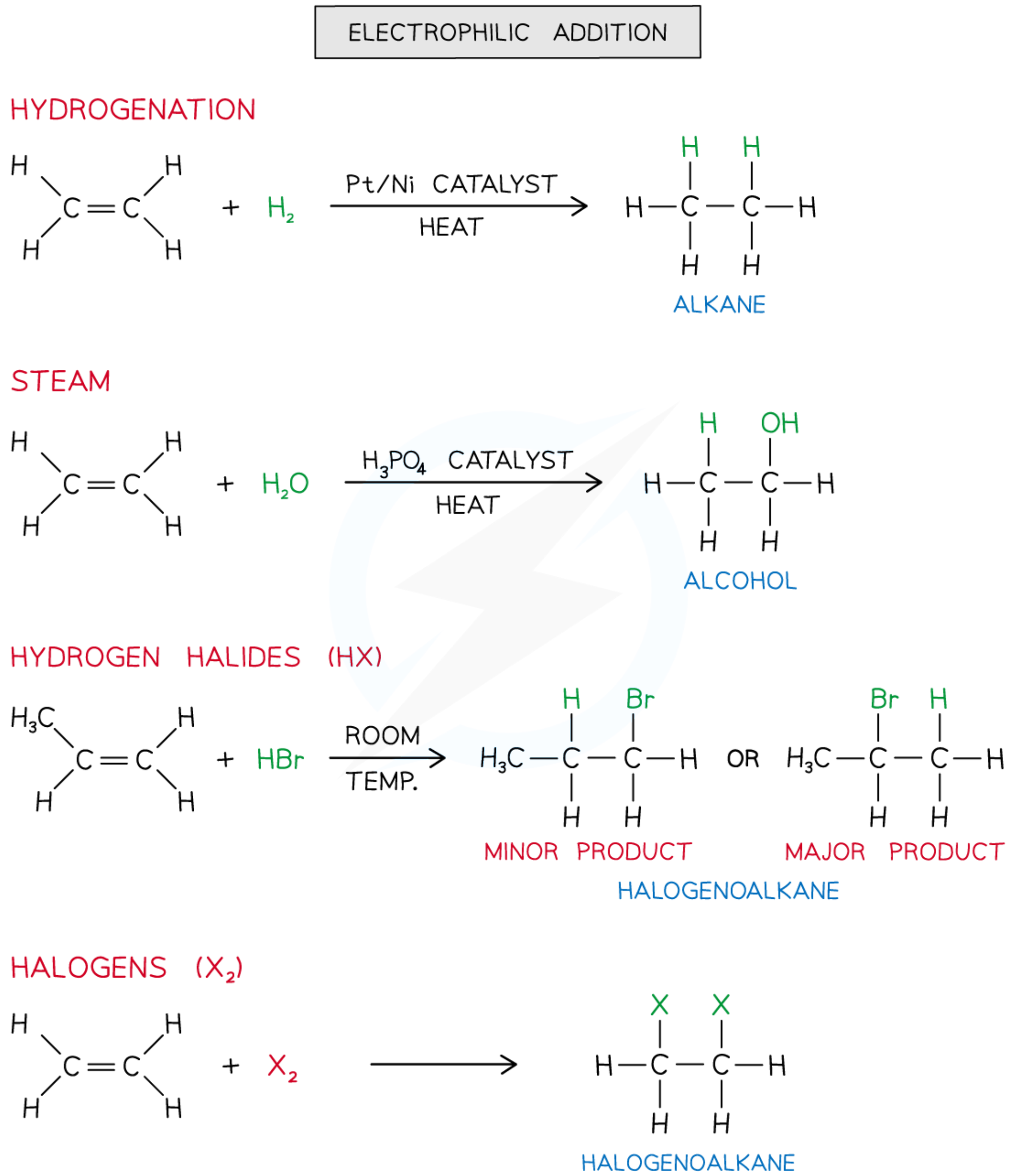
Compound X

- **Step 1: Apply the CIP priority rules**
  - Look at R_1 and R_3:
    - Carbon is the first atom attached to the C=C bond, on the left hand side
  - Look at R_2 and R_4:
    - Carbon is the first atom attached to the C=C bond, on the right hand side
  - This means that we cannot deduce if compound X is an *E* or *Z* isomer by applying the CIP priority rules to the first atom attached to the C=C bond
    - Therefore, we now have to look at the second atoms attached
  - Look again at R_1 and R_3:
    - The second atoms attached to R_1 are hydrogens and another carbon
    - The second atoms attached to R_3 are hydrogens and bromine
    - We can ignore the hydrogens as both R groups have hydrogens
    - Bromine has a higher atomic number than carbon, so bromine is the higher priority
      - Therefore, the CH_2Br group has priority over the CH_3CH_2 group
  - Look again at R_2 and R_4:
    - The second atoms attached to R_2 are hydrogens
    - The second atoms attached to R_3 are hydrogens and an oxygen
    - Oxygen has a higher atomic number than hydrogen, so oxygen is the higher priority
      - Therefore, the CH_2OH group has priority over the CH_3 group
- **Step 2: Deduce *E* or *Z***
  - In compound X, the two highest priority groups are on the same side (both below) the C=C bond
    - Therefore, compound X is the *Z* isomer

Your notes

Alkenes – Reactions

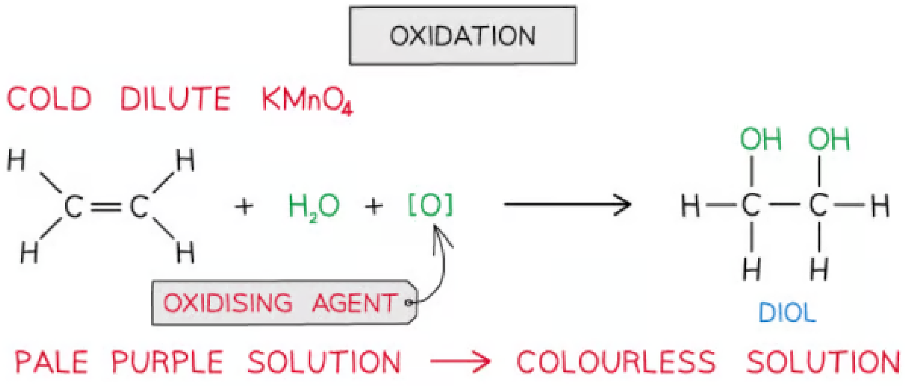
- The double bond in alkenes is an area of high electron density (there are four electrons found in this double bond)
- This makes the double bond susceptible to attack by electrophiles (electron-loving species)
- An **electrophilic addition** is the addition of an **electrophile** to a double bond
-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



The diagram shows an overview of the different electrophilic addition reactions alkenes can undergo

Oxidation

- Alkenes can also be **oxidised** by **acidified potassium manganate(VII)** ($KMnO_4$) which is a very powerful **oxidising agent**
- When shaken with cold dilute **$KMnO_4$** the **pale purple** solution turns **colourless** and the product is a **diol**
  - This colour change means this reaction can be used, like bromine, to distinguish alkanes from alkenes (alkanes do not have double bonds and so are not oxidised in this way)

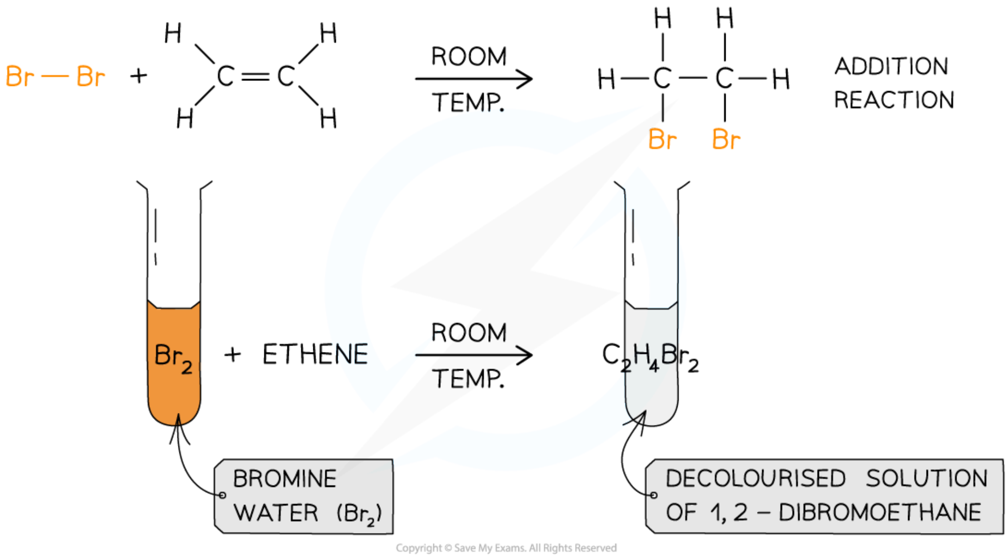


- Although you do not need to know the full details of the working of this reaction you can think of it as an oxidation followed by an addition
  - The potassium manganate provides an oxygen atom (oxidation)
  - Then water in the solution provides another oxygen atom and two hydrogen atoms, so there is addition of two OH groups across the double bond

Your notes

Saturation Test

- Halogens can be used to test if a molecule is **unsaturated** (i.e. contains a double bond)
- Br_2(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

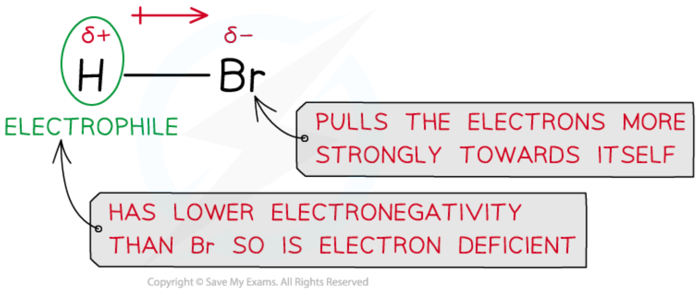


The decolourisation of bromine water by an unsaturated compound as a result of an addition reaction

Electrophilic Addition – Mechanism

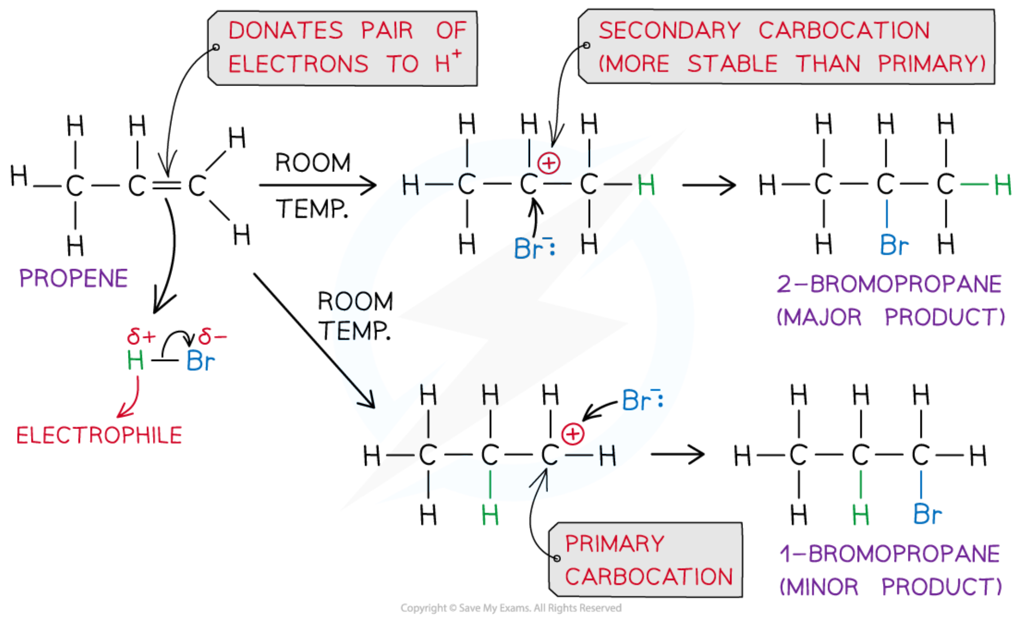
Electrophilic addition of hydrogen halides

- Hydrogen halides such as hydrogen bromide (HBr) are polar as the hydrogen and halogen 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



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

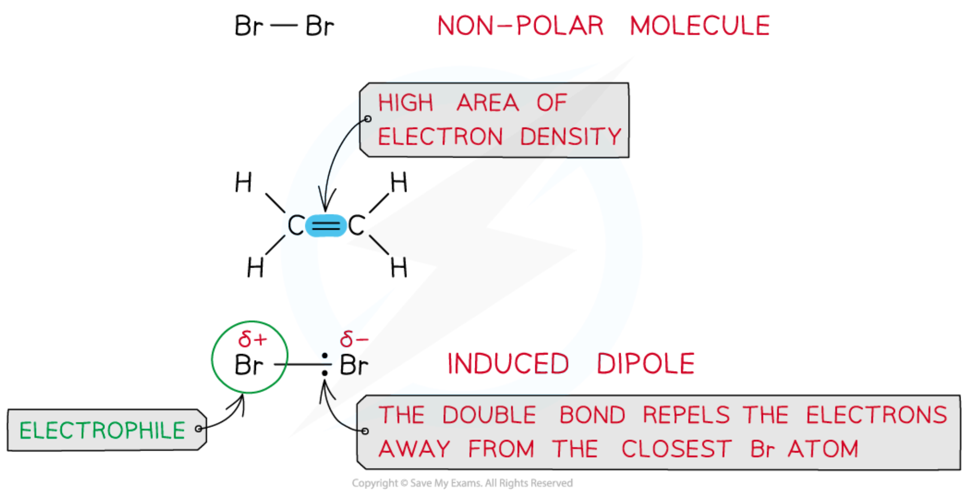
- In an addition reaction, the H atom acts as an electrophile and accepts a pair of electrons from the C-C bond in the alkene
  - The H-Br bond breaks heterolytically, forming a Br^- ion
- This result in the formation of a highly reactive carbocation intermediate which reacts with the Br^- (nucleophile)



Example of an electrophilic addition reaction of HBr and propene to form 1-bromopropane and 2-bromopropane

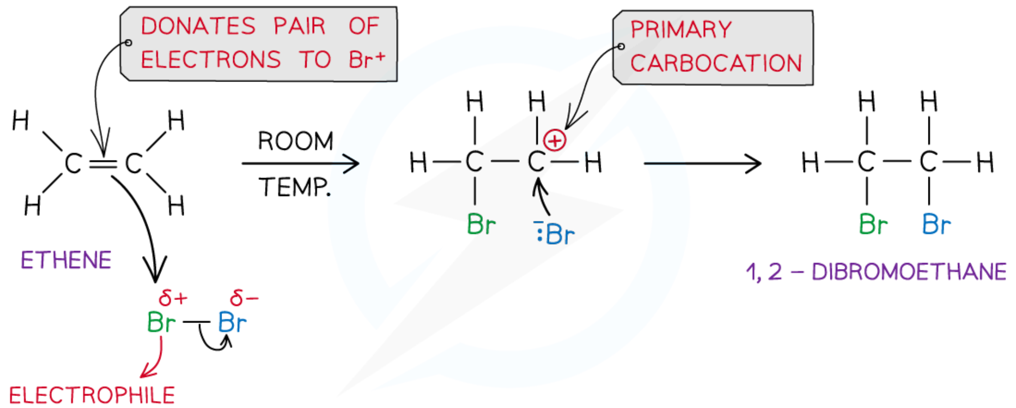
Electrophilic addition of Halogens

- Halogens such as bromine (Br_2) are a non-polar molecules 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



Br_2 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)



Example of an electrophilic addition reaction of Br_2 and ethene to form dibromoethane

Examiner Tips and Tricks

The stability of the carbocation intermediate is as follows:

tertiary > secondary > primary

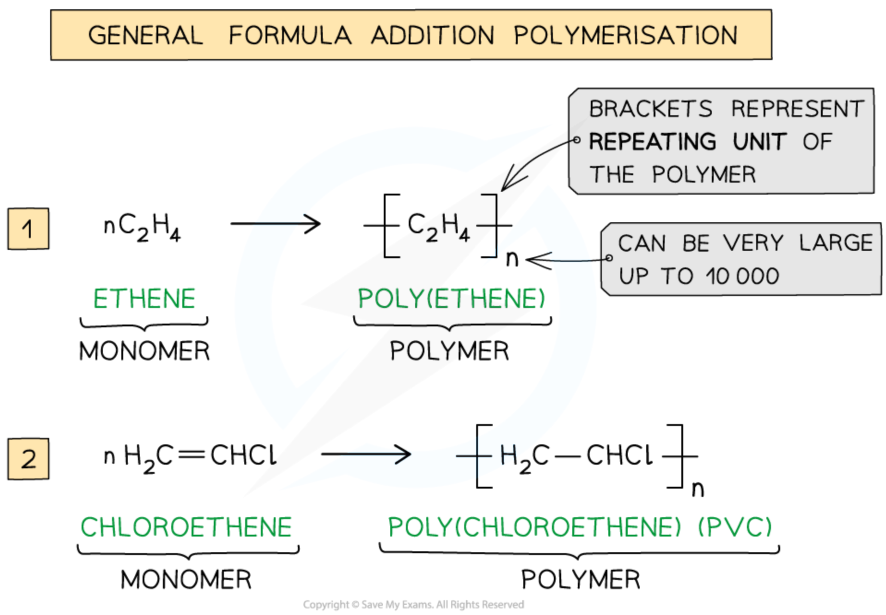
When more than one carbocations can be formed, the major product of the reaction will be the one that results from the nucleophilic attack of the most stable carbocation.

Your notes

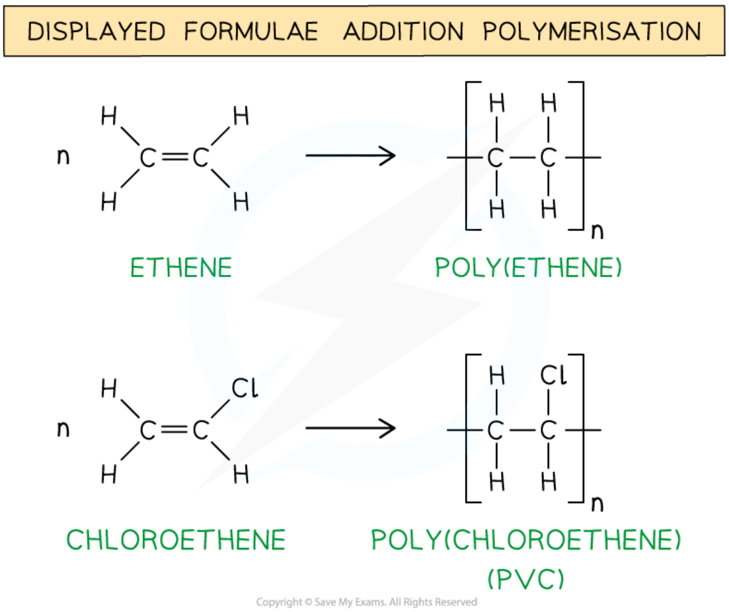
Addition Polymerisation

Addition polymerisation

- **Addition polymerisation** is one of the most important addition reactions of alkenes which form the basis of the plastics 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 join together to form the polymer are called **monomers**
- A polymerisation reaction can be represented by a **general formula** or by using **displayed formulae**
  - Eg. 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)

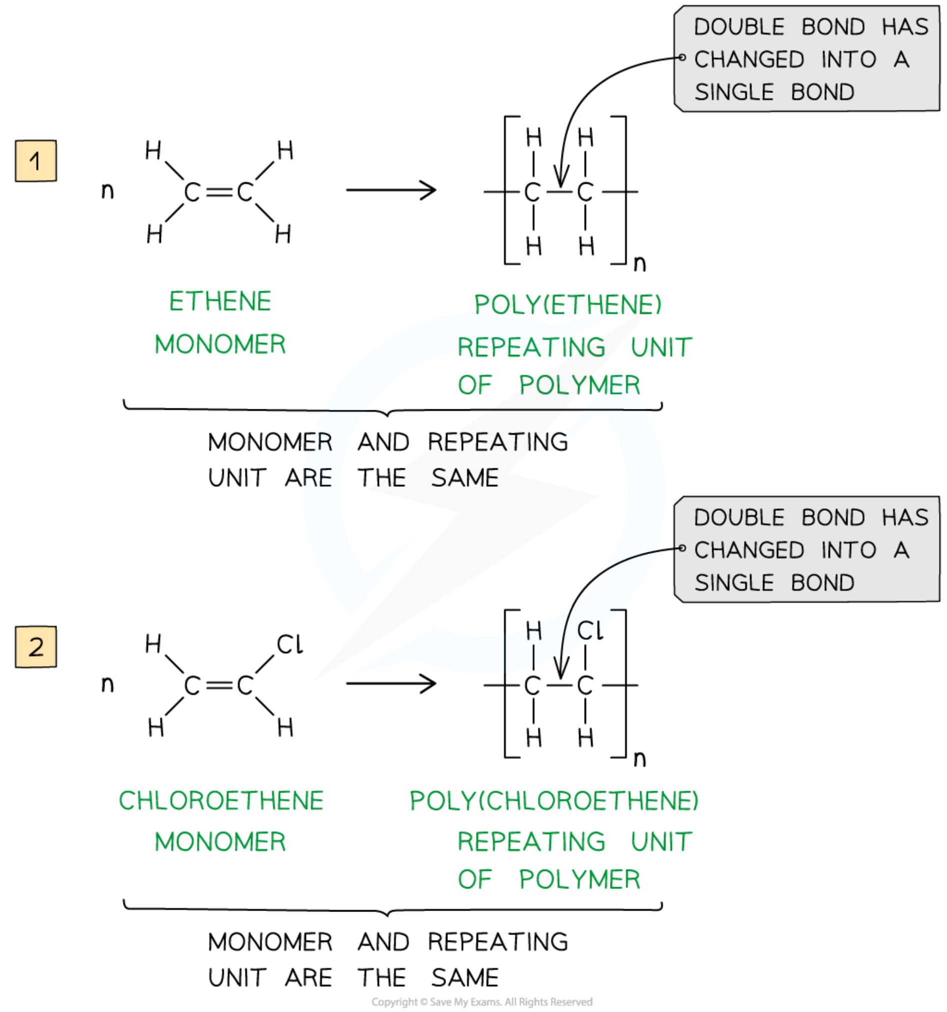


The displayed formulae of the addition polymerisation of ethene (1) and chloroethene (2)

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

Deducing repeat units

- 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

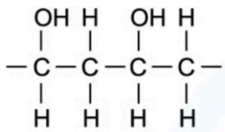
Worked Example

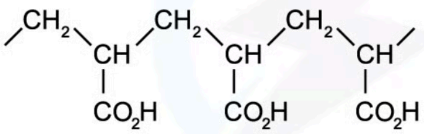
Identifying monomers

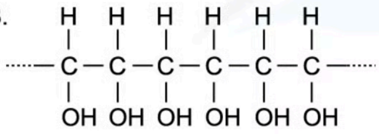
Identify the monomers present in the given sections of addition polymer molecules:

Your notes

Your notes

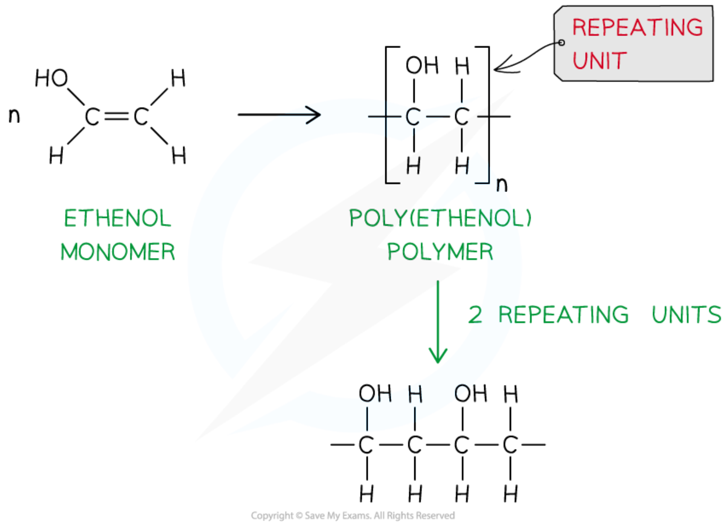
1. 

2. 

3. 

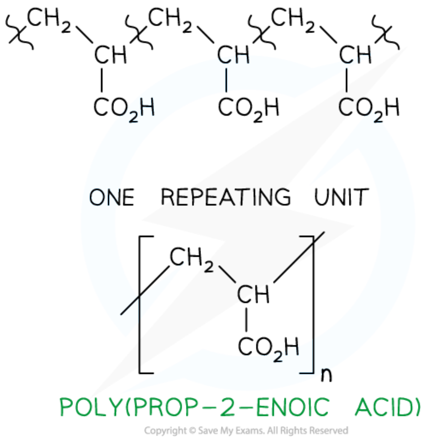
Answer 1:

- When ethenol, $CH(OH)=CH_2$, is polymerised, the C=C double bond opens to produce a repeating unit of $-CH(OH)-CH_2-$ This gives the polymer poly(ethenol)

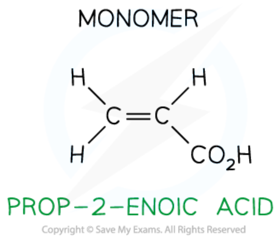


Answer 2:

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

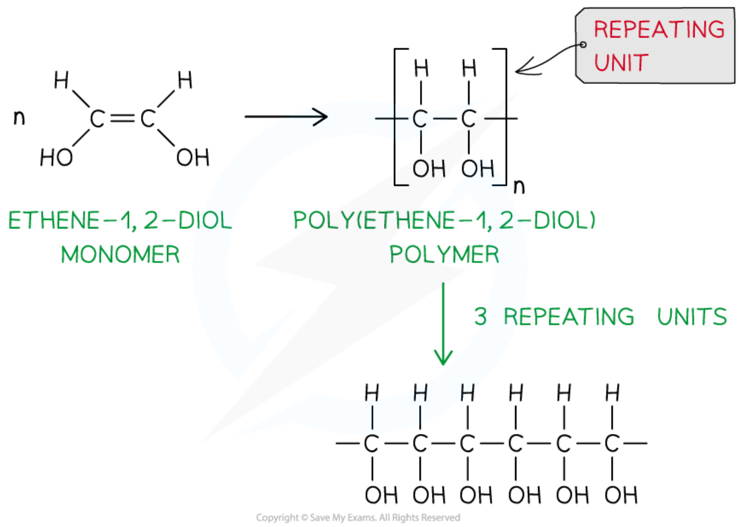


- Since the repeating unit is now found, it can be concluded that the monomer is prop-2-enoic acid



Answer 3:

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



Your notes

Examiner Tips and Tricks

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

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

Your notes

Polymer Disposal

- The three main methods to dispose of plastics are:
  - Landfill waste disposal
  - Incineration / burning
  - Recycling

Landfill waste disposal

- Landfill sites are not desirable because they take up valuable land
- Since polymers are nonbiodegradable, micro-organisms such as decomposers cannot break them down
- Therefore, plastic items will not decompose for hundreds of years which causes landfill sites to fill rapidly

Incineration

- Polymers release a lot of heat energy when they burn
- However, incineration / burning of plastic is not a good solution to the waste issue as it produces the greenhouse gas carbon dioxide, which contributes to climate change
- Some polymers release toxic fumes when they burn
  - An example of this is poly(vinylchloride) which releases toxic hydrogen chloride gas when burned
  - Chemists have designed ways to remove toxic waste products like HCl before they are emitted into the atmosphere
  - The waste gases from the incinerator are scrubbed/reacted with a base or carbonate
  - The base reacts with the acidic HCl gas, neutralising it
    - eg. $CaO (s) + 2HCl (aq) \rightarrow CaCl_2 (aq) + H_2O (l)$

Recycling

- Recycling plastic reduces the amount of water that goes to landfill sites or is burned
- It can also help to conserve crude oil reserves as less energy is required to recycle plastics than produce them
- This means that finite natural resources, such as crude oil and other fossil fuels, can be better managed as they are not being used:
  - As raw materials for plastics in the manufacture of plastics

- To power the industrial processes to manufacture plastics

Biodegradable polymers

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

Compostable polymers

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

Your notes