

CIE Chemistry A Level

15 : Hydrocarbons

Notes



Alkanes

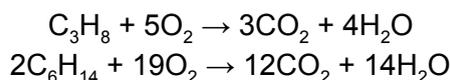
Reactivity of alkanes

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.

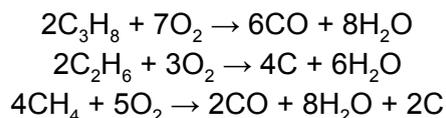
Alkanes are also '**non polar**' because there is only a very **small difference in electronegativity** of the carbon and hydrogen atoms. This means alkanes are also generally not very reactive with **polar reagents**.

Combustion of alkanes

Complete combustion occurs in **excess oxygen**. Complete combustion of alkanes produces water and carbon dioxide. Examples of balanced combustion equations:



Incomplete combustion of alkanes occurs when there is **insufficient oxygen**. This leads to the formation of water and various other products including, **carbon particulates**, **C**, **carbon monoxide**, **CO**, and some **carbon dioxide**, **CO₂**. Examples of these reactions:

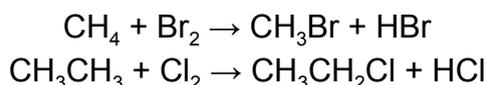


Substitution of alkanes

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 (**Cl₂** or **Br₂**). When this reaction takes place, a halogenoalkane is produced.

For example:

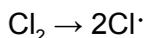


Free radical substitution

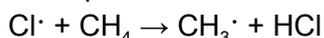
When the substitution reaction above takes place, the mechanism is called **free radical substitution**. This mechanism requires a **free radical** (a particle with an **unpaired electron**). A free radical is denoted by having a dot next to the chemical symbol, e.g. $\text{Cl}\cdot$. There are three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

Example: The reaction of methane with chlorine

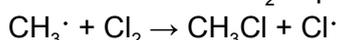
Initiation - Free radicals are produced. UV light is required to split the covalent bond in Cl_2 and form two chlorine atoms each with an unpaired electron (free radicals):



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

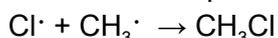


A methyl radical, $\text{CH}_3\cdot$, is produced which reacts with Cl_2 to produce more radicals.



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:



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** than the heavier fractions. Large fractions can be cracked (broken down) into smaller alkanes and alkenes.

There are two types of cracking:

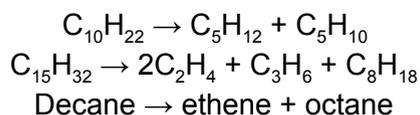
Thermal cracking

- 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



Alkenes

Alkenes are **unsaturated** hydrocarbons. This means they contain at least one **C=C** double bond.

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
- 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.

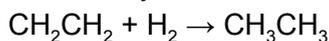
Addition with hydrogen halides:

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.



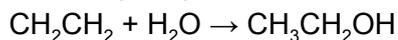
Addition with hydrogen:

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 nickel catalyst.

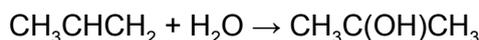


Addition with steam:

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



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:



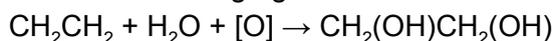
Using Markovnikov's rule, propan-2-ol is the major product and propan-1-ol is the minor product. The reaction will mostly produce propan-2-ol.

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.

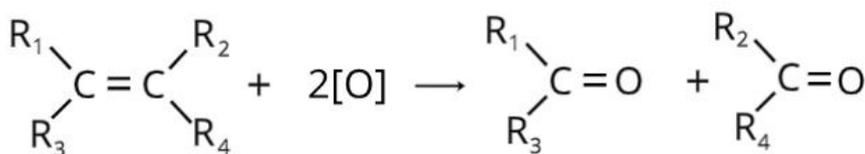
In the reaction below, [O] denotes the oxidising agent:



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 form **water and carbon dioxide**.

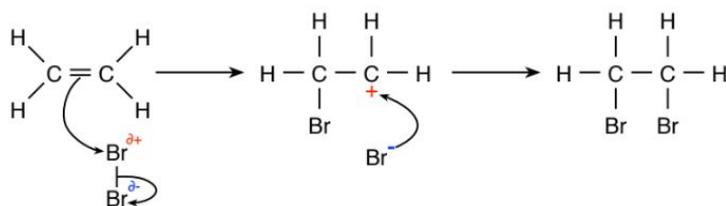


Polymerisation

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. Further details about addition polymerisation can be seen through the examples of **poly(ethene)** and **PVC** in 'Characteristics of addition polymerisation'.

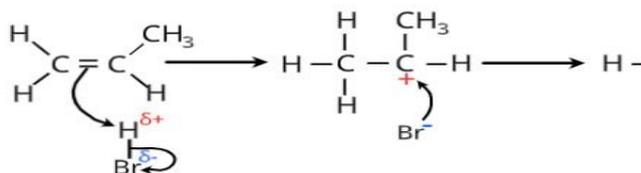
Electrophilic addition

Mechanism for Br₂ and ethene



The **electron dense double bond** in ethene causes an **uneven distribution of electrons in Br₂**. This causes a difference in charge between the two bromine atoms (dipoles form). The electron pair in the double bond attracts the **Br^{δ+}**, 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

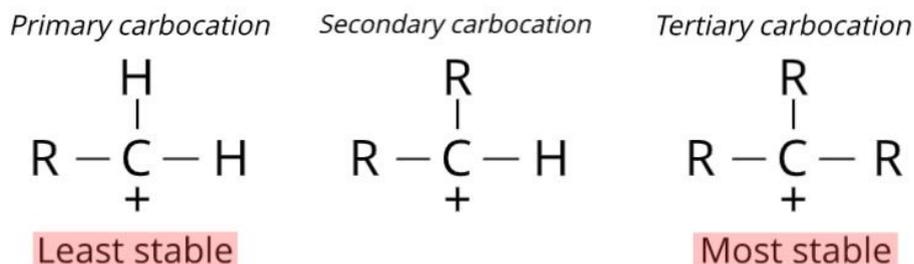


Hydrogen bromide is **polar** due to the difference in the electronegativities of hydrogen and bromine. The **electron pair** in the double bond attracts **H^{δ+}**, forming a covalent bond between carbon and hydrogen. This produces a positively charged **carbocation intermediate** which attracts the negatively charged bromide ion. According to **Markovnikov's rule**, the hydrogen joins 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**.



Characteristics of addition polymerisation

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

The chains are held together by **van der Waals** forces since there is generally no polarity in the main carbon chain. Polymers made up of **straight chains are strong and rigid** because the chains are able to **lie closer** together and so there are more points of contact and stronger **van der Waals forces**. Polymers made up of branched chains are usually weaker by comparison

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.

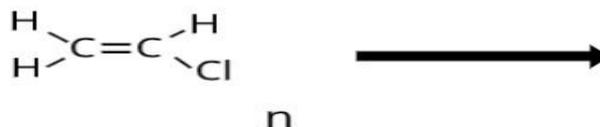


For the equation above, the '**n**' denotes a **large number of units** reacting together to form a chain with this unit length.



Poly(chloroethene) (PVC)

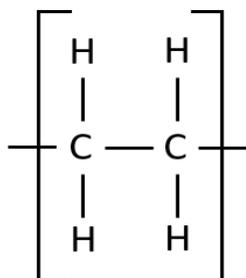
Poly(chloroethene), otherwise known as PVC, is produced from the addition polymerisation of **chloroethene**. Chloroethene is the **monomer** which forms the polymer poly(chloroethene).



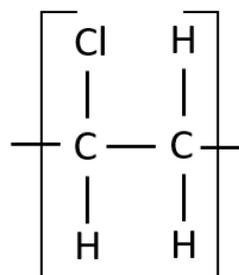
Repeat units

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:



Disposal of polymers

Polymers produced by addition polymerisation cause problems when it comes to disposal. This is because they are **not biodegradable**.

This means many polymers have to be **incinerated** or put into **landfill**, both of which have issues associated with them.

Landfill takes up a lot of land which could otherwise be used as **habitats for wildlife**. It is also **unattractive**.

Incineration of polymers **release harmful gases like carbon dioxide and HCl** (if the polymer contains chlorine) during combustion. However, the incineration of polymers produces a lot of energy which can be used to generate electricity.



Hydrocarbons as fuels

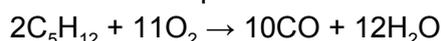
Combustion of alkanes

Alkanes make **good fuels** because they release **huge amounts of energy** when burnt. They are also relatively readily **available**, they **burn cleanly** in excess oxygen and are **easy to transport**. Alkanes are used as fuels in industry, cars and in the home.

However, the combustion of alkanes produces a **variety of pollutants**.

Carbon monoxide

When a hydrocarbon is combusted in a limited supply of oxygen, **incomplete combustion** occurs which can produce carbon monoxide. For example:



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. This can **kill** people if they too much is inhaled.

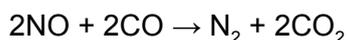
Oxides of nitrogen

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** (see 'Unburnt hydrocarbons' below).

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**.

Oxides of nitrogen can be removed from car exhaust fumes with **catalytic converters**. Catalytic converters contain a ceramic honeycomb structure which is coated in a thin layer of metal catalysts like **rhodium** and **platinum**. This creates a **larger surface area** of metal. Catalytic converters catalyse the reaction between carbon monoxide with nitrogen monoxide (harmful gases) to produce nitrogen and carbon dioxide.



Unburnt hydrocarbons

Unburnt hydrocarbons are released when **engines don't completely burn all the fuel molecules**. These hydrocarbons and oxides of nitrogen react in the **presence of sunlight** to form O_3 , **ground level ozone**. This is an **irritant** to people's eyes and causes **respiratory problems**. It can ultimately cause **lung damage**.



Greenhouse gases

Greenhouse gases include **carbon dioxide**, **methane** and **water vapour**.

The greenhouse effect

- **Electromagnetic radiation** from the sun passes through the Earth's atmosphere.
- The Earth **absorbs some radiation** and warms up.
- Heat is radiated from the Earth as **infrared radiation**.
- Some of the **infrared radiation is absorbed by greenhouse gases** in the atmosphere which warms the atmosphere.

Infra-red spectroscopy to monitor air pollution

Infra-red spectroscopy **identifies particular bonds** within molecules. Different polluting gases contain different bonds so they will have a **different infra-red spectrum**. This can be used to identify which gases are in the air. It is then possible to measure the **concentration of each pollutant**. This can be recorded over a period of time to monitor the changes in air pollution.

Arenes (A Level only)

Arenes are aromatic hydrocarbons.

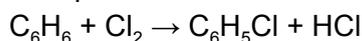
Substitution

Aromatic hydrocarbons, such as benzene, are able to undergo **electrophilic substitution**.

Benzene's **delocalised electron system** makes it a very **stable** molecule. Benzene is highly **attractive to electrophiles** because of the high electron density in the benzene ring. Electrophiles can be a positive ion or a positive end of a polar molecule. When the reaction takes place, the delocalised electron system remains in the compound and one of the **hydrogen atoms swaps places with the electrophile**. Various different types of substitution reactions can take place:

Substitution with chlorine

The reaction of benzene with chlorine requires an **aluminium chloride catalyst**.

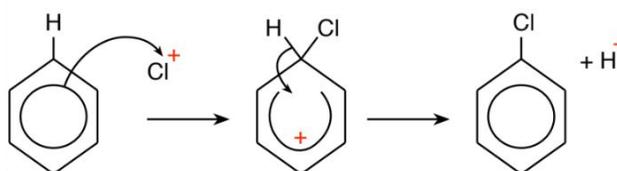


The mechanism for the electrophilic substitution reaction:

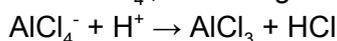
Stage 1: The aluminium chloride catalyst generates the electrophile from chlorine.



Stage 2: The electrophile reacts with the benzene molecule.



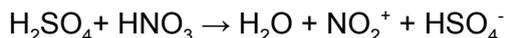
Stage 3: The hydrogen ion reacts with the AlCl_4^- , reforming the AlCl_3 catalyst.



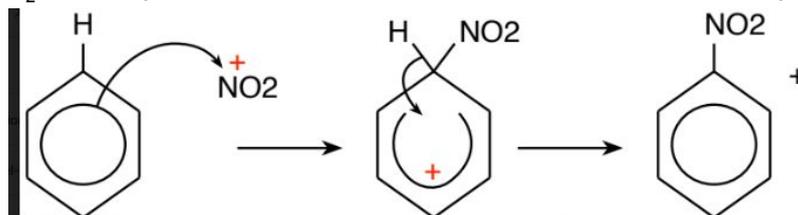
Substitution - nitration

The reaction of benzene to form nitrobenzene requires a mixture of **concentrated nitric acid and concentrated sulfuric acid to generate the electrophile.**

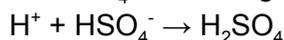
Stage 1: The electrophile is generated from concentrated nitric acid and concentrated sulfuric acid.



Stage 2: The NO_2^+ electrophile reacts with the benzene molecule in electrophilic substitution.



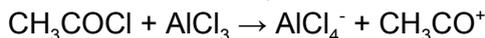
Stage 3: The hydrogen ion reacts with the HSO_4^- , reforming the H_2SO_4 catalyst.



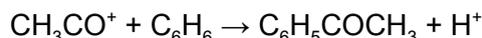
Acylation

Acylation of benzene involves the **substitution of an acyl group**. This reaction takes place when benzene is reacted with **ethanoyl chloride** in the presence of an **aluminium chloride catalyst**.

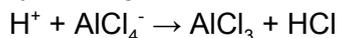
Stage 1: The electrophile is generated from ethanoyl chloride and aluminium chloride.



Stage 2: The CH_3CO^+ electrophile reacts with the benzene molecule.



Stage 3: The aluminium chloride catalyst is regenerated.



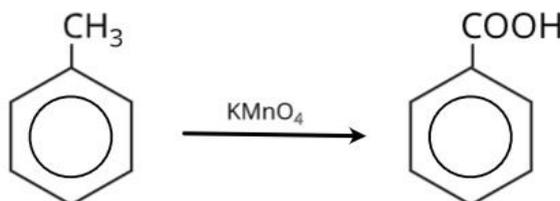
Alkylation

Alkylation of benzene involves the **substitution of an alkyl group**. The reaction occurs in the same way as the acylation reaction takes place above. It requires a **halogenoalkane** as a reactant as they contain a **polar bond** between the carbon and halogen.



Complete oxidation of side chains

If an alkyl group is attached to benzene, it can be easily oxidised to form benzoic acid. They can be oxidised using the oxidising agent, **potassium manganate(VII)**.

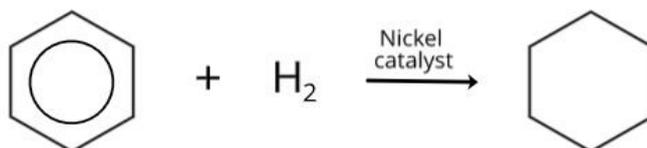


Hydrogenation

Hydrogenation takes place when **hydrogen atoms are added all around the benzene ring**, removing the delocalised electron system. A **cycloalkane** is formed as the product. The reaction is



carried out with hydrogen, in the presence of a **nickel catalyst**. A temperature around **150°C** is required.



Difference in reactivity between chlorobenzene and chloroalkane

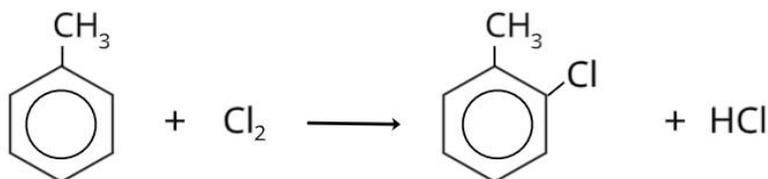
Chlorobenzene is much less reactive than chloroalkane. This is because the C-Cl bond in chlorobenzene is much stronger than in an halogenoalkane. **The aromatic C-Cl bond is stronger** due to one of the lone pairs on the chlorine atom interacting with the delocalised electron system, strengthening the bond. For reactions, like nucleophilic substitution, the C-Cl bond would require breaking. Since the chlorobenzene bond requires more energy to break, chlorobenzene is less reactive.

Halogenation (A Level only)

When a halogen reacts with methylbenzene, two possible reactions can take place depending on the conditions. The halogen can bond to the benzene ring or the methyl group.

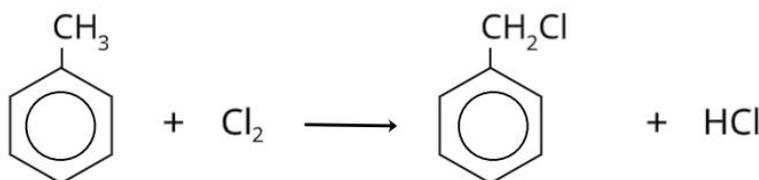
Substitution in the benzene ring

This reaction happens in the presence of **aluminium chloride** and in the **absence of UV light**.



Substitution in the methyl group

This reaction happens in the **presence of UV light**, without a catalyst.



The reaction can **continue to undergo substitution** so that all the hydrogen atoms on the methyl group are replaced by chlorine atoms, forming $\text{C}_6\text{H}_5\text{CCl}_3$.

