CAIE Chemistry A-level

14: Hydrocarbons

Notes

Alkanes

Reactivity of Alkanes

Alkanes are generally **unreactive**. This is because alkanes are largely made up of **C-C** and **C-H** covalent bonds which require a lot of energy to break.

Alkanes are also **‘non polar’** because there is only a very **small difference in electronegativity** of the carbon and hydrogen atoms. This means alkanes are also generally not very reactive with **polar reagents**.

Combustion of Alkanes

Alkanes make **good fuels** because they release **huge amounts of energy** when burnt. They are also relatively readily **available** and are **easy to transport**. **Complete combustion** occurs in **excess oxygen**. Complete combustion of alkanes produces water and carbon dioxide. Examples of balanced combustion equations:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$
$$2C_6H_{14} + 19O_2 \rightarrow 12CO_2 + 14H_2O$$

Incomplete combustion of alkanes occurs when there is **insufficient oxygen**. This leads to the formation of water and various other products and pollutants including, **carbon particulates**, C, **carbon monoxide**, CO, and some **carbon dioxide**, CO_2. Examples of these reactions:

$$2C_3H_8 + 7O_2 \rightarrow 6CO + 8H_2O$$
$$2C_2H_6 + 3O_2 \rightarrow 4C + 6H_2O$$
$$4CH_4 + 5O_2 \rightarrow 2CO + 8H_2O + 2C$$

Carbon monoxide is a **toxic colourless and odourless gas**. It binds haemoglobin molecules in red blood cells (to the same sites as oxygen), **preventing oxygen being transported** around the body.

Carbon particulates are also produced, they are small fragments of unburned hydrocarbon. Unless removed from the waste products in industry, these can cause serious **respiratory problems** as they pollute the air.

Oxides of nitrogen are formed when nitrogen and oxygen react in a **car engine** due to the high pressure and temperature. Oxides of nitrogen react with unburnt hydrocarbons to produce **ground level ozone**

Oxides of nitrogen can lead to **acid rain**. This occurs when nitrogen oxides react with oxygen and water vapour in clouds. Acid rain causes various problems, including:

- **Acidification of lakes** and **rivers** (kills aquatic life)
- Destruction of **vegetation**.
- Damage to **limestone buildings**.

The pollutants of car exhaust fumes can be removed with **catalytic converters**. Catalytic converters contain a ceramic honeycomb structure which is coated in a thin layer of **heterogeneous catalysts** like **rhodium** and **platinum**. This creates a **larger surface area** of metal.

$$2NO + 2CO \rightarrow N_2 + 2CO_2$$

Substitution of Alkanes

Alkanes can undergo **substitution reactions with halogens**. This reaction only occurs in the presence of **ultraviolet light**.

A substitution takes place when a hydrogen atom is replaced by a halogen atom from a halogen molecule (Cl_2 or Br_2). When this reaction takes place, a halogenoalkane is produced.
For example:

$$CH_4 + Br_2 \rightarrow CH_3Br + HBr$$
$$CH_3CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + HCl$$

Free Radical Substitution

When the substitution reaction above takes place, the mechanism is called **free radical substitution**. This mechanism requires a **free radical** (a particle with an **unpaired electron**). A free radical is denoted by having a dot next to the chemical symbol, e.g. $Cl^{\cdot}$.
There are three stages to free radical substitution: initiation, propagation and termination.

Example: The reaction of methane with chlorine

Initiation - Free radicals are produced. UV light is required to split the covalent bond in Cl_2 and form two chlorine atoms each with an unpaired electron (free radicals):

$$Cl_2 \rightarrow 2Cl^{\cdot}$$

Propagation - The free radicals are used up and recreated in chain reactions:

$$Cl^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + HCl$$

A methyl radical, $CH_3^{\cdot}$, is produced which reacts with Cl_2 to produce more radicals.

$$CH_3^{\cdot} + Cl_2 \rightarrow CH_3Cl + Cl^{\cdot}$$

These reactions continually occur in a chain until the termination stage.

Termination - All the free radicals are completely used up. When two radicals react, they form a covalent bond. Several termination reactions can take place:

$$Cl^{\cdot} + CH_3^{\cdot} \rightarrow CH_3Cl$$
$$Cl^{\cdot} + Cl^{\cdot} \rightarrow Cl_2$$
$$CH_3^{\cdot} + CH_3^{\cdot} \rightarrow C_2H_6$$

Crude Oil

Crude oil is **unrefined petroleum** found in the ground. It contains a **mixture of hydrocarbons**. Crude oil isn't very useful unless it is **separated** into the different hydrocarbon fractions by fractional distillation.

The process of **fractional distillation**:

1. The crude oil is vaporised.
2. The crude oil vapours are placed into the fractionating column. The column has a temperature gradient where it is hotter at the bottom and cooler at the top.
3. The vapours rise up the column. Different hydrocarbon vapours have different boiling points so they condense at different temperatures. The separated liquid hydrocarbons leave the column.
4. The largest hydrocarbons have higher boiling points, so they are rarely vaporised. They run off the bottom as a sticky residue.

Crude oil is a source of **aliphatic and aromatic hydrocarbons**. Aliphatic hydrocarbons are straight chain hydrocarbons (e.g. alkanes and alkenes). Aromatic hydrocarbons contain at least one benzene ring.

Cracking

Shorter alkane chains are **more in demand** and useful than the heavier fractions. Large fractions can be cracked (broken down) into smaller alkanes and alkenes.
There are two types of cracking:

Thermal cracking

- High temperatures (around 1000°C).
- High pressures (around 70 atm)
- Produces lots of alkenes

Catalytic cracking

- Zeolite catalyst
- Slight pressure
- High temperature (around 450°C)
- Produces mostly aromatic hydrocarbons and motor fuels

Examples of cracking

$$C_{10}H_{22} \rightarrow C_5H_{12} + C_5H_{10}$$

$$C_{15}H_{32} \rightarrow 2C_2H_4 + C_3H_6 + C_8H_{18}$$

Decane → ethene + octane

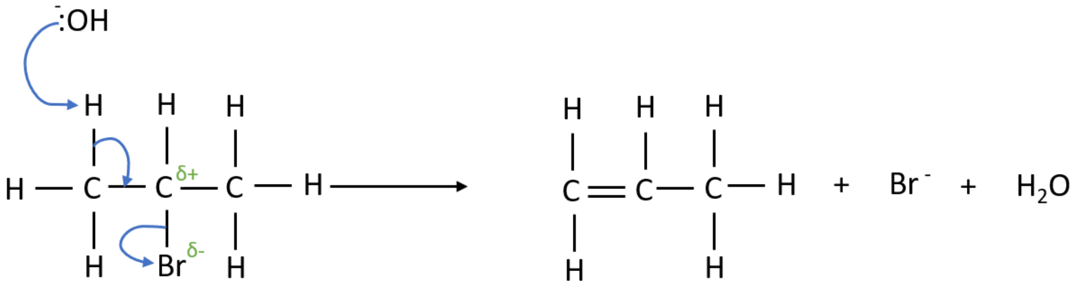
Alkenes

Alkenes are **unsaturated** hydrocarbons. This means they contain at least one **C=C** double bond. To identify alkenes aqueous bromine is added, the bromine will turn from a brown solution to a colourless solution if alkenes are present.

Formation of Alkenes

Elimination

Halogenoalkanes can also undergo an **elimination** reaction when they are **heated under reflux with ethanolic sodium hydroxide**. The hydroxide ions can’t be dissolved in water as this would cause hydrolysis would occur.



Dehydration of Alcohol

Alcohols can be dehydrated to form **alkenes**. This can be carried out using **aluminium oxide** or a concentrated **acid** as a **catalyst**.

Dehydration of alcohol using aluminium oxide

If **ethanol vapour** is passed over an aluminium oxide catalyst, the ethanol is **cracked**, producing ethene and water.

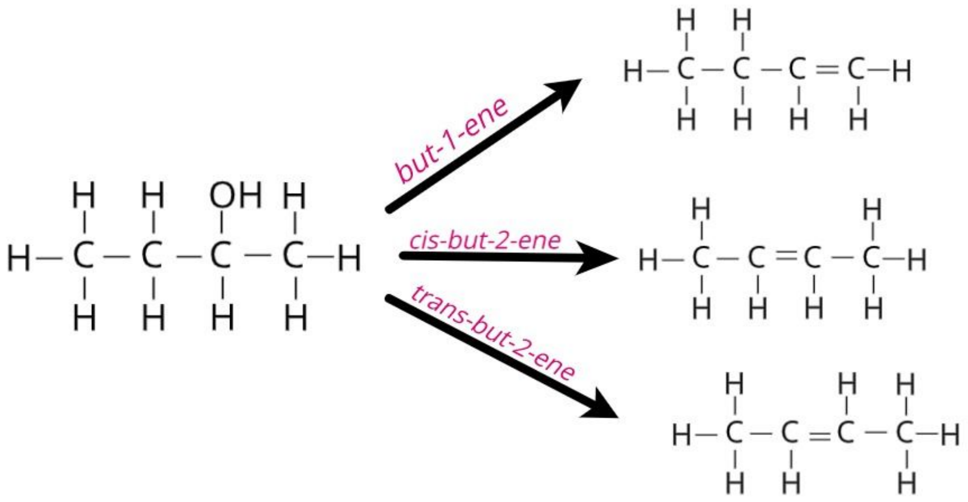
$$CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$$

Dehydration of ethanol using acid catalyst

Concentrated sulfuric or phosphoric acid can be used as acid catalysts to produce ethene from ethanol. When ethanol is heated with excess sulfuric acid (a strong oxidising agent), the alcohol is further oxidised to carbon dioxide and the acid is reduced to sulfur dioxide. These **gases must be removed** from the reaction. Phosphoric acid is often used in place of concentrated sulfuric acid because it is a weaker oxidising agent meaning the reaction is safer.

$$CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$$

If an alcohol is unsymmetrical, a **variety of products** will be produced from dehydration. For example, dehydration of **butan-2-ol** will produce but-2-ene, cis-but-1-ene and trans-but-1-ene. A diagram demonstrating this can be seen on the following page:



Chemistry of Alkenes

Addition

Alkenes undergo addition reactions because they contain at least one C=C double bond. This is when **two compounds combine to form a larger compound**.
Alkenes can undergo addition with different compounds:

- Halogens
- Hydrogen halides
- Hydrogen(g) and Pt/Ni
- Water (in the form of steam)

Addition with Halogens:

When alkenes react with halogens, covalent bonds form between the halogen atoms and the carbons on either side of the double bond, producing a di-halogenoalkane. The mechanism is called electrophilic addition and can be seen in ‘Electrophilic addition’ on the following page.

Addition with Hydrogen Halides:

A hydrogen halide is polar due to the difference in electronegativity between hydrogen and the much more electronegative halogen atom. This polarity means both the hydrogen and the halide bond to carbon atoms in the alkene, forming a halogenoalkane.

Addition with Hydrogen:

Alkenes undergo hydrogenation when they react with hydrogen. The C=C double bond opens up to form covalent bonds with the new hydrogen atoms. The reaction requires excess hydrogen, a temperature of around 150°C and a platinum/nickel catalyst.

$$CH_2CH_2 + H_2 \rightarrow CH_3CH_3$$

Addition with Steam:

Alkenes are hydrated when they react with steam to form alcohols. This requires an acid catalyst such as phosphorus acid or sulfuric acid.

$$CH_2CH_2 + H_2O \rightarrow CH_3CH_2OH$$

When steam reacts with propene, according to Markovnikov's rule of addition, the OH group joins to the carbon atom in the double bond which is directly bonded to the most carbons atoms. This can be seen in the equation below:

$$CH_3CHCH_2 + H_2O \rightarrow CH_3C(OH)CH_3$$

Using Markovnikov's rule, propan-2-ol is the major product and propan-1-ol is the minor product. The reaction will mostly produce propan-2-ol.

Oxidation

Cold, dilute acidified manganate(VII) ions

Potassium manganate(VII) contains manganate(VII) ions meaning it is a strong oxidising agent. Manganate(VII) ions can oxidise alkenes to form diols (alkane with two alcohol groups). For this reaction to take place, the manganate ions must be cold, dilute and acidified.

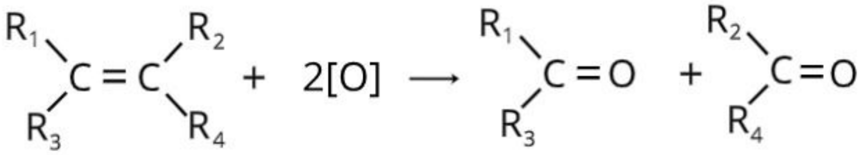
In the reaction below, [O] denotes the oxidising agent:

$$CH_2CH_2 + H_2O + [O] \rightarrow CH_2(OH)CH_2(OH)$$

During this reaction, the purple solution will decolourise.

Hot, concentrated acidified manganate(VII) ions

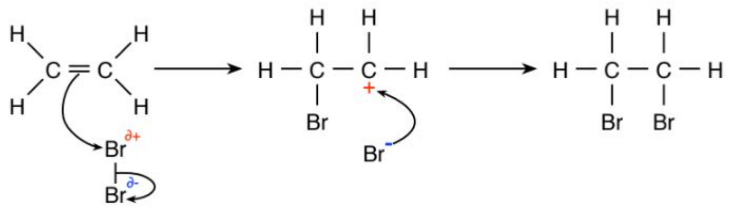
When an alkene reacts with hot, concentrated, acidified manganate(VII) ions the C=C double bond, ruptures. The manganate(VII) ions oxidise the alkene by breaking the C=C bond and replacing it with a C=O double bond on each new molecule. Further reactions then take place, depending on the groups attached to the carbons:



- If both the R groups in the product are alkyl groups then a **ketone** will form. Ketones are not easily oxidised so **no further oxidation** takes place.
- If a product has one alkyl group and one hydrogen then an **aldehyde** will be produced. Aldehydes are **easily oxidised** to carboxylic acids meaning that the final product will be a **carboxylic acid**.
- If both R groups in the product are hydrogen atoms, methanal will be formed. This is oxidised to **methanoic acid** which is then oxidised to **water and carbon dioxide**.

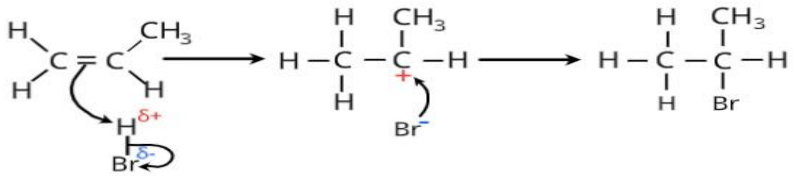
Electrophilic Addition

Mechanism for Br_2 and ethene



The **electron dense double bond** in ethene causes an **uneven distribution of electrons in Br_2**. This causes a difference in charge between the two bromine atoms (dipoles form). The electron pair in the double bond attracts the **$Br^{\delta+}$**, forming a covalent bond between carbon and a bromine atom. This produces a positively charged **carbocation intermediate** which attracts the **negatively charged bromide ion**. Dibromoethane is produced.

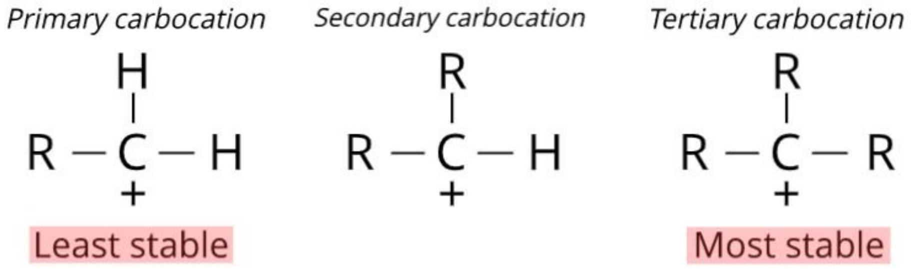
Mechanism for HBr and propene



Hydrogen bromide is **polar** due to the difference in the electronegativities of hydrogen and bromine. The **electron pair** in the double bond attracts **$H^{\delta+}$**, forming a covalent bond between carbon and hydrogen. This produces a positively charged **carbocation intermediate** which attracts the negatively charged bromide ion. According to **Markovnikov's rule**, the hydrogen bonds to the carbon atom which is bonded to the most hydrogen atoms. The bromide ion bonds to the carbon atom which is joined to the most carbon atoms. This is why **2-bromopropane** forms more often than 1-bromopropane.

Inductive Effects of Alkyl Groups

When a hydrogen halide bonds to an **unsymmetrical alkene**, there are two possible products. The quantities of each product produced depends on how **stable** the **carbocation intermediate** is. Carbocations with **more alkyl groups are more stable**. This is because alkyl groups have a **positive inductive effect** on the carbon atom and feed electrons towards the positive charge.



The more stable carbocation is more likely to form so there will be higher quantities of this product. It is often referred to as the **major product.**

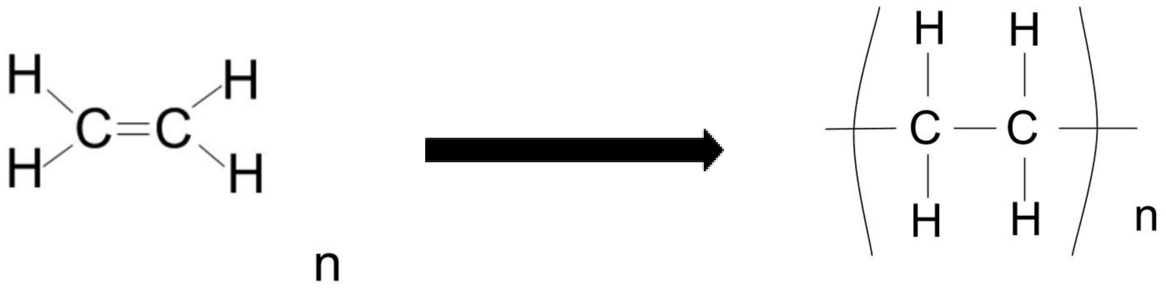
Addition Polymerisation

Alkenes can undergo **addition polymerisation.** In this reaction, many **alkene monomers** join together to form a **polymer.** Alkenes are able to react and form polymers because their **C=C double bonds can open up**, allowing the carbons to join together. The polymers produced are saturated because they do not contain any carbon-carbon double bonds.

Addition polymers are very **unreactive**. This is because the polyalkene chains are **saturated** and the main carbon chain is **non-polar.**

Poly(ethene)

Poly(ethene) is produced from the addition polymerisation of **ethene**. During this reaction, lots of **ethene monomers** join together to produce one long chain polymer product.

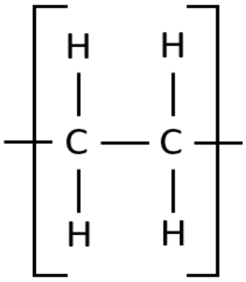


For the equation above, the **'n'** denotes a **large number of units** reacting together to form a chain with this unit length.

Repeat Units

Repeat units are the **section of polymer which repeats** throughout the whole chain. They can be easily drawn as they look the same except that the double carbon-carbon bond is drawn as a single bond and single bonds are drawn coming out the sides of each carbon atom:

Repeat unit of poly(ethene):



Repeat unit of PVC: