1 (a) The rates of hydrolysis of three bromoalkanes are compared.

2 cm^3 of ethanol is added to three test tubes, **A**, **B** and **C**.

Three drops of bromoalkane are added to each of these three test tubes.

1-bromobutane is added to test tube **A**.
2-bromobutane is added to test tube **B**.
2-bromo-2-methylpropane is added to test tube **C**.

2 cm^3 of hot aqueous silver nitrate solution is added to each test tube.

(i) Explain why ethanol is added to each test tube.

(1)

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(ii) Complete the general equation for the hydrolysis of these bromoalkanes.

State symbols are not required.

(1)

$C_4H_9Br + H_2O \rightarrow$

(iii) Eventually a precipitate is formed in each test tube. Give the colour of the precipitate formed and write the ionic equation, with state symbols, for its formation.

(2)

Colour .....

Ionic Equation

(iv) Identify the reagent you could add to dissolve the precipitate.

(1)

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(v) Give the order in which the precipitates form in the test tubes **A**, **B** and **C**, giving the fastest first.

(1)

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*(vi) State how the rates of hydrolysis depend on the structure of the bromoalkane. Suggest a reason for this difference. You are not required to give detailed mechanisms for the reactions.

(2)

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(b) (i) When 1-bromobutane reacts with an alcoholic solution of sodium hydroxide, a different reaction occurs.

Draw a fully labelled diagram to show the apparatus needed for carrying out this reaction in the laboratory and collecting the gaseous organic product.

(2)

(ii) Name the organic product for this reaction and draw its **skeletal** formula.

(2)

Name .....

Skeletal formula

(c) 1-bromobutane reacts with alcoholic ammonia when heated under pressure.

(i) State the type and mechanism of this reaction.

(2)

Type .....

Mechanism .....

(ii) Name the organic product of this reaction.

(1)

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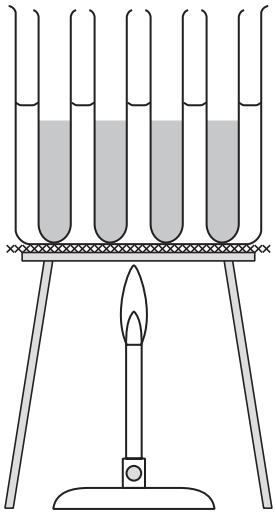
(Total for Question = 15 marks)

2 Halogenoalkanes react slowly with water to form alcohols. The equation for the reaction is

$$RX + H_2O \rightarrow ROH + H^+ + X^-$$

(a) The rate of this reaction for different halogenoalkanes was investigated using the apparatus below.



In one experiment, equal amounts of 1-chlorobutane, 1-bromobutane and 1-iodobutane were placed in separate test tubes with 5 cm^3 of ethanol. These test tubes were placed in the water bath together with a test tube containing aqueous silver nitrate. After about 5 minutes, 1 cm^3 of the silver nitrate solution was added to each test tube containing a halogenoalkane and the time taken for a precipitate to form in each test tube was noted. The temperature of the water bath was maintained at 50 °C.

(i) Why is ethanol used as a solvent in this experiment?

(1)

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(ii) Explain why the apparatus was left for 5 minutes before the silver nitrate was added.

(1)

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(iii) **Name** the precipitate formed in the test tube containing 1-bromobutane and write an **ionic** equation for the formation of this precipitate. State symbols are not required.

(2)

Precipitate .....

Ionic equation

(iv) Predict the order (fastest first) in which the halogenoalkanes form precipitates. Explain your answer.

(2)

Order .....

.....

Explanation .....

.....

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(b) Alcohols are usually prepared from halogenoalkanes using aqueous alkali, rather than water, as the reaction is faster.

(i) Name the mechanism and type of reaction occurring when 1-bromobutane reacts with aqueous alkali.

(2)

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(ii) Explain why the formation of alcohols is faster with aqueous alkali than with water.

(1)

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(iii) Give the mechanism for the reaction of 1-bromobutane with aqueous alkali.

Show the lone pair involved in the mechanism and any relevant dipoles and curly arrows.

(3)

(iv) One student suggested that the final reaction mixture could be tested for the presence of an alcohol using phosphorus(V) chloride while another suggested using potassium dichromate(VI) with sulfuric acid.

Describe the result of a positive test for alcohols using each of these reagents.

Explain which test is better for the final reaction mixture.

(3)

Observation with PCl_5 .....

Observation with acidified $K_2Cr_2O_7$ .....

Explanation .....

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(c) 1-bromobutane is classified as a **primary** halogenoalkane and is one of the four structural isomers with a molecular formula C_4H_9Br.

Give the **skeletal** formula of the three isomers, other than 1-bromobutane, classifying the halogenoalkane in each case.

(3)

Skeletal formula	Classification

(Total for Question = 18 marks)

3 When trichloromethane, $CHCl_3$, reacts with chlorine, the organic product is tetrachloromethane, CCl_4. The reaction proceeds by free radical substitution.

The equation for this reaction is

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

(a) State the essential condition for this reaction to occur at room temperature.

(1)

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(b) The reaction mechanism involves free radicals. Explain what is meant by the term **free radical**.

(1)

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(c) The reaction takes place in a series of steps.

(i) The initiation step is

$$Cl_2 \rightarrow 2Cl\bullet$$

Suggest why this initiation step is more likely than

$$CHCl_3 \rightarrow CCl_3\bullet + H\bullet$$

(1)

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(ii) Write equations for the two propagation steps.

(2)

First propagation step

Second propagation step

(iii) Write an equation for the termination step in which tetrachloromethane is formed.

(1)

(d) Tetrachloromethane can be manufactured using the by-products of chlorination reactions.

$$C_2Cl_6 + Cl_2 \rightarrow 2CCl_4$$

Compare the atom economy of this process with that of the reaction which produces tetrachloromethane from trichloromethane and chlorine. A calculation is not required.

(1)

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(Total for Question = 7 marks)

4 (a) The products of the reaction when 2-chlorobutane is heated with sodium hydroxide depend on the conditions.

(i) What condition, other than a suitable temperature and sodium hydroxide concentration, would produce a mixture of but-1-ene and but-2-ene?

(1)

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(ii) What type of reaction occurs in (a)(i)?

(1)

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(iii) What condition, other than a suitable temperature and sodium hydroxide concentration, would produce butan-2-ol in the reaction of 2-chlorobutane with sodium hydroxide?

(1)

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(iv) Suggest the mechanism for the reaction of 2-chlorobutane with hydroxide ions to form butan-2-ol. Use curly arrows to show the movement of electron pairs.

(2)

(b) Phosphorus(V) chloride, PCl_5, can be used to test for the –OH group.

Describe what would be seen when phosphorus(V) chloride is added to butan-2-ol. Give the equation for the reaction. State symbols are not required.

(2)

Observation .....

Equation

(c) A tertiary alcohol, **A**, is an isomer of butan-2-ol.

(i) Butan-2-ol and **A** can be distinguished by warming separate samples with a mixture of potassium dichromate(VI) and sulfuric acid. State the observations which would be made with each alcohol.

(2)

Observation with butan-2-ol .....

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Observation with **A** .....

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(ii) Give the structural formula of the organic product which forms when butan-2-ol is oxidized.

(1)

(iii) Explain how infrared spectroscopy could be used to detect whether butan-2-ol has been oxidized.

(1)

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(Total for Question = 11 marks)