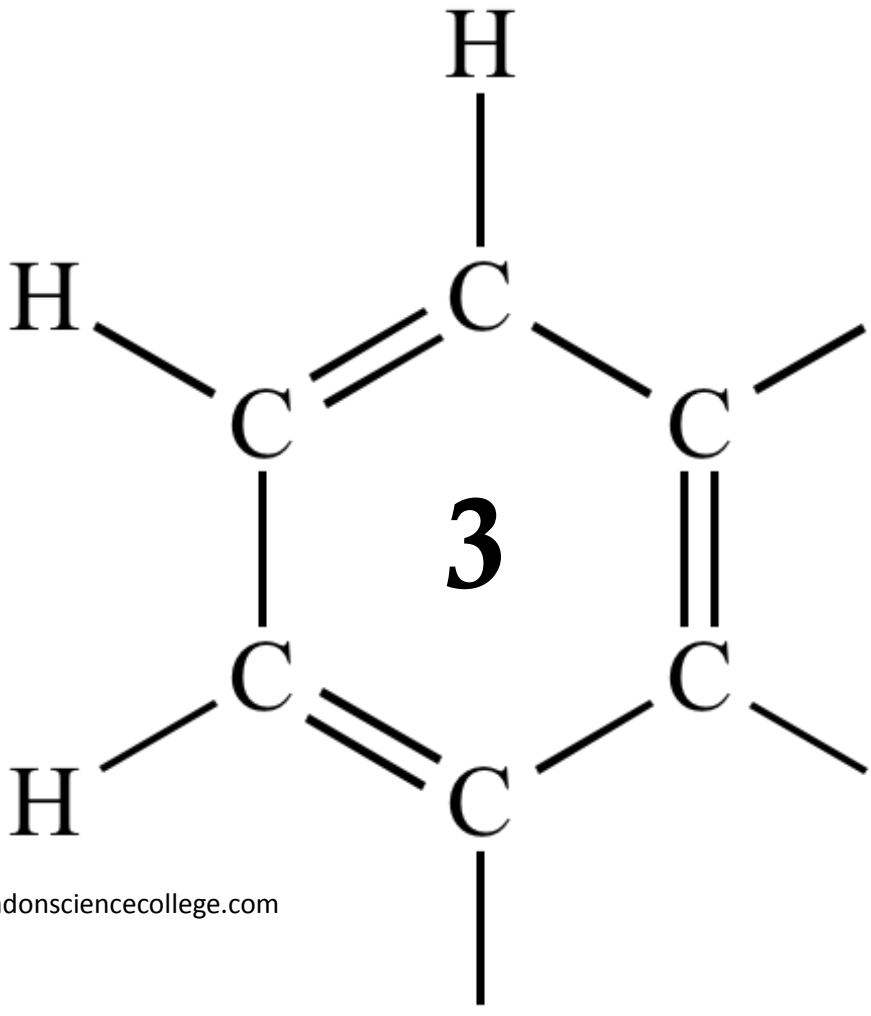
LONDON SCIENCE COLLEGE

AQA AS CHEMISTRY

HALOALKANES



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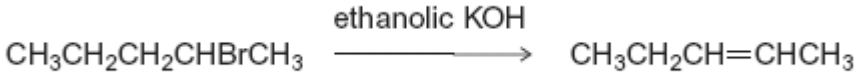
1 Organic reaction mechanisms help chemists to understand how the reactions of organic compounds occur.
The following conversions illustrate a number of different types of reaction mechanism.

(a) When 2-bromopentane reacts with ethanolic KOH, two structurally isomeric alkenes are formed.

(i) Name and outline a mechanism for the conversion of 2-bromopentane into pent-2-ene as shown below.



(4)

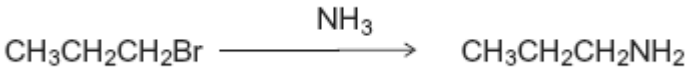
(ii) Draw the structure of the other structurally isomeric alkene produced when 2-bromopentane reacts with ethanolic KOH.

(1)

(b) Name and outline a mechanism for the following conversion.

(5)

(c) Name and outline a mechanism for the following conversion.



(5)
(Total 15 marks)

2 Oxygen and ozone (O_3) both occur as gases in the upper atmosphere.
Chlorine atoms catalyse the decomposition of ozone and contribute to the formation of a hole in the ozone layer.
These chlorine atoms are formed from chlorofluorocarbons (CFCs) such as CF_3Cl

(a) (i) Give the IUPAC name of CF_3Cl

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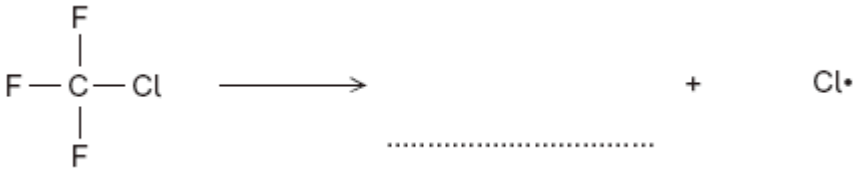
(1)

(ii) Complete the following equation that shows the formation of a chlorine atom from a molecule of CF_3Cl



(1)

(iii) State what the • represents in Cl•

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(1)

(b) Write two equations that show how chlorine atoms catalyse the decomposition of ozone into oxygen.

Equation 1 .....

Equation 2 .....

(2)

(c) An equilibrium is established between oxygen and ozone molecules as shown below.

$$3O_2(g) \rightleftharpoons 2O_3(g) \qquad \Delta H = +284 \text{ kJ mol}^{-1}$$

(i) State Le Chatelier's principle.

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(1)

(ii) Use Le Chatelier's principle to explain how an increase in temperature causes an increase in the equilibrium yield of ozone.

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(2)

(d) Chemists supported the legislation to ban the use of CFCs. Modern refrigerators use pentane rather than CFCs as refrigerants.
With reference to its formula, state why pentane is a more environmentally acceptable refrigerant.

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(1)
(Total 9 marks)

3 A student read the following passage on the Internet.

> Haloalkanes contain a polar covalent bond. The carbon atom of the polar covalent bond can be attacked by nucleophiles. Nucleophilic attack enables haloalkanes to undergo substitution reactions.
> A nucleophilic substitution reaction occurs when a haloalkane undergoes hydrolysis; the rate of hydrolysis of the haloalkane is influenced by the carbon–halogen bond enthalpy.

(a) Explain the meaning of each of the following terms in the information given above.

(i) *nucleophile*

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(1)

(ii) *substitution,* as applied to nucleophilic substitution in a haloalkane

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(1)

(iii) *hydrolysis*

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(1)

(iv) *bond enthalpy,* as applied to a carbon–halogen bond.

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(1)

(b) Outline a mechanism for the nucleophilic substitution reaction in which 2-bromopropane ($CH_3CHBrCH_3$) reacts with potassium hydroxide to form propan-2-ol.

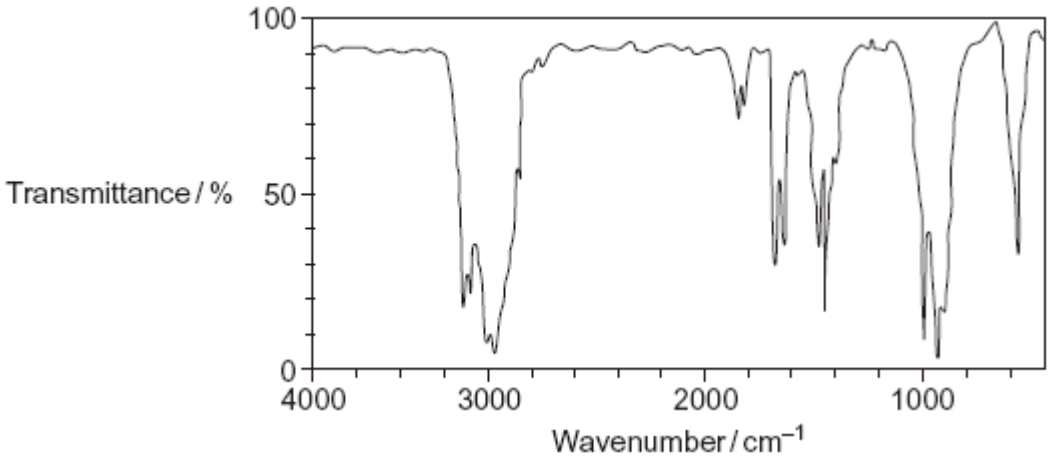
(2)

(c) Haloalkanes also undergo elimination reactions to produce alkenes.

(i) Outline a mechanism for the elimination reaction in which 2-bromopropane reacts with potassium hydroxide to form propene.

(3)

(ii) A student obtained the following infrared spectrum for the product from this elimination reaction.



Use information from the infrared spectrum to state and explain how the student deduced that the product was an alkene.
You may find it helpful to refer to **Table 1** on the Data Sheet.

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(2)
(Total 11 marks)

4 A student carried out an experiment to study the rates of hydrolysis of some haloalkanes.

(a) In the experiment, two different haloalkanes were placed in separate test tubes containing silver nitrate solution. The haloalkanes reacted with the water in the silver nitrate solution. The student timed how long it took for the first appearance of the silver halide precipitate in each tube at a constant temperature. This time was used to provide a measure of the initial rate of reaction.
The student obtained the following results.

	1-bromobutane	1-iodobutane
Time to form a precipitate / s	480	15

(i) State the meaning of the term *hydrolysis*.

.....

.....

(1)

(ii) State the colour of the precipitate formed when iodide ions react with silver nitrate and write the **simplest** ionic equation for this reaction.

Colour of precipitate .....

Simplest ionic equation

.....

(2)

(iii) Use your knowledge of the reactions of halide ions with silver nitrate to suggest why the student did **not** include 1-fluorobutane in this experiment.

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(2)

(b) The student used the following enthalpy data to try to account for the different initial rates of hydrolysis of the haloalkanes used in part (a). The student deduced that the rate of hydrolysis of a haloalkane is influenced by the strength of the carbon–halogen bond in the haloalkane.

	C–Br	C–I
Bond enthalpy / kJ mol^{-1}	276	238

State how the experimental evidence enabled the student to make this deduction.

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(1)

(c) The student had read that the reaction of water with haloalkanes was similar to the reaction of aqueous sodium hydroxide with haloalkanes and was an example of a nucleophilic substitution reaction.

(i) State the meaning of the term *nucleophile*.

.....

(1)

(ii) When a hydroxide ion collides with a molecule of 1-bromobutane, the following reaction occurs.

$$CH_3CH_2CH_2CH_2Br + OH^- \rightarrow CH_3CH_2CH_2CH_2OH + Br^-$$

Outline the nucleophilic substitution mechanism for this reaction.

(2)

(d) The reaction of hydroxide ions with 2-bromo-2-methylpropane may occur by a different mechanism from the one in part (c). This different mechanism involves the formation of a carbocation.

(i) Complete the following equation by drawing the structure of the carbocation formed when the C–Br bond in 2-bromo-2-methylpropane is broken.

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(1)

(ii) Suggest **one** reason why this reaction occurs by a mechanism involving a carbocation, but the reaction in part (c) (ii) does not.

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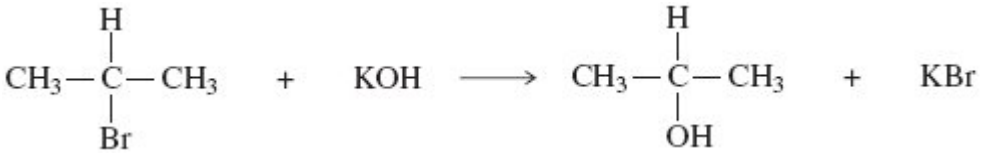
(1)

(Total 11 marks)

5 (a) Consider the following reaction.



(i) Name and outline a mechanism for this reaction.

Name of mechanism .....

Mechanism

(3)

(ii) Name the haloalkane in this reaction.

.....

(1)

(iii) Identify the characteristic of the haloalkane molecule that enables it to undergo this type of reaction.

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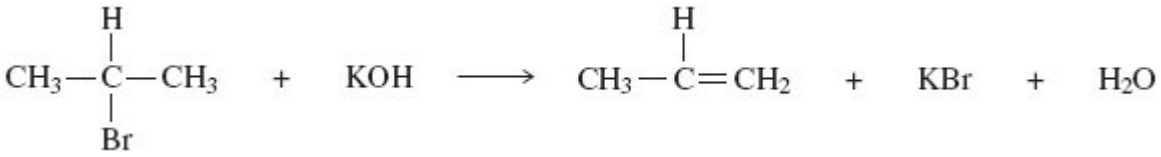
(1)

(b) An alternative reaction can occur between this haloalkane and potassium hydroxide as shown by the following equation.



Name and outline a mechanism for this reaction.

Name of mechanism .....

Mechanism

(4)

(c) Give **one** condition needed to favour the reaction shown in part (b) rather than that shown in part (a).

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(1)

(d) Alkenes can be polymerised to produce poly(alkenes).

(i) State the type of polymerisation that alkenes undergo.

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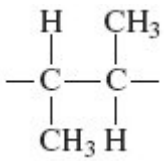
(1)

(ii) Name the alkene that gives a polymer with the repeating unit shown below.

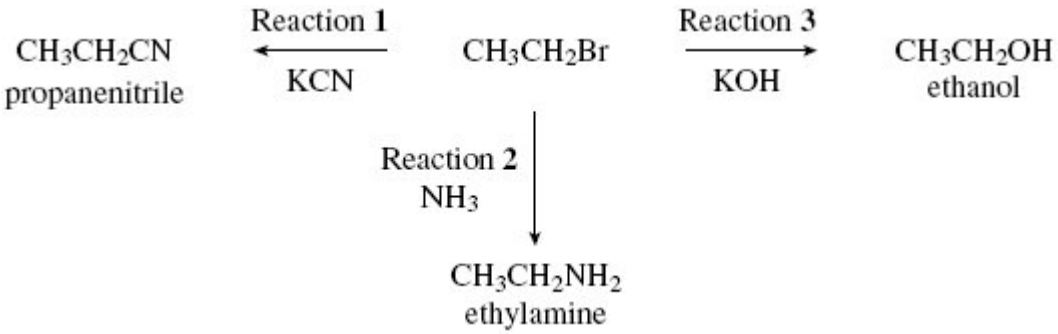


Name of alkene .....

(1)

(Total 12 marks)

6 Nucleophiles react with bromoethane in substitution reactions. This type of reaction is illustrated in the following scheme.



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

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(1)

(b) Outline a mechanism for the reaction of potassium cyanide with bromoethane (Reaction **1**).

(2)

(c) Explain why an excess of ammonia is needed in Reaction **2** to produce a high yield of ethylamine.

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(1)

(d) When potassium hydroxide reacts with bromoethane, ethene can also be formed. Name and outline a mechanism for this reaction.

Name of mechanism .....

Mechanism

(4)
(Total 8 marks)

7 One of the first substances used as an anaesthetic in medicine was chloroform (trichloromethane, $CHCl_3$). By 1950, *halothane* was in common use but by 1990 this had been replaced by more acceptable anaesthetics such as *desflurane*.

$CF_3CHBrCl$	$CF_3CHFOCHF_2$
halothane	*desflurane*

One reason for replacing *halothane* was that it is an organic compound that contains chlorine. Chlorine-containing organic compounds are thought to cause damage to the ozone layer in the upper atmosphere.

(a) Name and outline a mechanism for the reaction of chlorine with methane to form chloromethane (CH_3Cl).

Write an overall equation for the reaction of chlorine with methane to form trichloromethane ($CHCl_3$).

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(5)

(b) Explain how chlorine atoms are formed from chlorine-containing organic compounds in the upper atmosphere.

Explain, with the aid of equations, how chlorine atoms act as a catalyst in the decomposition of ozone into oxygen.

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(6)

(c) Use the formulae of the two anaesthetics, *halothane* and *desflurane*, to help to explain why *desflurane* is considered to be a more **environmentally** acceptable anaesthetic than *halothane*.

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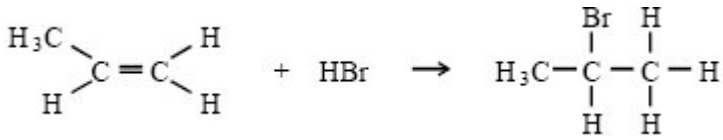
(2)
(Total 13 marks)

8 Organic reaction mechanisms help to develop an understanding of how and why reactions occur.

(a) Propene reacts with hydrogen bromide by an electrophilic addition mechanism forming 2-bromopropane as the major product.

The equation for this reaction is shown below.



(i) Outline the mechanism for this reaction, showing the structure of the intermediate carbocation formed.

(ii) Give the structure of the alternative carbocation which could be formed in the reaction between propene and hydrogen bromide.

(5)

(b) A substitution reaction occurs when 2-bromopropane reacts with aqueous sodium hydroxide.

(i) Draw the structure of the organic product of this reaction and give its name.

Structure

Name .....

(ii) Name and outline the mechanism for this reaction.

Name of mechanism .....

Mechanism

(5)

(c) Under different conditions, 2-bromopropane reacts with sodium hydroxide to produce propene.

(i) Name the mechanism for this reaction

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(ii) State the role of sodium hydroxide in this reaction

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(2)
(Total 12 marks)

9 How many different alkenes are formed when 2-bromo-3-methylbutane reacts with ethanolic potassium hydroxide?

A 2

B 3

C 4

D 5

(Total 1 mark)

10 Which one of the following statements explains best why fluoroalkanes are the least reactive haloalkanes?

A Fluorine is much more electronegative than carbon.

B The F^- ion is the most stable halide ion.

C The C–F bond is the most polar carbon–halogen bond.

D The C–F bond is the strongest carbon–halogen bond.

(Total 1 mark)