Edexcel International AS Chemistry

Your notes

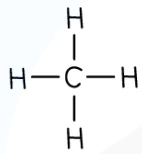
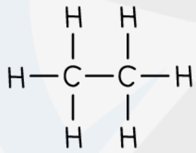
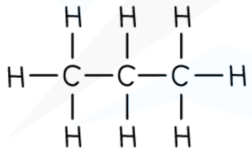
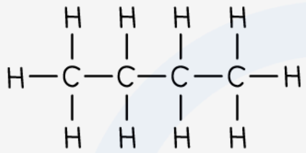
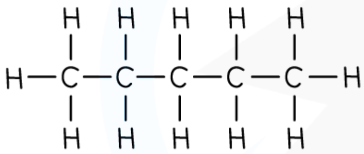
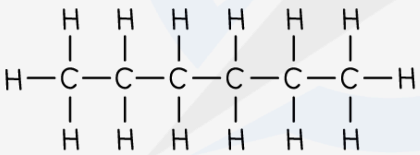
Alkanes

Contents

Alkanes – Introduction

- **Hydrocarbons** are compounds containing hydrogen and carbon only
- Some of the hydrocarbon families that you are expected to know include: **alkanes, alkenes** and **arenes**
  - Alkanes and alkenes can be described as **aliphatic**
  - Arenes can be described as **aromatic**
- Alkanes have the general molecular formula $\mathbf{C_nH_{2n+2}}$
- They contain only **single bonds** and are said to be **saturated**
- Alkanes are named using the nomenclature rule **alk + ane**
  - The **alk** portion of the name depends on the number of carbons
    - 1 carbon = meth
    - 2 carbons = eth
    - 3 carbons = prop
    - 4 carbons = but
    - 5 carbons = pent
    - After 5 carbons, the naming of alkanes matches the names of the polygons in Maths
  - The **ane** portion of the name suggests single bonds between the carbon atoms

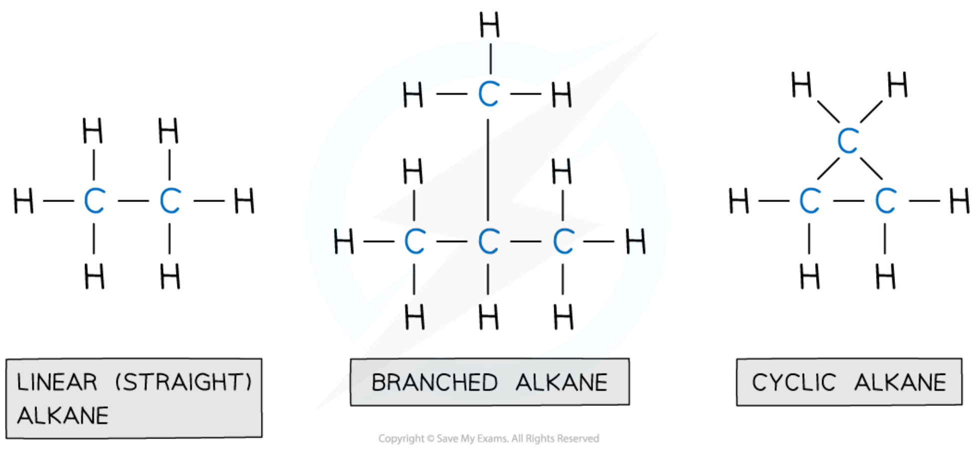
The First Six Members of the Alkane Family

Structural Formula	Name	Molecular Formula
	methane	CH_4
	ethane	C_2H_6
	propane	C_3H_8
	butane	C_4H_{10}
	pentane	C_5H_{12}
	hexane	C_6H_{14}

- Alkanes can be linear, branched or cyclic
  - The key points are that there are no functional groups and only single bonds between the carbon atoms
- Cycloalkanes have the general formula $\mathbf{C_nH_{2n}}$
  - This general formula is the same as the alkene general formula but cycloalkanes are still saturated
  - Cycloalkanes are named using the nomenclature rule **cyclo + alk + ane**

Your notes

- The **cyclo** portion of the name shows that there is a ring stucture
- As with alkanes, the **alk** portion of the name depends on the number of carbons
- The **ane** portion of the name suggests single bonds between the carbon atoms



Alkanes are compounds made up of carbon and hydrogen atoms only and contain no functional group

Alkanes – Reactions

- The **unreactive** nature of alkanes can be explained by two factors
  - The **high bond enthalpies** of the C-C and C-H bonds
  - The very **low polarity** of the sigma (σ) bonds present

Bond enthalpy

- The C-C bond has a bond enthalpy of 316 kJ mol^{-1} and the C-H bond has a bond enthalpy of 411 kJ mol^{-1}
- The C-H bond is stronger as the bond length is less than the C-C bond
  - This is because the hydrogen atom only consists of one shell, so the distance between the nuclei is shorter
  - Creating greater force of attraction to the nuclei and the pair of electron between them

Polarity

- The electronegativities of carbon and hydrogen are very similar, therefore the bonds will have very low polarity

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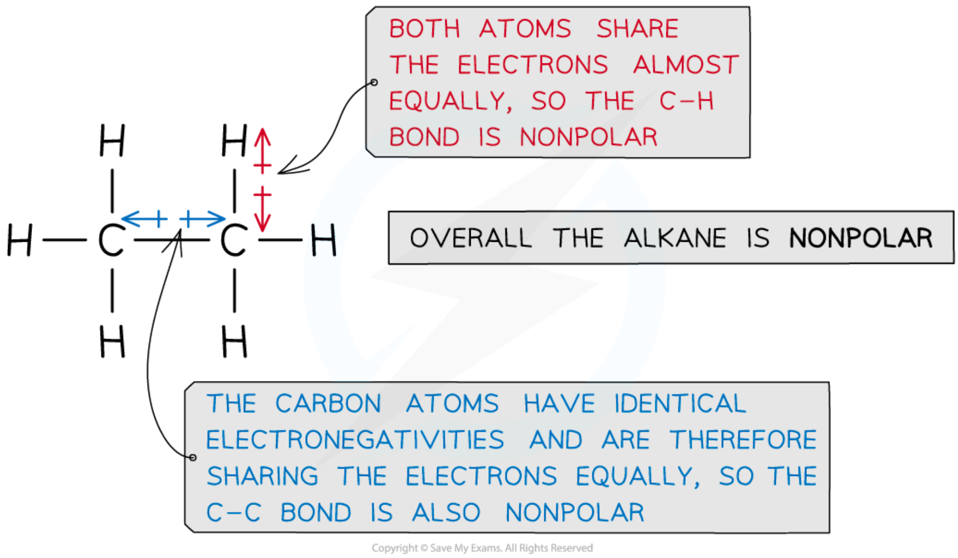
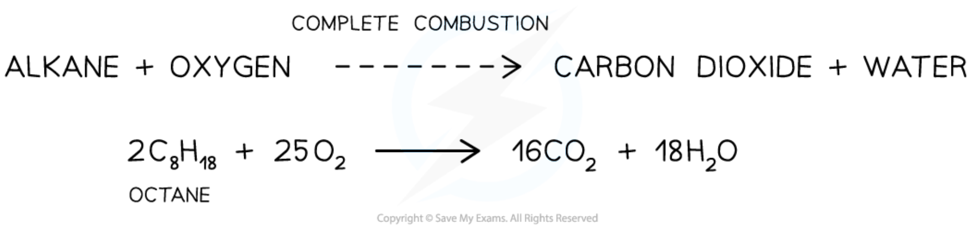


Ethane is an example of an alkane that lacks polarity due to almost similar electronegativities of the carbon and hydrogen atoms

Alkanes are **combusted** (burnt) on a large scale for their use as fuels

Complete combustion

- When alkanes are burnt in **excess** (plenty of) oxygen, **complete combustion** will take place and all carbon and hydrogen will be oxidised to **carbon dioxide** and **water** respectively
    - For example, the complete combustion of octane to carbon dioxide and water



The complete combustion of alkanes

Incomplete combustion

- When alkanes are burnt in only a **limited supply** of oxygen, **incomplete combustion** will take place and not all the carbon is fully oxidised
- Some carbon is only **partially** oxidised to form **carbon monoxide**
    - For example, the incomplete combustion of octane to form carbon monoxide

Your notes

$$\text{ALKANE} + \text{OXYGEN} \xrightarrow{\text{INCOMPLETE COMBUSTION}} \text{CARBON MONOXIDE} + \text{WATER}$$

$$\underset{\text{OCTANE}}{2C_8H_{18}} + 17\,O_2 \xrightarrow{\text{INCOMPLETE COMBUSTION}} 16CO + 18H_2O$$

The incomplete combustion of alkanes

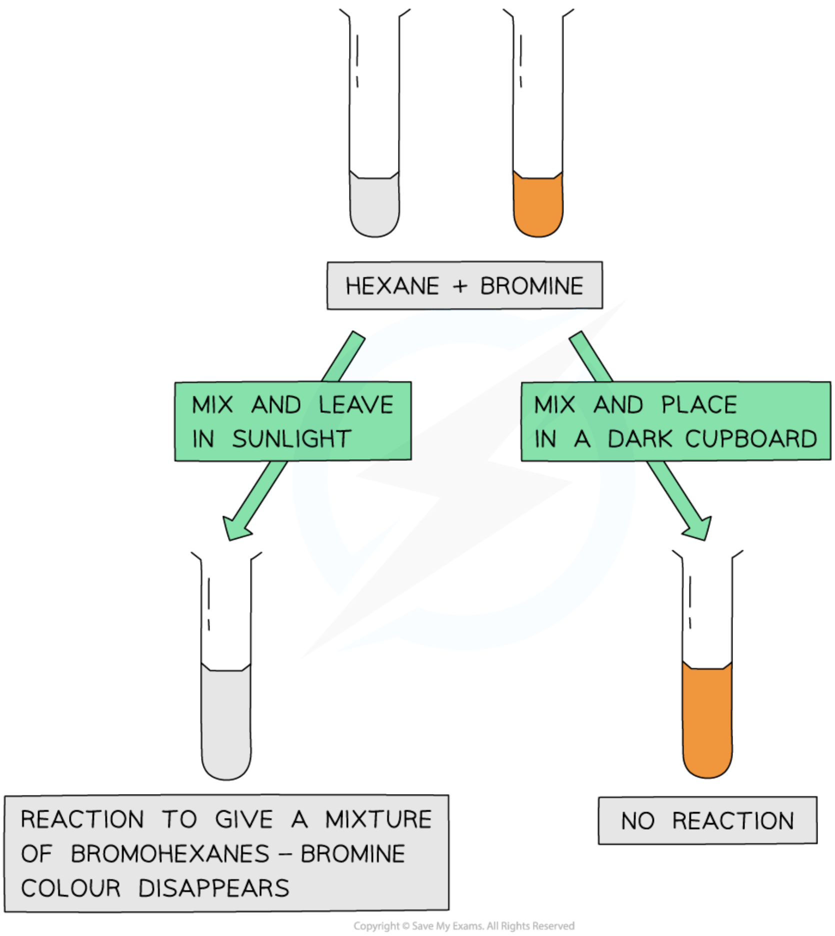
- Incomplete combustion often takes place inside a **car engine** due to a limited amount of oxygen present
- With a reduced supply of oxygen, **carbon** will be produced in the form of soot:

$$\text{ALKANE} + \text{OXYGEN} \xrightarrow{\text{INCOMPLETE COMBUSTION}} \text{CARBON} + \text{WATER}$$

$$2C_8H_{18} + 9O_2 \xrightarrow{\text{INCOMPLETE COMBUSTION}} 16C + 18H_2O$$

Free-radical substitution

- Alkanes can undergo **free-radical substitution** in which a hydrogen atom gets **substituted** by a halogen (chlorine / bromine)
- Since alkanes are very unreactive, **ultraviolet** light **(sunlight)** is needed for this substitution reaction to occur
- The free-radical substitution reaction consists of three steps:
  - In the **initiation step**, the halogen bond (Cl-Cl or Br-Br) is broken by UV energy to form two radicals
  - These radicals create further radicals in a chain reaction called the **propagation step**
  - The reaction is terminated when two radicals collide with each other in a **termination step**
- Alkanes can undergo **free-radical substitution** in which a hydrogen atom gets **substituted** by a halogen (chlorine/bromine)
  - **Ultraviolet** light **(sunlight)** is needed for this substitution reaction to occur



The fact that the bromine colour has disappeared only when mixed with an alkane and placed in sunlight suggests that the ultraviolet light is essential for the free radical substitution reaction to take place

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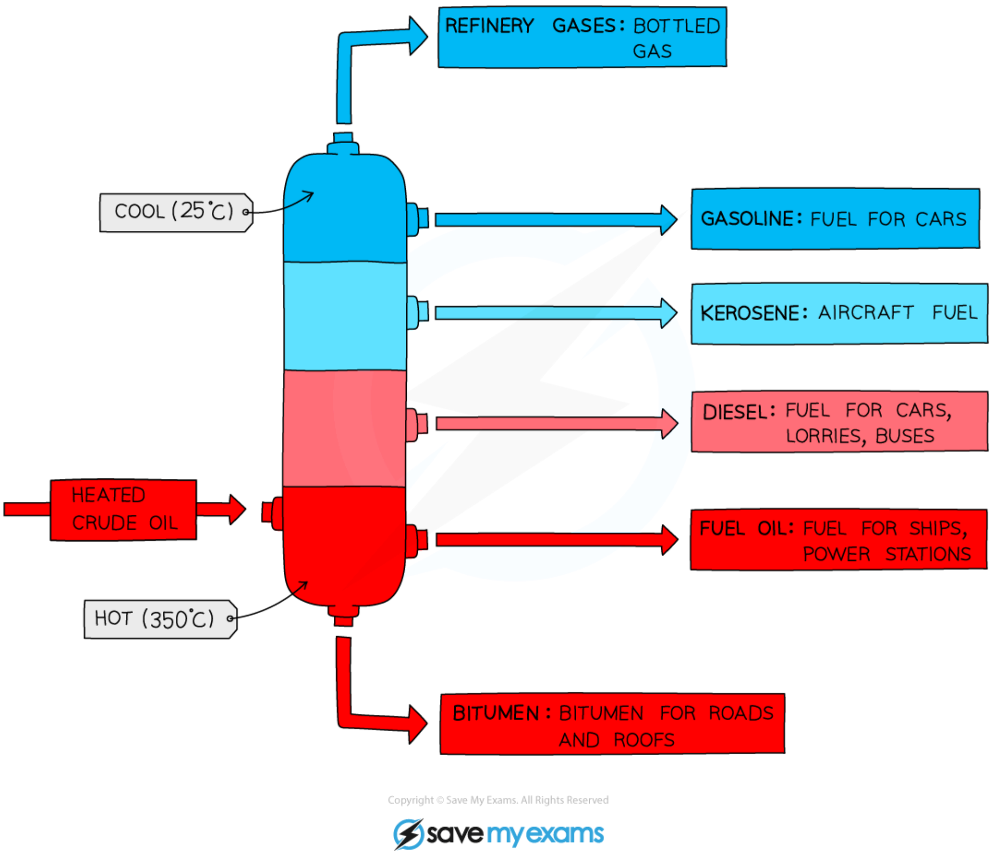
Alkanes as Fuels

- Alkanes are obtained from the **fractional distillation** and **cracking** of crude oil

Fractional distillation of crude oil

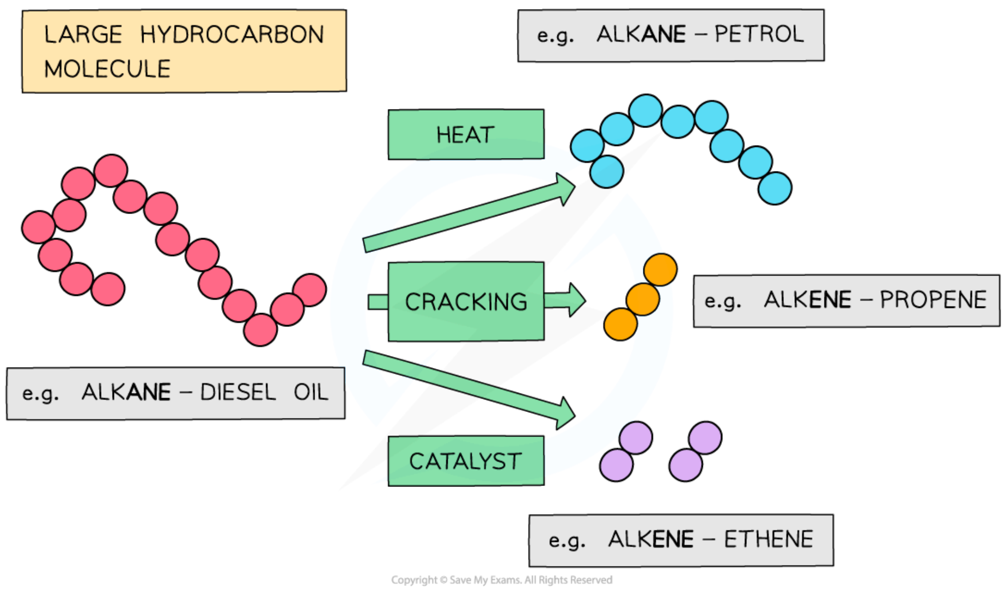
- Crude oil is a **mixture** of hydrocarbons containing **alkanes**, **cycloalkanes** and **arenes** (compounds with a benzene ring)
- The crude oil is extracted from the earth in a drilling process and transported to an oil refinery
- At the oil refinery the crude oil is separated into useful fuels by fractional distillation
  - This is a separating technique in which the wide range of different hydrocarbons are separated into fractions based on their boiling points



Crude oil is initially separated into fractions with similar boiling points in a process called fractional distillation

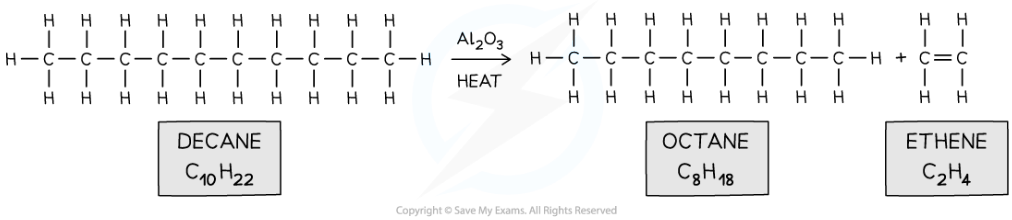
Cracking of crude oil fractions

- However, the smaller hydrocarbon fractions (such as gasoline fractions) are in high demand compared to the larger ones
- Therefore, some of the **excess** heavier fractions are broken down into smaller, **more useful compounds**
- These more useful compounds include **alkanes** and **alkenes** of **lower** relative formula mass (**M_r**)
- This process is called **cracking**



The heavier fractions that are obtained in fractional distillation are further cracked into useful alkane and alkenes with lower M_r values

- When a large hydrocarbon is cracked, a **smaller alkane** and **alkene** molecules are formed
  - E.g.. octane and ethene from decane



Long hydrocarbon fraction is cracked into two smaller ones

- The **low-molecular mass alkanes** formed make good fuels and are in high demand
- There are two types of cracking:

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- **Thermal cracking** requires high temperatures (up to 1000 °C) and high pressure (up to 70 atmospheres) and produces alkanes and a lot of alkenes
- **Catalytic cracking** uses a lower temperature (around 450 °C) and slight pressure in the presence of a catalyst such as a zeolite or aluminium oxide to produce mainly aromatic hydrocarbons

Reforming alkanes

- Many vehicles run on petrol or diesel which are both a mixture of alkanes along with other hydrocarbons, impurities and additives
- Many of the alkanes in these fuels are straight chain alkanes
- These straight chain alkanes are more likely to explode, rather than combust, inside the engine
  - This is known as **knocking** and makes the combustion less efficient
- To reduce this straight chain alkanes are **reformed** into:
  - Branched alkanes, e.g. octane → 2,5-dimethylhexane

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 \rightarrow CH_3CH\mathbf{(CH_3)}CH_2CH_2CH\mathbf{(CH_3)}CH_3$$

- Cycloalkanes, e.g. hexane → cyclohexane

$$CH_3CH_2CH_2CH_2CH_2CH_3 \rightarrow C_6H_{12} + H_2$$

- Reforming often uses a platinum catalyst

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Problems of Pollution – General

- When alkanes are burnt in **excess** (plenty of) oxygen, **complete combustion** will take place and all carbon and hydrogen will be oxidised to **carbon dioxide** and **water** respectively
- When alkanes are burnt in only a **limited supply** of oxygen, **incomplete combustion** will take place and not all the carbon is fully oxidised
  - Some carbon is only **partially** oxidised to form **carbon monoxide**
- Incomplete combustion often takes place inside a **car engine** due to a limited amount of oxygen present
- With a reduced supply of oxygen, **carbon** will be produced
- Solid carbon particles (or **particulates**) released from incomplete combustion clump together to form **soot** which gradually falls back to the ground

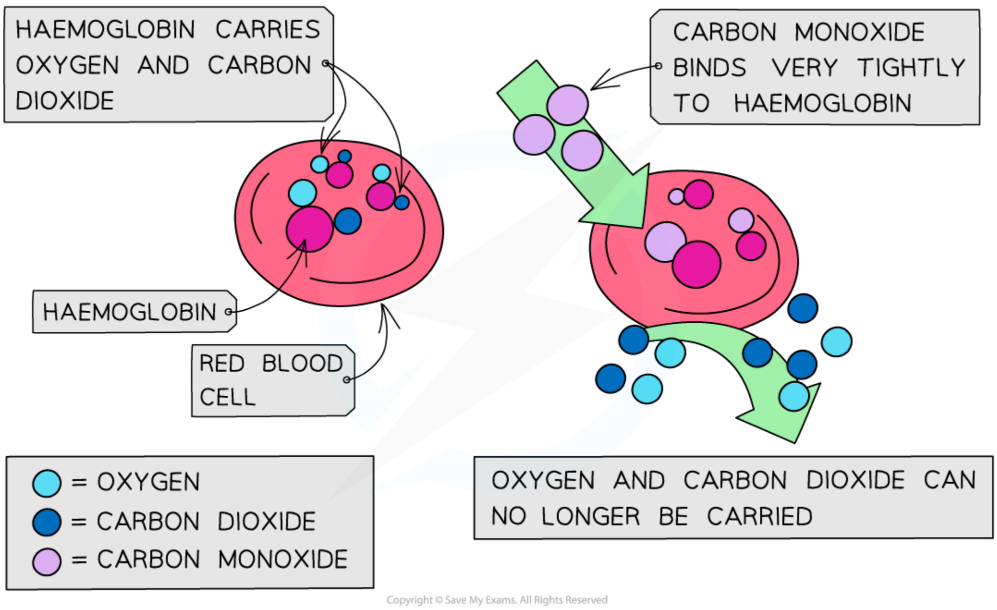
$$\text{ALKANE} + \text{OXYGEN} \xrightarrow{\text{INCOMPLETE COMBUSTION}} \text{CARBON} + \text{WATER}$$

$$2C_8H_{18} + 9O_2 \xrightarrow{\text{INCOMPLETE COMBUSTION}} 16C + 18H_2O$$

- Car **exhaust fumes** include toxic gases such as **carbon monoxide** (CO), **oxides of sulfur**, **oxides of nitrogen** (NO/NO_2) and **volatile organic compounds** (VOCs)
- When released into the atmosphere, these pollutants have serious environmental consequences damaging nature and health

Carbon monoxide

- CO is a toxic and odourless gas which can cause dizziness, loss of consciousness and eventually death
  - The CO binds well to haemoglobin which therefore cannot bind oxygen and carbon dioxide
  - Oxygen is transported to organs
  - Carbon dioxide is removed as waste material from organs



The high affinity of CO to haemoglobin prevents it from binding to O_2 and CO_2

Oxides of sulfur

- Some of the crude oil products from fractional distillation, cracking and reforming contain sulfur atoms
- When these molecules are combusted, the sulfur atoms form sulfur dioxide and sulfur trioxide
  - Both of these sulfur oxides are acidic

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

- When these acidic sulfur oxides dissolve into water in the atmosphere, they form sulfurous and sulfuric acid

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

- Both of these acids contribute to acid rain, which is responsible for various environmental issues:
  - Damage / death of aquatic life
  - Damage / death to crops and forests
  - Release of carbon dioxide from carbonate rocks and building materials
  - Corrosion of metallic structures

Oxides of nitrogen

Your notes

Your notes

- Normally, nitrogen is too unreactive to react with oxygen in air
- However, in a car engine, high temperatures and pressures are reached causing the oxidation of nitrogen to take place:

$$N_2 + O_2 \rightarrow 2NO$$

$$N_2 + 2O_2 \rightarrow 2NO_2$$

- The **oxides of nitrogen** are then released in the exhaust fumes into the atmosphere
- Car exhaust fumes also contain **unburnt hydrocarbons** from fuels and their **oxides** (VOCs)
- In air, the nitrogen oxides can react with these VOCs to form **peroxyacetyl nitrate** (PAN) which is the main pollutant found in **photochemical smog**
  - PAN is also harmful to the lungs, eyes and plant-life
- Nitrogen oxides can dissolve in water to form nitrous and nitric acid:

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

- Nitrogen oxides can also react with water and oxygen to form nitric acid:

$$4NO_2\,(g) + 2H_2O\,(l) + O_2\,(g) \rightarrow 4HNO_3\,(aq)$$

- Nitric and nitrous acids are a cause of **acid rain**, which can corrode buildings, endanger plant and aquatic life (as lakes and rivers become too **acidic**) as well as directly damaging human health

Pollutants, their Effect & Removal Table

Your notes

	Formation	Environmental Consequence	Catalytic Removal
Carbon Monoxide	Incomplete combustion of alkanes in car engines	Toxic gas	Oxidation to CO_2: $2CO + O_2 \longrightarrow 2CO_2$ OR $2CO + 2NO \longrightarrow 2CO_2 + N_2$
Oxides of Nitrogen	Oxidation of nitrogen in car engines	Dissolve in and react in water with oxygen to form acid rain	Reduction to nitrogen gas: $2CO + 2NO \longrightarrow 2CO_2 + N_2$
VOCs	Unburnt hydrocarbons from fuels and their oxides formed in car engines	React with oxides of nitrogen in the atmosphere to produce PAN	Oxidise unburnt hydrocarbons to carbon dioxide and water: $C_nH_{2n+2} + (3n + 1)[O] \longrightarrow nCO_2 + (n + 1)H_2O$
PAN	From the photochemical reaction of VOCs and nitrogen oxides in the atmosphere	Photochemical smog	Oxidise unburnt hydrocarbons and reduce nitrogen oxides to prevent formation of PAN in the atmosphere

Reducing Emissions

- To reduce the amount of pollutants released in car exhaust fumes, many cars are now fitted with **catalytic converters**
- Precious metals (such as platinum, rhodium and palladium) are coated on a honeycomb to provide a **large surface area**
- The reactions that take place in the catalytic converter include:
  - Oxidation of unburnt hydrocarbons:

$$C_nH_{2n+2} + (3n+1)[O] \rightarrow nCO_2 + (n+1)H_2O$$

- Oxidation of CO to CO_2:

$$2CO + O_2 \rightarrow 2CO_2$$

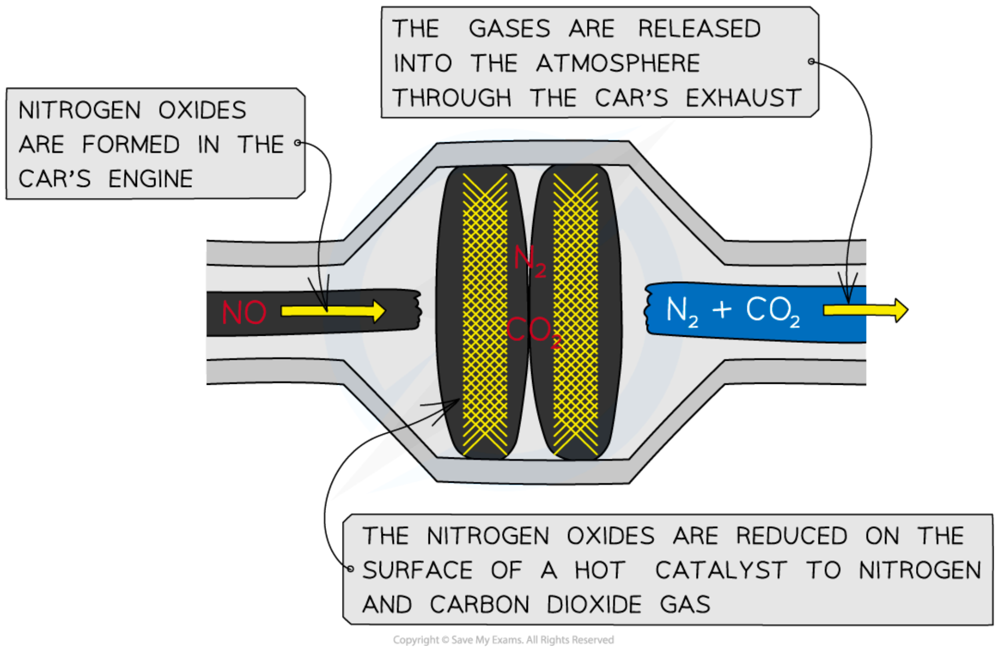
or

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

Catalytic removal of NO_x and CO

- Carbon monoxide and the nitrogen oxides released through cars' exhaust fumes **pollute** the atmosphere
- The nitrogen oxides are **reduced** on the surface of the **hot catalyst** to form the unreactive and harmless nitrogen gas which is then released from the vehicle's exhaust pipe into the atmosphere
- The chemical reaction for the reduction of nitrogen oxide to nitrogen gas by the catalyst is as follows:

$$2CO\,(g) + 2NO\,(g) \rightarrow 2CO_2\,(g) + N_2\,(g)$$



A catalytic converter helps reduce the pollutants from motor vehicles

Alternative fuels

- There are a number of reasons for finding and developing alternative fuels:
  - Reducing pollution from the combustion of fossil fuels, including issues associated with global warming and climate change
  - The limited amount and depletion of **non-renewable fossil fuels** are two reasons for finding alternative fuels
- Biofuels are **renewable** fuels
  - Renewable meaning that they can be replaced over a short period of time
  - The bio part of biofuel meaning that it comes from living matter
- The three main biofuels are **biodiesel**, **bioethanol** and **biogas**
  - Biodiesel - made by refining renewable fats and oils
  - Bioethanol - made by fermentation
  - Biogas - made / released when organic waste breaks down

Benefits of biofuels

- Biofuels are often considered as **carbon neutral**
- Biodiesel and biogas can reduce the amount of waste going to landfill as the waste can be used to produce them
- Biofuel production could provide money for less developed countries as they have the space to grow the crops required

Your notes

Drawbacks of biofuels

- The cost of converting engines and machinery to run on biofuels instead of petrol / diesel
- Many developed countries don't have the space to be able to produce enough plants to make the biofuels because the land is needed for food production

Greenhouse Gases

- When shortwave radiation from the sun strikes the Earth's surface it is absorbed and re-emitted from the surface of the Earth as infrared radiation
- Much of the radiation, however, is trapped inside the Earth's atmosphere by greenhouse gases which can absorb and store the energy
- **Carbon dioxide**, **methane** and **water vapour** are gases that have this effect
- Increasing levels of carbon dioxide, although present in only a small amount, is causing significant upset to the Earth's natural conditions by trapping extra heat energy
- This process is called the enhanced greenhouse effect

Carbon Neutrality

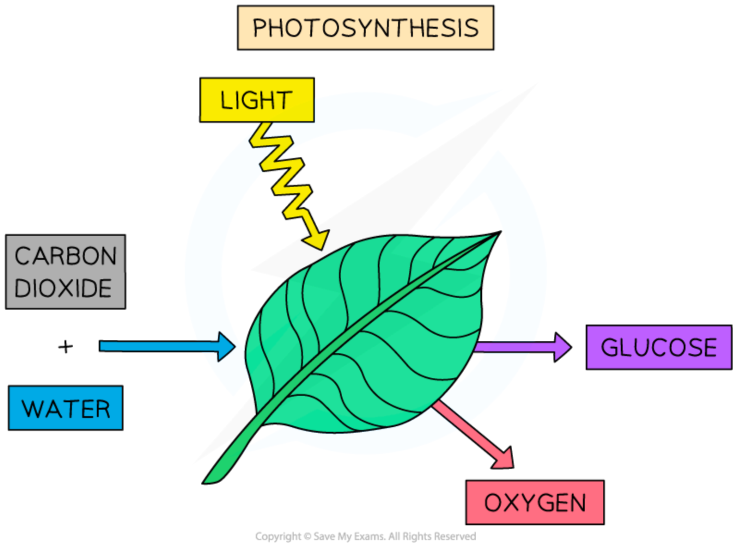
- Carbon neutral is defined as a net-zero effect on the amount of carbon dioxide in the atmosphere
- Hydrogen gas is an important carbon neutral fuel that produces only water when it combusts

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$$

- Although it produces a large amount of energy, the low density of hydrogen means you need large amounts compared to fossil fuels to give the same amount of energy per gram
  - Along with its explosive nature, this results in storage problems when using hydrogen as a fuel
  - Producing hydrogen is not cheap, so although it qualifies as a carbon neutral fuel its widespread use remains limited
- Biofuels are commonly thought of as being plant-based
  - As a plant grows, it absorbs carbon dioxide from the atmosphere during photosynthesis
  - When the plant is then burnt as a fuel it releases the carbon that is stored as carbon dioxide
  - If the amount of carbon dioxide during growth is the same as the amount of carbon dioxide released during combustion, then this is considered to be carbon neutral

Your notes

Your notes



As a plant grows, it absorbs carbon dioxide from the atmosphere during photosynthesis

- There is an argument for fossil fuels being carbon neutral because they are releasing the carbon dioxide that they absorbed millions of years ago
  - However, they are not carbon neutral because they absorbed carbon dioxide millions of years ago when the levels of carbon dioxide in the atmosphere were higher than the present day
- Biofuels are considered to be carbon neutral, although this is not necessarily true
  - There is no consideration for the carbon dioxide used in their production, harvesting, manufacture and any transport involved
- Biofuel is a generic term applied to any fuel that is considered to have a biological (often plant-based) origin and is an indication of the way that the fuel was produced
- One of the most common biofuels is bioethanol, which is the same as ethanol
- It is produced by the fermentation of sugars using yeast enzymes
- There is a limit to the concentration of ethanol in solution that can be produced using this method, although more efficient and higher yield processes are being developed
- The separation of the ethanol from the solution is one of the reasons that bioethanol can be argued not to be carbon neutral
- The following four points are the major considerations for biofuels:
  1. Land - should the land used for biofuel production be used for food production instead?
  2. Yield - what volume of biofuel can be produced in the land provided? What percentage of the crop becomes useful fuel?
  3. Manufacture and transport - what are the energy costs involved in growing, harvesting, processing and transporting the biofuel from crop to finished product?

4. Carbon neutrality - how close is the finished product (including manufacture and transport) to being carbon neutral?

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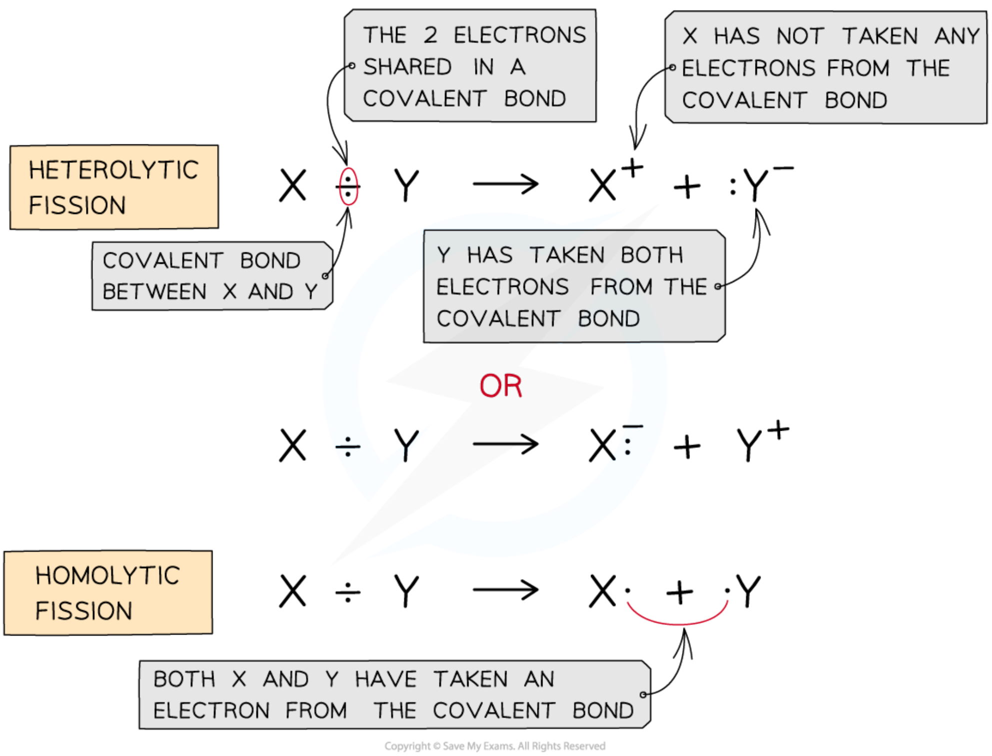
Free Radicals & Fission

- In chemical reactions, there are two types of fission or bond breaking:

  1. **Heterolytic fission**
  2. **Homolytic fission**

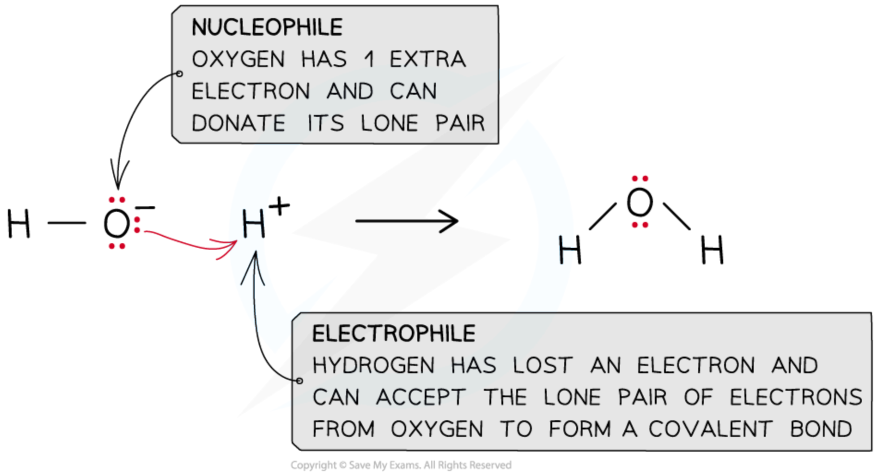


The diagram shows heterolytic fission in which the most electronegative atom takes both electrons in the covalent bond and homolytic fission in which each atom takes one electron from the covalent bond

Heterolytic fission

- Heterolytic fission is breaking a covalent bond in such a way that the more electronegative atom takes both the electrons from the bond to form a negative ion and leaving behind a positive ion
- In heterolytic fission, a double-headed arrow is used to show the movement of a **pair of electrons**
- The resulting negative ion is an electron-rich species that can **donate** a pair of electrons
  - This makes the negative ion a **nucleophile**
- The resulting positive ion is an electron-deficient species that can **accept** a pair of electrons

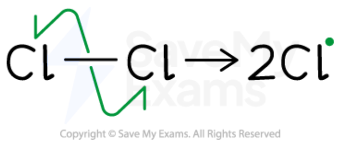
- This makes the positive ion an **electrophile**



A nucleophile 'loves' a positive charge and an electrophile 'loves' a negative charge

Homolytic fission

- Homolytic fission is breaking a covalent bond in such a way that each atom takes an electron from the bond to form two free radicals
  - A free radical is a species that contains an unpaired electron
- In homolytic fission, single-headed (or fishhook) arrows are used to show the movement of a **single electron**



The homolytic fission of a chlorine-chlorine bond results in the formation of two chlorine-free radicals

- Each atom involved in the original bond receives one of the two bonding electrons
  - This makes each atom into a free radical

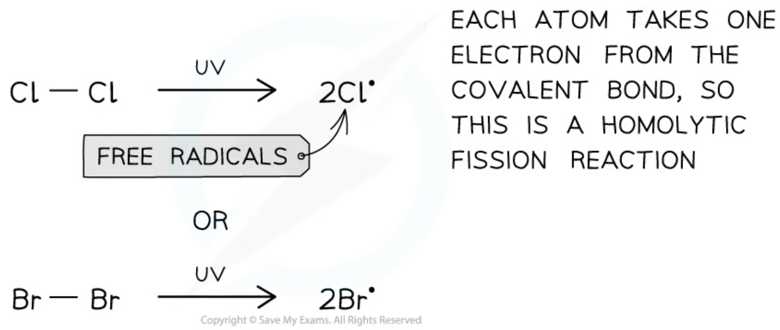
Your notes

Free Radical Substitution – Mechanism

- The free-radical substitution reaction consists of three steps:

Initiation step

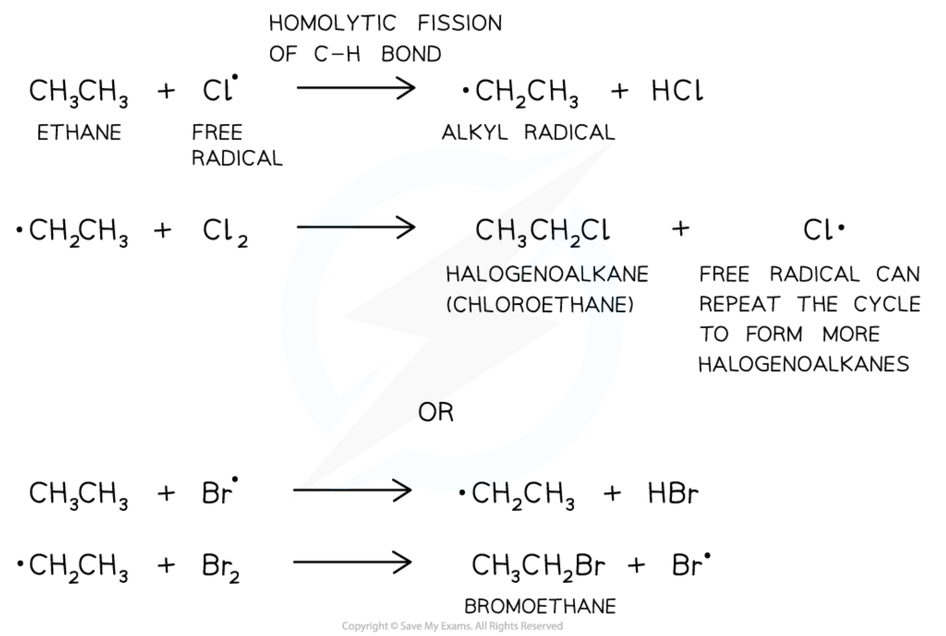
- In the **initiation step**, the Cl-Cl or Br-Br is broken by energy from the UV light
- This produces two radicals in a **homolytic fission** reaction



The first step of the free-radical substitution reaction is the initiation step, in which two free radicals are formed by sunlight

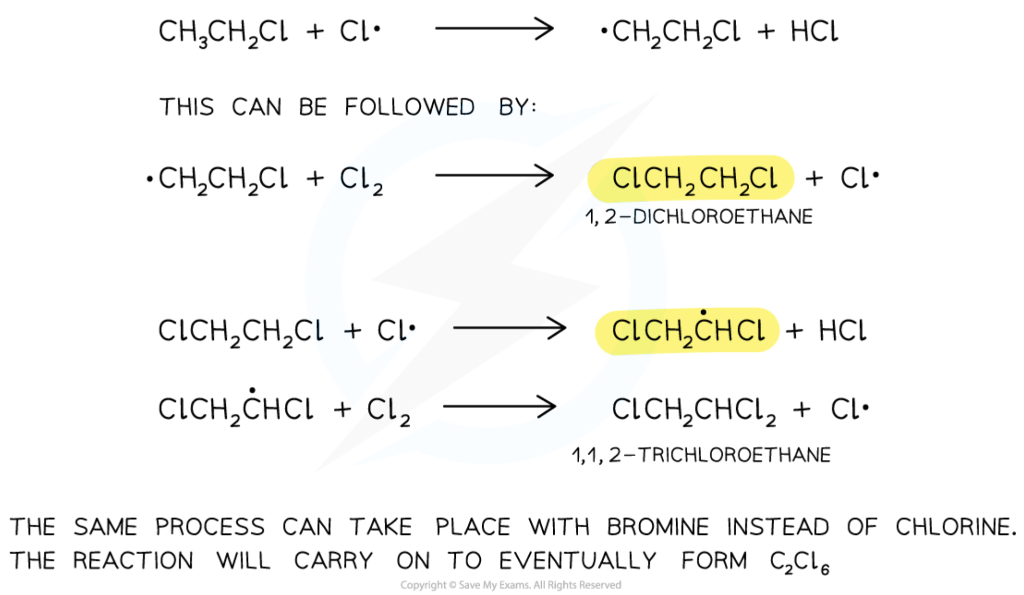
Propagation step

- The **propagation step** refers to the **progression** (growing) of the substitution reaction in a **chain reaction**
  - **Free radicals** are very reactive and will attack the unreactive alkanes
  - A C-H bond breaks **homolytically** (each atom gets an electron from the covalent bond)
  - An **alkyl** free radical is produced
  - This can attack another chlorine/bromine molecule to form the **halogenoalkane** and **regenerate** the chlorine/bromine free radical
  - This free radical can then **repeat** the cycle



The second step of the free-radical substitution reaction is the propagation step in which the reaction grows in a chain reaction

- This reaction is not very suitable for preparing specific halogenoalkanes as a **mixture** of substitution products are formed
    - If there is enough chlorine/bromine present, all the hydrogens in the alkane will eventually get substituted (eg. ethane will become C_2Cl_6/C_2Br_6)



The free-radical substitution reaction gives a variety of products and not a pure halogenoalkane

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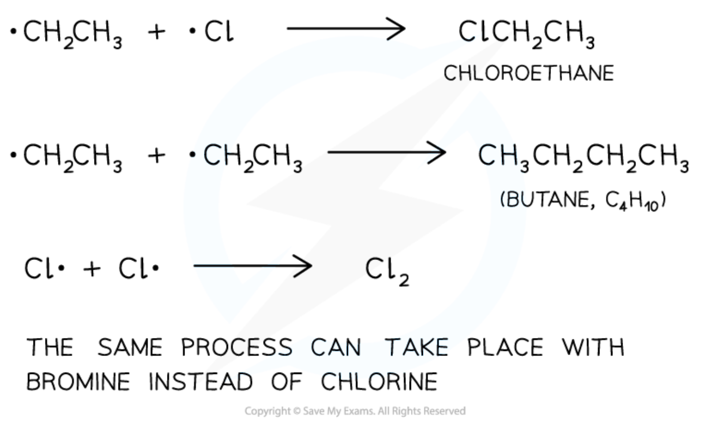
Termination step

- The **termination step** is when the chain reaction **terminates** (stops) due to two free radicals reacting together and forming a single unreactive molecule
  - Multiple products are possible



The final step in the substitution reaction to form a single unreactive molecule

Limitations of the free radical mechanism

- In the termination step, there are a number of possibilities
- Remember that termination involves any free radical bonding with another free radical
- If we have two $^{\bullet}CH_3$ radicals, they can bond to form ethane, CH_3CH_3
  - $^{\bullet}CH_3 + {}^{\bullet}CH_3 \rightarrow CH_3CH_3$
  - If we are trying to form a chloroalkane, then ethane is an impurity

Further substitution

- Excess chlorine present when reacted with methane in the presence of UV light will promote further substitution and could produce CH_2Cl_2, $CHCl_3$, CCl_4
- Further substitution can occur as follows
  - $CH_3Cl + {}^{\bullet}Cl \rightarrow HCl + {}^{\bullet}CH_2Cl$
  - $^{\bullet}CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + {}^{\bullet}Cl$
- These reactions could occur
  - $CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$
  - $CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$
  - $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$

Substitution of different carbon atoms

- If we have an alkane with a middle carbon such as propane, substitution can occur here

- Propagation steps for the substitution of propane with excess bromine in the presence of UV light on the middle carbon are as follows:
  - $CH_3CH_2CH_3 + {}^{\bullet}Br \rightarrow CH_3{}^{\bullet}CHCH_3 + HBr$
  - $CH_3{}^{\bullet}CHCH_3 + Br_2 \rightarrow CH_3CH(Br)CH_3 + {}^{\bullet}Br$
- If the question asks for the halogen to be substituted onto a middle carbon, you must show the radical dot in the correct place, so on the electron-deficient carbon

Your notes