Chapter 12 - The petroleum industry

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Substances from oil

What do the modes of transport shown in Figure 12.1 have in common? They all use liquids obtained from crude oil as fuels.

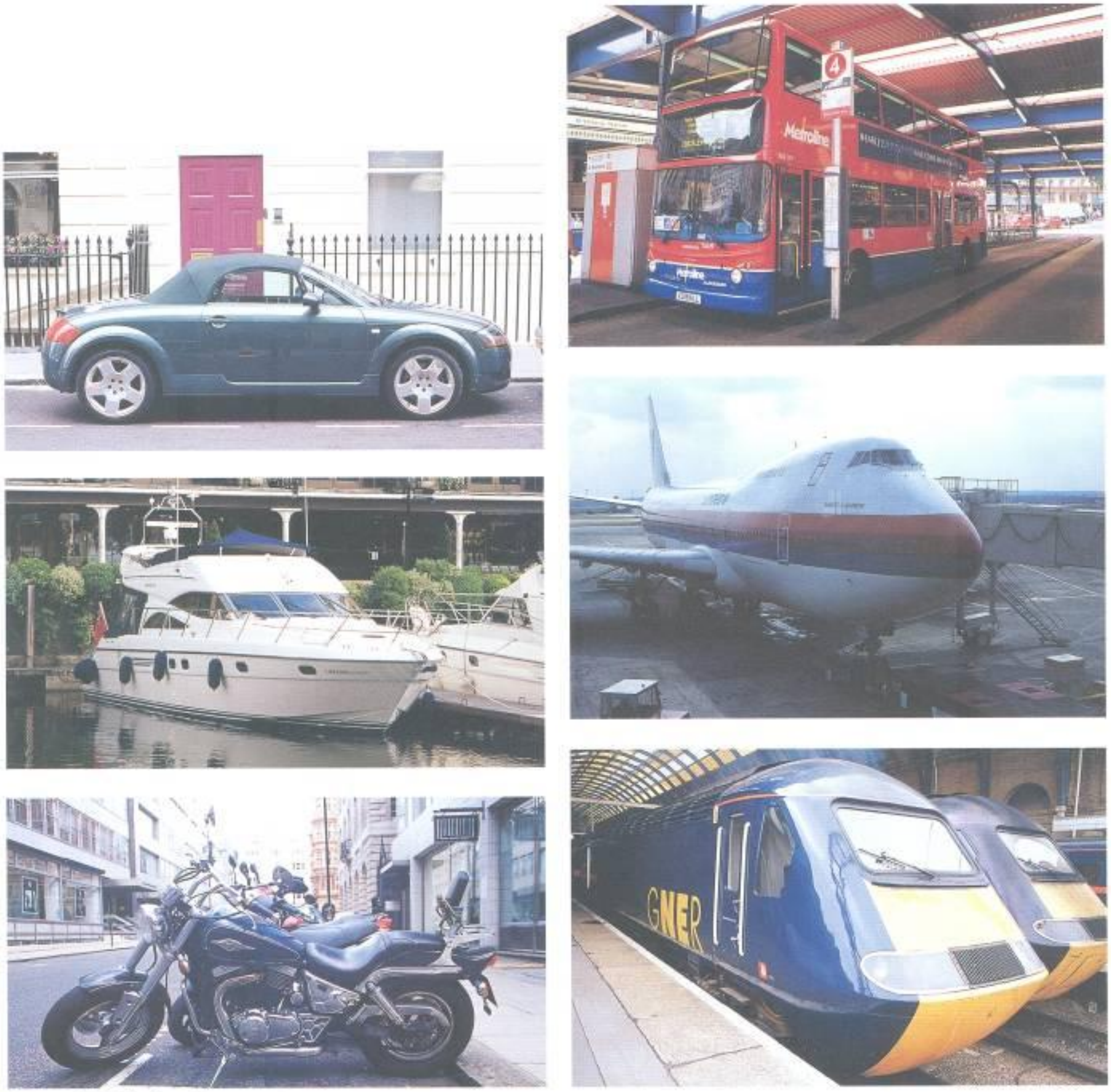


Figure 12.1 Modes of transport.

Oil refining

Crude oil is a complex mixture of compounds known as **hydrocarbons** (Figure 12.2a). Hydrocarbons are molecules which contain only the elements carbon and hydrogen bonded together covalently (Chapter 4). These carbon compounds form the basis of a group called **organic compounds**. All living things are made from organic compounds based on chains of carbon atoms similar to those found in crude oil. Crude oil is not only a major source of fuel but is also a raw material of enormous importance. It supplies a large and diverse chemical industry to make dozens of products (Figure 12.2b).

Crude oil is not very useful to us until it has been processed. The process, known as **refining**, is carried out at an oil refinery (Figure 12.3).

a Crude oil is a mixture of hydrocarbons.

Figure 12.3 An oil refinery.

b The objects above are made from substances obtained from oil.

Figure 12.2

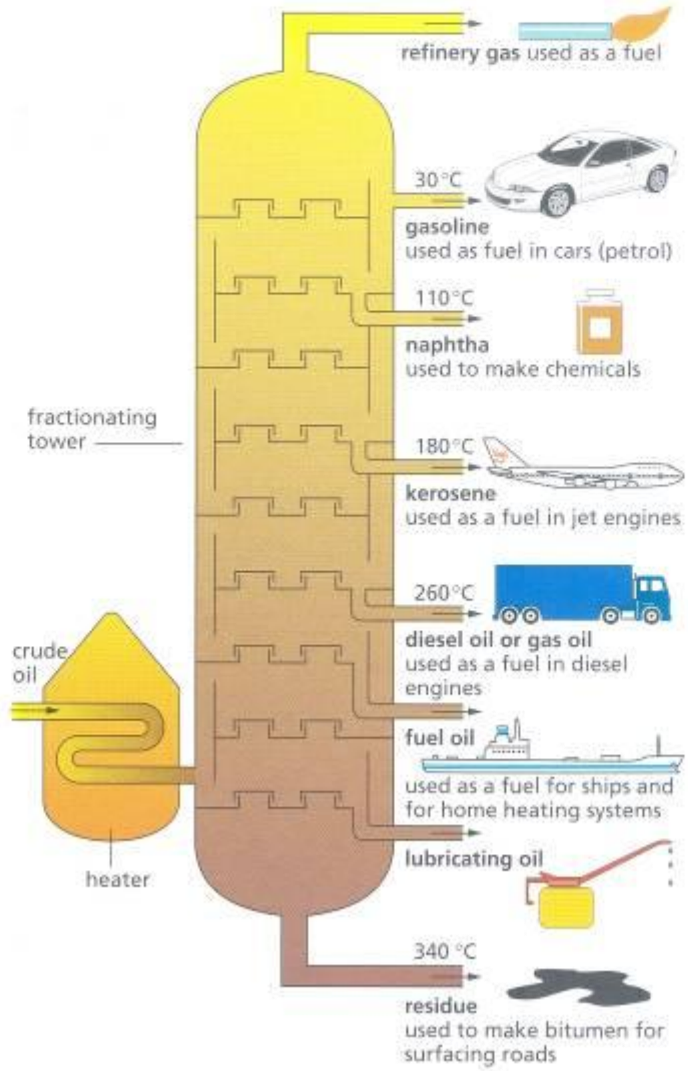


Figure 12.4 Fractional distillation of crude oil in a refinery.

Refining involves separating crude oil into various batches or **fractions**. Chemists use a technique called **fractional distillation** to separate the different fractions. This process works in a similar way as that discussed in Chapter 2, for separating ethanol (alcohol) and water. The different components (fractions) separate because they have different boiling points. The crude oil is heated to about 400°C to vaporise all the different parts of the mixture. The mixture of vapours passes into the fractionating column near the bottom (Figure 12.4). Each fraction is obtained by collecting hydrocarbon molecules which have a boiling point in a given range of temperatures (Figure 12.4). For example, the fraction we know as petrol contains molecules which have boiling points between 30°C and 110°C. The molecules in this fraction contain between five and ten carbon atoms. These smaller molecules with lower boiling points condense higher up the tower. The bigger hydrocarbon molecules which have the higher boiling points condense in the lower half of the tower.

The liquids condensing at different levels are collected on **trays**. In this way the crude oil is separated into different fractions. These fractions usually contain a number of different hydrocarbons. The individual single hydrocarbons can then be obtained, again by refining the fraction by further distillation.

It is important to realise that the uses of the fractions depend on their properties. For example, one of the lower fractions, which boils in the range 250-350°C, is quite thick and sticky and makes a good lubricant.

However, the petrol fraction burns very easily and this therefore makes it a good fuel for use in engines.

Questions

1. What do you understand by the term hydrocarbon?

2. All organisms are composed of compounds which contain carbon. Why do you think carbon chemistry is often called 'organic chemistry'?

3. List the main fractions obtained by separating the crude oil mixture and explain how they are obtained in a refinery.

Alkanes

Most of the hydrocarbons in crude oil belong to the family of compounds called **alkanes**. The molecules within the alkane family contain carbon atoms covalently bonded to four other atoms by single bonds. Because these molecules possess only single bonds they are said to be **saturated**, as no further atoms can be added (Figure 12.5). The physical properties of the first six members of the alkane family are shown in Table 12.1.

Table 12.1 Some alkanes and their physical properties.

Alkane	Formula	Melting point/°C	Boiling point/°C	Physical state at room temperature
Methane	CH_4	-182	-162	Gas
Ethane	C_2H_6	-183	-89	Gas
Propane	C_3H_8	-188	-42	Gas
Butane	C_4H_{10}	-138	0	Gas
Pentane	C_5H_{12}	-130	36	Liquid
Hexane	C_6H_{14}	-95	69	Liquid

You will notice from Figure 12.5 and Table 12.1 that the compounds have a similar structure and similar name endings. They also behave chemically in a similar way and the family of compounds can be represented by a general formula. In the case of the alkanes the general formula is:

$$C_nH_{(2n+2)}$$

where n is the number of carbon atoms present.

A family with the above factors in common is called a **homologous series**. As you go up a homologous series, in order of increasing number of carbon atoms, the physical properties of the compounds gradually change. For example, the melting and boiling points of the alkanes shown in Table 12.1 gradually increase. This is due to an increase in the intermolecular forces (van der Waals' forces) as the size and mass of the molecule increases (Chapter 4).

Under normal conditions molecules with up to four carbon atoms are gases, those with between five and 16 carbon atoms are liquids, while those with greater than 16 carbon atoms are solids.

Questions

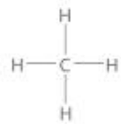
1. Estimate the boiling points for the alkanes with formulae:

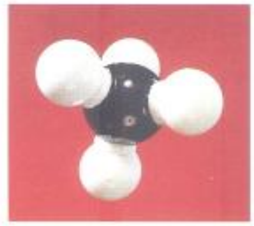
a. C_7H_{16}
b. C_8H_{18}

2. Name the alkanes which have the following formulae:

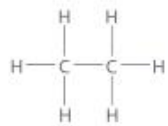
a. C_7H_{16}
b. $C_{10}H_{22}$

methane

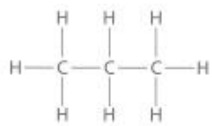




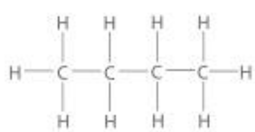
ethane

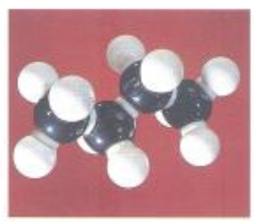


propane

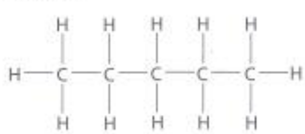


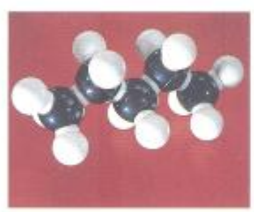
butane



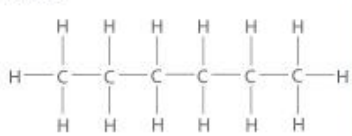


pentane





hexane



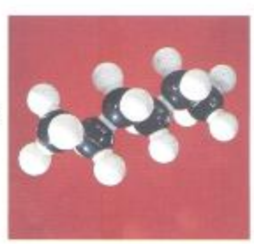


Figure 12.5 The alkane molecules look like the models in the photographs.

Naming the alkanes

All the alkanes have names ending in -ane. The rest of the name tells you the number of carbon atoms present in the molecule. For example, the compound whose name begins with:

- meth- has one carbon atom
- eth- has two carbon atoms
- prop- has three carbon atoms
- but- has four carbon atoms
- pent- has five carbon atoms

and so on.

Structural isomerism

Sometimes it is possible to write more than one structural formula to represent a molecular formula. The structural formula of a compound shows how the atoms are joined together by the covalent bonds. For example, there are two different compounds with the molecular formula C_4H_{10}. The structural formulae of these two substances along with their names and physical properties are shown in Figure 12.6.

Compounds such as those in Figure 12.6 are known as **isomers**. Isomers are substances which have the same molecular formula but different structural formulae. The different structures of the compounds shown in Figure 12.6 have different melting and boiling points. Molecule (b) contains a branched chain and has a lower melting point than molecule (a), which has no branched chain. All the alkane molecules with four or more carbon atoms possess isomers. Perhaps now you can see why there are so many different organic compounds!

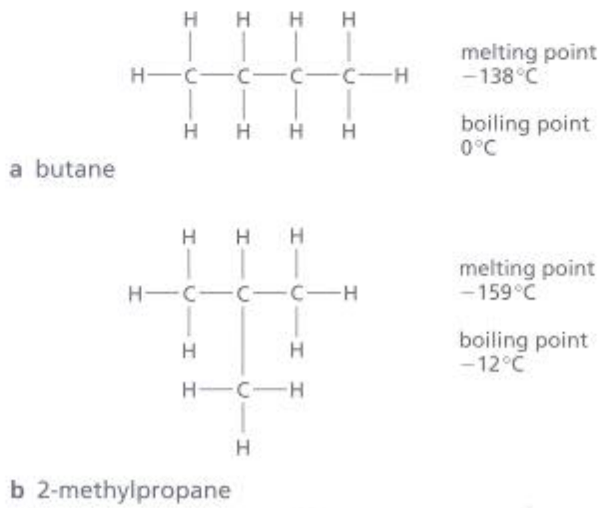


Figure 12.6 The isomers of C_4H_{10}.

Question

1. Draw the structural formulae for the isomers of:

a. C_5H_{12}
b. C_6H_{14}.

The chemical behaviour of alkanes

Alkanes are rather unreactive compounds. For example, they are generally not affected by alkalis, acids or many other substances. Their most important property is that they burn easily.

Gaseous alkanes, such as methane, will burn in a good supply of air, forming carbon dioxide and water as well as plenty of heat energy.

methane + oxygen → carbon dioxide + water + energy

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

The gaseous alkanes are some of the most useful fuels. Methane, better known as natural gas, is used for cooking as well as for heating our offices, schools and homes (Figure 12.7a). Propane and butane burn with very hot flames and they are sold as liquefied petroleum gas (LPG). In rural areas where there is no supply of natural gas, central heating systems can be run on propane gas (Figure 12.7b). Butane, sometimes mixed with propane, is used in portable blowlamps and in gas lighters.

a This is burning methane.

b Central heating systems can be run on propane.

Figure 12.7

Another useful reaction worth noting is that between the alkanes and the halogens. For example, methane and chlorine react in the presence of sunlight (or ultraviolet light). The ultraviolet light splits the chlorine molecules into atoms. When this type of reaction takes place, these atoms are called **free radicals** and they are very reactive.

$$\text{chlorine gas} \xrightarrow{\text{sunlight}} \text{chlorine atoms (free radicals)}$$

$$Cl_2(g) \rightarrow 2Cl(g)$$

The chlorine atoms then react further with methane molecules, and a hydrogen chloride molecule is produced along with a methyl free radical.

chlorine atom + methane → methyl radical + hydrogen chloride

$$Cl(g) + CH_4(g) \rightarrow CH_3(g) + HCl(g)$$

The methyl free radical reacts further.

methyl radical + chlorine gas → chloromethane + chlorine atom

$$CH_3(g) + Cl_2(g) \rightarrow CH_3Cl(g) + Cl(g)$$

This chlorine free radical, in turn, reacts further and the process continues until all the chlorine and the methane have been used up. This type of process is known as a chain reaction and it is very fast. The overall chemical equation for this process is:

methane + chlorine → chloromethane + hydrogen chloride

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$$

We can see from this final equation that one hydrogen atom of the methane molecule is **substituted** by a chlorine atom. This type of reaction is known as a **substitution reaction**.

Because we cannot control the chlorine free radicals produced in this reaction, we also obtain small amounts of other 'substituted' products – CH_2Cl_2 (dichloromethane), $CHCl_3$ (trichloromethane or chloroform) and CCl_4 (tetrachloromethane). Many of these so-called **halogenoalkanes** are used as solvents. For example, dichloromethane is used as a solvent in paint stripper (Figure 12.8).

Figure 12.8 Dichloromethane is used as a solvent in paint stripper.

Early anaesthetics relied upon trichloromethane, $CHCl_3$, or chloroform. Unfortunately, this anaesthetic had a severe problem since the lethal dose was only slightly higher than that required to anaesthetise the patient. In 1956, halothane was discovered by chemists working at ICI. This is a compound containing chlorine, bromine and fluorine. Its formula is $CF_3CHBrCl$. However, even this is not the perfect anaesthetic since evidence suggests that prolonged exposure to this sub-stance may cause liver damage. The search continues for even better anaesthetics.

A group of compounds were discovered in the 1930s and were called the chlorofluorocarbons or CFCs for short. Because of their inertness they found many uses, especially as a propellant in aerosol cans. CFC-12 or dichlorodifluoromethane, CF_2Cl_2, was one of the most popular CFCs in use in aerosols. Scientists now believe that the CFCs released from aerosols are destroying the ozone layer.

The ozone hole problem

Our atmosphere protects us from harmful ultraviolet radiation from the Sun. This damaging radiation is absorbed by the relatively thin ozone layer found in the stratosphere (Figure 12.9).

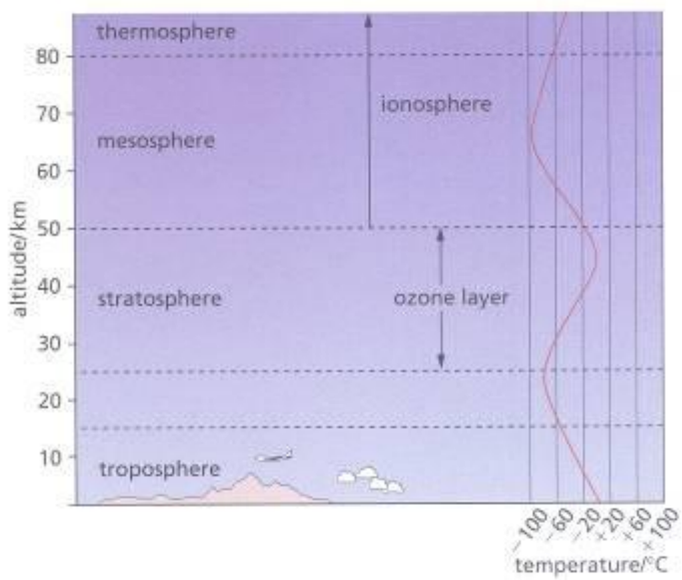


Figure 12.9 The ozone layer is between 25 km and 50 km above sea level.

Large holes have recently been discovered in the ozone layer over Antarctica, Australasia and Europe. Scientists think that these holes have been produced by CFCs such as CFC-12. CFCs escape into the atmo-sphere and, because of their inertness, remain without further reaction until they reach the stratosphere and the ozone layer. In the stratosphere the high-energy ultraviolet radiation causes a chlorine atom to split off from the CFC molecule. This chlorine atom, or free radical, then reacts with the ozone.

$$Cl(g) + O_3(g) \rightarrow OCl(g) + O_2(g)$$

This is not the only problem with CFCs. They are also significant 'greenhouse gases' (Chapter 8). The ozone depletion and greenhouse effects have become such serious problems that an international agreement

known as the Montreal Protocol on Substances that Deplete the Ozone Layer was agreed in 1987. The proposed controls were tightened in 1990 by the second meeting of the parties to the Montreal Protocol. Modifications have since been made at meetings held in 1992, 1995 and 1996.

Research is now going ahead, with some success, to produce safer alternatives to CFCs. At present, better alternatives called hydrochlorofluorocarbons (HCFCs) have been developed. These substances have lower ozone-depletion effects and are not very effective greenhouse gases.

Other uses of alkanes

Besides their major use as fuels (Chapter 13), some of the heavier alkanes are used as waxes (Figure 12.10), as lubricating oils and in the manufacture of another family of hydrocarbons — the alkenes.

Figure 12.10 Candles contain a mixture of heavier alkanes.

Questions

1. Write a balanced chemical equation to represent the combustion of propane.

2. In what mole proportions should chlorine and methane be mixed to produce:

   a. mainly chloromethane?
   b. mainly tetrachloromethane?

3. Describe a method you would use to separate chloromethane from the other possible reaction products when methane reacts with chlorine.

4. Why do you think that CFCs release chlorine atoms into the stratosphere and not fluorine atoms?

Alkenes

Alkenes form another homologous series of hydrocarbons of the general formula:

$$C_nH_{2n}$$

where n is the number of carbon atoms. The alkenes are more reactive than the alkanes because they each contain a double covalent bond between the carbon atoms (Figure 12.11). Molecules that possess a double covalent bond of this kind are said to be unsaturated, because it is possible to break one of the two bonds to add extra atoms to the molecule.

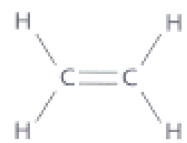


Figure 12.11 The bonding in ethene, the simplest alkene.

All alkenes have names ending in -ene. Alkenes, especially ethene, are very important industrial chemicals. They are used extensively in the plastics industry and in the production of alcohols such as ethanol and propanol. Table 12.2 gives the names, formulae and some physical properties of the first three members of the alkene family. Figure 12.12 shows the structure of these members as well as models of their shape.

Table 12.2 The first three alkenes and their physical properties.

Alkene	**Formula**	**Melting point/°C**	**Boiling point/°C**	**Physical state at room temperature**
Ethene	C_2H_4	-169	-104	Gas
Propene	C_3H_6	-185	-47	Gas
Butene	C_4H_8	-184	-6	Gas

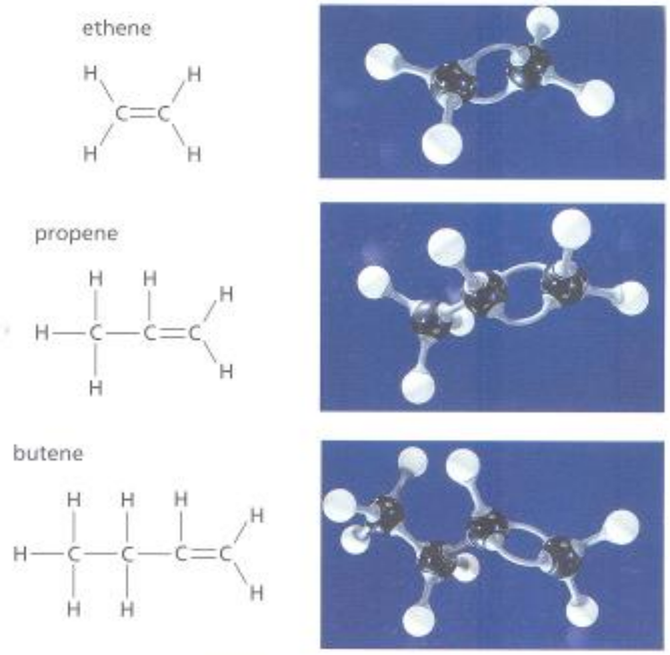


Figure 12.12 Structure and shape of the first three alkenes.

Where do we get alkenes from?

Very few alkenes are found in nature. Most of the alkenes used by the petrochemical industry are obtained by breaking up larger, less useful alkane molecules obtained from the fractional distillation of crude oil. This is usually done by a process called **catalytic cracking**. In this process the alkane molecules to be 'cracked' (split up) are passed over a mixture of aluminium and chromium oxides heated to about 500 °C.

$$\text{dodecane} \rightarrow \text{decane} + \text{ethene}$$

$$\underset{\text{(found in kerosene)}}{C_{12}H_{26}(g)} \rightarrow \underset{\text{shorter alkane}}{C_{10}H_{22}(g)} + \underset{\text{alkene}}{C_2H_4(g)}$$

Figure 12.13 shows the simple apparatus that can be used to carry out cracking reactions in the laboratory. You will notice that in the laboratory we may use a catalyst of broken, unglazed pottery.

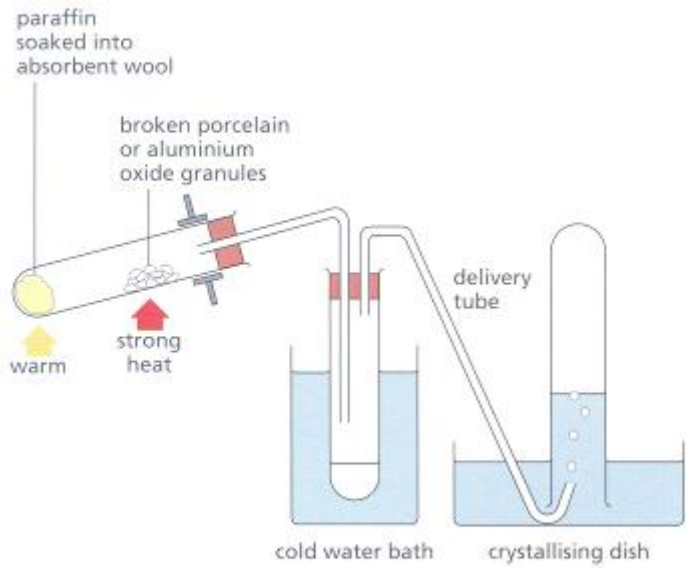


Figure 12.13 The cracking of an alkane in the laboratory.

The chemical behaviour of alkenes

The double bond makes alkenes more reactive than alkanes during chemical reactions. For example, hydrogen will add across the double bond of ethene, under suitable conditions, forming ethane (Figure 12.14).

$$\text{ethene} + \text{hydrogen} \xrightarrow[\text{Ni/Pt catalyst}]{150-300\,^\circ\text{C}} \text{ethane}$$

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

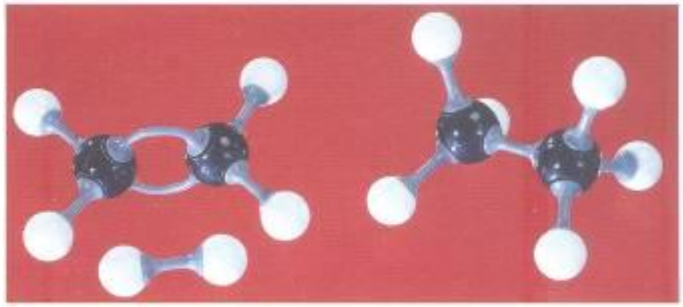
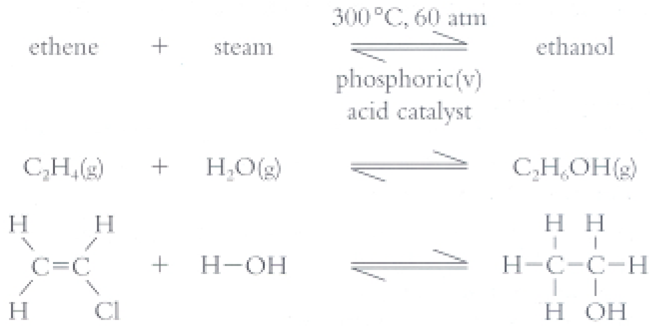


Figure 12.14 The addition of hydrogen to ethene using molecular models.

This reaction is called **hydrogenation**. Hydrogenation reactions like the one shown with ethene are used in the manufacture of margarines from vegetable oils. Vegetable oils contain fatty acids, such as linoleic acid ($C_{18}H_{32}O_2$). These are unsaturated molecules, containing several double bonds. These double bonds make the molecule less flexible. Hydrogenation can convert these molecules into more saturated ones. Now the molecules are less rigid and can flex and twist more easily, and hence pack more closely together. This in turn causes an increase in the intermolecular forces and so raises the melting point. The now solid margarines can be spread on bread more easily than liquid oils.

There is another side to this process. Many doctors now believe that unsaturated fats are more healthy than saturated ones. Because of this, many margarines are left partially unsaturated. They do not have all the C=C taken out of the fat molecules. However, the matter is far from settled and the debate continues.

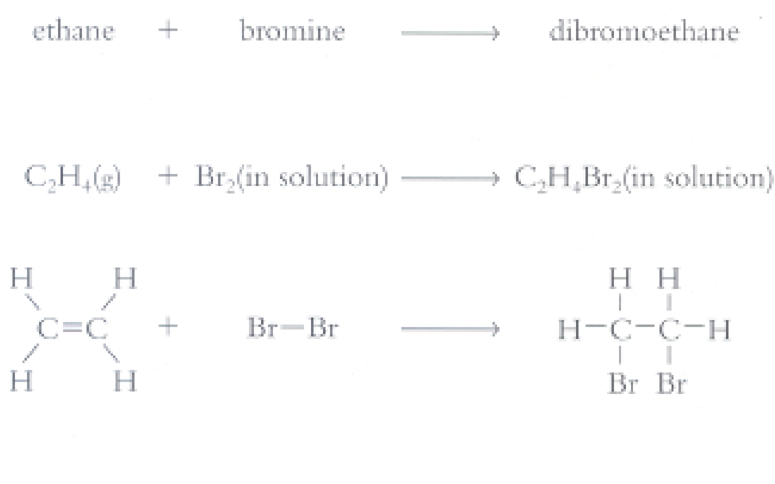
Another important **addition reaction** is the one used in the manufacture of ethanol. Ethanol has important uses as a solvent and a fuel. It is formed when water (as steam) is added across the double bond in ethene. For this reaction to take place, the reactants have to be passed over a catalyst of phosphoric (v) acid (absorbed on silica pellets) at a temperature of 300 °C and pressure of 60 atmospheres (1 atmosphere = 1×10^5 pascals).



This reaction is reversible as is shown by the equilibrium (⇔) sign. The conditions have been chosen to ensure the highest possible yield of ethanol. In other words, the conditions have been chosen so that they favour the forward reaction.

A test for unsaturated compounds

The addition reaction between bromine dissolved in an organic solvent, or water, and alkenes is used as a chemical test for the presence of a double bond between two carbon atoms. When a few drops of this bromine solution are shaken with the hydrocarbon, if it is an alkene, such as ethene, a reaction takes place in which bromine joins to the alkene double bond. This results in the bromine solution losing its red/brown colour. If an alkane, such as hexane, is shaken with a bromine solution of this type, no colour change takes place (Figure 12.15). This is because there are no double bonds between the carbon atoms of alkanes.



Questions

1. Using the information in Table 12.2, make an estimate of the boiling point of pentene.

2. Write a balanced chemical equation to represent the process that takes place when decane is cracked.

3. What is meant by the term 'addition reaction'?

4. Write a word and balanced chemical equation for the reaction between ethene and hydrogen chloride.

5. Write the structural formula for pentene.

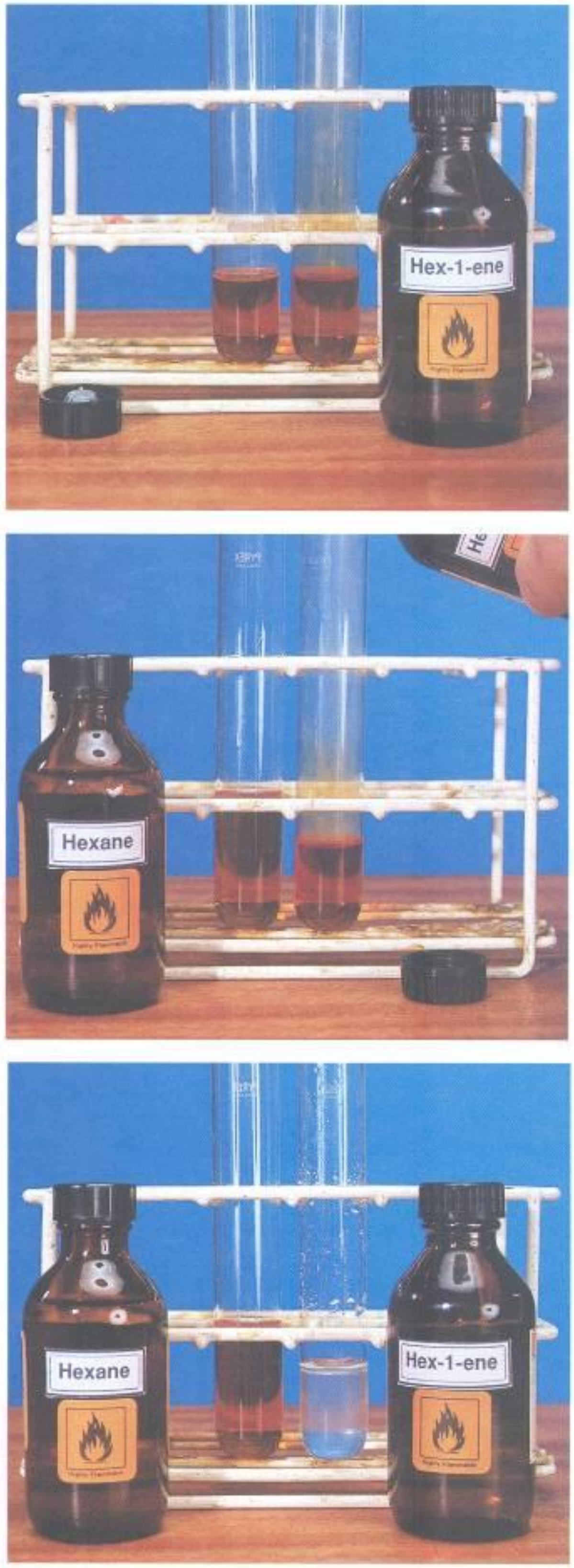


Figure 12.15 The alkene decolorises bromine in 1,1,1-trichloroethane.

Checklist

After studying Chapter 12 you should know and understand the following terms.

Alkanes A family of saturated hydrocarbons with the general formula C_nH_{2n+2}. The term 'saturated', in this context, is used to describe molecules that have only single bonds. The alkanes can only undergo substitution reactions in which there is replacement of one atom in the molecule by another atom.

Alkenes A family of unsaturated hydrocarbons with the general formula C_nH_{2n}. The term 'unsaturated', in this context, is used to describe molecules which contain one or more double carbon–carbon bonds. Unsaturated compounds undergo addition reactions across the carbon–carbon double bonds and so produce saturated compounds. The addition of hydrogen across the carbon–carbon double bonds is used to reduce the amount of unsaturation during the production of margarines.

Catalytic cracking The decomposition of higher alkanes into alkenes and alkanes of lower relative molecular mass. The process involves passing the larger alkane molecules over a catalyst of aluminium and chromium oxides, heated to 500°C.

CFC Abbreviation for chlorofluorocarbon, a type of organic compound in which some or all of the hydrogen atoms of an alkane have been replaced by fluorine and chlorine atoms. These substances are generally unreactive but they can diffuse into the stratosphere where they break down under the influence of ultraviolet light. The products of this photochemical process then react with ozone (in the ozone layer). Because of this, their use has been discouraged. They are now being replaced by hydrochlorofluorocarbons (HCFCs).

Chain reaction A reaction which is self-sustaining owing to the products of one step of the reaction assisting in promoting further reaction.

Free radicals Atoms or groups of atoms with unpaired electrons and are therefore highly reactive. They can be produced by high-energy radiation such as ultraviolet light in photochemical reactions.

Halogenoalkanes Organic compounds in which one or more hydrogen atoms of an alkane have been substituted by halogen atoms such as chlorine.

Hydrocarbon A substance which contains atoms of carbon and hydrogen only.

Isomers Compounds which have the same molecular formula but different structural arrangements of the atoms.

Oil refining The general process of converting the mixture that is collected as crude oil into separate fractions. These fractions, known as petroleum products, are used as fuels, lubricants, bitumens and waxes. The fractions are separated from the crude oil mixture by fractional distillation.

Organic chemistry The branch of chemistry concerned with compounds of carbon found in living organisms.

Test for unsaturation A few drops of bromine dissolved in an organic solvent are shaken with the hydrocarbon. If it is decolorised, the hydrocarbon is unsaturated.

The petroleum industry

Additional questions

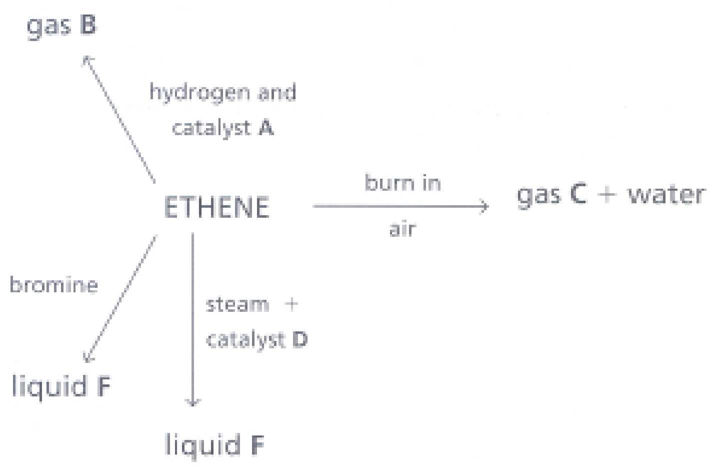
1. Explain the following.

a. Ethene is called an unsaturated hydrocarbon.

b. The cracking of larger alkanes into simple alkanes and alkenes is important to the petrochemical industry.

c. The conversion of ethene to ethanol is an example of an addition reaction.

2. The following question is about some of the reactions of ethene.



a. Give the names and formulae for substances A to F.

b.(i) Write a word and balanced chemical equation to represent the reaction in which liquid E is formed.

(ii) What reaction conditions are required for the process to take place?

(iii) Hydrogen is used in the production of margarine to remove unsaturation. Explain what you understand by this statement.

c. Name the homologous series that gas B belongs to.

d. Describe a chemical test which would allow you to identify gas C.

3a. Crude oil is a mixture of **hydrocarbons** which belong to the **homologous series** called the **alkanes**. This mixture can be separated into fractions by the process of **fractional distillation**. Some of the fractions obtained are used as **fuels**. Some of the other fractions are subjected to **catalytic cracking** in order to make **alkenes**.

Explain the meaning of the terms in blue.

b. Alkanes can be converted into substances which are used as solvents. To do this the alkane is reacted with a halogen, such as chlorine, in the presence of ultraviolet light.

(i) Write a word and balanced chemical equation for the reaction between methane and chlorine.

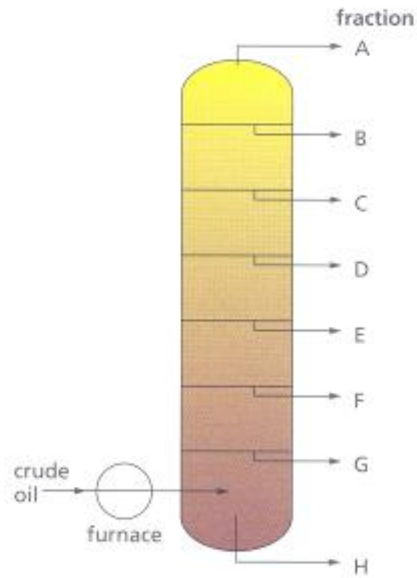
(ii) Name the type of reaction taking place.

(iii) Highly reactive chlorine atoms are produced in the presence of ultraviolet light. When atoms are produced in this way, what are they called?

(iv) Write a balanced chemical equation for the reaction which takes place between CHF_3 and Cl_2 to produce a chlorofluorocarbon (CFC).

(v) Why are CFCs such a problem?

4. Crude oil is a mixture of hydrocarbons. The refining of crude oil produces fractions which are more useful to us than crude oil itself. Each fraction is composed of hydrocarbons which have boiling points within a specific range of temperature. The separation is carried out in a fractionating column, as shown below.



a. Which separation technique is used to separate the fractions?

b. Name each of the fractions A to H and give a use for each.

c. Why do the fractions come from the fractionating column in this order?

d. What is the connection between your answer to c and the size of the molecules in each fraction?

e. Which of the fractions will be the most flammable?

5. Alkanes and alkenes are hydrocarbons. They are composed of molecules which contain covalent bonds. For each of the molecules below, use a dot and cross diagram to show the bonding it contains.

a. Methane, CH_4.

b. Propene, C_3H_6.

c. Propane, C_3H_8.

d. Ethene, C_2H_4.

6. Crude oil is an important source of organic chemical fuels. It is refined by fractional distillation. Use the information in the table below to answer the questions which follow.

Fraction	**Boiling point/°C**
A	40
B	80
C	200
D	350
E	above 350

a. For each of the questions that follow, give the letter of the fraction which is most appropriate as an answer. You should also give a reason for your answer in each case.

(i) Which fraction would contain the most volatile substances?

(ii) Which of the fractions would collect at the bottom of the fractionating column?

(iii) Which fraction could be used as a fuel for cars?

(iv) Which fraction would contain the largest molecules?

b. Some of the fractions undergo a further process called cracking to produce further substances.

(i) Explain what you understand by the term 'cracking'. What conditions are employed when cracking occurs?

(ii) Write a word and balanced chemical equation to show how octane can be produced by the cracking of $C_{15}H_{32}$.

7a. A hydrocarbon contains 92.3% by mass of carbon. Work out the empirical formula of this hydrocarbon.

b. The relative molecular mass of this hydrocarbon was found by mass spectrometry to be 78. Work out its molecular formula. (A_r: H = 1, C = 12)

8a. Which of the following formulae represent alkanes, which represent alkenes and which represent neither?

CH_3, C_6H_{12}, C_5H_{12}, C_6H_6, C_9H_{20},

$C_{12}H_{24}$, $C_{20}H_{42}$, C_2H_4, C_8H_{18}, C_3H_7

b. Draw all the possible isomers which have the molecular formula C_6H_{14}.