14 Hydrocarbons

With the exception of arenes (dealt with in Chapters 29 and 30), this chapter covers the chemistry of hydrocarbons for AS Level. Some of the content has been covered previously or you may have studied it at IGCSE.

Combustion of alkanes

Due to their general lack of reactivity, the single most important use of **alkanes** is as fuels. You may already know about the importance of crude oil, and the cracking of less useful fractions to form more useful products.

KEY TERM

Alkanes are hydrocarbons that contain only carbon–carbon single bonds. They have the general formula C_nH_{2n+2}.

Ethane is used as an example of an alkane. It has the molecular formula C_2H_6.

Ethane reacts differently with oxygen depending on how much oxygen is available.

Plenty of oxygen: $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

Less oxygen: $2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O$

Restricted oxygen: $2C_2H_6 + 3O_2 \rightarrow 4C + 6H_2O$

Progressively restricting the amount of oxygen reduces the amount by which the carbon in ethane is oxidised, until it cannot be oxidised at all. Midway it produces poisonous carbon monoxide, which has been known to kill people using faulty gas heaters.

Crude oil as a source of hydrocarbons

- The use of oil as a major fuel is less than 170 years old and results from the revolutions in land and air transport brought about by the development of the internal combustion engine.
- Crude oil is often talked about as if it is a mixture with fixed composition.

  However, it can vary enormously in the proportions of the various hydrocarbons that make up the mix. This variation affects how much processing the oil requires to yield useful products.
- Not all sources of crude oil have high proportions of the hydrocarbons that are most in demand. However, chemists have developed ways of converting less useful hydrocarbons into more useful ones. The main process for achieving this is cracking.
- The cracking process involves using either high pressures and temperatures without a catalyst, or lower temperatures and pressures in the presence of a catalyst.
- The source of the large-hydrocarbon molecules is often the naphtha fraction or the gas-oil fraction from the fractional distillation of crude oil.
- Although these fractions are obtained as liquids, they have to be vaporised before cracking can occur.

KEY TERM

Cracking is a process in which a large-molecule hydrocarbon of limited use is broken into small-molecule hydrocarbons that are in greater demand. In the laboratory this can be done by passing paraffin vapour over heated aluminium oxide, Al_2O_3. This usually produces a smaller alkane and an alkene.

There is no unique reaction in the cracking process. In general, a large hydrocarbon molecule produces one or more smaller alkane hydrocarbons and one or more alkenes – for example:

$$C_{15}H_{32} \rightarrow 2C_2H_4 + C_3H_6 + C_8H_{18}$$

$$C_{12}H_{26} \rightarrow C_3H_6 + C_9H_{20}$$

$$C_8H_{18} \rightarrow C_6H_{14} + C_2H_4$$

The alkanes produced are usually used for motor fuel – either petrol (gasoline) or diesel – while the alkenes formed are used in the polymer industry.

Some of the most important processes in an oil refinery are shown in Figure 14.1.

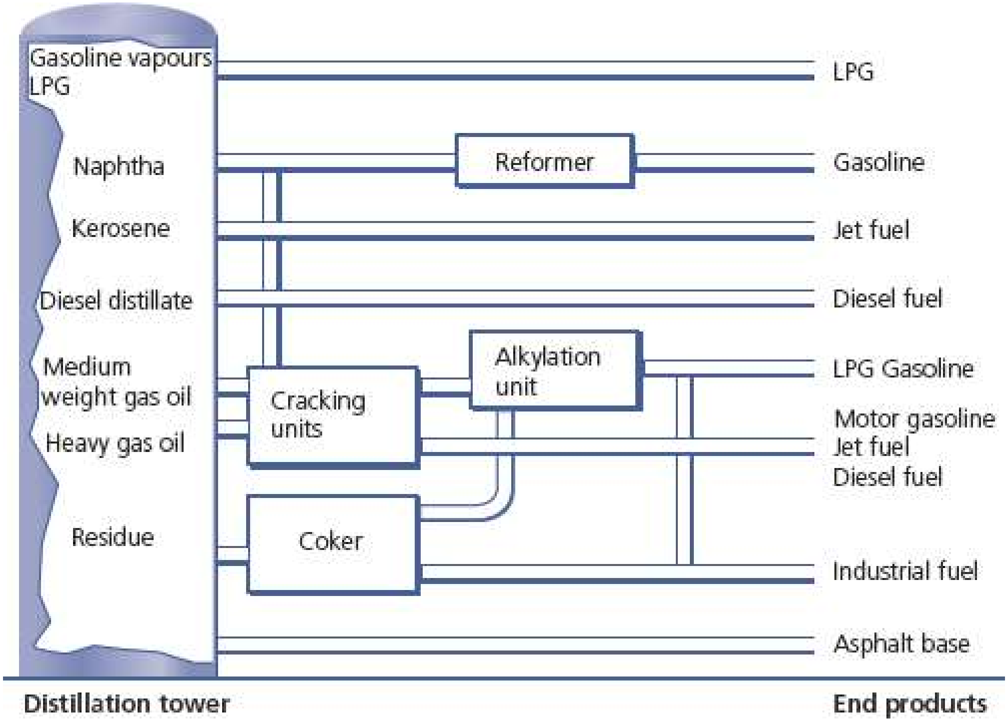


Figure 14.1 Processes in an oil refinery

Substitution reactions of alkanes

Alkanes react with difficulty with both chlorine and bromine. In order to react, alkanes need energy from ultraviolet light (sunlight) and, as you might expect, chlorine reacts more easily than bromine. Taking ethane as the example, the hydrogen atoms are replaced one at a time in substitution reactions:

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$

$$C_2H_5Cl + Cl_2 \rightarrow C_2H_4Cl_2 + HCl$$

$$C_2H_4Cl_2 + Cl_2 \rightarrow C_2H_3Cl_3 + HCl \text{ and so on}$$

The mechanism for the equivalent reaction with methane was covered on page 83.

NOW TEST YOURSELF

1 What sort of substitution reaction is shown above?

Alkenes

Ethene is used as an example of an **alkene**, noting that it has the formula C_2H_4 and that the general formula for alkenes is C_nH_{2n}.

KEY TERM

Alkenes are hydrocarbons that contain a carbon–carbon double bond. They have the general formula C_nH_{2n}.

Addition reactions of alkenes

Because alkenes have a double bond, it is reasonable to expect addition reactions to be particularly important.

With hydrogen

Ethene reacts with hydrogen at a temperature of about 150°C in the presence of finely divided (powdered) nickel. The hydrogen adds across the double bond, forming ethane:

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3{-}CH_3$$

This is not a very useful reaction, but for larger alkenes – such as those found in vegetable oils – the addition of hydrogen across double bonds is more important. These oils are ‘hardened’, or turned into solid fats, by hydrogenation – a process that is necessary for the manufacture of margarine.

With steam

Water, in the form of steam, can be added across ethene's double bond to form ethanol. This is carried out industrially at a temperature of about 300°C and a pressure of about 60 atm in the presence of a phosphoric(v) acid catalyst.

For alkenes other than ethene, there is the possibility of adding the hydrogen to two different carbons. In propene, for example, the hydrogen can be added to either the end carbon or the middle carbon, forming propan-2-ol or propan-1-ol respectively:

$$CH_3{-}CH{=}CH_2 + H_2O \rightarrow CH_3CHOHCH_3 \text{ or } CH_3CH_2CH_2OH$$

Markovnikov's rule means that in the above reaction, propan-2-ol is favoured.

KEY TERM

Markovnikov's rule states that when a molecule of the form HX is added across a double bond, the hydrogen usually becomes attached to the carbon that is already attached to the most hydrogen atoms.

With hydrogen halides

If a gaseous alkene is bubbled through, or a liquid alkene is shaken with either a concentrated aqueous solution of hydrogen bromide or hydrogen bromide dissolved in a non-polar solvent, the hydrogen bromide is added across the double bond.

The reaction is similar to the addition of water and follows Markovnikov's rule:

$$CH_3{-}CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3$$

With halogens

Ethene reacts with halogens by adding across the double bond. Therefore, with bromine at room temperature the reaction forms 1,2-dibromoethane:

$$CH_2{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$$

Chlorine, being more reactive, reacts faster than bromine. Iodine reacts more slowly.

The reaction above refers to ethene reacting with a pure halogen. Often, as in testing for alkenes using bromine water, a competing reaction can take place:

$$CH_2{=}CH_2 + Br_2 + H_2O \rightarrow CH_2BrCH_2OH + HBr$$

The new compound is 1-bromo-2-hydroxyethane (or 2-bromoethanol).

NOW TEST YOURSELF

2 a Write an equation to show the addition of HBr to but-1-ene.

b Give the systematic name for the product of this reaction.

Oxidation reactions of alkenes

Alkenes react with oxidising agents such as acidified manganate(VII) ions. The extent of the reaction, and hence the nature of the products, depends on the concentration of the oxidising agent and the temperature.

With cold, dilute, acidified manganate(VII) ions

Under these conditions ethene is oxidised to the diol 1,2-dihydroxyethane:

$$CH_2{=}CH_2 + [O] + H_2O \rightarrow CH_2OHCH_2OH$$

With hot, concentrated, acidified manganate(VII) ions

Acidified manganate(VII) is such a strong oxidising agent that in concentrated solution and with heat, the carbon–carbon double bond of the alkene is ruptured. You may not think that this is a very useful reaction, but by identifying the products the position of a double bond in an unknown alkene can be determined.

The symbol R is used to represent a hydrocarbon group or a hydrogen atom. So, any alkene can be represented by the formula shown in Figure 14.2.

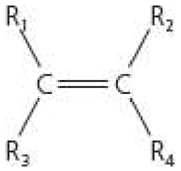


Figure 14.2

When the acidified manganate(VII) ions oxidise the alkene, two C=O double bonds are formed (Figure 14.3).

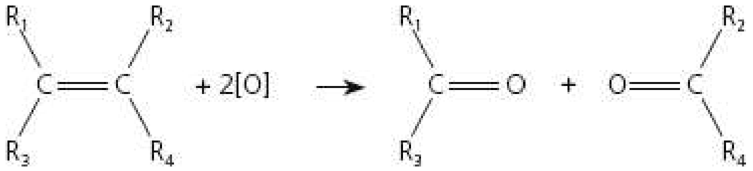


Figure 14.3

A compound that contains a C=O functional group is known as a **carbonyl compound**. A carbonyl compound with two hydrocarbon groups is called a **ketone**. If one of the R groups is hydrogen, the carbonyl compound formed is called an **aldehyde** (Figure 14.4) and this can be oxidised further by acidified manganate(VII) to form a **carboxylic acid**.

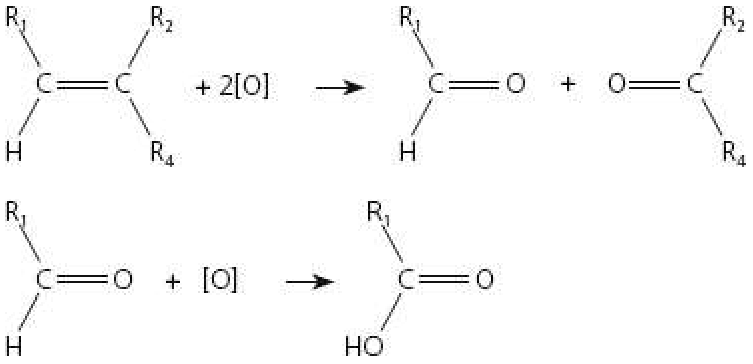


Figure 14.4

There is one further complication that occurs when there are no R groups at one end of the double bond (Figure 14.5). The carboxylic acid formed under those circumstances (methanoic acid) is itself oxidised by the acidified manganate(VII) ions to form carbon dioxide and water.

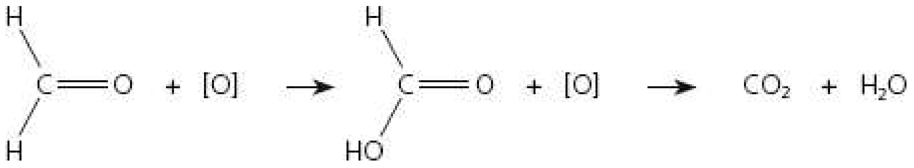


Figure 14.5

STUDY TIP

Here are some rules that might help you to work out the structure of the original alkene:

- Think about each end of the double bond separately.
- If there are two hydrocarbon groups at one end of the bond then that part of the molecule will give a ketone.
- If there is one hydrocarbon group and one hydrogen atom at one end of the bond then that part of the molecule will give a carboxylic acid.
- If there are two hydrogen atoms at one end of the bond then that part of the molecule will give carbon dioxide and water.

Combine the information to work back to the structure of the original alkene.

NOW TEST YOURSELF

3 Name the products of reacting propene with:

a cold, dilute, acidified manganate(VII) ions

b hot, concentrated, acidified manganate(VII) ions

Electrophilic addition in alkenes

You saw in Chapter 13 that halogens behave as electrophiles, and you know that alkenes have a relatively high concentration of electrons round the double bond. You need to understand the mechanism of electrophilic addition, including the specific example of bromine reacting with ethene. The reaction takes place in two stages.

First, bromine molecules approach the ethene molecules, and the π-electrons in ethene induce a dipole on the bromine molecules (Figure 14.6). A bond is formed between the carbon and the bromine, forming a positively charged species called a **carbocation.**

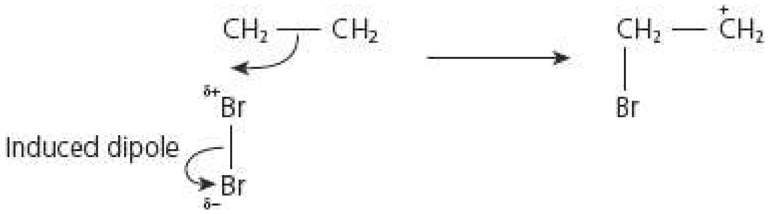


Figure 14.6

Second (Figure 14.7), the carbocations are rapidly attacked by Br^- ions to form the dibromide product.

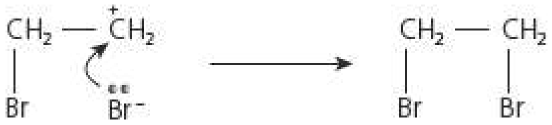


Figure 14.7

You need to be aware of the **inductive effects** of alkyl groups in stabilising such carbocations. Alkyl groups tend to push electrons towards the carbon they are attached to, and this helps to stabilise a carbocation.

KEY TERM

An **inductive effect** exists with alkyl groups. This refers to alkyl groups attached to a carbon which is electron deficient in some way. The alkyl groups act as reservoirs of electrons, partially compensating for the deficiency.

NOW TEST YOURSELF

4 The reaction between bromine and ethene only occurs ‘cleanly’ in a non-aqueous solvent. Explain what other product(s) might be formed if the bromine is dissolved in water.

Polymerisation

Carbon is one of the few elements to form rings and extended chains of atoms. Alkenes can join together to form long chains, or **polymers**. This does not apply to hydrocarbon alkenes only but also to substituted alkenes such as chloroethene (CH_2=CHCl), which is used to make PVC.

Poly(ethene)

Addition polymerisation takes place when molecules containing a C=C double bond are joined together to form a long chain. The simplest of these reactions is the polymerisation of ethene:

$$n\mathrm{CH_2{=}CH_2} \rightarrow \mathrm{\!\left(CH_2{-}CH_2 \right)\!}_n$$

- In this reaction, the conditions needed are a temperature of around 200°C, a pressure of around 2000 atmospheres and a small amount of oxygen to initiate the reaction.
- Under these conditions the resulting chain could be made up of anything between 2000 and 20 000 molecules.
- This reaction produces a form of poly(ethene) called **low-density poly(ethene)** due to the fact that the chains made are branched and do not allow close packing.
- This polymer is used to make plastic bags and for other low-strength sheet applications.

KEY TERM

Addition polymerisation occurs in alkenes and substituted alkenes. The double bond reacts, linking monomers together and without the formation of any other product.

Another form of poly(ethene), **high-density poly(ethene)**, can be produced but the conditions used are very different:

- The temperature is much lower, at around 60°C, the pressure is only a few atmospheres and a catalyst is required. These conditions cause the chains to grow in a much more ordered way, enabling them to pack together much more closely, hence increasing the density of the bulk polymer.
- This tougher polymer is used to make plastic containers, washing-up bowls and some plastic pipes.

Poly(propene)

Propene is similar to ethene, but its molecules have one hydrogen atom replaced by a methyl group. The double bond is still present and so the molecule can be polymerised:

$$n\mathrm{CH_2{=}CHCH_3} \rightarrow \left(\mathrm{CH_2{-}CHCH_3}\right)_n$$

Poly(propene) is used in containers and packaging, carpets and thermal clothing such as fleeces.

Poly(chloroethene)

Other addition polymers can be formed by substituting a hydrogen in ethene as we did with propene, e.g. with chlorine to form poly(chloroethene). The polymer formed is still commonly called after the old name for chloroethene – vinyl chloride – so you will see it referred to as polyvinylchloride or PVC. Although the reaction is the same, it is usual to draw the molecules showing the chlorine atoms all bonded to one side of the chain (Figure 14.8).

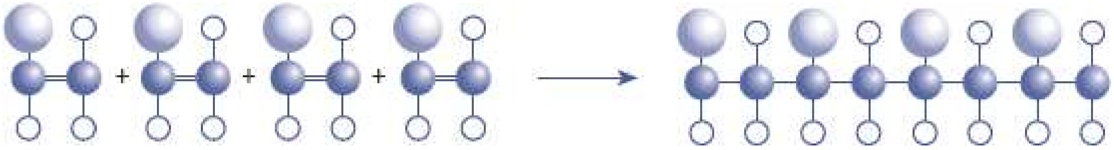
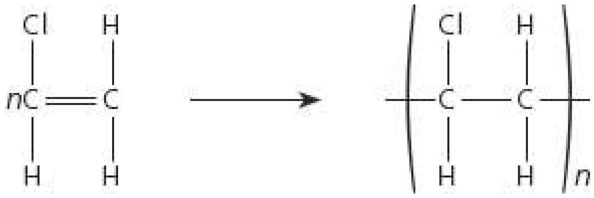


Figure 14.8

The equation used to show this is given in Figure 14.9.



$$n\,\begin{matrix}\mathrm{Cl} & & \mathrm{H}\\ | & & |\\ \mathrm{C} & = & \mathrm{C}\\ | & & |\\ \mathrm{H} & & \mathrm{H}\end{matrix} \longrightarrow \left(\begin{matrix} & \mathrm{Cl} & & \mathrm{H} & \\ & | & & | & \\ - & \mathrm{C} & - & \mathrm{C} & -\\ & | & & | & \\ & \mathrm{H} & & \mathrm{H} & \end{matrix}\right)_n$$

Figure 14.9

Poly(chloroethene) is used to make a wide range of products, including guttering and plastic window frames. It can be rather hard and rigid. Chemicals called plasticisers can be added to increase the flexibility. This increases the range of uses – for example electrical cable insulation, sheet materials for flooring, footwear and clothing.

As well as knowing the polymers formed from alkenes (and substituted alkenes) you will need to be able to identify the monomer from which a given addition polymer has been formed, and also the repeat unit for the polymer (Figure 14.10).

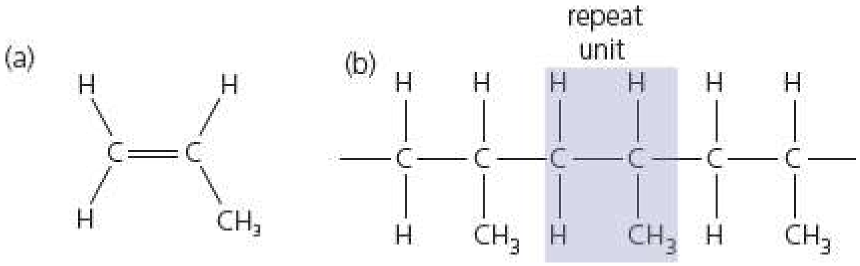


Figure 14.10 (a) Monomer, (b) repeat unit

NOW TEST YOURSELF

5 Figure 14.11 shows a section of a polymer.

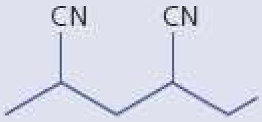


Figure 14.11

What monomer was used to produce this polymer?

REVISION ACTIVITY

a Why are large alkane molecules often subjected to cracking?
b What other type of hydrocarbon is formed in the cracking process?

END OF CHAPTER CHECK

By now you should be able to:

- recall the reactants and conditions by which alkanes can be produced
- describe the combustion of alkanes and the free radical substitution by Cl_2 and Br_2 in the presence of sunlight, including the mechanism; recognise the environmental consequences of the products of the combustion of alkanes
- suggest how cracking can be used to produce more useful alkanes and alkenes from heavier crude oil fractions

- understand the general unreactivity of alkanes in terms of the strength and relative lack of polarity of the C–H bond
- recall the reactants and conditions by which alkenes can be produced
- describe the reactions of alkenes – electrophilic addition; oxidation with cold dilute and hot concentrated KMO_4; addition polymerisation
- describe the mechanism of electrophilic additions using Br_2/ethene and HBr/propene as examples
- describe and explain the inductive effect of alkyl groups on the stability of primary, secondary and tertiary cations formed during electrophilic addition