

## Alkanes

Alkanes are saturated hydrocarbons

**General formula** alkane  $C_nH_{2n+2}$

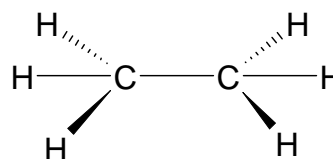
**Saturated:** Contain single carbon-carbon bonds only

**Hydrocarbon** is a compound consisting of hydrogen and carbon **only**

Methane	$CH_4$
Ethane	$C_2H_6$
Propane	$C_3H_8$
Butane	$C_4H_{10}$
Pentane	$C_5H_{12}$
Hexane	$C_6H_{14}$
Heptane	$C_7H_{16}$
Octane	$C_8H_{18}$
Nonane	$C_9H_{20}$
Decane	$C_{10}H_{22}$

Remember that the shape around the carbon atom in saturated hydrocarbons is tetrahedral and the bond angle is  $109.5^\circ$

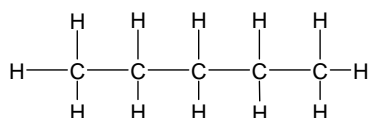
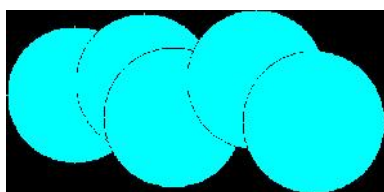
The shape is tetrahedral as a result of the four bond pairs of electrons equally repelling.



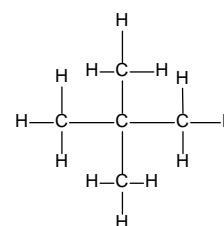
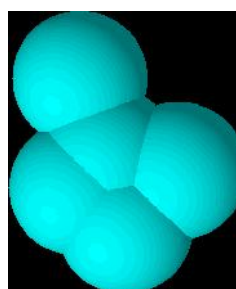
### Physical properties- boiling point

The increasing boiling points of the alkane homologous series can be explained by the increasing number of electrons in the bigger molecules causing an increase in the size of the London forces between molecules.

The shape of the molecule can also have an effect on the size of the London forces. Long chain alkanes have a larger surface area of contact between molecules for London forces to form than compared to spherical shaped branched alkanes and so have stronger London forces and higher boiling points.



Pentane B.p.  $36^\circ C$



2,2 Dimethylpropane  
B.p.  $10^\circ C$

### Chemical Reactivity

Alkanes do not react with many reagents.

This is because the C-C bond and the C-H bond are relatively strong and so cannot form stronger bonds with other elements that easily and there are no polar side groups.

Their main reactions are combustion reactions in air although they can react with halogens in the presence of UV light

## Fuels from crude oil

They are obtained from the crude oil in the order of fractional distillation, cracking and reformation of crude oil

Alkanes are used as fuels

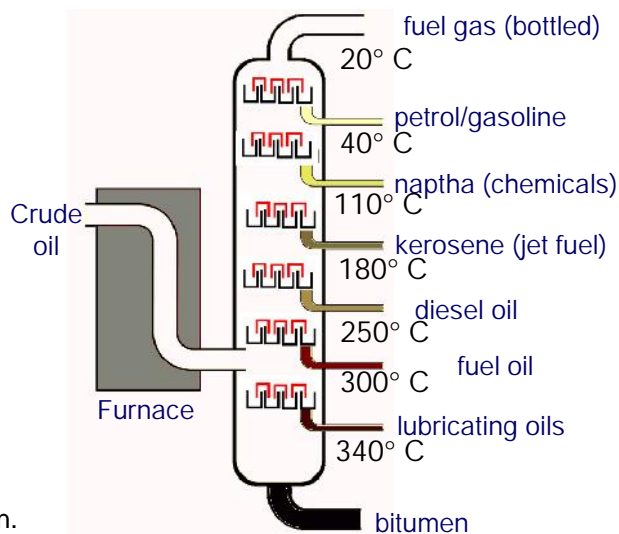
## Refining crude oil

### Fractional Distillation:

Petroleum is a mixture consisting mainly of alkane hydrocarbons

Fractional distillation of crude oil works because different components (fractions) of this mixture can be drawn off at different levels in a fractionating column because of the temperature gradient in the column. The temperature of column decreases upwards.

The crude oil is preheated in a furnace and then passed into the column. The smaller molecules with lower boiling points will evaporate in the column and move upwards in the column. They will pass through the many bubble caps on the trays in the column. As they move up to a colder part of the column that is equal to their boiling point they will start to condense on the trays. Similar molecules of similar size and boiling point will condense at the same level. This fraction of similar molecules will be tapped off from the tray. Note that fractions are a mixture of hydrocarbons with a similar chain length and boiling point range. The larger molecules with stronger London forces and higher boiling points will condense at lower points in the column where the temperature is higher



This is a physical process involving the splitting of weak London forces between molecules

### Vacuum distillation unit

The column shown above is a simplification of the real process. The larger heavier fractions are tapped off from the fractionating column and are distilled again under a lower pressure. Lowering the pressure over a liquid will lower its boiling point.

Vacuum distillation allows heavier fractions to be further separated without high temperatures which could break them down.

## Cracking

Cracking is the next process that occurs in a oil refinery after the initial fractional distillation of the crude oil. Cracking is the conversion of large hydrocarbons to smaller molecules of by breakage of C-C bonds. This is a chemical process involving the splitting of strong covalent bonds so requires high temperatures. There are two main types of cracking: thermal and catalytic. The two processes are used to produce different types of useful products

### Economic reasons for cracking

There is a general imbalance between the abundance of certain fractions in crude oil with their economic demand

The petroleum fractions with shorter carbon chains such as petrol and naphtha are in more demand than the larger fractions.

The larger hydrocarbons are abundant but have a lower demand. To make use of excess larger hydrocarbons and to supply demand for shorter ones the longer hydrocarbons are cracked.

The products of cracking are more useful and valuable than the starting materials (e.g. ethene used to make poly(ethene) and ethane-1,2-diol, and ethanol) The smaller alkanes are used for motor fuels which burn more efficiently.

The two main types of cracking, **thermal** and **catalytic**, need different conditions and are used to produce different products

### Thermal Cracking

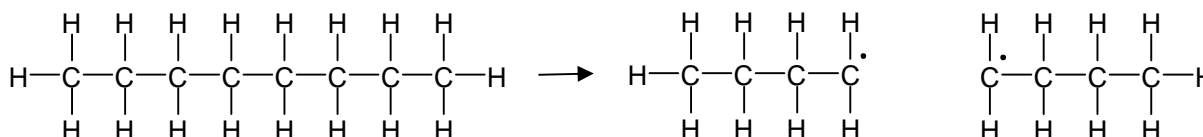
#### Conditions:

**High Pressure** (7000 kPa)

**High Temperature** (400°C to 900°C)

The molecules only need to be exposed to the high temperature for a second for the reaction to occur

The high temperatures involved in this process can break bonds anywhere in the molecule by C-C bond fission and C-H bond fission. The fission of the bond is called homolytic and reactive free radicals are formed.

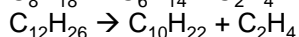
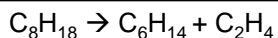


These radicals can then undergo a series of reaction to form more stable compounds. For example they can lose a hydrogen to form a stable alkene plus a hydrogen radical. Hydrogen radicals can then react together to form hydrogen gas. There are several other possible reactions that can occur and this process will always produce a mixture of products. It does produce a high proportion of alkenes that can be useful for manufacturing polymers and many other chemicals. The hydrogen gas produced can also be used in the Haber Process and in margarine manufacture

### Example Equations

Many different overall equations can be written for the process.

High Mr alkanes  $\rightarrow$  smaller Mr alkanes + alkenes + (hydrogen)



## Catalytic Cracking

**Conditions:**  
**Slight/moderate pressure**  
**High Temperature (450°C)**  
**Zeolite Catalyst**

Catalytic cracking is cheaper than thermal cracking because it saves energy as lower temperatures and pressures are used. It produces very different products.

This type of cracking still involves breaking C-C bonds, but the bonds are broken heterolytically and carbocations are produced instead of free radicals. In the process the large hydrocarbon chains can rearrange to form branched chain alkanes, cyclic alkanes and aromatic hydrocarbons. These products are added to motor fuels. Branched and cyclic hydrocarbons burn more cleanly and are used to give fuels a higher octane number.

## Reforming

Reforming is a similar process to catalytic cracking that is used in addition to cracking to turn straight chain alkanes into branched and cyclic alkanes. Reforming is generally used to turn smaller straight chain alkanes into branched or cyclic hydrocarbons of the same size. The products are added to motor fuels to increase their octane number



## Octane number

Knocking occurs in four stroke motor car engines when some hydrocarbons ignite too early. It causes a knocking sound and reduces the engines performance.

We measure the problem using the **octane number**. The higher the number, the better the fuel.

The scale is based on the tendency to auto-ignite of two hydrocarbons:

2,2,4-trimethylpentane, which used to be called iso-octane is given an octane number of 100.

Heptane is given an octane number of zero.

For most of the 20<sup>th</sup> century pre-ignition in motor cars was reduced by the addition of a lead compound, tetraethyl lead (CH<sub>3</sub>CH<sub>2</sub>)<sub>4</sub>Pb. The problem was the lead in the petrol was emitted into the atmosphere via the exhaust gases. Lead is a toxic element and caused significant health problems. Lead was phased out in petrol in the late 20<sup>th</sup> century but we still refer to lead free petrol.

To improve the octane number of petrol and lessen the need for lead additives, the products of the reforming and catalytic cracking processes described above are now added to petrol.

### Questions on Distillation and Cracking

1.a) Describe how fractional distillation of crude oil works. In your answer you should refer to the temperature gradient in the column, the type and varying strength of the intermolecular forces between the molecules, and why the fractions collect at different levels in the fractionating column

b) Why do fractions have a range of boiling points?

2. Catalytic cracking and thermal cracking of petroleum fractions produce different types of products, both of which are valuable.

Discuss both **catalytic cracking and thermal cracking** of a petroleum fraction. In your answer you should quote the conditions used for both cases. Identify the products formed and state their uses for both cases.

3. a) Explain the economic reasons for the catalytic cracking of alkanes and why catalytic cracking is cheaper to carry out than thermal cracking.

b) Explain why high temperatures are needed for thermal cracking

4) Thermal cracking of large hydrocarbon molecules is used to produce alkenes. Write an equation for the thermal cracking of  $C_{21}H_{44}$  in which ethene and propene are produced in a 3:2 molar ratio together with one other product.

5) Cetane ( $C_{16}H_{34}$ ) can be cracked to produce hexane, butene and ethene.

Write an equation to show how one molecule of cetane can be cracked to form hexane, butene and ethene.

6) The cracking of one molecule of compound **X** produces pent-1-ene, ethene and butane in a 1:2:1 mol ratio. Deduce the molecular formula of **X** and write the equation for the reaction

7) One molecule of  $C_9H_{20}$  can be cracked to form one molecule of pentane and one other product.

Write an equation for this cracking reaction.

8) Find out some of the major uses of the alkene products from the thermal cracking reactions.

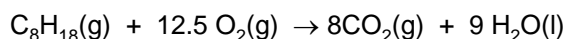
## COMBUSTION

**Alkanes** readily burn in the presence of oxygen. This combustion of alkanes is highly exothermic, explaining their use as **fuels**.

### Complete Combustion

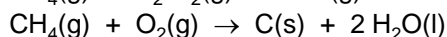
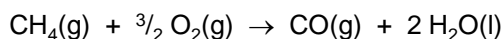
In excess oxygen alkanes will burn with complete combustion

The products of *complete* combustion are CO<sub>2</sub> and H<sub>2</sub>O.



### Incomplete Combustion

If there is a **limited amount of oxygen** then *incomplete* combustion occurs, producing CO (which is very toxic) and/or C (producing a sooty flame)



Incomplete combustion produces less energy per mole than complete combustion

Carbon (soot) can cause global dimming- The small solid particles in the atmosphere reflect the sun's light leading to cooling effect.

Carbon monoxide is an highly toxic but odourless gas. It can cause death if it builds up in a enclosed space due to faulty heating appliances.

CO is toxic to humans as CO can form a strong bond with haemoglobin in red blood cells. This is a stronger bond than that made with oxygen and so it prevents the oxygen attaching to the haemoglobin.

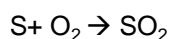
## Sulfur dioxide

Sulfur containing impurities are found in petroleum fractions which produce SO<sub>2</sub> when they are burned.

One impurity found in fuels is methanethiol CH<sub>3</sub>SH. It combusts according to the following equation

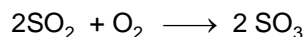


Coal is high in sulfur content, and large amounts of sulfur oxides are emitted from power stations.

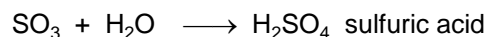


SO<sub>2</sub> will dissolve in atmospheric water and can produce **acid rain** by the following two reactions

Reaction with oxygen in the atmosphere form SO<sub>3</sub>



The SO<sub>3</sub> dissolves in atmospheric water to form acid



Rain is naturally acidic because of dissolved CO<sub>2</sub> and has a pH of 5.6. Acid rain deposition from pollution has a pH below 5.6

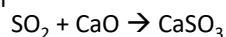
### Removing sulfur by Pre-combustion method

Crude oil can have its sulfur content removed by reacting it with hydrogen gas during the refining process. The sulfur is converted to hydrogen sulfide gas that can be separated.

The hydrogen sulfide can be converted back to sulfur and then used in other processes like vulcanization of rubber

### Removing sulfur by Post-combustion method

SO<sub>2</sub> can be removed from the waste gases from furnaces (e.g. coal fired power stations) by flue gas desulfurisation. The gases pass through a scrubber containing **basic** calcium oxide which reacts with the **acidic** sulfur dioxide in a **neutralisation** reaction



The calcium sulfite which is formed can be used to make calcium sulphate for plasterboard.

## Nitrogen Oxides NO<sub>x</sub>

NO<sub>x</sub> gases react to form smog and acid rain in the atmosphere

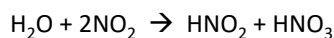
Nitrogen oxides form from the reaction between N<sub>2</sub> and O<sub>2</sub> inside the car engine.

The high temperature and spark in the engine provides sufficient energy to break strong N<sub>2</sub> bond

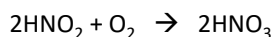


NO can oxidise to NO<sub>2</sub> in the atmosphere  $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$

NO<sub>2</sub> easily dissolves in moisture in the atmosphere to form an acidic solution

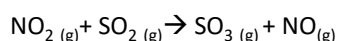


The nitric(III) acid formed in this reaction can also react with oxygen in the atmosphere to produce more nitric(V) acid

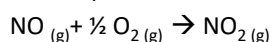


Nitrogen dioxide catalyses the conversion of sulfur dioxide to sulfur trioxide.

The first step of the reaction is



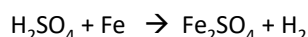
The second step of the reaction is



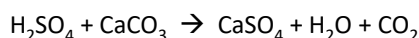
The nitrogen dioxide is regenerated at the end of the reaction so is classed as a catalyst.

Acid Rain can acidify lakes resulting in problems for aquatic creatures. A pH of <4 is fatal for nearly all fish and invertebrate animals. It can also destroy forests and corrode buildings and statues made from limestone.

Sulfuric acid in acid rain will react with metal objects made from iron

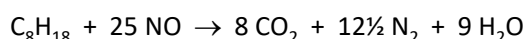
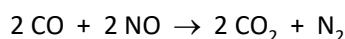


Sulfuric acid in acid rain will react with objects made from limestone which is mostly calcium carbonate.

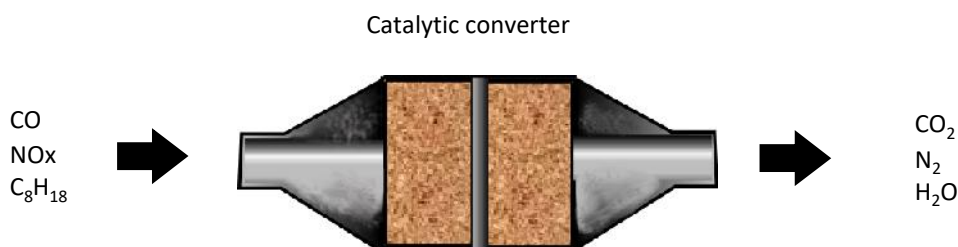


## Catalytic converters

These remove CO, NO<sub>x</sub> and unburned hydrocarbons (e.g. octane, C<sub>8</sub>H<sub>18</sub>) from the exhaust gases of motor vehicles, turning them into 'harmless' CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O.



Converters have a ceramic honeycomb coated with a thin layer of catalyst metals **Platinum, Palladium, Rhodium** – to give a large surface area.



### How Catalytic converter works

- CO and NO are adsorbed onto surface of catalyst
- This weakens bonds in the CO and NO, thereby lowering activation energy
- Reaction occurs
- CO<sub>2</sub> and N<sub>2</sub> desorbs from the surface

Bonding to the catalyst surface must be weak enough for adsorption and desorption to take place but strong enough to weaken bonds and allow reaction to take place.

## The 'Greenhouse Effect' and Global Warming

- Carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and water vapour (H<sub>2</sub>O) are all greenhouse gases. (They trap the Earth's radiated infra red energy in the atmosphere).
- Water is the main greenhouse gas (but is natural), followed by carbon dioxide and methane.

### The Greenhouse Effect

Ultraviolet radiation from the sun comes and heats up the earth. The earth like all hot objects then emits infra red radiation. Some of the infra red radiation is absorbed by greenhouse gases such as CO<sub>2</sub>. Infrared radiation is absorbed by C=O, O-H and C-H bonds in H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub>.

The greenhouse gases then radiates infra red radiation back to the earth's surface. This makes the atmosphere warmer

The 'Greenhouse Effect' of a given gas is dependent both on its **atmospheric concentration** and its **ability to absorb infrared radiation** and also its **residence time**. (Time it stays in atmosphere)

Concentrations of Carbon dioxide in the atmosphere have risen significantly in recent years due to increasing burning of fossil fuels. Carbon dioxide is a particularly effective greenhouse gas and its increase is thought to be largely responsible for global warming.

The Earth is thought to be getting warmer, and many scientists believe it is due to increasing amounts of greenhouse gases in the atmosphere.

### Role of chemists in minimising climate change resulting from global warming

Chemists provide scientific evidence to governments to verify that global warming is taking place such as monitoring atmospheric changes

Chemists are investigating solutions to environmental problems, such as developing **carbon capture and storage, CCS**.

Chemists can monitor progress against initiatives such as the Kyoto protocol

### Carbon Capture and Storage, CCS

Carbon dioxide could potentially be stored in a number of different ways

- removal of waste carbon dioxide as a liquid injected deep in the oceans or on the sea-bed.
- storage in geological formations or under the sea-bed by the reaction of carbon dioxide with metal oxides to form stable solid carbonates, which can be stored

Chemists can also develop

- alternative energy sources such as developing fuel cells or developing solar power or fuels that do not produce CO<sub>2</sub>
- Develop more efficient engines for transport or lean burn engines
- Develop uses for carbon dioxide e.g. dry cleaning or making decaffeinated coffee OR blowing agent in polymer or making fizzy drinks.



## Questions on Combustion and Pollution

### Complete Combustion:

- Cetane ( $C_{16}H_{34}$ ) is a major component of diesel fuel.
  - Write an equation to show the complete combustion of cetane.
  - Cetane has a melting point of  $18^{\circ}C$  and a boiling point of  $287^{\circ}C$ . In polar regions vehicles that use diesel fuel may have ignition problems. Suggest **one** possible cause of this problem with the diesel fuel.
  - What are the environmental consequences of this combustion reaction?
  - How can complete combustion of a fuel be maximised?
  - Another fuel, propane has a boiling point of  $-42^{\circ}C$ , it is usually supplied as a liquid for use in camping stoves. Why is it supplied as a liquid?
- Write equations to show how the following compounds burn completely in air
  - pentane
  - ethanol  $C_2H_5OH$

### Incomplete combustion

- Write an equation to show the incomplete combustion of ethanol to form only carbon monoxide
  - What are the environmental and economic problems of incomplete combustion forming carbon monoxide
- Give the name of a solid pollutant which may form when pentane burns incompletely in air. Write an equation for the combustion of pentane for the formation of this solid pollutant
  - What are the environmental problems caused by the formation of this solid pollutant?

### Nitrogen Oxides

- The pollutant gas NO is found in the exhaust gases from petrol engines. Explain why NO is formed in petrol engines but is not readily formed when petrol burns in the open air.
  - Write an equation to show how NO is formed in the combustion engine and give a condition needed for its formation.
  - The oxide NO reacts with oxygen to form nitrogen dioxide. Write an equation for this reaction. Then deduce an equation to show how  $NO_2$  reacts with water and oxygen to form nitric acid ( $HNO_3$ )
  - What are the environmental consequences of the formation of nitrogen oxides.

### Sulfur dioxide

- There are sometimes sulfur-containing impurities naturally found in crude. One impurity is called methanethiol ( $CH_3SH$ ). This impurity causes environmental problems when burned. Write an equation to show the complete combustion of methanethiol, and explain what are the environmental consequences of this reaction?
  - Describe how the sulfur dioxide can be removed from the waste gases produced when sulphur containing fuels are burnt on a large scale in industry by reacting with calcium oxide on a mesh. As part of your answer include the following
    - Write an equation to show how the  $SO_2$  is removed and explain what type of reaction this is.
    - Why is CaO placed on a mesh?
    - Give a use for the product formed.
    - Give reasons why the method you have described may not be 100% efficient.

## Catalytic Convertors

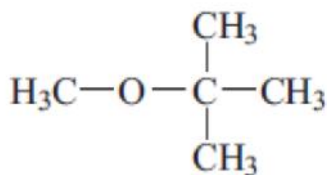
- 7a)** What is the main role of a catalytic convertor in a car?
- b)** What metals is a catalytic convertor made from and explain why these metals are coated on an inert ceramic honeycomb structure.
- c)** Outline, with an equation, how a catalytic convertor removes CO and NO from the exhaust gases of the engine.
- d)** Catalytic convertors can also remove unburnt hydrocarbons. Write an equation to show how inside a catalytic convertor the unburnt octane reacts with nitrogen monoxide to form carbon dioxide, water and nitrogen only. What are the environmental consequences of unburnt hydrocarbons escaping into the atmosphere?
- \*e)** The combustion of diesel is less efficient than that of petrol. Despite an excess of oxygen, unburnt hydrocarbons, CO and even solid carbon are produced. Whilst the first two pollutants may be removed as before in the catalytic converter, the carbon formed would simply block it up were it not removed. At the operating temperatures within the catalyst, very little of the carbon reacts with oxygen; it is, however, oxidised by nitrogen dioxide, NO<sub>2</sub>, forming CO<sub>2</sub> and NO. Write an equation for the reaction between carbon and NO<sub>2</sub>.
- \*8 a)** The catalysts in a catalytic convertor work by a process called heterogeneous catalysis. Explain this term, and describe (with the help of diagrams) the adsorption and desorption mechanism by which heterogeneous catalysts work.
- b)** Explain why the adsorption strength of the catalyst is an important factor in determining its success.

## Pre-ignition

**\*9)** In petrol engines, the vaporised petrol–air mixture is compressed before it is sparked. Some hydrocarbons with a low octane rating, however, ignite under pressure before sparking so that pre-ignition, called knocking, occurs which causes the engine to run unevenly. The octane rating is based on a scale on which 2,2,4-trimethylpentane has an octane rating of 100.

One way to reduce knocking and improve the octane rating is to add tetraethyllead, Pb(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (TEL), and 1,2-dibromoethane. During the combustion, TEL reacts with oxygen and 1,2-dibromoethane to form a mixture of products including lead(II) bromide. Use of TEL is banned in Britain because of the danger to health of lead compounds in the exhaust gases being released into the atmosphere.

- a)** Using molecular formulae, write equations for
- (i)** the complete combustion of 2,2,4-trimethylpentane;
- (ii)** the complete combustion of TEL in the presence of 1,2-dibromoethane to form a mixture of products. Assume that all the bromine and lead combine to form lead(II) bromide.
- b)** Find out what types of hydrocarbons have a large octane numbers and how petrol is stopped from pre-igniting now TEL cannot be used
- c)** Another way to improve the octane rating of petrol is to add compounds such as ethers or alcohols. The ether functional group is R-O-R. The most commonly used ether is methyl tertiary butyl ether (MTBE)



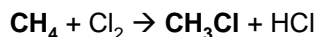
Explain why the ether MTBE is more volatile than its isomeric alcohols

## Free Radical Substitution Reactions of Alkanes

### Reaction of alkanes with bromine / chlorine in UV light

In the presence of **UV light** alkanes react with chlorine to form a mixture of products with the halogens substituting hydrogen atoms.

#### Overall Reaction



methane      chloromethane

*This is the overall reaction, but a more complex mixture of products is actually formed*

In general, alkanes do not react with many reagents. This is because the C-C bond and the C-H bond are relatively strong

The mechanism for this reaction is called a free radical substitution

It proceeds via a series of steps:

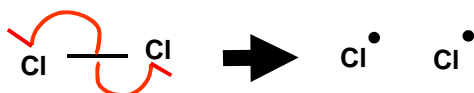
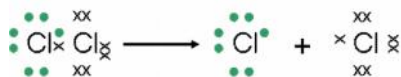
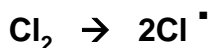
Step one: **Initiation**

Step two: **Propagation**

Step three: **Termination**

#### Step one Initiation

Essential condition: UV light



The UV light supplies the energy to break the Cl-Cl bond. It is broken in preference to the others as it is the weakest.

UV light does not have enough energy to break the C-H bond

The bond has broken in a process called **homolytic fission**.

*each atom gets **one** electron from the covalent bond*

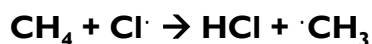
When a bond breaks by homolytic fission it forms **Free Radicals**.

**Free Radicals** do not have a charge and are represented by a  $\cdot$

#### Definition

A **Free Radical** is a reactive species which possess an **unpaired electron**

#### Step two Propagation



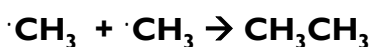
The chlorine free radicals are very reactive and remove an H from the methane leaving a methyl free radical

The methyl free radical reacts with a  $\text{Cl}_2$  molecule to produce the main product and another Cl free radical

All propagation steps have a **free radical** in the **reactants** and in the **products**.

As the Cl free radical is regenerated, it can react with several more alkane molecules in a chain reaction

#### Step three Termination



Collision of two free radicals *does not generate* further free radicals: the chain is **terminated**.

Minor step leading to impurities of ethane in product. **Write this step using structural formulae** and don't use molecular formulae

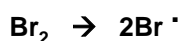
### Applying the mechanism to other alkanes

Example: Write mechanism of Br<sub>2</sub> and Propane

The same mechanism is used: Learn the patterns in the mechanism

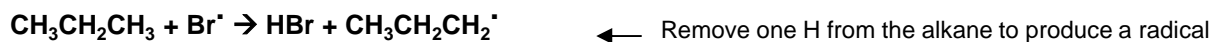
#### STEP ONE Initiation

Essential condition: UV light

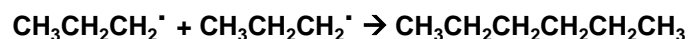


Br<sub>2</sub> splits in the same way as Cl<sub>2</sub>

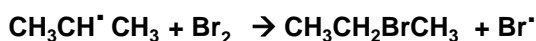
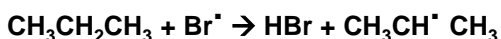
#### STEP TWO Propagation



#### STEP THREE Termination



### Propagation steps for substituting a halogen on a 'middle' carbon

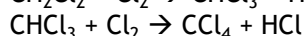
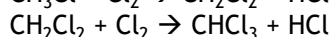
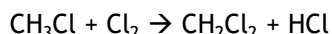


If the question asks for the halogen to be substituted onto a middle carbon in the chain, it is important to put the free radical 'dot' on the correct carbon in the propagation stages.

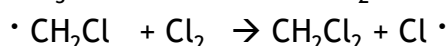
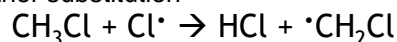
### Further substitution reactions

Excess Cl<sub>2</sub> present will promote further substitution and could produce CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CCl<sub>4</sub>

These reactions could occur



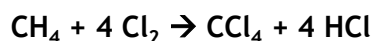
Example propagation steps that would lead to further substitution



### Overall reaction equations

You should be able to write overall reaction equations for various reactions

Example 1. Write the overall reaction equation for the formation of CCl<sub>4</sub> from CH<sub>4</sub> + Cl<sub>2</sub>



Example 2. Write the overall reaction equation for the formation of CFCI<sub>3</sub> from CH<sub>3</sub>F + Cl<sub>2</sub>



Note HCl is always the side product – never H<sub>2</sub>

### Free Radical Substitution questions

**1a)** Explain what is meant by homolytic bond fission. Draw a dot and cross diagram to show the outer electrons in  $\text{CH}_3\text{Cl}$ . Then draw dot and cross diagrams of the two species formed when the C-Cl bond in  $\text{CH}_3\text{Cl}$  undergoes homolytic fission.

**b)** Explain what a free radical is. Use the species formed in 1a) to illustrate your answer.

**2) a)** Name and outline a mechanism for the reaction of chlorine with methane to form chloromethane ( $\text{CH}_3\text{Cl}$ ).

*Include: Initiation step, First propagation step, Second propagation step, 2 different termination steps*

**b)** What is the essential condition needed for the initiation step? Explain why it is the Cl-Cl bond that breaks in this step rather than the C-H bond in the methane

**c)** Write an overall equation for the reaction of chlorine with methane to form trichloromethane ( $\text{CHCl}_3$ ).

**3.** The mechanism for the reaction of methane with fluorine is a free-radical substitution similar to the chlorination of methane.

**(a)** Outline the following steps in the mechanism for the reaction of methane with fluorine to form fluoromethane,  $\text{CH}_3\text{F}$

*Include: Initiation step, First propagation step, Second propagation step, 2 different termination steps*

**(b)** Write an overall equation for the reaction of fluorine with fluoromethane to form tetrafluoromethane.

**4.** When chlorine reacts with trichloromethane, tetrachloromethane,  $\text{CCl}_4$ , is formed.

**(a)** Write the overall equation for this reaction and state the essential condition for this reaction.

**(b)** The mechanism for the chlorination of trichloromethane is free-radical substitution, which proceeds by a series of steps. Write equations for the steps named below in this chlorination.

*Include: Initiation step, First propagation step, Second propagation step, 2 different termination steps*

**5. a)** Outline the following steps in the mechanism for the reaction of bromine with ethane to form 1-Bromoethane

*Include: Initiation step, First propagation step, Second propagation step, 2 different termination steps*

**b)** Further substitution in the reaction of bromine with ethane produces a mixture of liquid organic compounds.

**(i)** Name a technique which could be used to separate the different compounds in this mixture.

**(ii)** Write an overall equation for the reaction between bromine and ethane which produces hexabromoethane,  $\text{C}_2\text{Br}_6$ , by this substitution reaction.

**6.** When bromine reacts with methane. The main product will be  $\text{CH}_3\text{Br}$ . A mixture of other halogenoalkane products are also formed due to further propagation and termination steps.

**a)** Work out the formulae of the other 3 halogenoalkanes formed with 1 carbon atom and explain how they are formed.

**b)** Work out the formulae of at least four of the halogenoalkanes formed with 2 carbon atom and explain how they are formed