Cambridge

AS Level

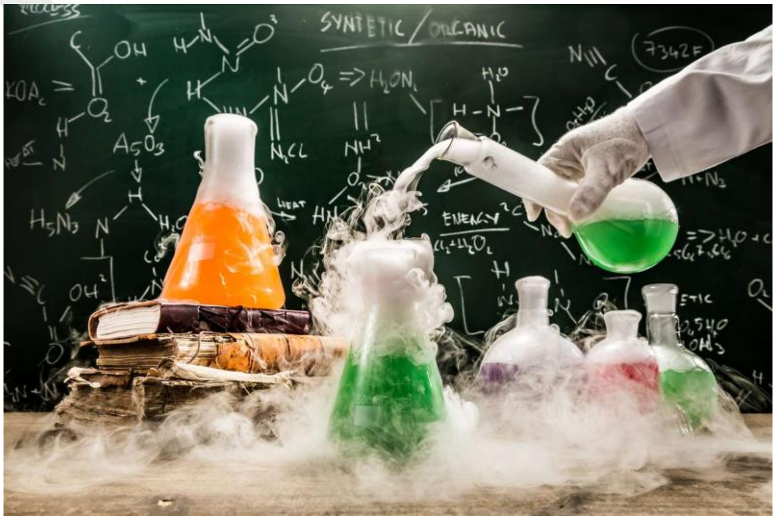
Chemistry

CODE: (9701)

Chapter 15 and 16

Hydrocarbons and

Halogenoalkanes



The homologous group of alkanes

The majority of compounds found in the mixture of hydrocarbons we call crude oil are **alkanes**. Figure 15.2 shows some different ways of representing pentane molecules.

The carbon atoms all display sp^3 hybridisation. This means that alkanes have the maximum number of hydrogen atoms in their molecules and are known as saturated hydrocarbons.

Sources of the alkanes

Crude oil is found trapped in layers of rock beneath the surface of the Earth. The actual composition of crude oil varies in different oilfields around the world.

■■ Crude oil is a complex mixture of hydrocarbons – alkanes, cycloalkanes and aromatic compounds.

■■ Cycloalkanes are saturated hydrocarbons in which there is a 'ring' consisting of three or more carbon atoms. Imagine the two carbon atoms at each end of a straight-chain alkane bonding to each other.

Aromatic hydrocarbons, also known as arenes, are based on hexagonal benzene rings. Crude oil is transported to refineries for processing into fuels. Fractional distillation separates hydrocarbons into fractions with similar boiling points. The lower the molecular mass, the more volatile they are. High-demand compounds, like gasoline and naphtha, are collected near the top of fractionating columns.

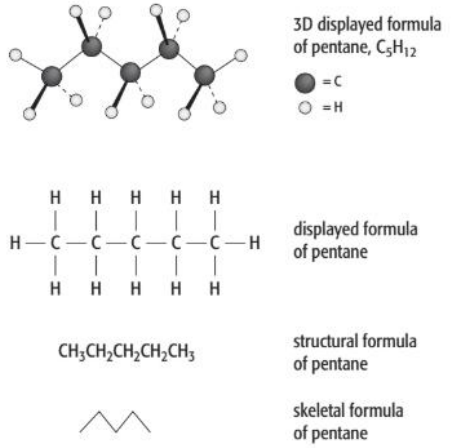


Figure 15.2 The 3D displayed formula shows the tetrahedral arrangement of atoms around each carbon atom (approximate bond angles of 109.5°).

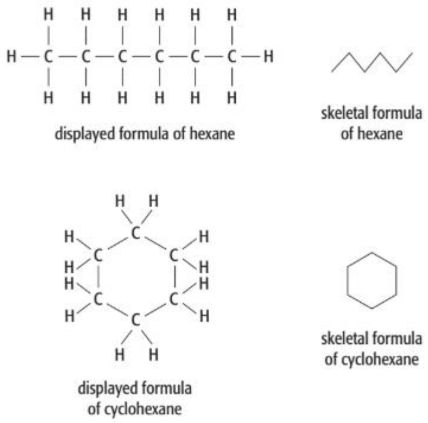


Figure 15.3 Hexane, C_6H_{14}, and cyclohexane, C_6H_{12}.

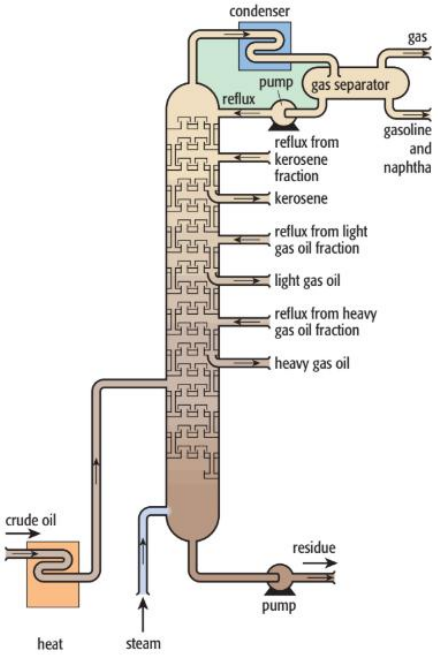


Figure 15.4 The fractional distillation of crude oil takes place in a fractionating column. The top of the column is at a lower temperature than the bottom of the column. The crude oil enters as vapour and liquid. The liquids are drawn off at the bottom of the column while more volatile hydrocarbons rise up the column. They condense at different levels as the temperature gradually falls and are collected as liquids. The most volatile hydrocarbons, which are short-chain alkanes (methane to butane), leave the top of the column as gases.

Reactions of alkanes

Alkanes are unreactive compounds due to their small difference in electronegativity between carbon and hydrogen and their non-polar nature. They do react with oxygen in combustion reactions and undergo substitution by halogens in sunlight.

Figure 15.5 Non-polar alkanes do not react with polar compounds such as water. The hexane (which is dyed with iodine to make it more clearly visible) and water shown here are immiscible – they do not mix and they do not react with each other.

Combustion of alkanes

Alkanes are often used as fuels (Figure 15.6). We burn them for many reasons:

- to generate electricity in power stations
- to heat our homes and cook our food
- to provide energy needed in industrial processes
- to provide power for ships, aeroplanes, trains, lorries, buses, cars and motorbikes.

Figure 15.6 Alkanes are useful fuels.

If an alkane is burnt in plenty of oxygen, it will undergo complete combustion. The carbon will be oxidised fully to form carbon dioxide and the hydrogen will be oxidised to form water:

$$\text{alkane} + \text{oxygen} \xrightarrow[\text{combustion}]{\text{complete}} \text{carbon dioxide} + \text{water}$$

Pollution from burning hydrocarbon fuels

When the petrol or diesel is mixed with air inside a car engine, there is a limited supply of oxygen. Under these conditions, not all the carbon in the hydrocarbon fuel is fully oxidised to carbon dioxide. Some of the carbon is only partially oxidised to form carbon monoxide gas. This is called incomplete combustion.

$$\text{octane} + \text{oxygen} \xrightarrow[\text{combustion}]{\text{incomplete}} \text{carbon monoxide} + \text{water}$$

$$2C_8H_{18} + 17O_2 \longrightarrow 16CO + 18H_2O$$

or

$$C_8H_{18} + 8\tfrac{1}{2}O_2 \longrightarrow 8CO + 9H_2O$$

Carbon monoxide is a toxic gas that bonds with blood haemoglobin, causing dizziness and loss of consciousness. It is odourless, making it dangerous in poorly ventilated rooms. Road traffic releases acid nitrogen oxides, contributing to acid rain, which can kill trees and aquatic animals and corrode metals like iron.

Figure 15.7 These trees have been badly damaged by acid rain.

In normal combustion, nitrogen gas in the air does not get oxidised. However, in the very high temperatures in car engines oxidation of nitrogen does take place. A variety of nitrogen oxides can be formed and released in the car's exhaust fumes (Figure 15.8).

Cars can now be fitted with a catalytic converter in their exhaust system (Figure 15.9). Once warmed up, a catalytic converter can cause the following reactions to take place:

- the oxidation of carbon monoxide to form carbon dioxide
- the reduction of nitrogen oxides to form harmless nitrogen gas
- the oxidation of unburnt hydrocarbons to form carbon dioxide and water.

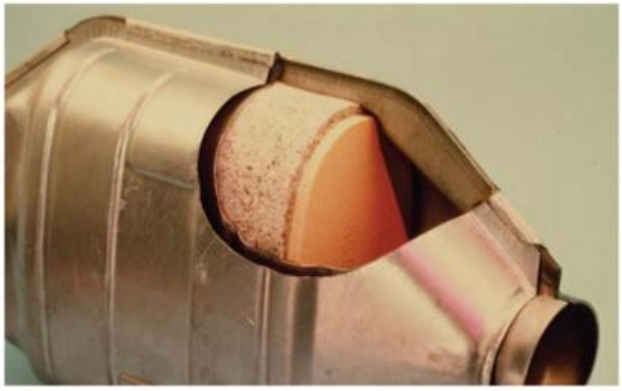


Figure 15.9 Catalytic converters reduce the pollutants from car exhausts. Precious metals, such as platinum, are coated on a honeycomb structure to provide a large surface area on which the reactions can occur.

Figure 15.8 The vast numbers of cars on the roads pollute our atmosphere.

The following equation describes the reaction between carbon monoxide and nitrogen monoxide. It takes place on the surface of the precious metal catalyst in a catalytic converter:

$$2CO + 2NO \longrightarrow 2CO_2 + N_2$$

Without it all the water on our planet would be constantly frozen. The problem of **enhanced global warming** has arisen because of the huge increase in the amount of CO2 produced by human activity in the last 200 years.

Infrared spectroscopy is a technique used by environmental scientists to monitor pollutants like nitrogen dioxide, sulfur dioxide, carbon monoxide, carbon dioxide, over 100 VOCs, and low-level ozone. It uses characteristic wavelengths to identify pollutants and analyze their concentrations. Over time, it provides valuable information on pollution control measures.

Substitution reactions of alkanes

The alkanes will undergo substitution reactions with halogens in sunlight. For example:

$$\underset{\text{methane}}{CH_4} + Cl_2 \xrightarrow{\text{sunlight}} \underset{\text{chloromethane}}{CH_3Cl} + HCl$$

In this reaction a hydrogen atom in the methane molecule gets replaced by a chlorine atom. However, the reaction does not take place in darkness (Figure 15.10). So what role does the sunlight play in the mechanism of the substitution reaction?

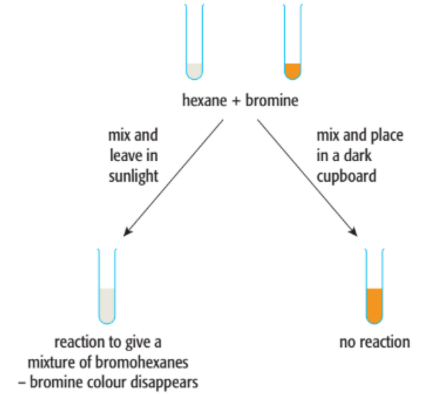


Figure 15.10 A substitution reaction takes place between alkanes and bromine in sunlight, but there is no reaction in darkness.

Initiation step

The first step in the mechanism is the breaking of the Cl= Cl bond by ultraviolet light from the Sun. This is an example of homolytic fission of a covalent bond. This is called the initiation step in the mechanism:

$$Cl_2 \xrightarrow{\text{UV light}} 2Cl\bullet$$

As the Cl—Cl bond breaks, each chlorine atom takes one electron from the pair of electrons in the Cl—Cl bond. Two Cl• atoms are formed. These Cl• atoms, each with an unpaired electron, are called free radicals.

Propagation steps

Free radicals are very reactive. They will attack the normally unreactive alkanes. A chlorine free radical will attack the methane molecule:

$$CH_4 + Cl\bullet \longrightarrow \bullet CH_3 + HCl$$

The propagation process involves a chain reaction where a chlorine free radical attacks another methane molecule, forming methyl free radicals and regenerating others. This method is not suitable for preparing specific halogenoalkanes as it results in a mixture of substitution products.

$$CH_3Cl + Cl\bullet \longrightarrow \bullet CH_2Cl + HCl$$

This can then be followed by:

$$\bullet CH_2Cl + Cl_2 \longrightarrow \underset{\text{dichloromethane}}{CH_2Cl_2} + Cl\bullet$$

Termination steps

Whenever two free radicals meet they will react with each other. A single molecule is the only product.
As no free radicals are made that can carry on the reaction sequence, the chain reaction stops.

$$\bullet CH_3 + Cl\bullet \longrightarrow CH_3Cl$$
$$\bullet CH_3 + \bullet CH_3 \longrightarrow C_2H_6$$

■■ In the initiation step we start with a molecule and get two free radicals formed.

■■ In the propagation steps we start with a molecule plus a free radical and get a different molecule and a different free radical formed.

■■ In the termination steps we start with two free radicals and end up with a molecule and no free radicals.

The alkenes

We have looked at the nature of the double bond found in the hydrocarbons called **alkenes.** Alkenes with one double bond per molecule have the general formula C_nH_{2n}.

alkenes are described as **unsaturated hydrocarbons**. The lighter fractions, such as the gasoline fraction, are in high demand. So, some of the excess heavier fractions are converted to lighter hydrocarbons. The large, less useful hydrocarbon molecules are broken down into smaller, more useful molecules. The process is called **cracking**.

When large alkane molecules are cracked they form smaller alkane molecules and alkene molecules.

$$CH_3(CH_2)_8CH_3 \longrightarrow CH_3(CH_2)_4CH_3 + CH_2{=}CHCH_2CH_3$$
$$C_{10}H_{22} \longrightarrow C_6H_{14} + C_4H_8$$

Low-molecular mass alkanes are highly sought after fuels, while the more reactive alkenes (C4H8) are used in the chemical industry as starting compounds for new products like plastics.

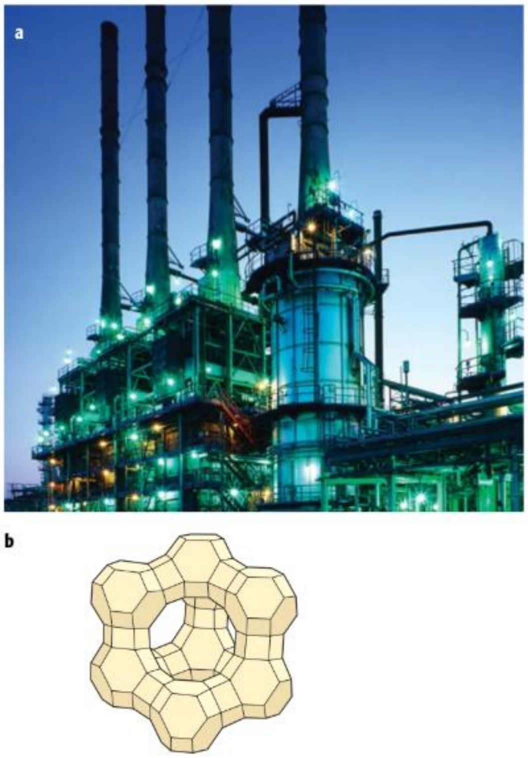


Figure 15.11 **a** A catalytic cracker occupies the bulk of the central part of this view of an oil refinery. **b** A computer graphic showing a zeolite catalyst used to crack hydrocarbons.

Addition reactions of the alkenes

Most reactions of the alkenes are examples of **addition** reactions. In these reactions one of the two bonds in the carbon–carbon double bond is broken and a new single bond is formed from each of the two carbon atoms.

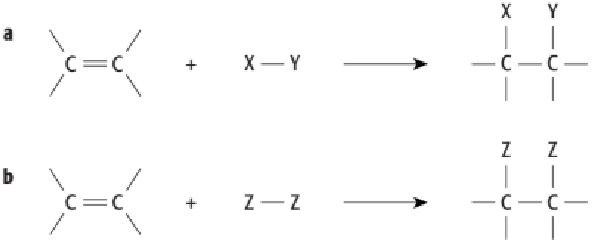


Figure 15.12 General equations for addition reactions of the alkenes: **a** with a hydrogen halide such as hydrogen bromide, and **b** with a halogen such as chlorine. In an addition reaction a single product is always formed.

Addition of hydrogen, H_2(g)

When hydrogen and an alkene are passed over a finely divided nickel catalyst at 140 °C, the addition reaction produces an alkane:

$$\underset{\text{ethene}}{CH_2{=}CH_2} + H_2 \xrightarrow{\text{Ni catalyst}} \underset{\text{ethane}}{CH_3CH_3}$$

The addition reaction with hydrogen is used in the manufacture of margarine (Figure 15.13).

Figure 15.13 Unsaturated oils, such as sunflower oil, contain hydrocarbon chains with several C=C double bonds. These become partially saturated by reacting them with hydrogen. This raises the melting points of the oils, changing them from liquids to soft solids that can be spread easily.

Addition of steam, H_2O(g)

The addition of steam to alkenes is used in industry to make alcohols. Steam and the gaseous alkene, in the presence of concentrated phosphoric acid as the catalyst, are reacted at a temperature of 330 °C and a pressure of 6MPa. When the alkene is ethene, the product is ethanol (Figure 15.14).

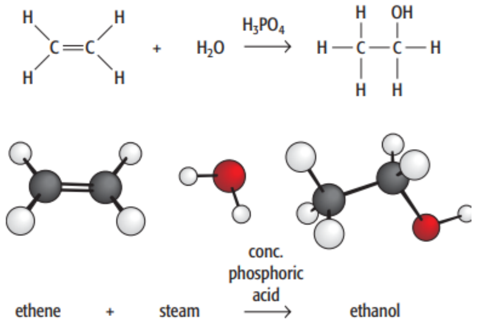


Figure 15.14 The reaction between ethene and steam.

Addition of hydrogen halides, HX(aq)

When an alkene is bubbled through a concentrated solution of a hydrogen halide (HF, HCl, HBr, HI) at room temperature, the product is a halogenoalkane

$$\underset{\text{ethene}}{CH_2{=}CH_2} + HBr \longrightarrow \underset{\text{bromoethane}}{CH_3CH_2Br}$$

With longer, asymmetric alkenes there are always two possible products that could be formed. For example, with propene:

$$\underset{\text{propene}}{CH_3CH{=}CH_2} + HBr \longrightarrow \underset{\text{1-bromopropane}}{CH_3CH_2CH_2Br}$$

and

$$\underset{\text{propene}}{CH_3CH{=}CH_2} + HBr \longrightarrow \underset{\text{2-bromopropane}}{CH_3CHBrCH_3}$$

Where two products are formed, the major product is the one that has the halogen atom bonded to the carbon with the least number of hydrogen atoms (in this case $CH_3CHBrCH_3$). This is because the $CH_3CHBrCH_3$ is formed from a secondary carbocation intermediate. On page 197 we saw that this ion is more stable than the primary carbocation so is more readily formed in the course of a reaction. The mechanism that follows shows how a carbocation forms and is then attacked by a negative ion to give the product of the addition reaction.

Addition of halogens, X_2(aq)

If we bubble an alkene through a solution of chlorine or bromine at room temperature, we again get an addition reaction. The colour of the halogen molecules in solution, which is pale green for chlorine water and orange/yellow for bromine water, is removed.

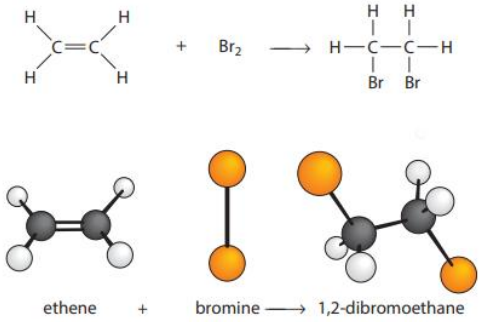


Figure 15.15 The reaction between ethene and bromine.

The mechanism of electrophilic addition to alkenes

The double bond in ethene, formed from a σ and π bond, makes it a non-polar molecule. However, the high electron density around the C= C bond makes alkenes vulnerable to electrophile attack. An electrophile is an acceptor of a pair of electrons. In HBr, the H atom acts as an electrophile, accepting electrons from the C=C bond. However, Br₂ acts as an electrophile by repelling electrons in the Br- Br bond.

As the new bond between the C and Br atom forms, the Br- Br bond breaks heterolytically.

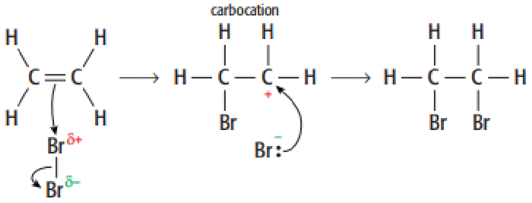


Figure 15.16 The mechanism of electrophilic addition of bromine to ethene.

Oxidation of the alkenes

Alkenes can be oxidised by acidified potassium manganate(VII) solution, which is a powerful oxidising agent. The products formed will depend on the conditions chosen for the reaction. In Figure 15.17, the R, R1 and R2 are alkyl groups.

Hot, concentrated manganate(VII) solution

Under these harsher conditions, the C=C bond in the alkene is broken completely. The O- H groups in the diol formed initially are further oxidised to ketones, aldehydes, carboxylic acids or carbon dioxide gas. The actual products depend on what is bonded to the carbon atoms involved in the C=C bond

To see what is formed when 2-methylprop-1-ene is heated with hot, concentrated potassium manganate(VII), look at equations 1 and 3 in Figure 15.17. The actual oxidation can be represented as:

$$\underset{\text{2-methylprop-1-ene}}{(CH_3)_2C{=}CH_2} + 4[O] \longrightarrow \underset{\text{propanone, a ketone}}{(CH_3)_2C{=}O} + CO_2 + H_2O$$

We can summarise the oxidations under harsh conditions (using a hot, concentrated solution of potassium managanate(VII)) in three reactions.

1 $H_2C{=}CH_2 \longrightarrow CO_2 + CO_2$

If a carbon atom is bonded to two hydrogen atoms we get oxidation to a CO_2 molecule.

2 $RHC{=}CHR \longrightarrow RCHO + RCHO$
$\longrightarrow RCOOH + RCOOH$

If a carbon atom is bonded to one hydrogen atom and one alkyl group we get oxidation to a —COOH (carboxylic acid) group.

3 $R^1R^2C{=}CR^3R^4 \longrightarrow R^1R^2C{=}O + R^3R^4C{=}O$

If a carbon atom is bonded to two alkyl groups we get oxidation to a C=O (ketone) group.

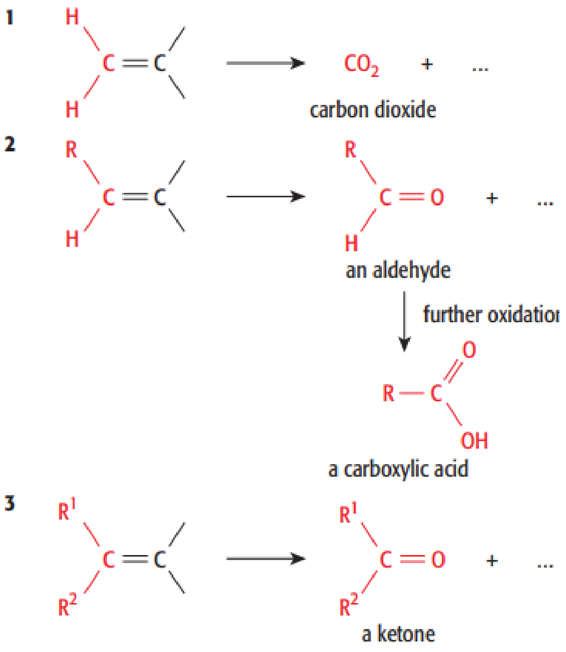


Figure 15.17 Oxidation with hot, concentrated manganate(VII) solution.

Addition polymerization

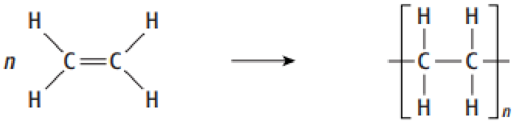
Molecules of ethene, as well as other unsaturated compounds, can react with each other under the right conditions to form **polymer** molecules

A polymer is a longchain molecule made up of many repeating units. The small, reactive molecules that react together to make the polymer are called **monomers**

We can show the polymerisation reaction of ethene as:

$$\underset{\text{ethene}}{nC_2H_4} \longrightarrow \underset{\text{poly(ethene)}}{\left[C_2H_4 \right]_n}$$

or by using the displayed formulae:



n is very large, e.g. up to 10 000

The section of the polymer shown in the brackets is the repeat unit of the polymer. The reaction is called **addition polymerisation.**

We can also use substituted alkenes, such as chloroethene, as monomers:

$$\underset{\text{chloroethene}}{nH_2C{=}CHCl} \longrightarrow \underset{\text{poly(chloroethene)}}{\left[H_2C{-}CHCl \right]_n}$$

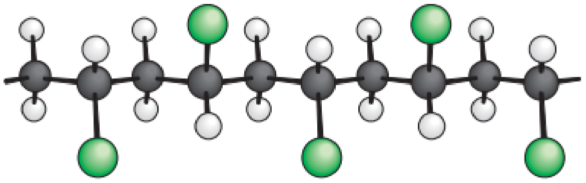


Figure 15.18 A 3D displayed formula of a small section of the poly(chloroethene) molecule. Its common name is PVC, as the old name for chloroethene was vinyl chloride.

In poly(alkenes) made of one type of monomer, the repeat unit is the same as the monomer except that the C=C double bond is changed to a C-C single bond. Notice that, as in any other addition reaction of the alkenes, addition polymerisation yields only one product.

Disposal of poly(alkene) plastics

Poly(alkene)s, widely used in everyday life, have a problem when disposed of due to their non-reactivity and long decomposition time in landfills. This creates waste that pollutes the environment for centuries, taking up valuable space.

Remember that:

- the section of the polymer chain shown inside the brackets in its structural or displayed formula is called its repeat unit
- addition polymerisation is characterised by:
  - monomers which are unsaturated, e.g. contain a C=C double bond
  - the polymer being the only product of the reaction.

Burning plastic waste

One way to solve this problem would be to burn the poly(alkene)s and use the energy released to generate electricity

This solution would not combat global warming but conserve fossil fuels for electricity generation. However, incomplete combustion of hydrocarbons produces toxic carbon monoxide. Recycling plants struggle to separate plastic waste from poly(alkene)s, releasing acidic hydrogen chloride gas and toxic compounds like dioxins. High temperatures in incinerators are needed to neutralize these gases.

Figure 15.19 A beach littered with poly(alkene) plastic waste.

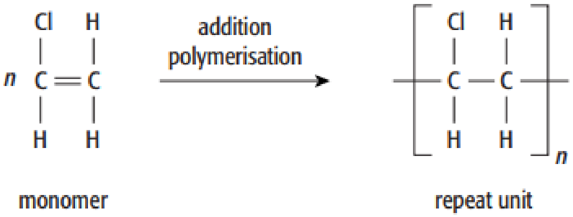
Tackling questions on addition polymers

In your exam, you might be asked to:

1. deduce the repeat unit of a polymer obtained from a given unsaturated monomer
2. identify the monomer(s) present in a given section of a polymer molecule.

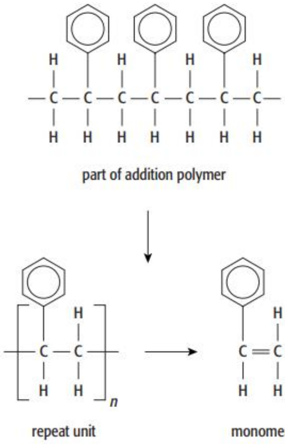
1. Deducing the repeat unit of an addition polymer for given monomer(s)

Given a monomer with a C=C bond, simply turn the double bond into a C-C single bond and show the bonds either side of the two C atoms that would continue the chain:



2. Identifying the monomer(s) present in a given section of an addition polymer molecule

First of all, you should split the polymer chain into its repeat units. With an addition polymer, you then need to put the C=C double bond back into the monomer:



Chapter 16 - Halogenoalkanes

Remember that the halogens are the elements in Group 17 of the Periodic Table, namely fluorine (F), chlorine (Cl), bromine (Br) and iodine (I).

Nucleophilic substitution reactions

We can think of the halogenoalkanes as alkanes that have one or more hydrogen atoms replaced by halogen atoms.

1. Substitution reactions with aqueous alkali, OH–(aq)

When an aqueous solution of sodium hydroxide is added to a halogenoalkane, a nucleophilic substitution reaction takes place. The halogen atom in the halogenoalkane is replaced by an OH, hydroxyl group, so the organic product formed is an alcohol:

$$\underset{\text{bromoethane}}{CH_3CH_2Br} + NaOH \longrightarrow \underset{\text{ethanol}}{CH_3CH_2OH} + NaBr$$

We can also show this equation as:

$$CH_3CH_2Br + OH^- \longrightarrow CH_3CH_2OH + Br^-$$

The aqueous hydroxide ion behaves as a nucleophile here, because it is donating a pair of electrons to the carbon atom bonded to the halogen in the halogenoalkane. This is why the reaction is called a **nucleophilic** substitution

Observing this reaction, we can time how long it takes for test tubes containing the halogenoalkanes and aqueous silver nitrate solution to become opaque. We find that:

■■ the fastest nucleophilic substitution reactions take place with the iodoalkanes

■■ the slowest nucleophilic substitution reactions take place with the fluoroalkanes.

The substitution reaction involves the breaking of the carbon halogen bond. Looking at the bond energies

Fluoroalkanes	least reactive
Chloroalkanes	↓
Bromoalkanes	↓
Iodoalkanes	most reactive

(Table 16.1) helps us to explain the rates of reaction. Notice that the C–I bond is the weakest, so it is broken most easily. It forms an I– ion during the substitution reaction. This is shown clearly in an ionic equation:

$$\underset{\text{iodoethane}}{CH_3CH_2I} + OH^- \longrightarrow \underset{\text{ethanol}}{CH_3CH_2OH} + I^-$$

HYDROLYSIS OF A HALOGENOALKANE

The reaction is carried out under reflux in the laboratory. This enables us to heat the reaction mixture without evaporating off the volatile organic compounds in the reaction flask. The apparatus is shown in Figure 16.2.

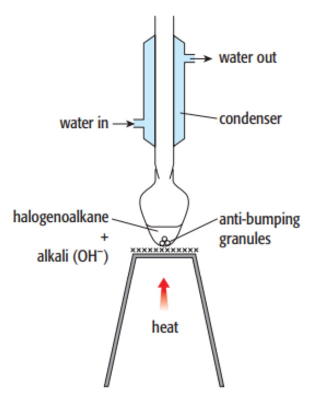


Figure 16.2 Reflux apparatus for hydrolysis of a halogenoalkane.

2 Substitution with cyanide ions, CN– (in ethanol)

In this reaction the nucleophile is the cyanide, CN–, ion. To carry out the reaction, a solution of potassium cyanide, KCN, in ethanol (known as an ethanolic or alcoholic solution of potassium cyanide) is made up. This is then heated under reflux with the halogenoalkane. An ionic equation for this reaction is:

$$\underset{\text{bromoethane}}{CH_3CH_2Br} + CN^- \longrightarrow \underset{\text{propanenitrile}}{CH_3CH_2CN} + Br^-$$

The reaction with cyanide ion adds an extra carbon atom to the halogenoalkane chain, converting bromoethane to propanenitrile. In industry, chemists can create new compounds with more carbon atoms by converting the starting compound to a halogenoalkane and refluxing with ethanolic KCN.

3 Substitution with ammonia, NH3 (in ethanol)

If a halogenoalkane is heated with an excess of ammonia dissolved in ethanol under pressure, an amine is formed.

$$\underset{\text{bromoethane}}{CH_3CH_2Br} + NH_3 \longrightarrow \underset{\text{ethylamine}}{CH_3CH_2NH_2} + HBr$$

Ammonia molecule acts as a nucleophile, forming primary amines like ethylamine. Excess ammonia results in a mixture of secondary amines, forming secondary amines.

Mechanism of nucleophilic substitution in halogenoalkanes

Many of the reactions of halogenoalkanes are nucleophilic substitutions. In these reactions, the nucleophile attacks the carbon atom bonded to the halogen.

Therefore the carbon atom carries a partial positive charge as the electron pair in the carbon–halogen bond is drawn nearer to the halogen atom (shown in Figure 16.3). The halogen atom is replaced by the nucleophile in the substitution reaction

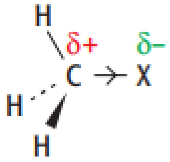
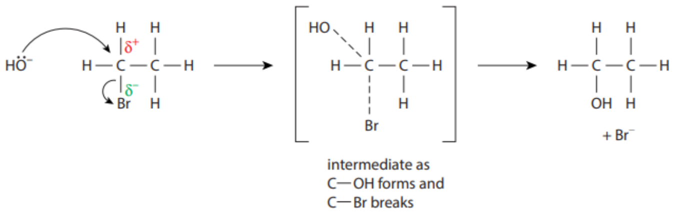


Figure 16.3 The carbon–halogen bond is polarised.

Mechanism for primary halogenoalkanes (S_N2)

In primary halogenoalkanes containing one halogen atom, the halogen atom is bonded to a carbon atom, which is itself bonded to one other carbon atom and two hydrogen atoms. This means that the carbon atom bonded to the halogen is attached to one alkyl group.



intermediate as C—OH forms and C—Br breaks

Figure 16.4 The mechanism of nucleophilic substitution in a primary halogenoalkane.

The OH– ion donates a pair of electrons to the δ+ carbon atom, forming a new covalent bond. At the same time, the C-Br bond is breaking. This mechanism is called an S_N2 mechanism. The 'S' stands for substitution and the 'N' stands for nucleophilic. The '2' tells us that the rate of the reaction, which is determined by the slow step in the mechanism, involves two reacting species

Mechanism for tertiary halogenoalkanes (S_N1)

In a tertiary halogenoalkane, the carbon atom bonded to the halogen atom is also bonded to three other carbon atoms (alkyl groups). For example, 2-bromo-2- methylpropane is a tertiary halogenoalkane. Its structure is shown in Figure 16.5.

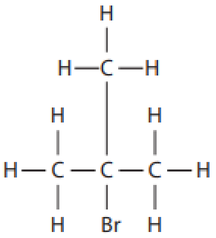


Figure 16.5 A tertiary halogenoalkane, 2-bromo-2-methylpropane.

The first step in the mechanism is the breaking of the carbon–halogen bond. This forms a tertiary carbocation, which is attacked immediately by the hydroxide ion (Figure 16.6).

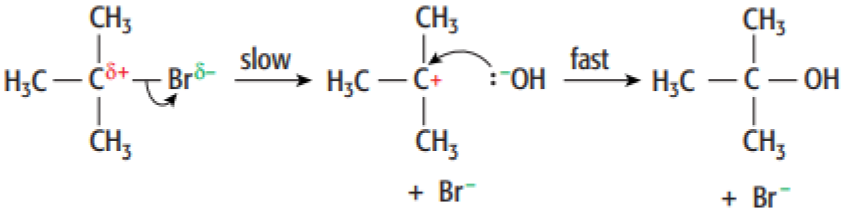


Figure 16.6 The mechanism of nucleophilic substitution in a tertiary halogenoalkane.

This mechanism is known as an S_N1 mechanism. The '1' tells us that the rate of the reaction only depends on one reagent, in this case the concentration of the halogenoalkane, as shown in the first (slow) step of the mechanism.

The S_N1 mechanism and the S_N2 mechanism are both likely to play a part in the nucleophilic substitution of secondary halogenoalkanes.

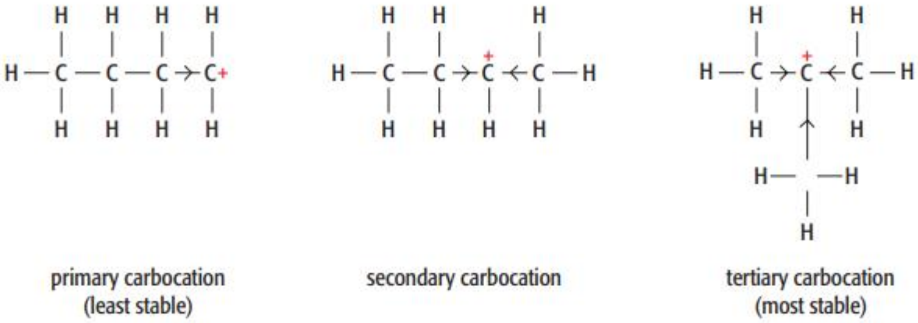


Figure 16.7 The trend in the stability of primary, secondary and tertiary carbocations.

Elimination reactions

Halogenoalkanes also undergo elimination reactions. An elimination reaction involves the loss of a small molecule from the original organic molecule.

The reagent used in these elimination reactions is ethanolic sodium hydroxide:

$$\underset{\text{2-bromopropane}}{CH_3CHBrCH_3} + NaOH(\text{ethanol}) \longrightarrow \underset{\text{propene}}{CH_2{=}CHCH_3} + H_2O + NaBr$$

The 2-bromopropane molecule loses H and Br atoms, resulting in HBr elimination from halogenoalkane. The ethanolic OH- ion forms water, while the C-Br bond breaks heterolytically, forming Br– ion and producing an alkene.

Uses of halogenoalkanes

Halogenoalkanes, often used as intermediates in the chemical industry, are also important anaesthetics due to their chemical inertness and strong C-F bonds. For instance, Teflon®, a non-stick lining in pans, is made from poly(tetrafluoroethene), a fluoropolymer with a strong C-F bond that can withstand high temperatures and is now used in ice-skating blades due to its durability and low friction properties.

CFC substitutes containing fluorine

CFCs are chlorofluorocarbons. Chemists refer to them as chlorofluoroalkanes. These organic compounds are all chemically inert (very unreactive). They are not flammable and are not toxic.

Dichlorodifluoromethane (CFC) was discovered in the 1930s and was initially unreactive. However, they become highly reactive in the atmosphere, releasing chlorine free radicals that can destroy a million ozone molecules. Most industrialized countries have banned CFC use. New compounds, such as hydrofluorocarbons (HFCs), have been developed for fridges and aerosols, breaking down more quickly once released into the air. Despite the depletion of the ozone layer, there are signs that the hole in the ozone layer is slowly closing up.

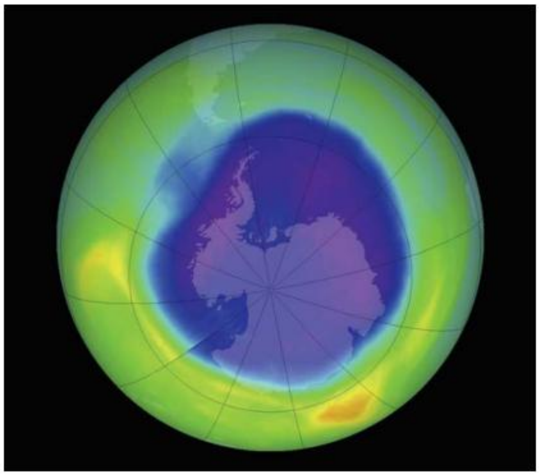


Figure 16.8 Banning the use of CFCs has meant that the hole in the ozone layer over Antarctica is now getting smaller.

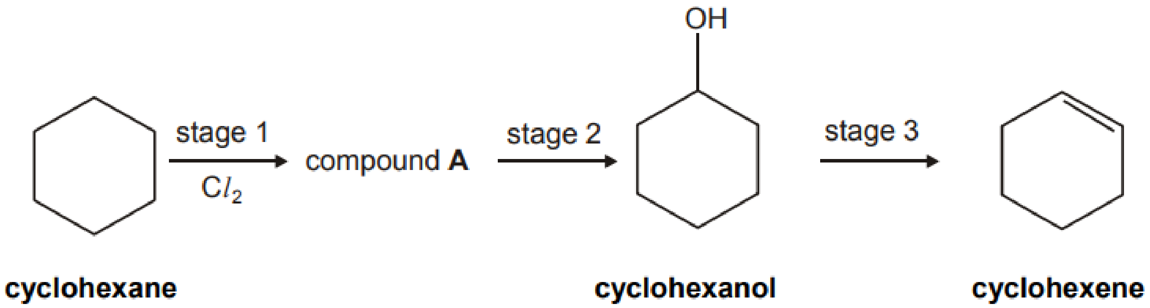
Revision questions

1. Chlorofluoroalkanes, CFCs, were developed from fluoroalkanes and were used in aerosols and as refrigerants. Under the Montreal Protocol, CFCs are now largely banned because of their ozone-depleting properties. CFCs have now been replaced in many applications. Suggest two reasons why there is still concern about ozone depletion.

2. A student reacted 8.72 g of bromobutane with an excess of OH–. The student produced 4.28 g of butan-1-ol. In this reaction the hydroxide ion acts as a nucleophile.

(i) What name is given to this type of reaction?
(ii) Explain the term nucleophile.
(iii) Outline the mechanism for this reaction. Show curly arrows and relevant dipoles.

3. (a) Cyclohexane can be converted into cyclohexene via a three-stage synthesis.



(i) In stage 1, cyclohexane reacts with chlorine to form the organic product, compound **A**.

Show the structure of compound **A**.

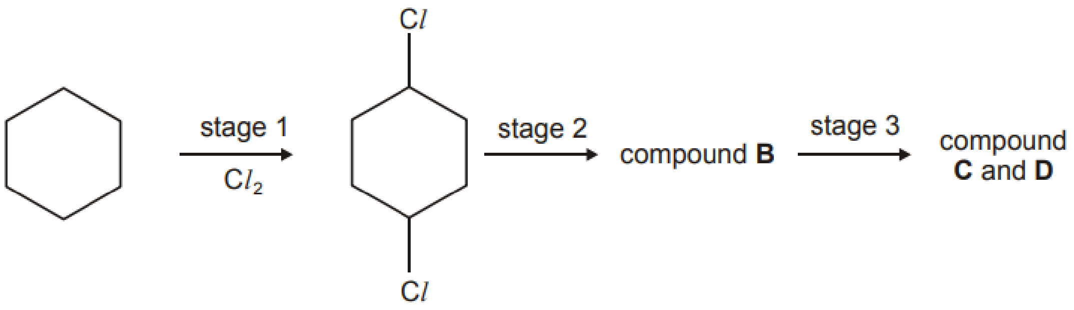
(ii) Stage 3 involves the dehydration of an alcohol.

State a suitable reagent for dehydrating an alcohol.

....

(iii) Write a balanced equation for the dehydration of cyclohexanol, $C_6H_{11}OH$.

(b) The reaction in stage 1 is difficult to control. One other possible chlorinated product is 1,4-dichlorocyclohexane. This is shown below.



cyclohexane **1,4-dichlorocyclohexane**

1,4-Dichlorocyclohexane reacts in the same way as compound **A** in stages 2 and 3.

(i) Suggest the structure of compound **B**.

(ii) Two cyclic alkenes, **C** and **D** are formed in stage 3. **C** and **D** are structural isomers. Suggest the structures of **C** and **D**.

4. Trifluorochloromethane, CF_3Cl, is an example of a chlorofluorocarbon, CFC, that was commonly used as a propellant in aerosols. Nowadays, CFCs have limited use because of the damage caused to the ozone layer.

(i) Draw a diagram to show the shape of a molecule of CF_3Cl.

[1]

(ii) Predict an approximate value for the bond angles in a molecule of CF_3Cl.

bond angle ....

[1]

(iii) Suggest a property that made CF_3Cl suitable as a propellant in an aerosol.

....

[1]

(iv) When CFCs are exposed to strong ultraviolet radiation in the upper atmosphere, homolytic fission takes place to produce free radicals.

Explain what is meant by the term *homolytic fission*.

(v) Suggest which bond is most likely to be broken when CF_3Cl is exposed to ultraviolet radiation. Explain your answer.

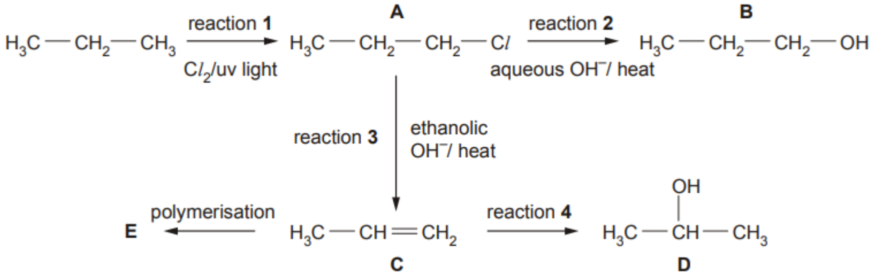
bond ....

reason ....

(vi) Identify the **two** free radicals most likely to be formed when CF_3Cl is exposed to ultraviolet radiation.

.... and ....

5. Propane, C_3H_8, is used in the reaction sequence shown below.



(a) The reaction sequence shows several important reaction mechanisms. Select from reactions **1** to **4**, the reaction that shows

(i) free radical substitution, reaction ....

[1]

(ii) electrophilic addition, reaction ....

[1]

(iii) elimination, reaction ....

[1]

(b) In reaction **2**, the aqueous OH^- acts as a nucleophile.

(i) State what is meant by the term *nucleophile*.

(ii) Complete, with the aid of curly arrows, the mechanism involved in reaction **2**. Show any relevant dipoles.

$$H_3C—CH_2—CH_2—Cl \longrightarrow H_3C—CH_2—CH_2—OH \quad + \quad ....$$

OH^-

6. In this question, one mark is available for the quality of spelling, punctuation and grammar.

The rates of hydrolysis of chloroethane, bromoethane and iodoethane are different.

- Describe how you would monitor the reaction rates.
- Explain why chloroethane, bromoethane and iodoethane react at different rates.

Use suitable equations in your answer.

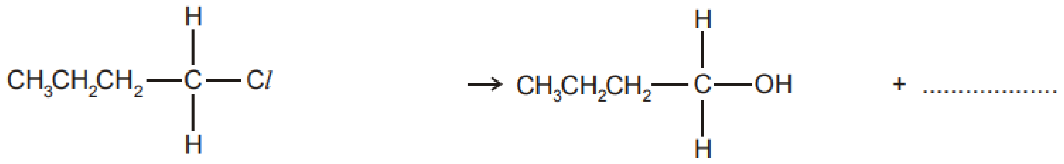
[Total 6 marks]

7. In 1930, an American engineer, Thomas Midgley, demonstrated a new refrigerant. As part of his demonstration, he inhaled a lung full of dichlorodifluoromethane, CCl_2F_2, and used it to blow out a candle.

Use Midgley's demonstration to suggest **two** properties of CCl_2F_2. Explain, with a reason, **two** other uses of chemicals such as CCl_2F_2, other than as a refrigerant.

8. Halogenoalkanes, such as 1-chlorobutane, are hydrolysed with hot aqueous alkali, $OH^-(aq)$, to form alcohols.

(a) Describe, with the aid of curly arrows, the mechanism of the hydrolysis of 1-chlorobutane with $OH^-(aq)$ ions to produce butan-1-ol. Show any relevant lone pairs of electrons and dipoles.



$$CH_3CH_2CH_2-\overset{H}{\underset{H}{C}}-Cl \rightarrow CH_3CH_2CH_2-\overset{H}{\underset{H}{C}}-OH + \ldots\ldots\ldots\ldots$$

[4]

(b) Another halogenoalkane, **H**, has a relative molecular mass of 127 and has the following composition by mass:
C, 37.8%; H, 6.3%; C*l*, 55.9%.

(i) Show that the empirical formula of compound **H** is C_2H_2Cl.

(ii) Deduce the molecular formula of compound **H**.

[1]

(iii) Compound **H** can also be hydrolysed with hot aqueous alkali to form butane-1,3-diol. Draw the structure of butane-1,3-diol

[1]

(iv) Deduce the structure of compound **H**.

[1]

[Total 9 marks]