

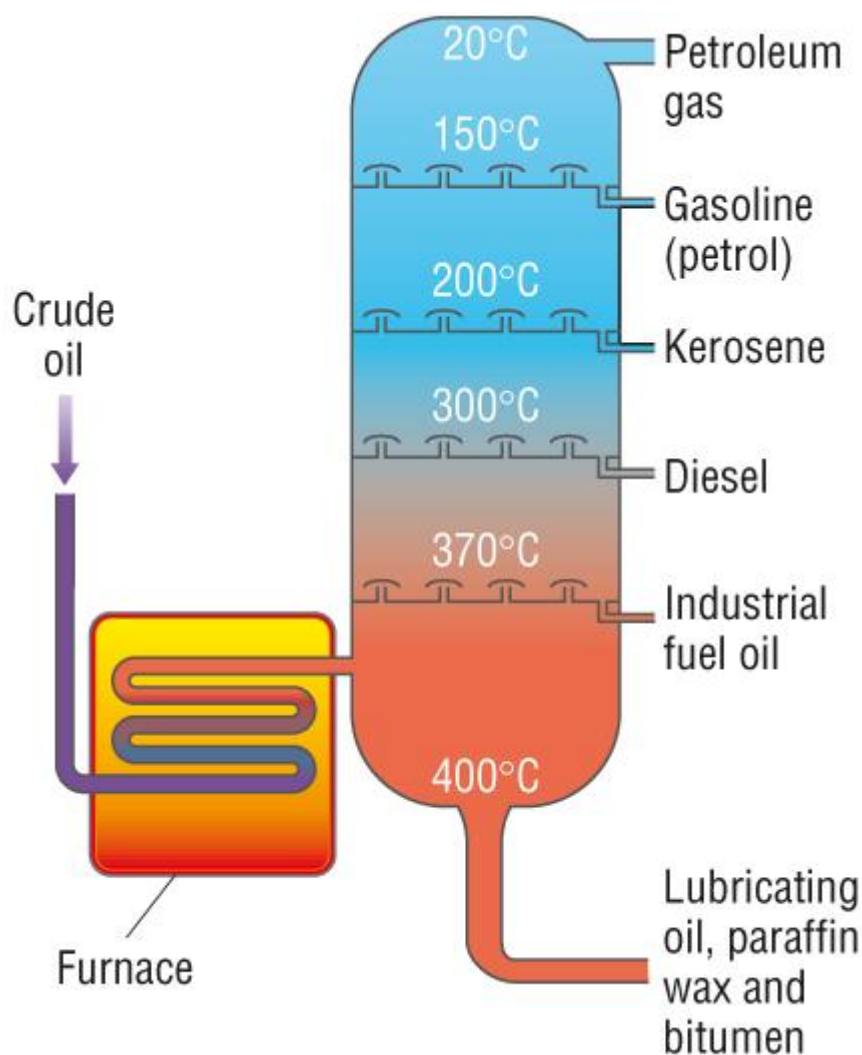
1B – Fuels, alkanes and alkenes

Hydrocarbons:

- Hydrocarbons contain only the elements hydrogen and carbon.
- Found as fossil deposits of crude oil and natural gas.
- They are made from naturally decaying plants and animals over millions of years
- Crude oil is a mixture of around 150 hydrocarbons which are mainly straight chain alkanes.
- Each source varies in its mixture slightly.
- Crude oil does not ignite easily. Only when separated into its constituent components is it valuable

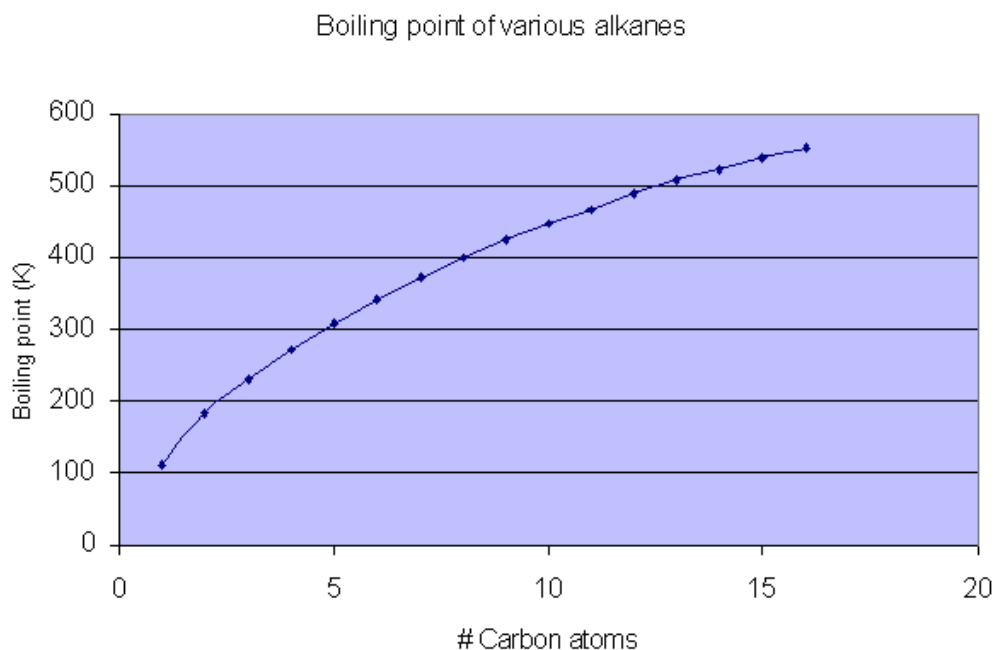
Fractional distillation of crude oil:

- Crude oil is a mixture of different hydrocarbons with a large range of boiling points.
- **Fractional distillation** is used to separate crude oil into fractions.
- Each fraction is made up of many different hydrocarbons but with more similar boiling points.
- Further distillation of these fractions can occur when a desired hydrocarbon is needed.




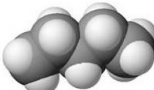




- The crude oil is vaporised before entering the column at 650K.
- The column has a temperature gradient – hot at the bottom getting gradually cooler as you go up the column.
- The column is divided into trays, each tray has bubble caps for vapour to rise
- As the hot vapour rises into a tray it comes in contact with cooler part of the column.
- Eventually the hydrocarbon will reach a part of the column where its temperature is lower than its boiling point. At this point it will condense in the tray.
- The top of the column has the most volatile hydrocarbons, those with the lowest boiling points.
- The bottom of the column has the least volatile hydrocarbons, those with the highest boiling points.

Boiling points of the alkanes:

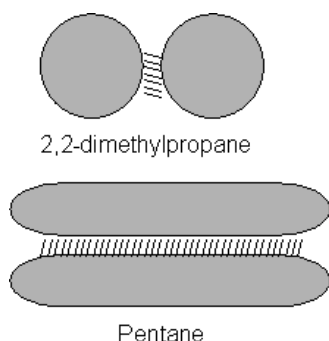


- The graph shows - the larger the carbon chain, the higher the boiling point:
- Weak Van der Waal's forces of attraction exist between the alkanes.
- The more carbons and hydrogen's there are, the more electrons there are in the molecule.
- The more electrons there are in the molecule, the stronger the Van der Waal's forces of attraction.
- This means that as the carbon chain increases, so does the strength of the Van der Waals forces of attraction.
- This means that more energy is needed to overcome these attractive forces.

Effect of branching:

Pentane	 	309K
2-methylbutane	 	301K
2,2-dimethylpropane	 	283K

- Each isomer has the same number of electrons but the strength of these forces are clearly not the same. This is indicated by the different boiling points.
- The shape of the molecule must have an effect on the boiling points. The more branches the lower the boiling point which means weaker Van Der Waals.
- The long shape of pentane allows close packing and maximum surface area for Van Der Waals. This gives optimum interactions
- More branches means the molecules can't pack as closely.
- It also means that the surface area for Van Der Waals is reduced, therefore the energy needed to overcome Van der Waals forces is reduced (lower boiling point)



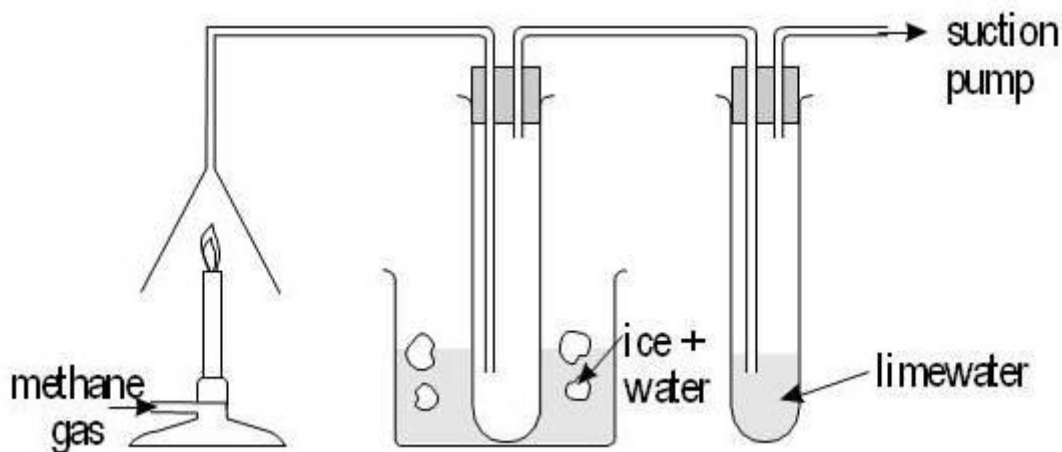
- Pentane can be described as sausage shape. These can get close and have maximum surface area.
- 2,2 – dimethylpropane is spherical in shape. It can't pack together quite as well and has a minimum surface area:

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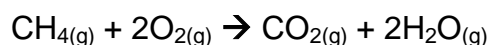
The Alkanes:

Hydrocarbons as Fuels

The combustion of alkanes:

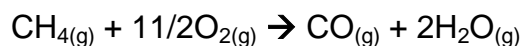


- The shorter the alkane the cleaner it burns.
- The yellow colour of the flames is due to incomplete combustion. In fact the yellow colour is due to particles of carbon glowing in the heat. More oxygen (air) increases oxidation of the carbon.
- The products of burning are water and carbon dioxide.
- The **C** in the hydrocarbon reacts with oxygen in the air forming **CO₂**
- The **H** in the hydrocarbon reacts with oxygen in the air forming **H₂O**



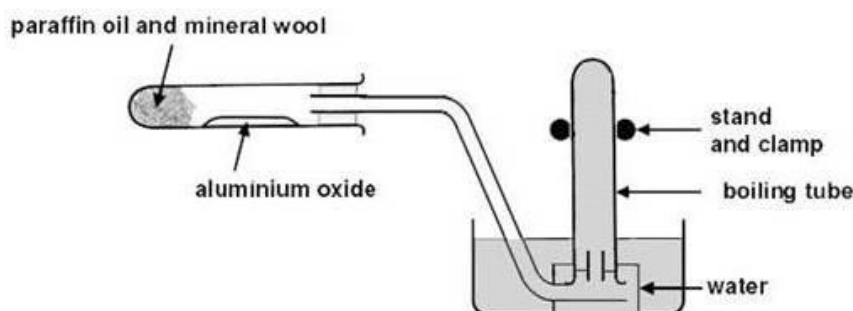
Incomplete combustion:

- Incomplete combustion is where there is an insufficient supply of oxygen. It produces carbon monoxide, **CO**

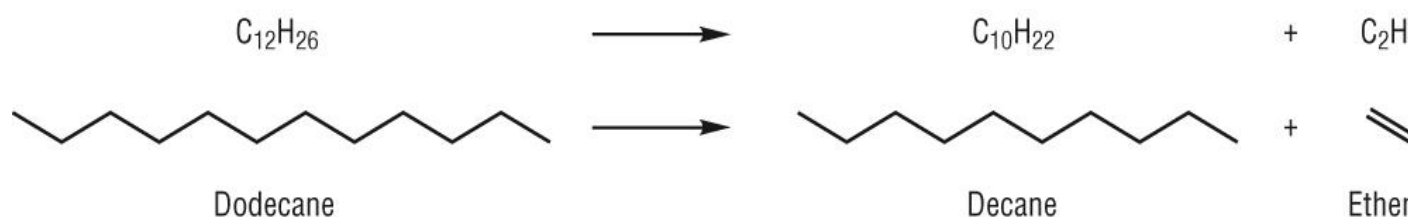


- Carbon monoxide is a poisonous gas. It has no colour or odour so is not noticed.
- It combines with haemoglobin in the blood in preference to oxygen.
- Deaths occur from faulty gas fires or boilers in poor ventilated rooms.
- Landlords are now required to have gas appliances serviced annually.

Cracking:

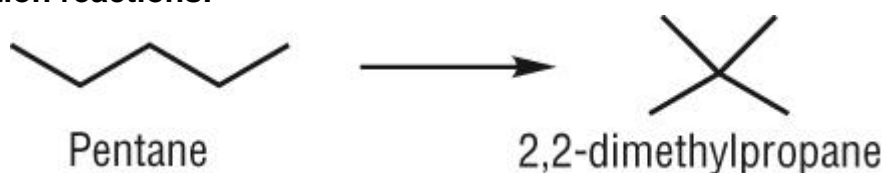


- Cracking breaks longer, less useful alkanes into shorter, more useful alkanes and alkenes.
- This is done at heating the alkanes with a catalyst.
- Both C – C and C – H bonds are broken in the process. Random bonds are broken which means a variety of products are produced including hydrogen. Some of the intermediates can react to produce branched chain alkanes.
- Alkenes are used in the polymer industry.
- One such reaction is:



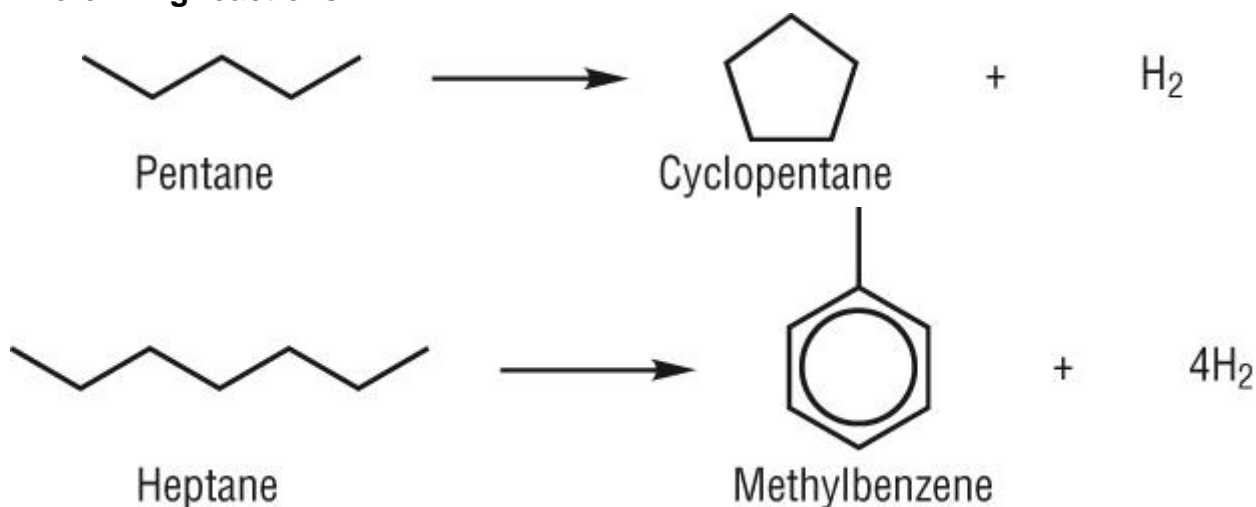
Producing branched chains:

- Straight chain alkanes have a tendency to pre ignite in a combustion engine whereas branched chains do not.
- Branched chain alkanes burn cleaner than straight chain alkanes so they are usually converted using:
- **Isomerisation reactions:**



Producing cyclic hydrocarbons:

- Again as straight chain alkanes have a tendency to pre ignite they are also converted to cyclic and aromatic hydrocarbons.
- Any hydrogen produced is used in other processes - **ammonia production, margarine**.
- These also burn cleaner than straight chain alkanes so they are usually converted using:
- **Reforming reactions:**



Improving fuels:

- Fuels have an octane rating (**Research Octane Rating, or RON**) which rates how well a fuel burns:

100% **Burns efficiently**
0% **Burns inefficiently**

- Branched and cyclic alkanes burn much more efficiently than straight chain alkanes hence the conversions (above).

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Fossil fuels and fuels of the future

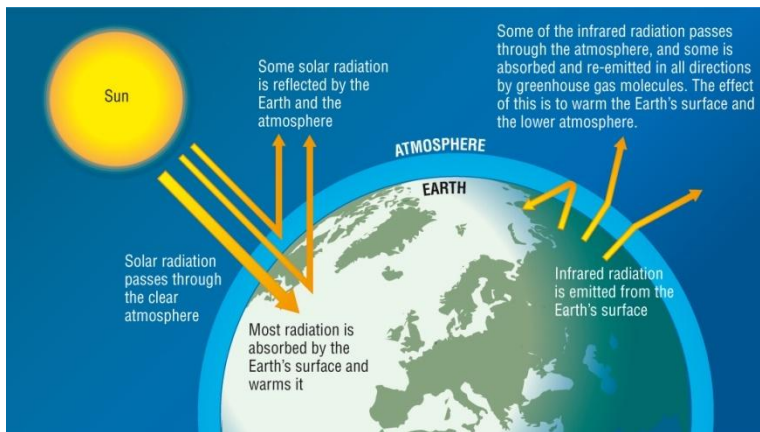
The crude oil economy:

- 90% of all crude oil is used as a source of fuels to generate electricity or used for transport.
- Plastics, pharmaceuticals, cosmetics etc are also sourced from crude oil.
- Our reliance on crude oil is worrying as oil deposits are running out!

The use of crude oil for fuels:

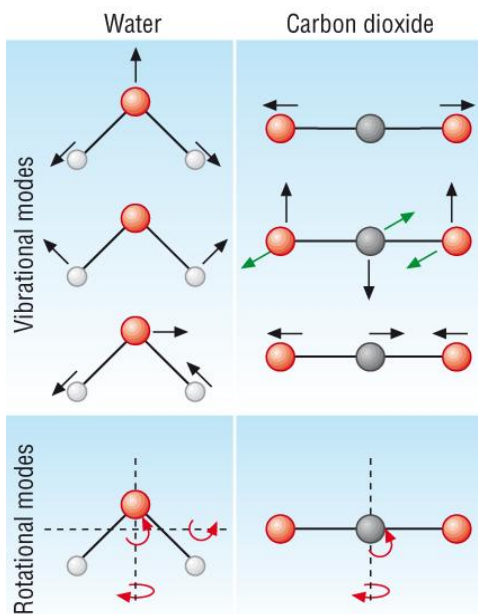
- The majority of crude oil is the alkanes - chains and branches. These are good fuels.
- As the availability of oil decreases the price increases.
- Crude oil as a fuel contributes to atmospheric pollutions:
 - Carbon monoxide** - **toxic gas**
 - Carbon dioxide** - **global warming**
 - Nitrogen oxides** - **acid rain / forest destruction**
 - Sulphur oxides** - **acid rain**
- All of these reasons has precipitated a shift away from the use of fossil fuels

The greenhouse effect - global warming:



- Radiation from the sun reaches the planet.
- The radiation is absorbed by the Earth and re emitted as IR radiation.
- Most of this IR radiation goes back into space but some is absorbed by gases in the atmosphere.
- These gas molecules absorb the IR radiation then re emit it as energy, this energy warms up the atmosphere.
- These gases are: water, methane and carbon dioxide.

How do gases absorb radiation?



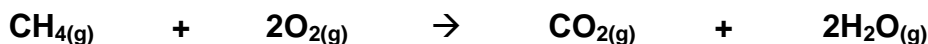
- Just like IR spectroscopy, the bonds in these greenhouse gases absorb IR radiation in their bonds.
- The bonds vibrate absorbing the IR radiation.
- Different gases will absorb different amounts of IR radiation.
- 3 factors determine the impact a gas has on Global warming:
 1. Its concentration in the atmosphere
 2. Its ability to absorb IR radiation
 3. Its lifetime in the atmosphere
- These 3 factors make up the GWP (Global Warming Potential)
- The term Climate Change explains that although the average temperature of the planet is rising, different areas around the planet will suffer from extreme weather patterns.

Solutions to the Greenhouse Effect:

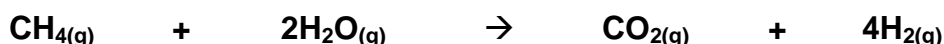
- Obviously alternative fuels such as: Wind, tidal, solar, nuclear. But we still need fossil fuels to meet the energy demands of the planet.

Carbon Capture and Storage, CCS:

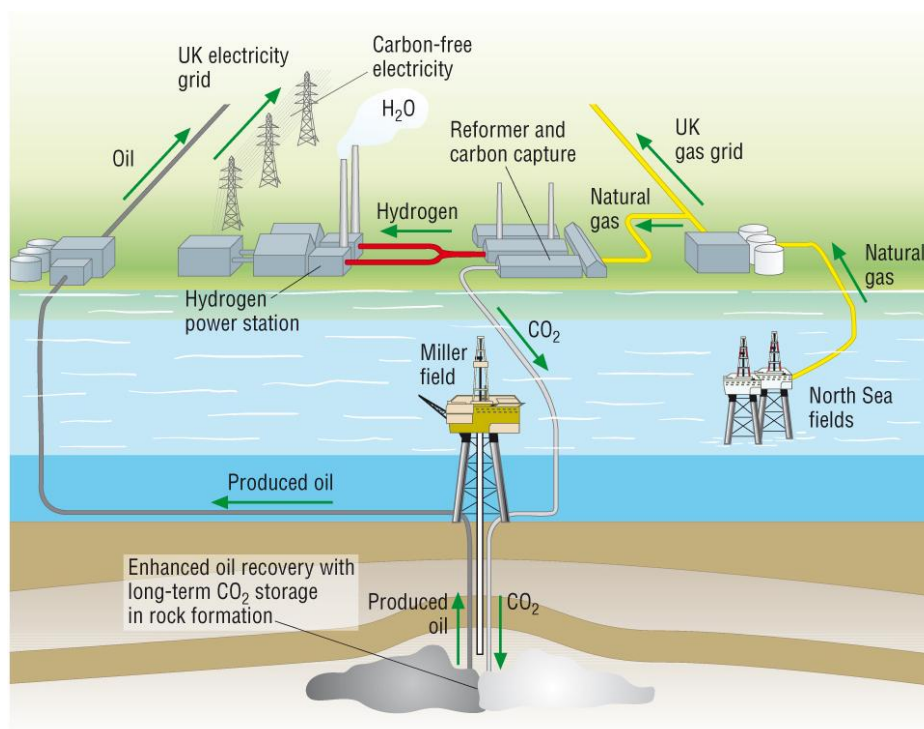
- When methane burns:



- Obviously this produces **CO₂** which is emitted into the atmosphere.
- The fuel can be decarbonised:

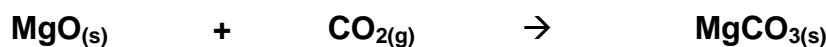
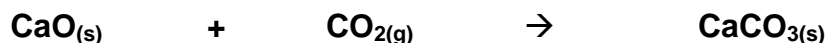


- The **CO₂** can be separated and pumped into oil wells to get the last bit of oil out.
- H₂** is produced which is a clean fuel as it only produces water vapour.
- The **CO₂** is now trapped in the oil well and not emitted into the atmosphere:



Storage as carbonates:

- Mineral storage aims to store the CO₂ locked up in minerals as carbonates, CO₃:



- This process occurs naturally but is very slow, More research is needed if this is to be a viable storage option.

Fuels of the future:

- Biofuel is made from the fermentation of plant material such as rape or sugar cane to produce ethanol.
- The idea is that as the plant grows it absorbs CO₂. When the ethanol is used as a fuel that CO₂ is released. This makes it 'carbon neutral'.
- The ethanol can be used as a fuel or added to petrol to make petrol burn more efficiently.
- Biodiesel is made from rapeseed. It can be used pure in a diesel engine but is more commonly added to normal diesel.

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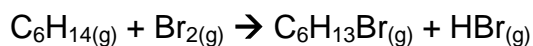
Substitution reactions of the alkanes

Halogenation of the alkanes:

- Alkanes are unreactive due to the lack of polarity. This is due to the fact that carbon and hydrogen are similar in electronegativities.
- In the presence of ultraviolet light (or 300°C) the halogen will substitute a hydrogen in an alkane, a halogenoalkane and hydrogen halide is produced:



- For the reaction with hexane:



- Reactions that occur in light are called photochemical reactions.

Mechanism for chlorination

- The overall reaction doesn't give any clues to how the reaction proceeds.
- The sequence of reactions leading to the products is known as the mechanism.
- The simplest alkane to consider is methane and chlorine:-

The mechanism:

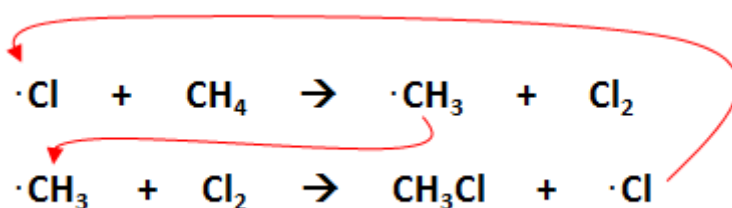
Step 1: Initiation:

- Absorption of UV light energy to break bond in the halogen.
- **Free radicals** are formed by **homolytic fission**.
- These chlorine atoms have an odd number of electrons. This means that 1 of the electrons are unpaired (represented by the dot).



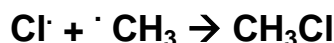
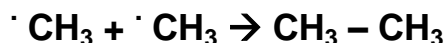
Step 2: Propagation:

- The chlorine radical breaks a C-H bond (homolytically) in the alkane forming an alkyl radical, and HCl.
- The alkyl radical can then go on to react with more chlorine to form the halogenoalkane and another chlorine radical.
- The chlorine radical can then repeat these stages until no more alkane or chlorine remains.
- These reactions are called **propagation reactions** (also called chain reaction) are fast and keep going until a reactant runs out.



Step 3: Termination:

- The reaction cannot go on indefinitely. There must be a point when the reaction stops.
- This occurs when 2 free radicals collide and give a stable product.
- There are many radical in the reaction giving rise to many products
- These are known as **termination reactions**



Overall



- This reaction is described as **free radical substitution**

Further reactions of chloromethane:

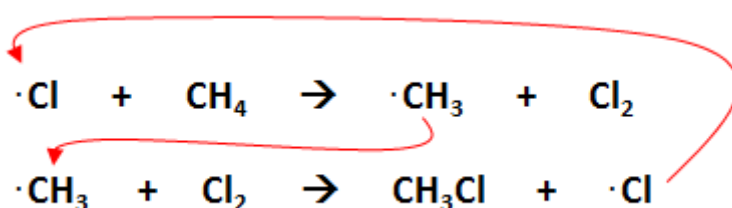
- In the termination steps 2 undesirable products are made - ethane and hydrogen chloride.
- Chloromethane formed in the propagation steps can react further with more chlorine radicals to give a mixture of multi substituted halogenoalkanes: CH_2Cl_2 , CHCl_3 , CCl_4

Summary of photochemical reaction:

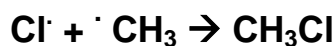
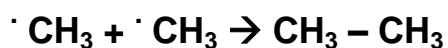
initiation



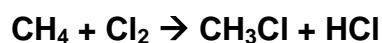
Propagation



Termination



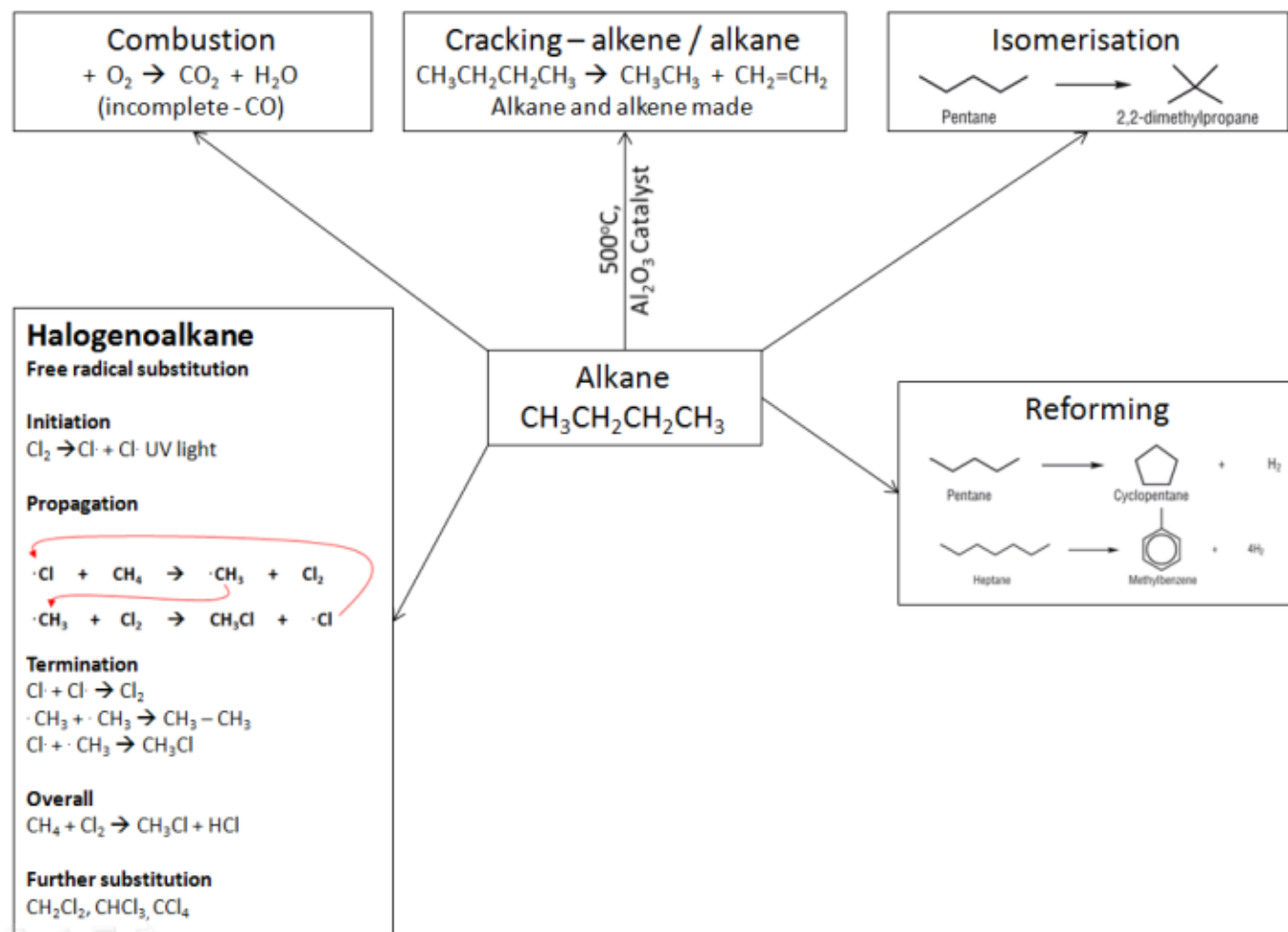
Overall



Further substitution



Revision: The alkanes:



Questions P125 Qu 1-2

Alkenes

The reactivity of the C=C double bond:

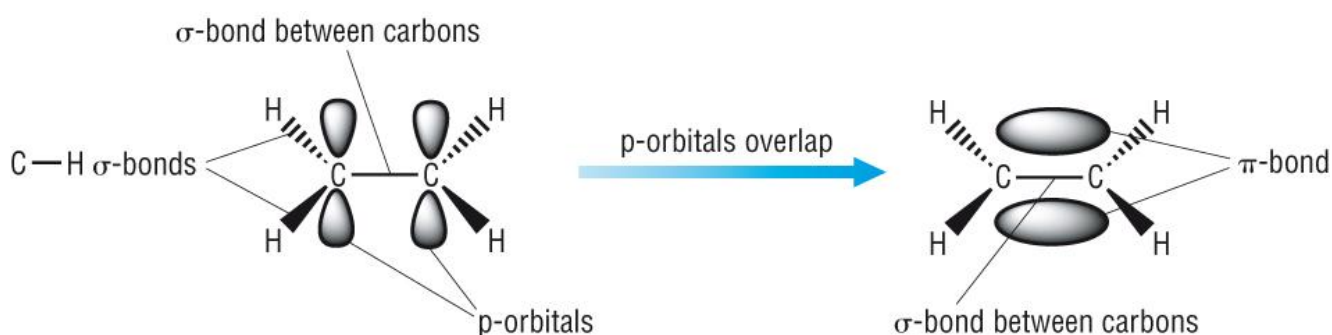
- Alkenes are more reactive than the alkanes due to the electron rich C=C

Physical properties of the alkenes

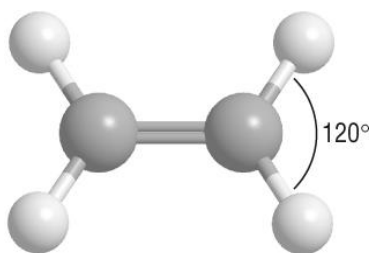
Introduction:

- Alkenes are unsaturated hydrocarbons containing at least 1 C=C.
- They have the general formula C_nH_{2n} .
- They typically take part in addition reactions (to the C=C).
- They exhibit E/Z isomers including the cis / trans isomerism.

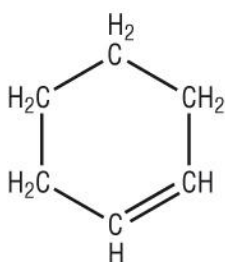
The nature of the double bond:



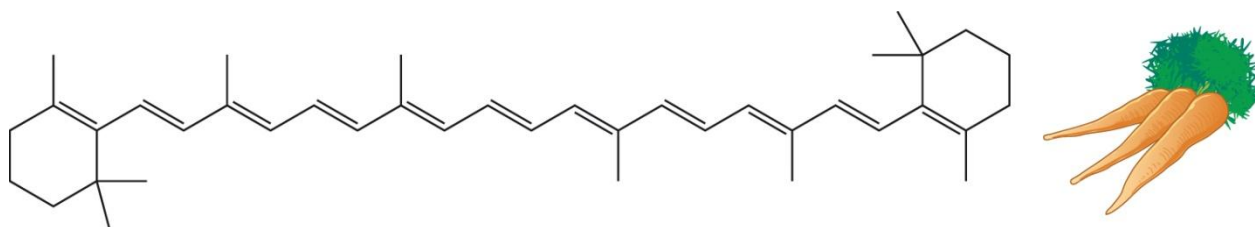
- The double bond consists of a **sigma bond (σ)** and a **pi bond (π)**.
- The π bond consists of 2 lobes one on each side of the sigma bond.
- The 2 lobes overlap to produce a π bond.
- To ensure maximum overlap, ethene must be a planar molecule.
- The asymmetric shape of the 2 bonds locks the molecule around the double bond
- This means that there is no free rotation about these bonds.
- The π bond changes the shape around the carbon atom to a trigonal planar with a bond angle of 120° :



Cyclic alkenes:



- Cyclic means that the carbon chain is joined at either end forming a ring.
- The reactions of cyclic alkenes is exactly the same as straight chain alkenes
- As there is no 'ends' to the molecule they have 2 H's less in the general formula.
- Carotene (below) has cyclic and straight chain double bonds (11)



Questions P127 1-4

Reactions of alkenes:

The reactivity of the C=C double bond:

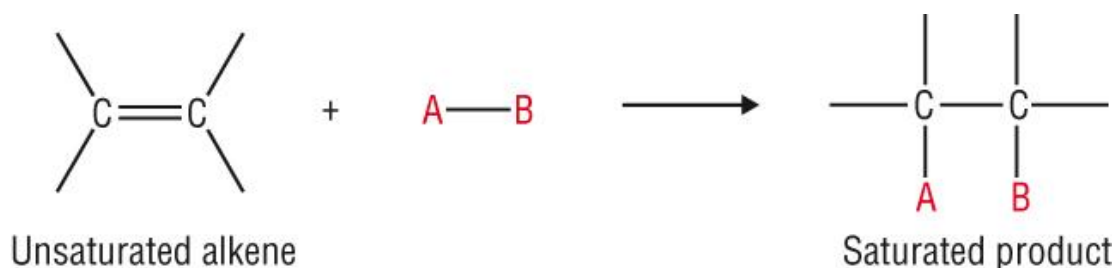
- The extra electrons in the C=C makes it more reactive as it is more electron rich.
- The relative strengths of the 2 bonds are:

Bond	Bond enthalpy KJ mol ⁻¹
C-C	+347
C=C	+265

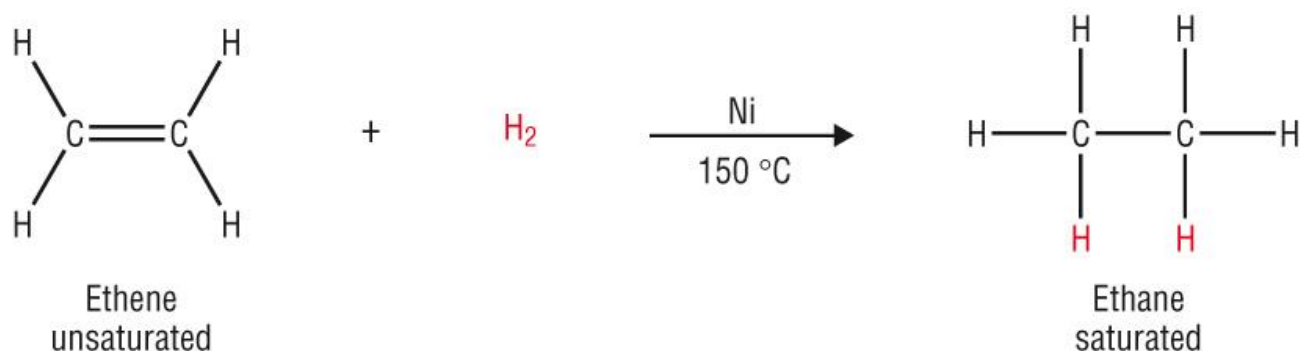
- The C=C requires 612 KJ Mol⁻¹ making it a lot stronger than just a C-C.
- The C=C is not however twice as strong as the C-C (due to orbital overlap)
- The **sigma bond (σ)** is a lot stronger than the **pi bond (π)** which means that the **pi bond (π)** breaks leaving the **sigma bond (σ)** intact.

Reactions of the alkenes:

- Alkenes undergo addition reactions as they are unsaturated.
- The reactant will add across the C=C forming a saturated product:

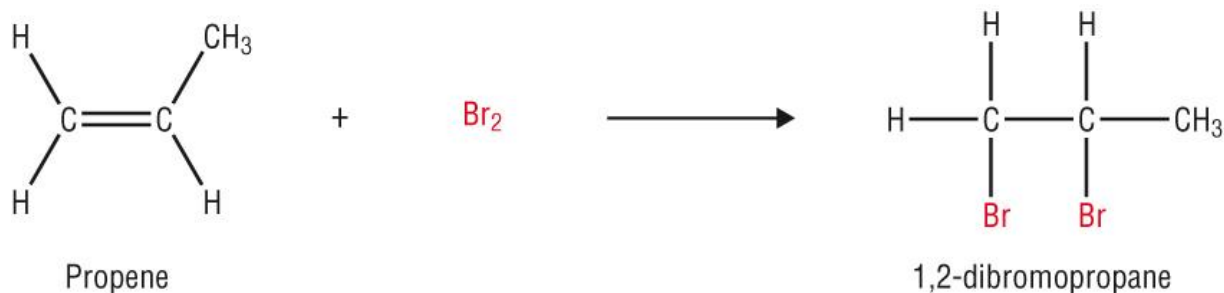
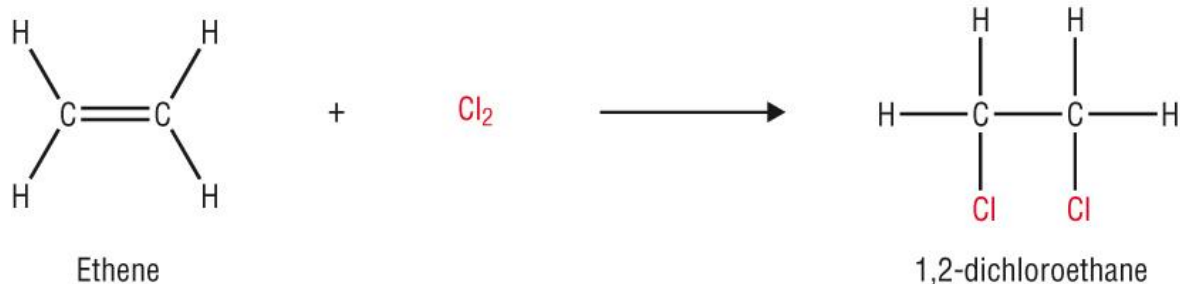


1) Addition of hydrogen:



- Each hydrogen joins to each carbon either side of the C=C.
- This reaction is also called **hydrogenation**
- It is also an example of a **reduction** reaction as hydrogen is added.

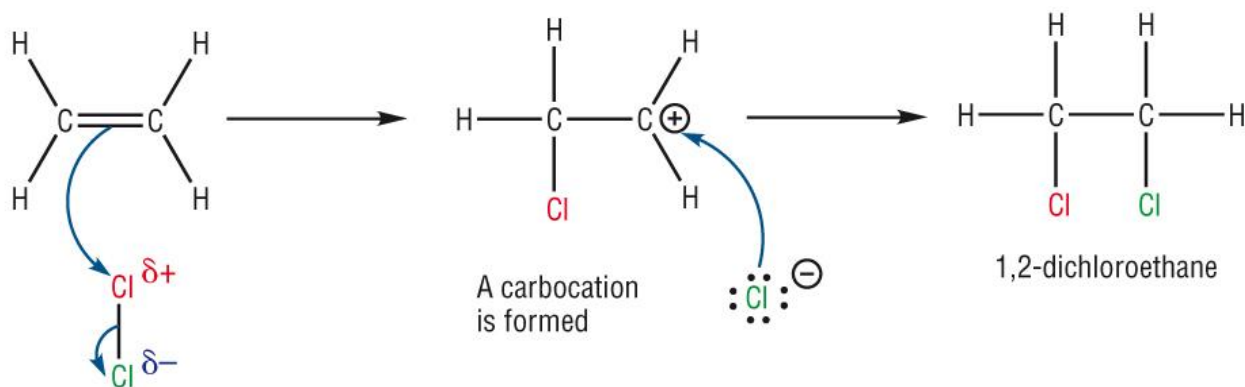
2) Addition of halogens:



- Each halogen joins to each carbon either side of the C=C.
- This reaction is also called **halogenation**, it makes a dihalogeno alkane
- It is also a test for **unsaturation**

The mechanism:

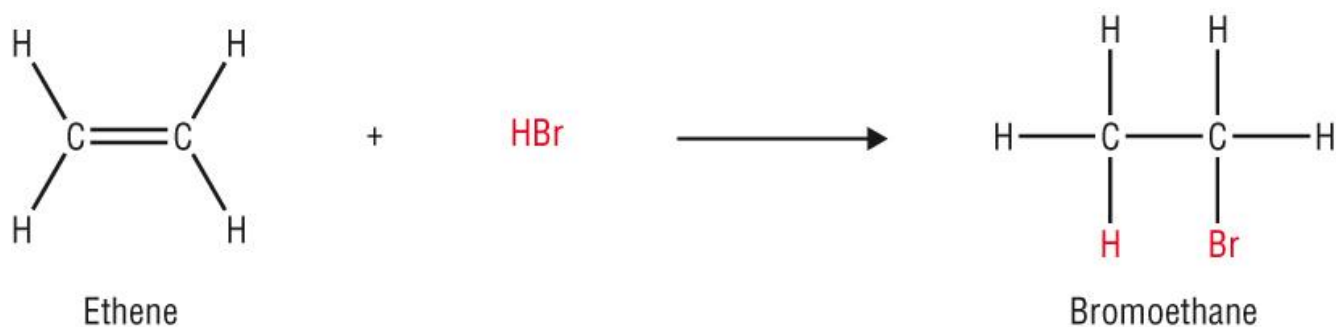
- The mechanism shows the movement of electrons with arrows.
- In Module 1A: An arrow with a double head shows the movement of a pair of electrons.



When Cl₂ approaches, the Cl-Cl bond becomes polar. A pair of electrons flows from the double bond to the slightly positive Cl^{δ+} and a bond formed.

- As Cl₂ comes towards the C = C, the electrons in the double bond repels electrons from the nearest chlorine in the chlorine molecule.
- This **polarises** the chlorine molecule giving a δ- and a δ+.
- The δ+ end of the chlorine molecule is attracted to the C = C.
- The π electrons from the C = C form a single bond with the δ+ Cl. At the same time the electrons from the Cl - Cl bond breaks **heterolytically**
- A carbocation and chloride ion is formed.
- The electrons from the chloride ion form a bond with the carbocation which is unstable, to form a single bond.
- This is an **electrophilic addition** reaction.
- It is used for the preparation of **dihaloalkanes**.

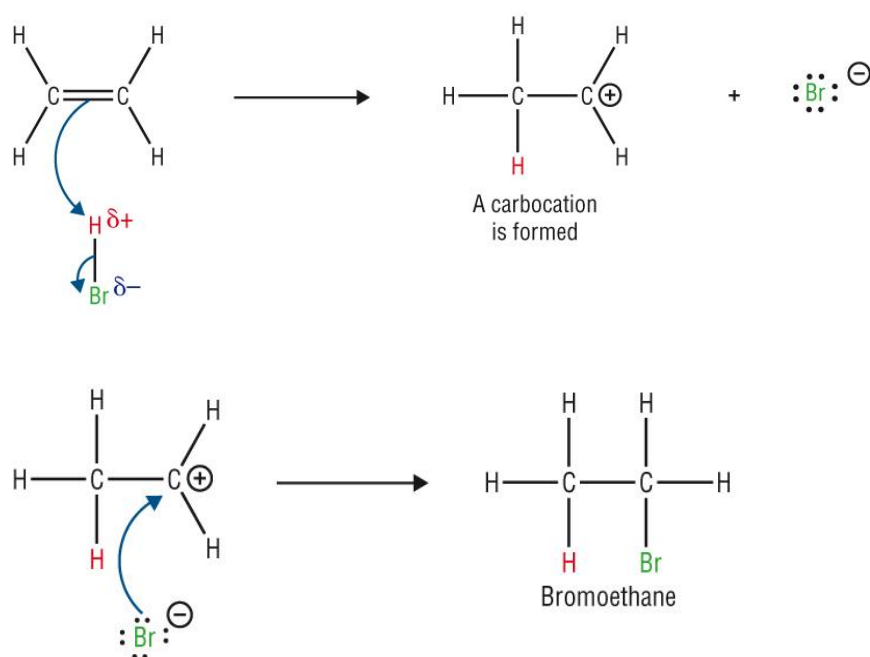
3) Addition of hydrogen halides:



- The hydrogen joins to one of the carbons while the halogen joins to the other carbon in the C=C.
- Any hydrogen halide will react, these are gases and are usually bubbled through the alkene.
- This reaction makes a **halogenoalkane**.

Mechanism:

- These show how a reaction proceeds in terms of the movement of electrons.
- A curly arrow represents the movement of 2 electrons.
- The C=C double bond is a region of high electron density due to the π electrons.
- This means it will attract **electrophiles** to itself.
- As all the reactions are **addition** reactions, the reactions are described as **electrophilic addition**

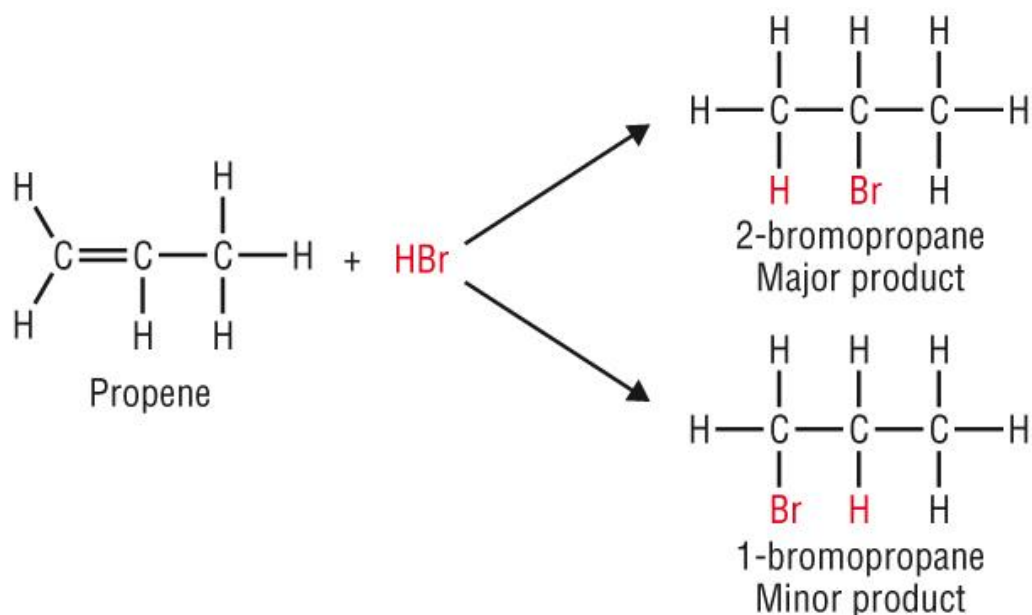


- HBr is a polar molecule due to the more electronegative bromine.
- The δ^+ **hydrogen** in HBr is attracted to the **electron rich** C=C.
- The π electrons in the double bond form a bond between one of the carbons and the δ^+ **hydrogen**.
- At the same time the H-Br bond breaks **heterolytically**.
- This forms a **bromide ion** and a **carbocation**:

Definition - Carbocation is an organic ion in which a carbon atom has a positive charge

- The carbocation is now unstable and quickly forms a bond with the bromide ion.

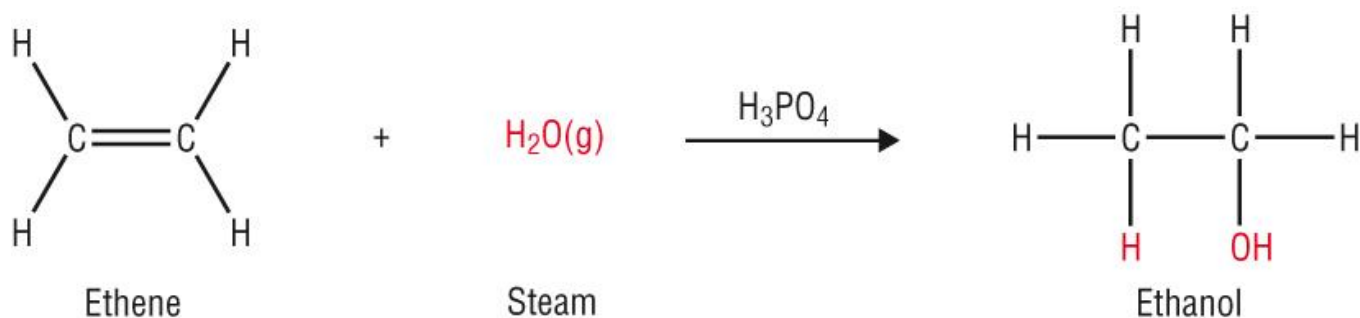
Addition to unsymmetrical alkenes:



- In this reaction the hydrogen and the halogen could add either way round across the $\text{C}=\text{C}$.
- This will give you a mixture of products of both halogenoalkanes.
- At first glance it would appear that both would be equally as likely.
- In fact one is more likely to be formed than the other.
- A rule of thumb is that the halogen adds nearer the centre of the molecule as possible.

You will be expected to identify both products. You will not need to identify the major / minor products

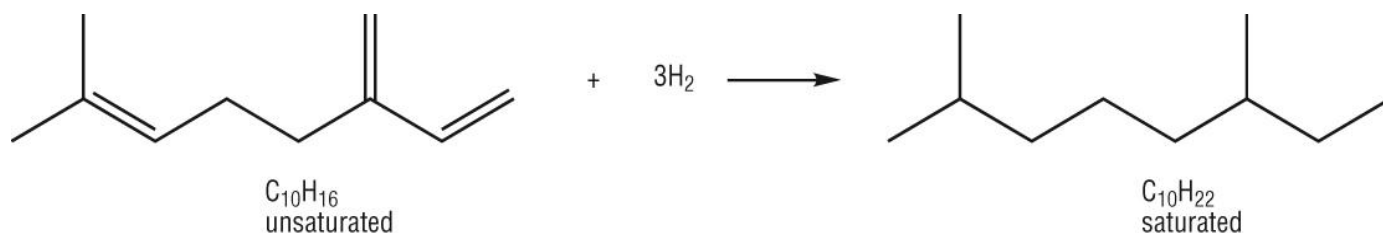
4) Addition of steam:



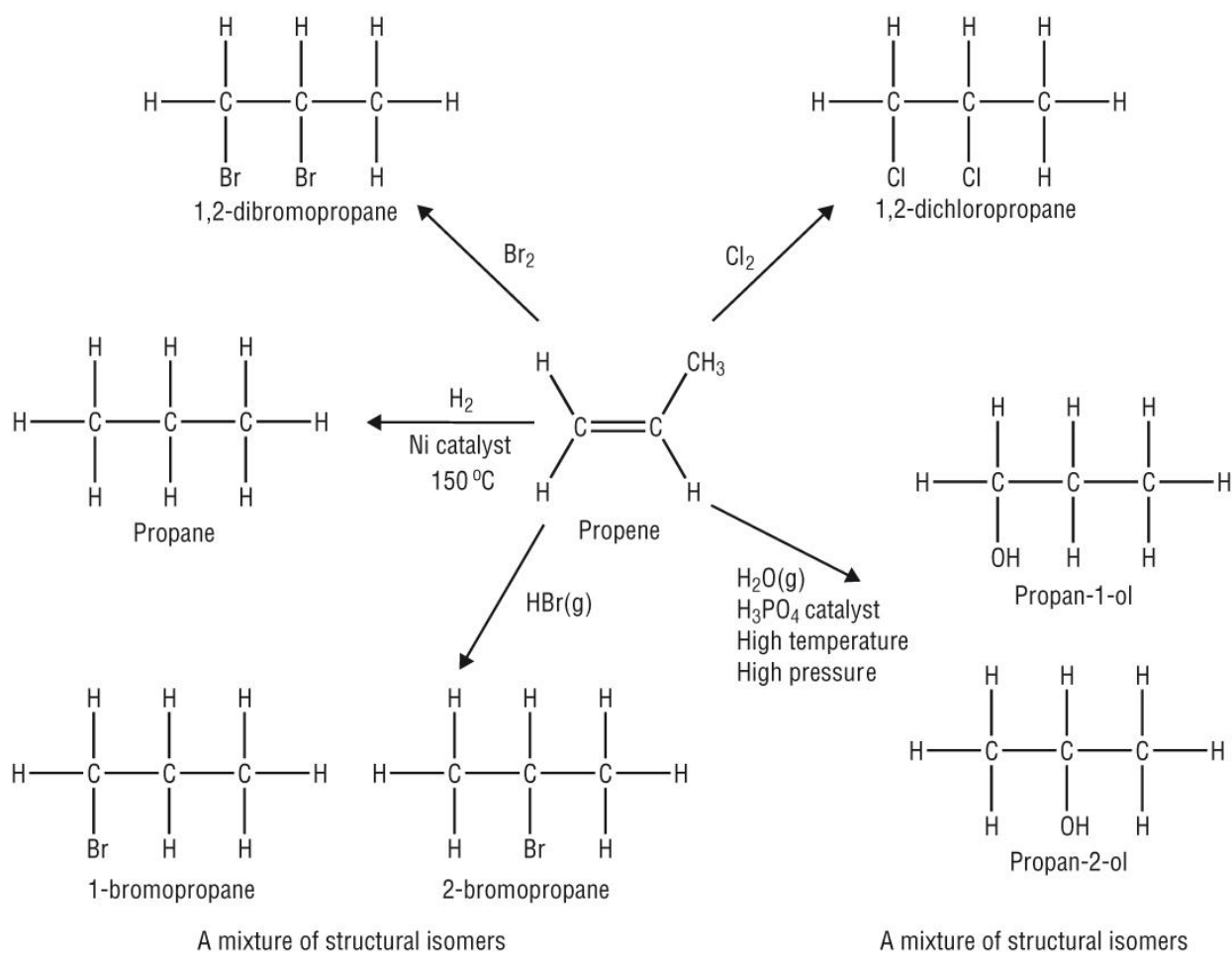
- The **H** joins to one of the carbons while the **OH** joins to the other carbon in the $\text{C}=\text{C}$.
- This reaction is also called **hydration** as water is added to the molecule.
- This reaction makes an **alcohol**

Alkenes with more than one double bond:

- Many naturally occurring alkenes contain more than one double bond. Terpenes are one type of these.
- The number of double bonds is equal to the number of hydrogen molecules needed to saturate it:



Revision: the chemistry of the alkenes



Questions P129 Qu 1-2 / P131 Qu 1-2 / P133 Qu 1-3 / P143 Qu 10 - 12, 14

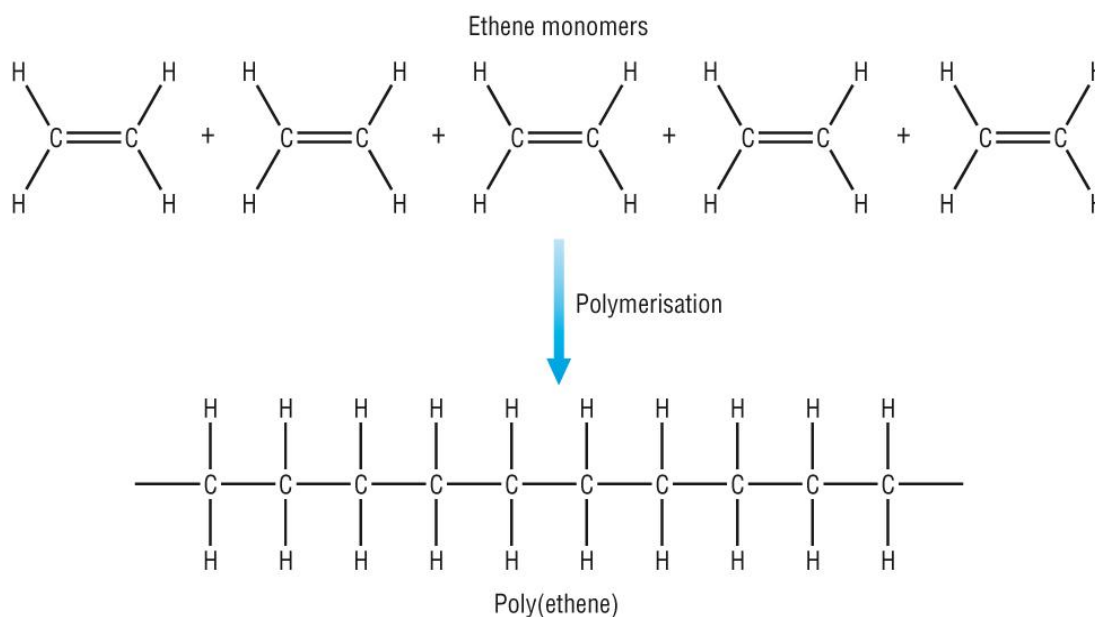
Industrial importance of alkenes:

Unsaturated compounds in industry:

- Unsaturated molecules can be used as starting materials for other molecules.
- The majority of alkenes are used in the polymer industry forming plastics

Making polymers

- Polymerisation is when an alkene undergoes an addition reaction to itself.
- The short starting alkenes are referred to as **monomers**
- A long molecule, **polymer** is formed with high Mr's.
- The type of reaction is **addition polymerisation**.
- Different polymers arise from different alkenes.
- Poly(ethene) is the simplest:



monomer polymer

Polymers and industry:

- Addition polymerisation is carried out in one of 2 ways:

1) Radical polymerisation:

- Carried out at 200°C and high pressures.
- This leads to branched chains in the polymers and polymer mixtures, eg poly(styrene)

2) Ziegler Natta process:

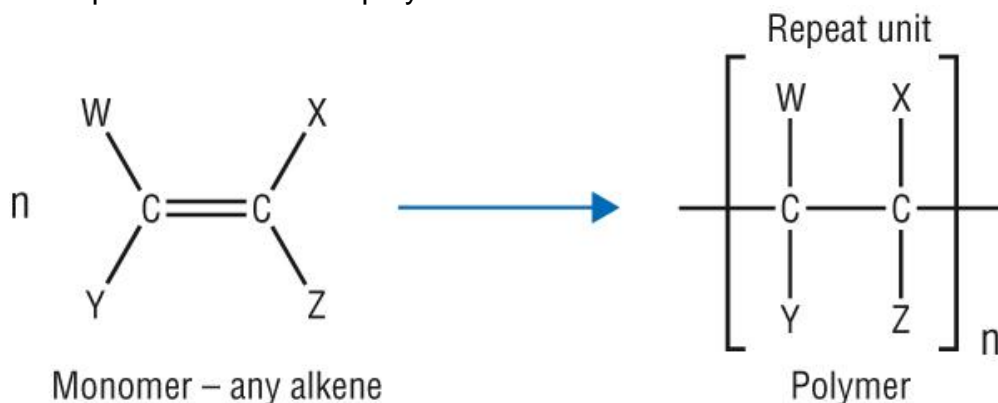
- This uses catalysts such as TiCl_3 / $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ at 60°C.
- This almost removes all branching in the polymer.

Questions P135 Qu 1-3

Polymer chemistry:

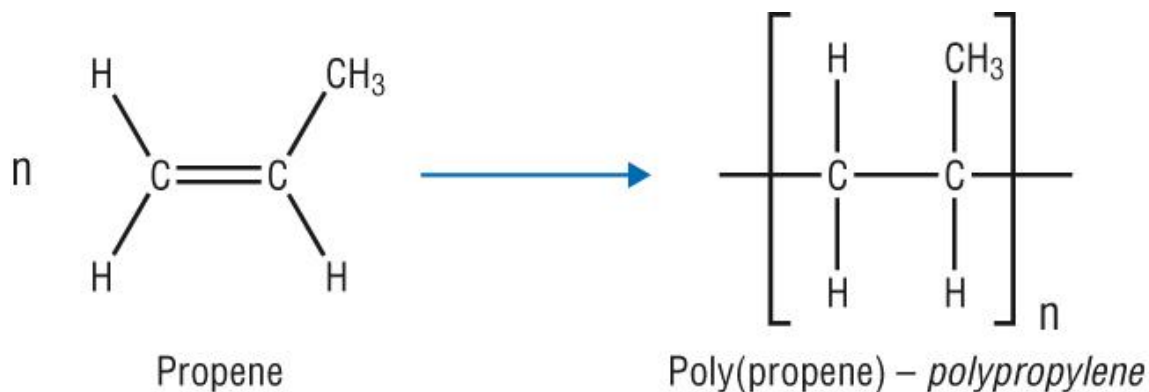
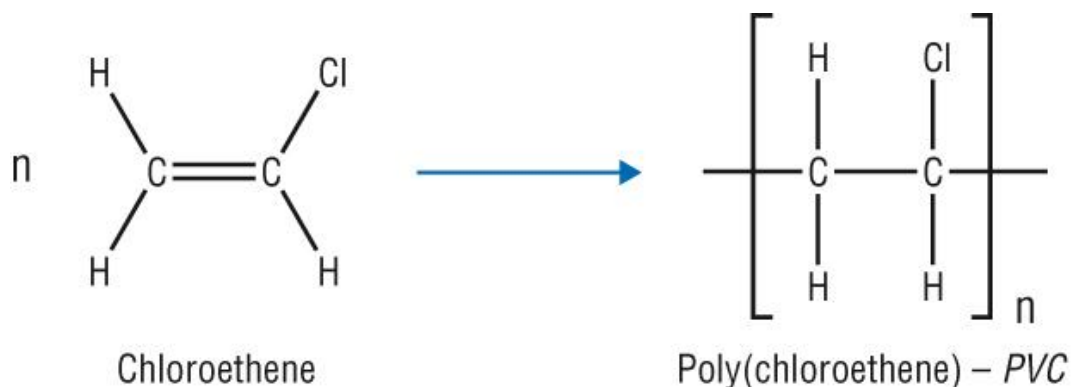
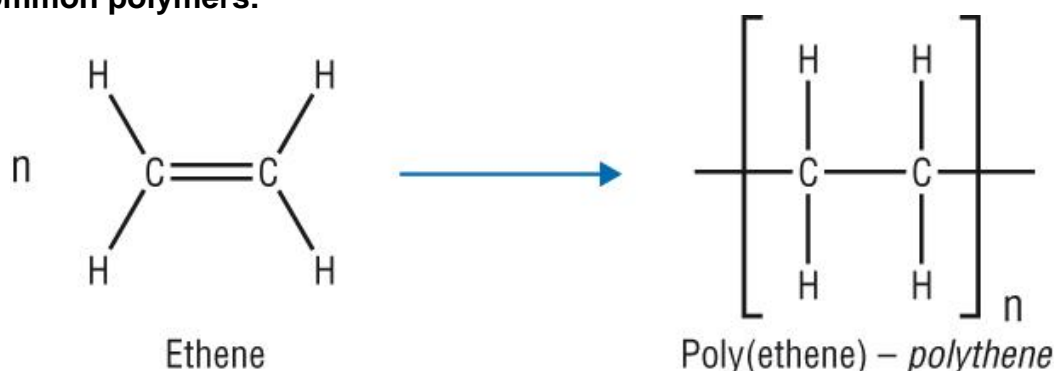
Addition polymerisation:

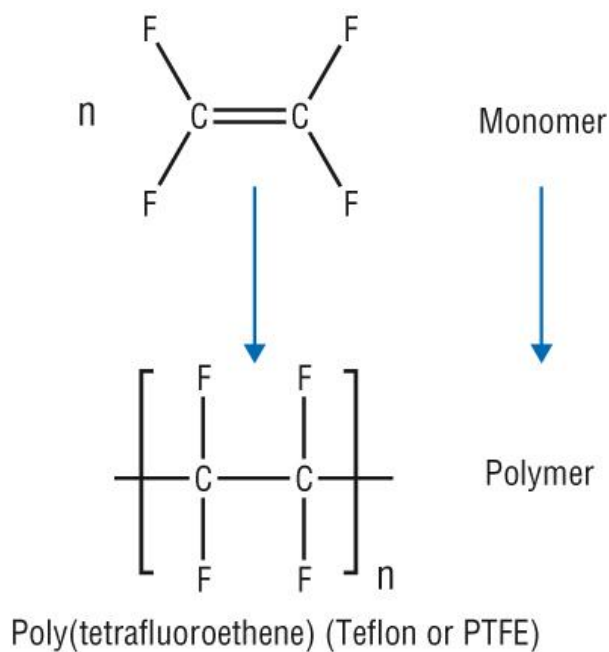
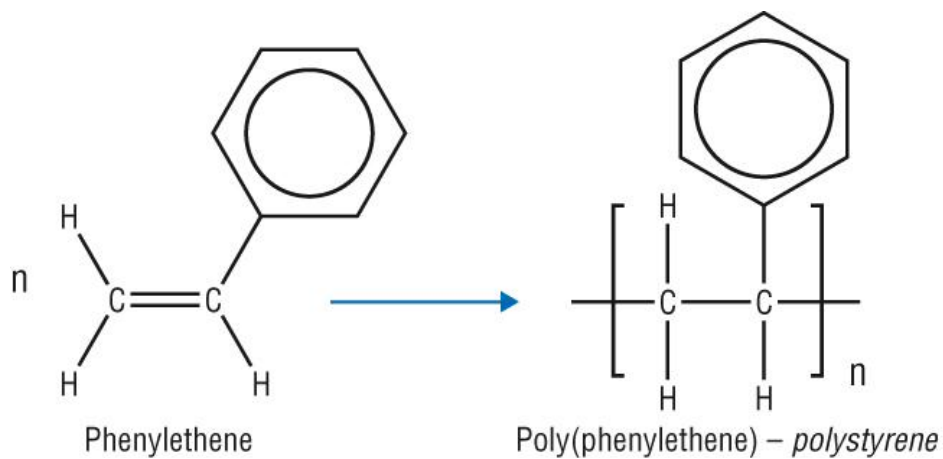
- A common equation for addition polymerisation is:



- Which ever groups come off the carbons on the double bond forms the groups that come off the polymer.

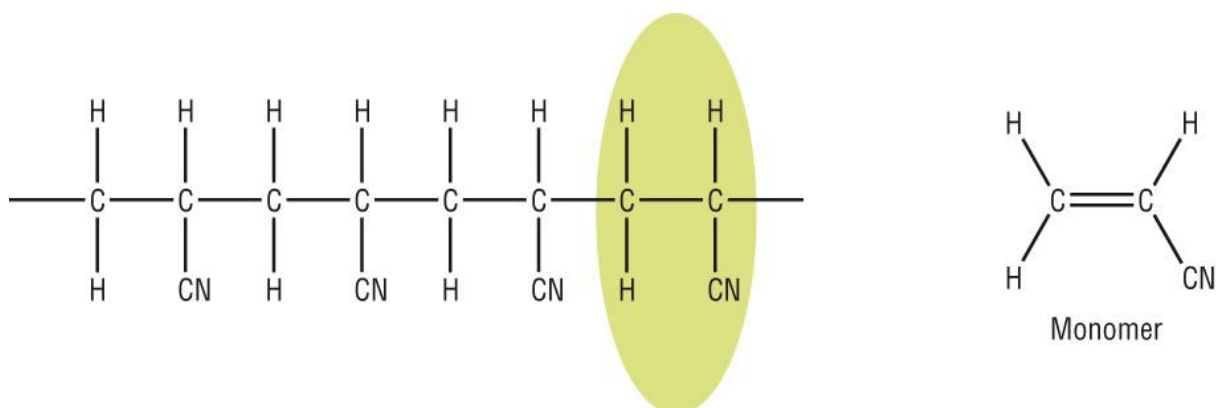
Some common polymers:





Identifying the monomer:

- The monomer is always identified by looking for the **repeat unit**.
- Once the repeat unit is found add a double bond between the carbons of the repeat unit.
- Then remove the 'branch' bonds linking it to the rest of the polymer:



Polymers - dealing with our waste:

- This has become quite a problem.
- As polymers are basically alkanes they are resistant to most chemicals and bacteria.
- This makes them **non – biodegradable**.

Recycling

- Recycling often costs more than it does to make new polymers.

Burning

- Burning polymers releases about the same energy that it took to make them.
- It reduces the use of fossil fuels.
- Burning with other household waste would save landfill site costs.
- Modern technology means that polymers can be burnt cleaner than traditional power stations.
- It would not add to CO₂ levels as these take the place of fossil fuels.
- Other gases like hydrogen chloride from PVC can be removed using gas scrubbers, the gases are removed by neutralisation with a spray of alkali.

Feedstock recycling

- Polymers are cracked to produce a mixture of alkanes, alkenes and arenes.
- These are used further in the chemical industry.
- Alkenes can be polymerised again.

Read P138 - 141, answer questions 1-4 P139 / 1 P141

Questions 13, 15 P 143 / 1-6 P 144,145