Cambridge (CIE) A Level Chemistry

Your notes

Alkanes

Contents

- Producing Alkanes
- Combustion & Free Radical Substitution of Alkanes
- Free Radical Substitution
- Cracking of Alkanes
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- Combustion of Alkanes

Your notes

Production of Alkanes: Hydrogenation & Cracking

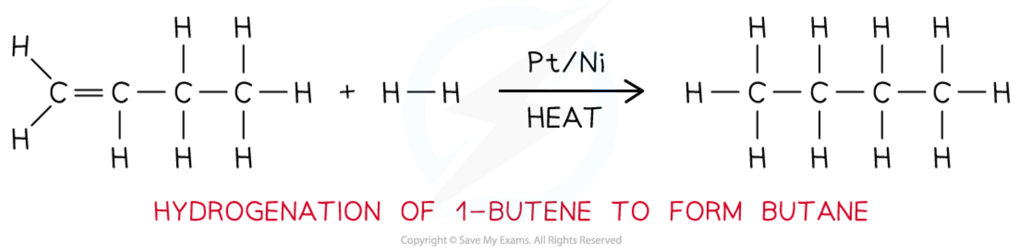
- **Alkanes** are hydrocarbons that can be produced by the **addition reaction** of hydrogen to an alkene or by **cracking** of longer alkane chains

Production of alkanes from addition reactions

- Alkenes are unsaturated organic molecules containing at least one C=C double bond
- Alkenes can be heated with hydrogen gas and a Pt/Ni catalyst
  - The Pt/Ni catalyst is finely divided to increase its surface area
  - This increases the overall rate of reaction
- This is an addition reaction which forms an alkane from an alkene, for example:

$$\textbf{butene + hydrogen} \xrightarrow{\text{Pt } H_2} \textbf{butane}$$

The hydrogenation reaction



Hydrogen gas is added to 1–butene which is then heated and passed over a Pt / Ni catalyst to produce butane

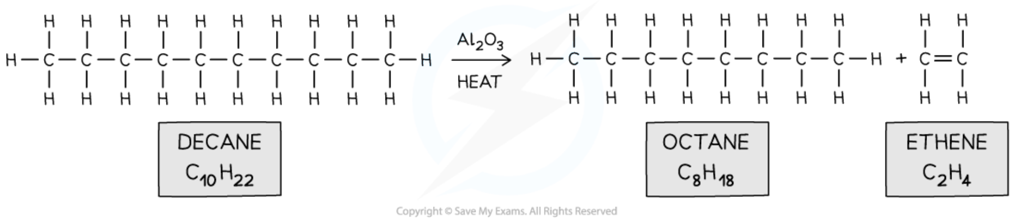
- The addition reaction of alkenes with hydrogen is called **hydrogenation**
- Hydrogenation is often used in the manufacture of **margarine** from **vegetable oil**
  - Vegetable oil is an unsaturated organic molecule with many C-C double bonds
  - When these are partially hydrogenated, their hydrocarbon chains become straighter
  - This raises the melting point of the oils which is why margarine is a soft solid and vegetable oil a liquid at room temperature

Production of alkanes from cracking

- In **cracking** large, less useful hydrocarbon molecules found in crude oil are broken down into smaller, more useful molecules

- The large hydrocarbon molecules are fed into a **steel chamber**, **heated** to a high temperature and then passed over an **aluminium oxide** (Al_2O_3) catalyst
    - The chamber does not contain any **oxygen** to prevent **combustion** of the hydrocarbon to water and carbon dioxide
- When a large hydrocarbon is cracked, a **smaller alkane** and **alkene** molecules are formed
    - E.g. octane and ethene from decane

An example of cracking



Long hydrocarbons are cracked by heating them and using an aluminium oxide catalyst into smaller hydrocarbons and an alkene

Examiner Tips and Tricks

Remember that hydrogenation is an **exothermic** reaction and cracking is an **endothermic** reaction

Your notes

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Combustion & Free Radical Substitution of Alkanes

- Alkanes are **combusted** (burnt) on a large scale for their use as fuels
- They also react in **free-radical substitution** reactions to form more reactive halogenoalkanes

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

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

$$\underset{\text{OCTANE}}{2C_8H_{18}} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

Complete combustion involves a plentiful supply of oxygen

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

The incomplete combustion of alkanes

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

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

Incomplete combustion involves a limited supply of oxygen

Your notes

- Carbon monoxide is a **toxic** gas as it will bind to haemoglobin in blood which can then no longer bind to **oxygen**
- As no oxygen can be transported around the body, victims will feel **dizzy, lose consciousness** and if not removed from the carbon monoxide, they can **die**
- Carbon monoxide is extra dangerous as it is **odourless** (it doesn't smell) and will not be noticed
- Incomplete combustion often takes place inside a **car engine** due to a limited amount of oxygen present

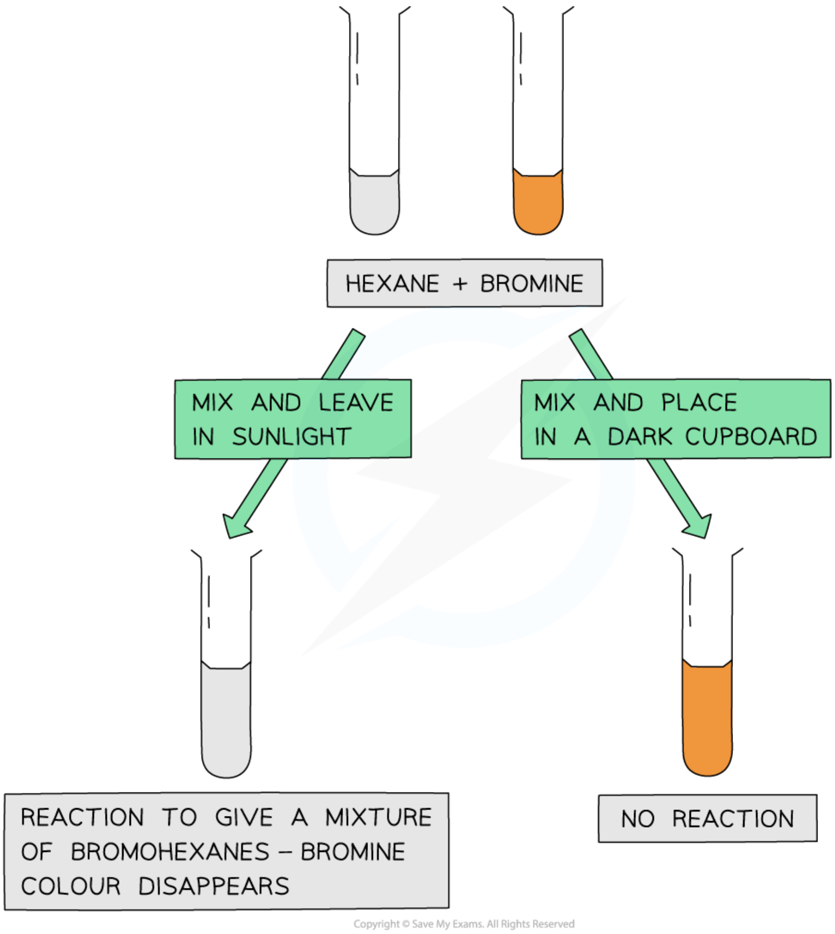
Free-radical substitution of alkanes

- 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 type reaction called the **propagation step**
  - The reaction is terminated when two radicals collide with each other in a **termination step**

Free Radical Substitution Mechanism

- 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

Reacting an alkane with bromine



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

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

Initiation step

- In the **initiation step**, the halogen bond (Cl-Cl or Br-Br) is broken by **UV energy** to form two radicals

Your notes

- The covalent Cl-Cl bond is broken by energy from the UV light
- Each atom takes **one electron** from the covalent bond
- This produces two radicals in a **homolytic fission** reaction

$$Cl{-}Cl\ 2Cl^{\bullet}$$

- For more information about the initiation step, see our revision note about homolytic fission

Propagation step

- The halogen free radicals are very reactive and will attack the unreactive alkanes
- One of the methane C-H bond breaks homolytically to produce an alkyl radical

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

- The alkyl radical can attack another chlorine molecule to form a halogenoalkane
- This also regenerates the chlorine free radical

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

- The regenerated chlorine free radical can then repeat the cycle
- For example, the **chlorination of ethane** is:

ethane + chlorine radical → ethyl radical + hydrogen chloride

$$CH_3CH_3 + Cl^{\bullet} \rightarrow {}^{\bullet}CH_2CH_3 + HCl$$

ethyl radical + chlorine molecule → chloroethane + regenerated chlorine radical

$${}^{\bullet}CH_2CH_3 + Cl_2 \rightarrow CH_3CH_2Cl + Cl^{\bullet}$$

- This reaction is not very suitable for preparing specific halogenoalkanes as a **mixture** of substitution products is formed
- If there is enough **halogen** present, all the hydrogens in the alkane will eventually get substituted
- For example, the chlorination of ethane could continue:

chloroethane + chlorine radical → radical + hydrogen chloride

$$CH_3CH_2Cl + Cl^{\bullet} \rightarrow {}^{\bullet}CH_2CH_2Cl + HCl$$

radical + chlorine molecule → 1,2-dichloroethane + regenerated chlorine radical

$${}^{\bullet}CH_2CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl^{\bullet}$$

- This process can repeat until **hexachloroethane**, C_2Cl_6, is formed

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
- For example, the single substitution of **ethane by chlorine** can form:

ethyl radical + chlorine radical → chloroethane

$$•CH_2CH_3 + Cl• \rightarrow CH_3CH_2Cl$$

ethyl radical + ethyl radical → butane

$$•CH_2CH_3 + •CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3$$

chlorine radical + chlorine radical → chlorine molecule

$$Cl• + Cl• \rightarrow Cl_2$$

Examiner Tips and Tricks

If you are asked to give an equation for the termination step of a free radical reaction / mechanism, you should not give the equation reforming the original halogen as this is often marked as "ignore" on mark schemes.

Free radical substitution using bromine instead of chlorine is possible and follows similar initiation, propagation and termination steps

Further substitution

- Often, free radical reactions are 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
- For example, methane could be substituted to become chloromethane and then further substituted
- Single substitution:

$$CH_4 + Cl• \rightarrow •CH_3 + HCl$$

$$•CH_3 + Cl_2 \rightarrow CH_3Cl + Cl•$$

- Second substitution:

$$CH_3Cl + Cl• \rightarrow •CH_2Cl + HCl$$

$$•CH_2Cl + Cl_2 \rightarrow CH_2Cl_2 + Cl•$$

- Third substitution:

$$CH_2Cl_2 + Cl• \rightarrow •CHCl_2 + HCl$$

$$•CHCl_2 + Cl_2 \rightarrow CHCl_3 + Cl•$$

- Complete substitution:

$$CHCl_3 + Cl• \rightarrow •CCl_3 + HCl$$

Your notes

$$\bullet CCl_3 + Cl_2 \rightarrow CCl_4 + Cl\bullet$$

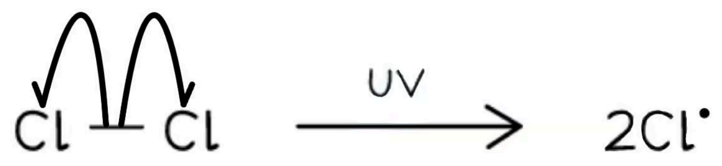
Examiner Tips and Tricks

You could be asked to draw the mechanism for initiation and termination steps for free radical substitution

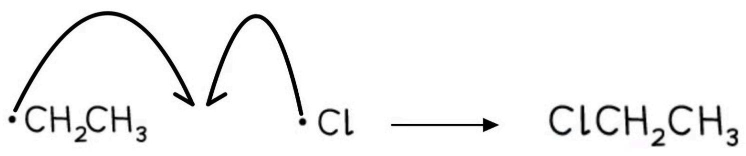
This mechanism will use half-headed arrows to show the movement of one electron (double-headed arrows show the movement of a pair of electrons)

A half-headed arrow is known as a ‘fish hook’ arrow.

Initiation:



Termination:



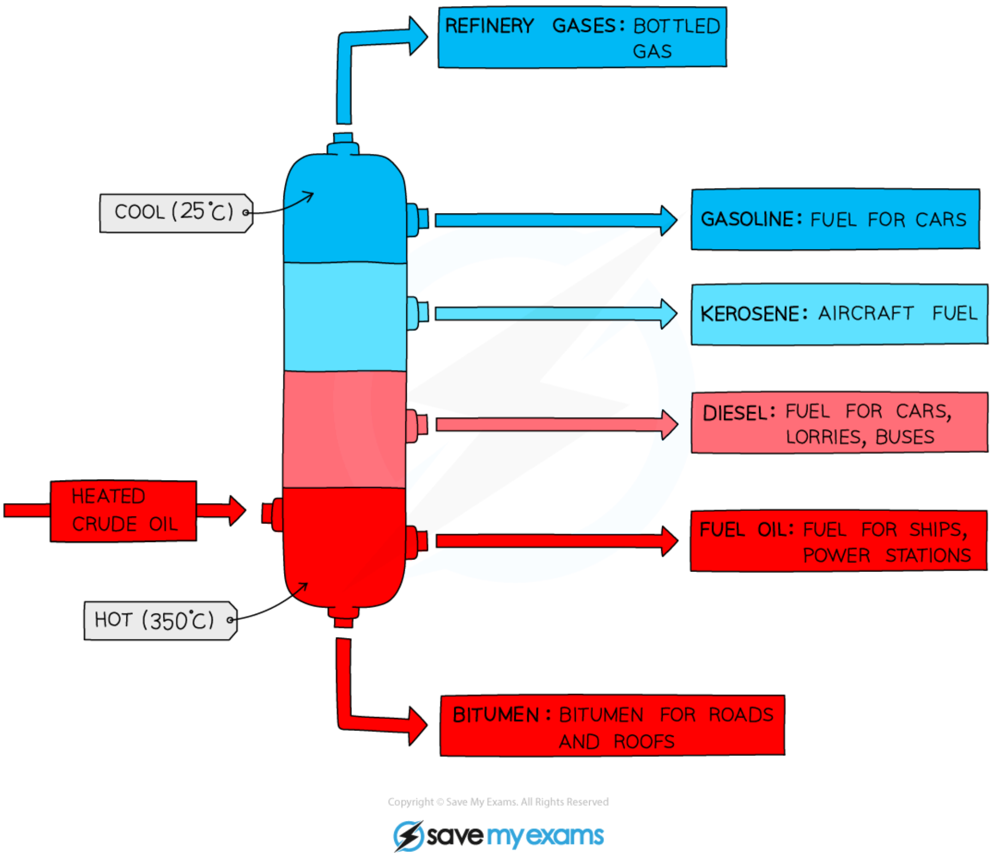
The key is the use of the ‘fish hook’ arrow to show the homolytic fission of the bond in initiation and the formation of the bond in termination.

Obtaining Useful Compounds by Cracking

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 a wide range of different hydrocarbons are separated into fractions based on their boiling points

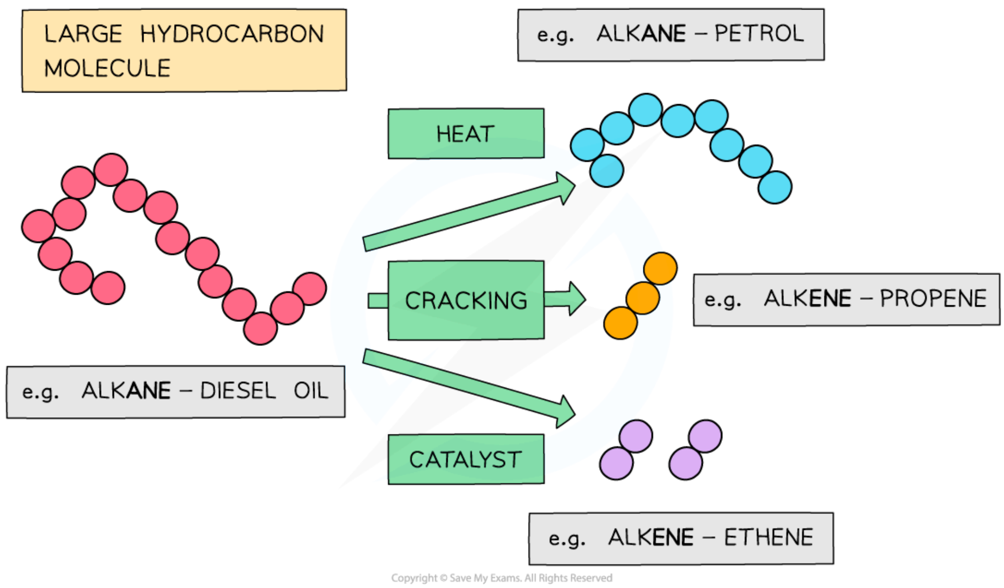
A fractional distillation column



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

- 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 process of cracking



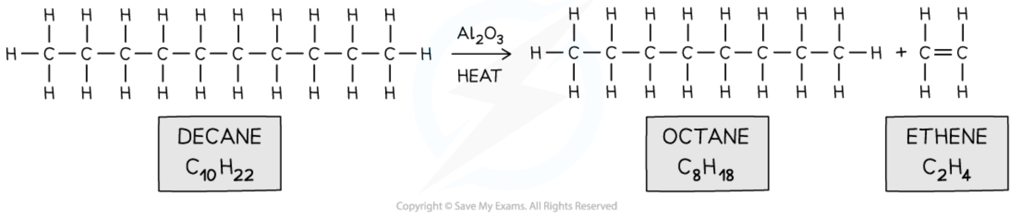
The heavier fractions that are obtained in fractional distillation are further cracked into useful alkanes and alkenes with lower Mr values

Cracking

- The large hydrocarbon molecules are fed into a **steel chamber**, **heated** to a high temperature and then passed over an **aluminium oxide** (Al_2O_3) catalyst
  - The chamber does not contain any **oxygen** to prevent **combustion** of the hydrocarbon to water and carbon dioxide
- When a large hydrocarbon is cracked, a **smaller alkane** and **alkene** molecules are formed
  - E.g. octane and ethene from decane

Cracking of long-chain hydrocarbons

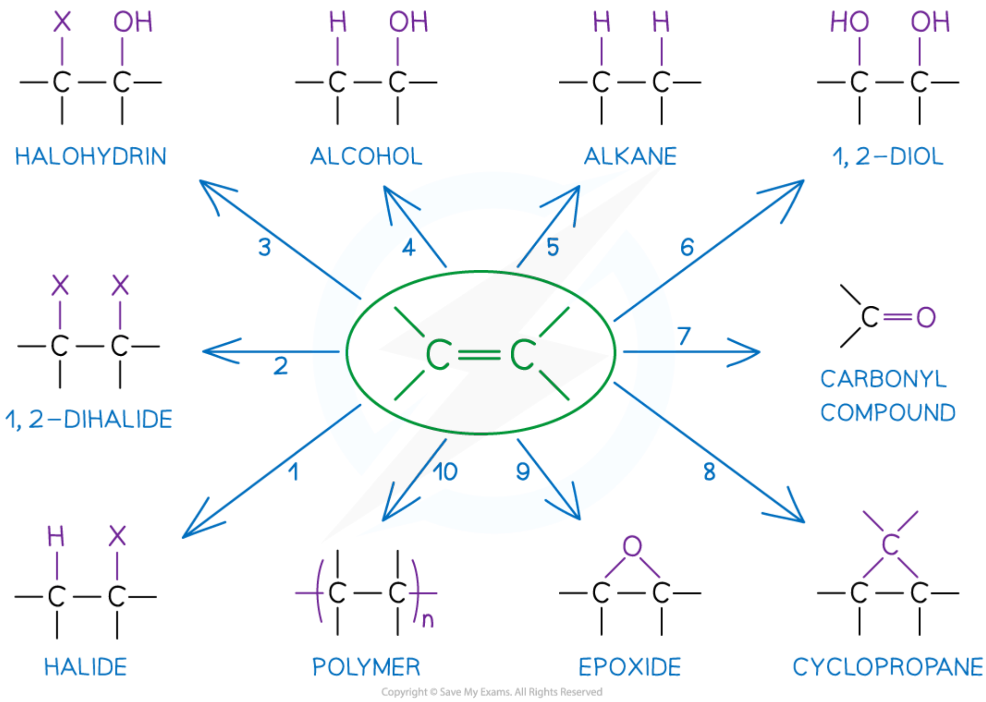
Your notes



The long hydrocarbon fraction is cracked into two smaller ones

- The **low-molecular mass alkanes** formed make good fuels and are in high demand
- The **low-molecular mass alkenes** are more reactive than alkanes due to their double bond
- This makes them useful for the chemical industry as the starting compounds (**feedstock**) for making new products
  - E.g. they are used as monomers in polymerisation reactions

Using alkenes to form other useful compounds



Alkenes are reactive molecules and can undergo many different types of reactions making them useful as starting compounds

Your notes

Unreactivity of Alkanes

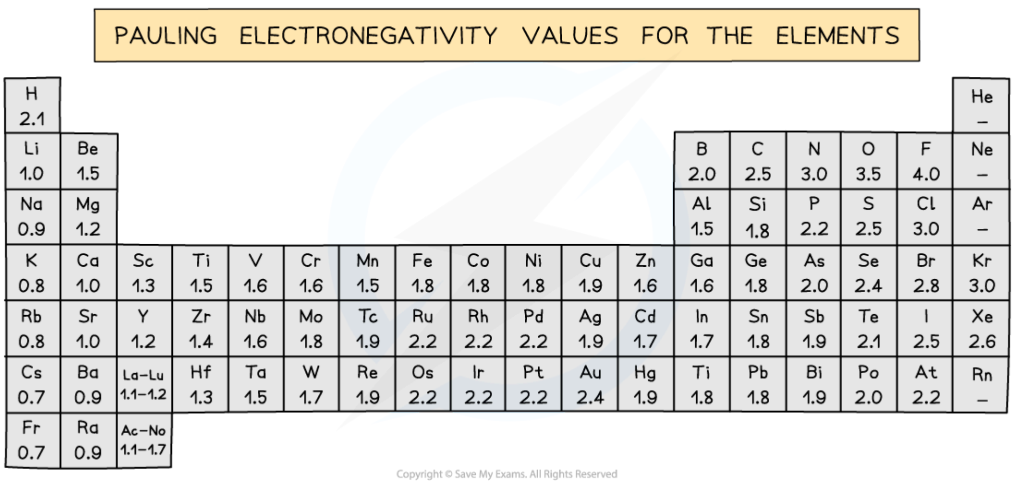
Strength of C-H bonds

- Alkanes consist of carbon and hydrogen atoms which are bonded together by **single bonds**
- Unless a lot of heat is supplied, it is difficult to break these **strong** C-C and C-H covalent bonds
- This decreases the alkanes' reactivities in chemical reactions

Lack of polarity

- The **electronegativities** of the carbon and hydrogen atoms in alkanes are almost the same
- This means that both atoms share the electrons in the covalent bond almost equally

The Pauling Scale



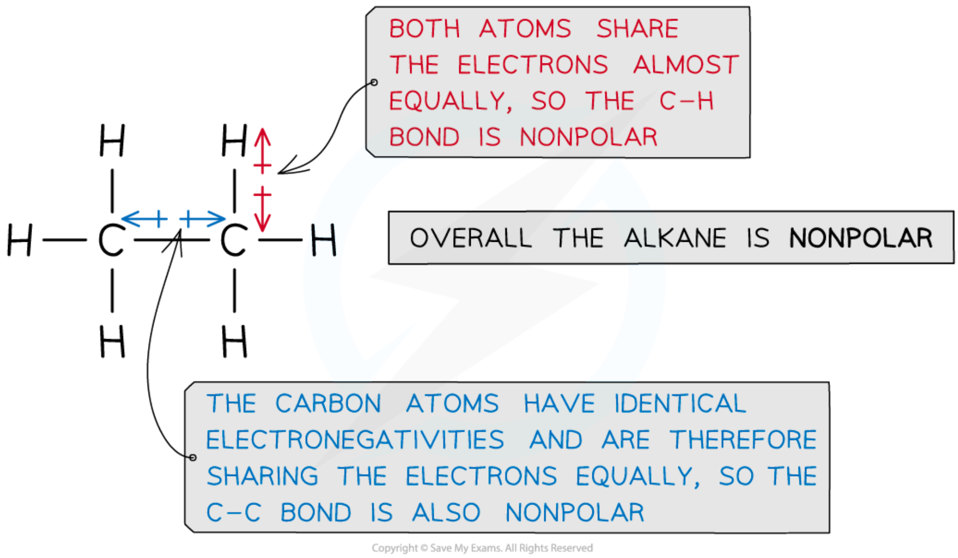
PAULING ELECTRONEGATIVITY VALUES FOR THE ELEMENTS

H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.2	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

The Pauling Scale shows that the difference in electronegativity between carbon and hydrogen is only 0.4

- As a result of this, alkanes are **nonpolar** molecules and have no partial positive or negative charges (δ^+ and δ^- respectively)
- Alkanes therefore do not react with **polar reagents**
  - They have no electron-deficient areas to attract **nucleophiles**
  - They also lack electron-rich areas to attract **electrophiles**

Examining bond polarity in ethane



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

- Due to the unreactivity of alkanes, they only react in combustion reactions and undergo substitution by halogens

Examiner Tips and Tricks

Remember: nucleophiles are negatively charged and are attracted to electron-deficient regions

Electrophiles are positively charged and attracted to electron-rich regions

Combustion of Alkanes & the Environment

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

Carbon monoxide

- When oxygen supply is limited, **carbon monoxide (CO)** forms instead of carbon dioxide:

fuel + oxygen → carbon monoxide + water

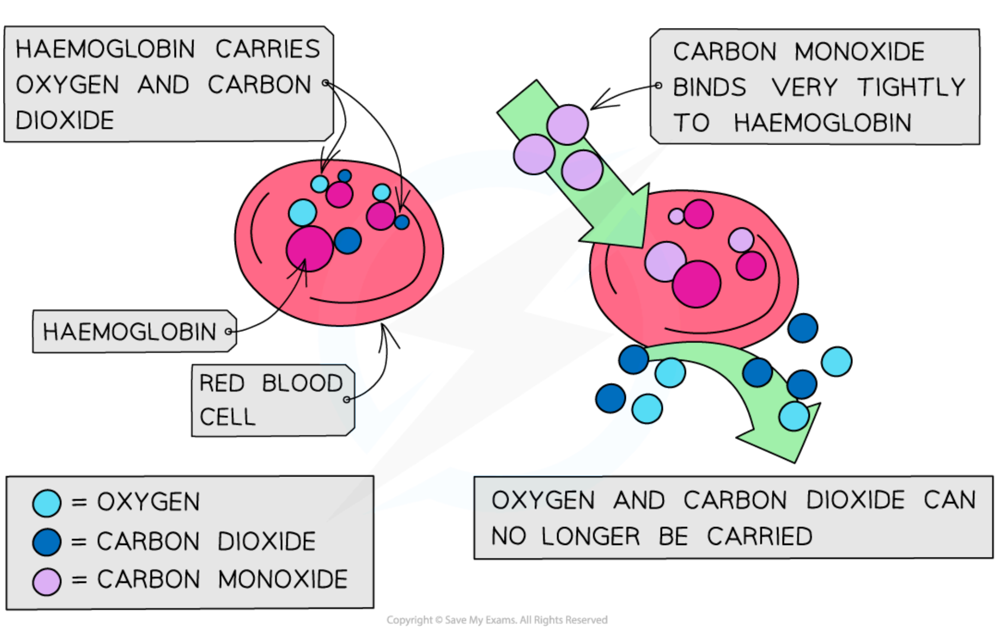
- For example, Incomplete combustion of **propane**:

propane + oxygen → carbon monoxide + water

$$C_3H_8 (l) + 3½O_2 (g) \rightarrow 3CO (g) + 4H_2O (l)$$

- **Carbon monoxide is extremely dangerous** because it is:
  - **Colourless** and **odourless** (can't be seen or smelled)
  - Hard to detect without a sensor
- It is a **toxic** and **poisonous** gas that binds **irreversibly** to **haemoglobin** in the blood.
  - This prevents haemoglobin from carrying **oxygen**.
- Lack of oxygen transport leads to:
  - **Dizziness**
  - **Loss of consciousness**
  - Potentially **death** if not treated

The effect of carbon monoxide on haemoglobin



The high affinity of CO to haemoglobin prevents it from binding to O2 and CO2

Your notes

Oxides of nitrogen

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

$$N_2\,(g) + O_2\,(g) \rightarrow 2NO\,(g)$$

$$N_2\,(g) + 2O_2\,(g) \rightarrow 2NO_2\,(g)$$

- The **oxides of nitrogen** are then released in the car's exhaust fumes into the atmosphere
- Car exhaust fumes also contain **unburnt hydrocarbons** from fuels and their **oxides** (VOCs)
- In the 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 also dissolve and react in water with oxygen to form nitric acid which is a cause of **acid rain**
  - Acid rain can cause corrosion of buildings, endanger plant and aquatic life (as lakes and rivers become too **acidic**) and directly damage human health

Catalytic removal

- To reduce the amount of pollutants released in cars' exhaust fumes, many cars are now fitted with **catalytic converters**
- Precious metals (such as platinum) are coated on a honeycomb to provide a **large surface area**

- The reactions that take place in the catalytic converter include:
  - Oxidation of CO to CO_2:

$$\mathbf{2CO + O_2 \rightarrow 2CO_2}$$

or

$$\mathbf{2CO + 2NO \rightarrow 2CO_2 + N_2}$$

- Reduction of NO/NO_2 to N_2:

$$\mathbf{2CO + 2NO \rightarrow 2CO_2 + N_2}$$

- Oxidation of unburnt hydrocarbons:

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

Pollutants, their effect & removal summary

- **Carbon Monoxide (CO)**
  - Formation:
    - Incomplete combustion of alkanes in car engines
  - Environmental consequence:
    - Toxic gas
  - Catalytic removal:
    - Oxidised to carbon dioxide (CO_2):

$$\mathbf{2CO + O_2 \rightarrow 2CO_2}$$

$$\mathbf{2CO + 2NO \rightarrow 2CO_2 + N_2}$$

- **Oxides of Nitrogen (NO, NO_2 etc.)**
  - Formation:
    - Oxidation of nitrogen in car engines (due to high temperatures)
  - Environmental consequence:
    - Dissolve in water and react with oxygen to form acid rain
  - Catalytic removal:
    - Reduced to nitrogen gas:

$$\mathbf{2CO + 2NO \rightarrow 2CO_2 + N_2}$$

- **Volatile Organic Compounds (VOCs)**
  - Formation:
    - Unburnt hydrocarbons from fuels
    - Oxides of these hydrocarbons formed in car engines

Your notes

Your notes

- Environmental consequence:
  - React with oxides of nitrogen in the atmosphere to form PAN
- Catalytic removal:
  - Oxidised to CO_2 and H_2O
  - General formula reaction:

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

- **PAN (peroxyacyl nitrate)**
  - Formation:
    - From the photochemical reaction of VOCs and nitrogen oxides in the atmosphere
  - Environmental consequence:
    - Contributes to photochemical smog
  - Catalytic removal:
    - Oxidise unburnt hydrocarbons
    - Reduce nitrogen oxides to prevent PAN formation

Examiner Tips and Tricks

Although CO_2 is not a **toxic** gas, it is still a **pollutant** causing **global warming** and **climate change**