2.7 Organic Chemistry

AQA 7405 · Calculator allowed · about 275 minutes · Write-in edition

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question is about naming organic compounds and identifying different types of structural isomerism.

(a) Give the IUPAC name of the following compound: CH_3-CH_2-$CH(CH_3)$-CH_2-OH **(2)**

(b) State the molecular formula of 2-methylbutan-1-ol, and give the structural formula of a chain isomer of this compound that is still an alcohol. **(2)**

(c) 1-Methoxybutane, CH_3-O-$CH_2CH_2CH_2CH_3$, is also an isomer of 2-methylbutan-1-ol. State the molecular formula of 1-methoxybutane, identify the type of isomerism shown between 1-methoxybutane and 2-methylbutan-1-ol, and explain your answer by reference to the functional groups present in each. **(3)**

(d) Define the term structural isomers. **(2)**

(Total for Question 1 is 9 marks)

2 This question is about alkane combustion and the free-radical substitution reaction between methane and chlorine.

(a) Write a balanced symbol equation for the complete combustion of propane, C_3H_8, in a plentiful supply of oxygen. **(2)**

(b) Incomplete combustion of hydrocarbon fuels in car engines can produce carbon monoxide gas. Explain why the formation of carbon monoxide is hazardous to health. **(2)**

(c) Methane reacts with chlorine gas in the presence of ultraviolet (UV) radiation, via a free-radical substitution mechanism, to form chloromethane. Write an equation for the initiation step of this reaction. **(1)**

(d) Write equations for the two propagation steps that lead to the formation of chloromethane. **(2)**

(e) Suggest why this reaction typically produces a mixture of chlorinated products (such as CH_2Cl_2 and $CHCl_3$), rather than pure chloromethane. **(2)**

(Total for Question 2 is 9 marks)

3 A technician has four unlabelled test tubes, each containing a different colourless liquid: propan-1-ol, propanal, propanoic acid and propanone. Simple chemical tests can be used to identify each compound.

(a) Describe a test, including the observation, that would distinguish propanoic acid from the other three liquids. **(2)**

(b) Describe a test, including the observations, that would distinguish propanal from propanone. **(2)**

(c) Both propanal and propanone react with 2,4-dinitrophenylhydrazine (Brady's reagent) to give an orange precipitate. State what this test confirms, and explain why it cannot be used alone to distinguish an aldehyde from a ketone. **(2)**

(d) Propan-1-ol gives no observable reaction with Tollens' reagent, 2,4-DNP or sodium carbonate. Explain why propan-1-ol gives none of these positive results. **(2)**

(Total for Question 3 is 8 marks)

4 Ethanoic acid reacts with ethanol in the presence of a small volume of concentrated sulfuric acid, under reflux, to form ethyl ethanoate.

(a) Write an equation for this esterification reaction, including state symbols. **(2)**

(b) State the role of concentrated sulfuric acid in this reaction. **(1)**

(c) In an experiment, 6.00 g of ethanoic acid (Mr = 60.0) was reacted with excess ethanol. The reaction produced 6.60 g of ethyl ethanoate (Mr = 88.0). Calculate the percentage yield of ethyl ethanoate. **(4)**

(d) Calculate the atom economy for the formation of ethyl ethanoate in this reaction, given Mr(ethanol) = 46.0. **(3)**

(e) Ethanoyl chloride, CH_3COCl, reacts much more readily with ethanol than ethanoic acid does, producing ethyl ethanoate without the need for a catalyst or heating. State one other observable difference between the reaction of ethanol with ethanoyl chloride and with ethanoic acid, and name the type of mechanism by which acyl chlorides react with alcohols. **(2)**

(Total for Question 4 is 12 marks)

5 An alkene, Y, is a gas at room temperature. Y has a relative molecular mass (Mr) of 56 and contains only carbon and hydrogen. Complete combustion of 0.560 g of Y produced 1.76 g of carbon dioxide and 0.720 g of water.

(a) Calculate the molecular formula of Y. Show your working. **(5)**

(b) Y has several structural isomers. One isomer, but-2-ene, shows E/Z isomerism, but another isomer, but-1-ene, does not. State the structural requirement for E/Z isomerism, and explain, in terms of this requirement, why but-1-ene does not show E/Z isomerism. **(3)**

(c) Propene reacts with hydrogen bromide in an electrophilic addition reaction, forming a mixture of 1-bromopropane and 2-bromopropane, with 2-bromopropane as the major product. Outline the mechanism for the formation of 2-bromopropane, naming the type of intermediate formed. **(3)**

(d) Explain, in terms of the stability of the carbocation intermediates, why 2-bromopropane is the major product. **(2)**

(Total for Question 5 is 13 marks)

6 Halogenoalkanes can undergo nucleophilic substitution or elimination reactions, and the carbon-halogen bond strength affects their reactivity.

(a) 1-chlorobutane, 1-bromobutane and 1-iodobutane are each warmed with aqueous silver nitrate dissolved in ethanol. State and explain the order in which precipitates form, in terms of carbon-halogen bond enthalpy. **(3)**

(b) 2-bromopropane can react with hydroxide ions to form either a substitution product (propan-2-ol) or an elimination product (propene), depending on the conditions used. Give the reagent and solvent, and state the type of mechanism, that would favour nucleophilic substitution to form propan-2-ol. **(2)**

(c) Give the reagent and solvent, and state the type of mechanism, that would favour elimination of 2-bromopropane to form propene. **(2)**

(Total for Question 6 is 7 marks)

7 Required practical: a student prepared a sample of 1-bromobutane from butan-1-ol using the following method. Butan-1-ol is heated under reflux with a mixture of sodium bromide and concentrated sulfuric acid; the crude product is then separated by distillation and purified.

(a) State the roles of sodium bromide and concentrated sulfuric acid in this preparation. **(2)**

(b) Write an equation for the reaction of butan-1-ol with hydrogen bromide to form 1-bromobutane. **(2)**

(c) Explain why the reaction mixture is heated under reflux, rather than in an open flask, during this stage of the preparation. **(2)**

(d) Describe how the crude 1-bromobutane product is purified after the reaction, explaining the purpose of each purification step. **(6)**

(e) A student reacted 7.40 g of butan-1-ol (Mr = 74.0) with excess sodium bromide and concentrated sulfuric acid, and obtained 9.13 g of pure 1-bromobutane (Mr = 137.0). Calculate the percentage yield of 1-bromobutane. **(4)**

(f) Suggest one reason, other than experimental or technique error, why the percentage yield of a preparation such as this is often less than 100%. **(2)**

(g) State how the student could show that the final 1-bromobutane product was pure. **(2)**

(h) State one safety precaution that should be taken when carrying out this preparation, giving a reason. **(2)**

(Total for Question 7 is 22 marks)

8 Butan-2-ol and butan-1-ol can each be oxidised, dehydrated or esterified, giving different products depending on the conditions used.

(a) Butan-2-ol is warmed with acidified potassium dichromate(VI) solution. State the colour change observed and identify the type of carbonyl product formed, explaining your answer with reference to the structure of butan-2-ol. **(3)**

(b) Butan-1-ol can be oxidised to either butanal or butanoic acid, depending on the technique used. Describe the practical technique used to obtain butanal as the main product, and explain why this method limits further oxidation to butanoic acid. **(3)**

(c) Butan-2-ol undergoes acid-catalysed dehydration when heated with concentrated sulfuric acid, forming a mixture of alkene products. Name the type of reaction mechanism and state a suitable catalyst. **(2)**

(d) Give the structural formulae of the two alkene products formed from the dehydration of butan-2-ol, and explain why a mixture is obtained. **(3)**

(Total for Question 8 is 11 marks)

9 2-methylbut-2-ene, $CH_3C(CH_3)=CHCH_3$, reacts with hydrogen bromide, HBr, in an electrophilic addition reaction.

(a) Outline the mechanism for the formation of the major product, 2-bromo-2-methylbutane, naming the type of intermediate formed. **(3)**

(b) Explain, in terms of carbocation stability, why 2-bromo-2-methylbutane is the major product rather than 2-bromo-3-methylbutane. **(2)**

(c) A sample of 2-methylbut-2-ene of mass 7.00 g (Mr = 70.0) is reacted with excess HBr. The reaction produces 11.6 g of pure 2-bromo-2-methylbutane (Mr = 151.0) after purification, although other bromobutane isomers also form in small amounts. Calculate the percentage yield of 2-bromo-2-methylbutane. **(4)**

(Total for Question 9 is 9 marks)

10 A student prepares a sample of the ester 3-methylbutyl ethanoate (isoamyl acetate) by heating 3-methylbutan-1-ol, $(CH_3)_2CHCH_2CH_2OH$, with an excess of glacial ethanoic acid and a few drops of concentrated sulfuric acid, under reflux. The crude ester is then purified by washing with sodium carbonate solution, separating the layers in a separating funnel, drying, and redistilling.

(a) Write an equation, including state symbols, for the esterification reaction between 3-methylbutan-1-ol and ethanoic acid to form 3-methylbutyl ethanoate. **(2)**

(b) State the role of concentrated sulfuric acid in this reaction, and explain why the reaction mixture is heated under reflux rather than in an open flask. **(2)**

(c) After washing the crude ester with aqueous sodium carbonate, the mixture separates into two layers in the separating funnel. State whether the ester forms the upper or lower layer, and explain your answer. **(2)**

(d) 4.40 g of 3-methylbutan-1-ol (Mr = 88.0) was reacted with excess ethanoic acid. After purification, 4.81 g of pure 3-methylbutyl ethanoate (Mr = 130.0) was obtained. Calculate the percentage yield. **(4)**

(e) The mass of 3-methylbutan-1-ol (4.40 g) was measured directly on a two-decimal-place balance with a reading uncertainty of ± 0.005 g. Calculate the percentage uncertainty in this mass measurement, to 3 significant figures. **(2)**

(Total for Question 10 is 12 marks)

11 Butanone, $CH_3COCH_2CH_3$, reacts with potassium cyanide (KCN) and dilute sulfuric acid to form 2-hydroxy-2-methylbutanenitrile via nucleophilic addition.

(a) Outline the mechanism for this nucleophilic addition reaction. **(4)**

(b) 2-hydroxy-2-methylbutanenitrile contains a chiral carbon atom. State what is meant by a chiral carbon atom, and identify the chiral carbon in this product. **(2)**

(c) Explain why the product of this reaction is a racemic mixture, and state the effect this has on plane-polarised light passing through the mixture. **(3)**

(Total for Question 11 is 9 marks)

12 This question is about the basicity of amines and the behaviour of amino acids in solution.

(a) Ethylamine, ammonia and phenylamine can all act as Bronsted-Lowry bases. Place these three compounds in order of increasing base strength, and explain this order in terms of the availability of the nitrogen lone pair. **(4)**

(b) Amino acids such as alanine, $CH_3CH(NH_2)COOH$, exist mainly as zwitterions in aqueous solution at neutral pH. State the structural formula of the zwitterion of alanine, and explain how it forms. **(3)**

(c) State the overall charge on an alanine molecule in a strongly acidic solution (low pH), and explain your answer. **(2)**

(d) Two amino acid molecules can react together to form a dipeptide. Name the type of reaction, the type of bond formed, and identify the small molecule released. **(3)**

(Total for Question 12 is 12 marks)

13 Two isomers, R and S, both have the molecular formula $C_4H_8O_2$ (Mr = 88.0). R is butanoic acid, $CH_3CH_2CH_2COOH$; S is methyl propanoate, $CH_3CH_2COOCH_3$.
Spectrum 1: broad absorption across 2500-3300 cm-1 and a sharp peak at 1710 cm-1.
Spectrum 2: no absorption in the 2500-3300 cm-1 region, but a sharp peak at 1740 cm-1.

(a) Identify which spectrum corresponds to R and which to S, explaining your reasoning by reference to the bonds present in each functional group. **(4)**

(b) In the mass spectrum of R, a fragment ion peak is observed at m/z = 71, in addition to the molecular ion peak at m/z = 88. Identify the species lost to form the m/z = 71 fragment and suggest its structure. **(2)**

(c) In the mass spectrum of S, a fragment ion peak is observed at m/z = 59. Identify the species lost to form this fragment and suggest its structure. **(2)**

(Total for Question 13 is 8 marks)

14 Benzene, C_6H_6, was originally proposed by Kekule to have a structure with alternating single and double carbon-carbon bonds arranged in a hexagonal ring.

(a) Give two pieces of experimental evidence that show that the Kekule structure of benzene is incorrect, and explain what this evidence suggests about the actual bonding in benzene. **(4)**

(b) Benzene reacts with a hot mixture of concentrated nitric acid and concentrated sulfuric acid to form nitrobenzene. Write an equation to show how the electrophile is generated from concentrated nitric acid and concentrated sulfuric acid. **(2)**

(c) Outline the mechanism for the electrophilic substitution reaction between benzene and NO_2^+, including the role of HSO_4^- in the final step. **(4)**

(Total for Question 14 is 10 marks)

15 Two isomeric carbonyl compounds, P and Q, both have molecular formula C_4H_8O (Mr = 72.0). The proton (1H) NMR spectrum of P shows four signals: a 1H signal at 9.75 ppm, a 2H signal at 2.42 ppm, a 2H signal at 1.68 ppm, and a 3H signal at 0.97 ppm. The 1H NMR spectrum of Q shows three signals: a 3H signal at 1.05 ppm, a 2H signal at 2.45 ppm, and a 3H signal at 2.12 ppm, with no signal beyond 3.5 ppm.

(a) Identify compound P, explaining your reasoning using the chemical shift and integration of its NMR signals. **(3)**

(b) Identify compound Q, explaining your reasoning. **(1)**

(c) Compound Q, butan-2-one, is reduced using sodium borohydride, $NaBH_4$, in aqueous solution to form butan-2-ol; one mole of $NaBH_4$ can reduce up to four moles of carbonyl compound. 1.44 g of butan-2-one (Mr = 72.0) is reacted with 0.400 g of $NaBH_4$ (Mr = 37.8). Show that $NaBH_4$ is in excess, and calculate the maximum mass of butan-2-ol (Mr = 74.0) that could be formed. **(4)**

(Total for Question 15 is 8 marks)

16 Ethanoic acid reacts with propan-1-ol in the presence of a strong acid catalyst to form propyl ethanoate in a reversible esterification reaction: $CH_3COOH + C_3H_7OH \rightleftharpoons CH_3COOC_3H_7 + H_2O$. This reaction is very slightly exothermic in the forward direction. In an experiment at 373 K, 1.00 mol of ethanoic acid and 1.00 mol of propan-1-ol (with no ester or water initially present) were mixed in a sealed 1.00 dm3 vessel and allowed to reach equilibrium. At equilibrium, the mixture was found to contain 0.667 mol of propyl ethanoate.

(a) Using the reaction stoichiometry, determine the equilibrium amounts, in mol, of ethanoic acid, propan-1-ol and water. **(3)**

(b) Write the expression for Kc for this reaction, and calculate its value at 373 K, stating its units. **(4)**

(c) State and explain the effect, if any, of increasing the temperature on the value of Kc, given that the esterification reaction is very slightly exothermic in the forward direction. **(2)**

(Total for Question 16 is 9 marks)

17 Ethane reacts with bromine in the presence of ultraviolet (UV) radiation via a free-radical substitution mechanism to form bromoethane and hydrogen bromide. Bond enthalpies: Br-Br = +193 kJ/mol; C-H (in ethane) = +413 kJ/mol; H-Br = +366 kJ/mol; H-Cl = +432 kJ/mol.

(a) Write an equation for the initiation step of this reaction, and state the type of bond fission involved. **(2)**

(b) Using the bond enthalpies given, calculate the enthalpy change for the first propagation step, $C_2H_6 + Br^* \rightarrow C_2H_5^* + HBr$. **(3)**

(c) Write an equation for the second propagation step that regenerates the bromine radical. **(2)**

(d) Give an equation for a termination step in this reaction, other than the reverse of the initiation step. **(1)**

(e) Initiation requires less energy for bromine than for chlorine, since the Br-Br bond (193 kJ/mol) is weaker than the Cl-Cl bond. Using the bond enthalpies given and your answer to part (b), explain why the overall reaction of ethane with bromine is nevertheless slower than the equivalent reaction with chlorine. **(2)**

(Total for Question 17 is 10 marks)

18 A student investigates the hydrolysis of 2-bromo-2-methylpropane, $(CH_3)_3CBr$, in aqueous acetone by withdrawing samples at intervals and titrating each against standard sodium hydroxide solution to determine the concentration of $(CH_3)_3CBr$ remaining. The results are shown below.

Time (s): 0, 300, 600, 900.

[$(CH_3)_3CBr$] remaining (mol dm-3): 0.0500, 0.0250, 0.0125, 0.00625.

Time (s)	[(CH3)3CBr] remaining (mol dm-3)
0	0.0500
300	0.0250
600	0.0125
900	0.00625

(a) Show that these data are consistent with the reaction being first order with respect to $(CH_3)_3CBr$. **(2)**

(b) Calculate the rate constant, k, for this first-order reaction using k = ln2 / half-life. Give your answer to 3 significant figures, with units. **(3)**

(c) Using your value of k, calculate the initial rate of reaction at t = 0, when $[(CH_3)_3CBr] = 0.0500$ mol dm-3, using rate = $k[(CH_3)_3CBr]$. Give your answer to 3 significant figures. **(2)**

(Total for Question 18 is 7 marks)

19 1-bromobutane (a primary halogenoalkane) and 2-bromo-2-methylpropane, $(CH_3)_3CBr$ (a tertiary halogenoalkane), both react with hydroxide ions in aqueous solution to form the corresponding alcohol, but by different mechanisms: a one-step mechanism for 1-bromobutane and a two-step mechanism, via a carbocation intermediate, for 2-bromo-2-methylpropane. Compare and explain these two mechanisms, including how the rate of each reaction depends on the concentrations of the halogenoalkane and hydroxide ion, the role of steric hindrance, and the role of carbocation stability, to explain why the two halogenoalkanes react by different routes.

(Total for Question 19 is 6 marks)

Mark scheme · 2.7 Organic Chemistry

Question 1

(a) longest carbon chain containing the -OH group correctly identified as a 4-carbon (butan-1-ol) chain **B1**

(a) 2-methylbutan-1-ol cao (correct locant and stem name) **B1**

(a) Answer: 2-methylbutan-1-ol

(b) $C_5H_{12}O$ cao **B1**

(b) any valid structural (chain) isomer that is an alcohol with formula $C_5H_{12}O$, e.g. pentan-1-ol ($CH_3CH_2CH_2CH_2CH_2OH$), pentan-2-ol, pentan-3-ol or 2,2-dimethylpropan-1-ol; must show a different carbon skeleton, not the same compound as (a) **B1**

(b) Answer: $C_5H_{12}O$; e.g. pentan-1-ol, $CH_3CH_2CH_2CH_2CH_2OH$

(c) $C_5H_{12}O$ cao (same molecular formula as 2-methylbutan-1-ol) **B1**

(c) functional group isomerism **B1**

(c) 2-methylbutan-1-ol contains an -OH (alcohol) functional group, whereas 1-methoxybutane contains a C-O-C (ether) linkage; same molecular formula but different functional groups oe **B1**

(c) Answer: $C_5H_{12}O$; functional group isomerism, because one compound is an alcohol (-OH) and the other is an ether (C-O-C), with the same molecular formula.

(d) compounds with the same molecular formula **B1**

(d) but a different structural arrangement of atoms (different connectivity/structural formula) oe **B1**

(d) Answer: Compounds with the same molecular formula but a different arrangement of atoms (different structural formula).

Question 2

(a) correct formulae for products, CO_2 and H_2O **M1**

(a) $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$, correctly balanced cao **A1**

(a) Answer: $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

(b) carbon monoxide binds to haemoglobin in red blood cells (forming carboxyhaemoglobin) in preference to oxygen **B1**

(b) this reduces the oxygen-carrying capacity of the blood, starving cells/tissues of oxygen, which can be toxic/fatal oe **B1**

(b) Answer: CO binds to haemoglobin in place of oxygen, reducing the oxygen-carrying capacity of the blood; this can starve cells of oxygen and is toxic.

(c) $Cl_2 \rightarrow Cl^* + Cl^*$ (homolytic fission of Cl-Cl, forming two chlorine radicals), initiated by UV light cao **B1**

(c) Answer: $Cl_2 \rightarrow 2Cl^*$ (homolytic fission, initiated by UV light)

(d) $CH_4 + Cl^* \rightarrow CH_3^* + HCl$ **M1**

(d) $CH_3^* + Cl_2 \rightarrow CH_3Cl + Cl^*$ cao (both equations needed, radical regenerated in step 2) **A1**

(d) Answer: Step 1: $CH_4 + Cl^* \rightarrow CH_3^* + HCl$. Step 2: $CH_3^* + Cl_2 \rightarrow CH_3Cl + Cl^*$.

(e) chloromethane formed can itself undergo further free-radical substitution with Cl_2 (the propagation steps can repeat on the substituted product) oe **B1**

(e) to minimise this and favour monosubstitution, methane is used in a large excess relative to chlorine oe **B1**

(e) Answer: Chloromethane can react further with Cl_2 in a repeat of the propagation steps, giving CH_2Cl_2, $CHCl_3$ etc; using excess methane favours monosubstitution.

Question 3

(a) add solid sodium carbonate (or sodium hydrogencarbonate solution) to a sample of each liquid **B1**

(a) propanoic acid produces effervescence/bubbles of gas (CO_2, which turns limewater cloudy); the other three liquids show no reaction oe **B1**

(a) Answer: Add sodium carbonate/hydrogencarbonate: propanoic acid fizzes (CO_2 gas evolved, turns limewater cloudy), the others do not react.

(b) add Tollens' reagent (ammoniacal silver nitrate) to a sample of each and warm gently in a water bath **B1**

(b) propanal produces a silver mirror (Ag^+ is reduced to Ag); propanone shows no reaction (remains colourless) oe; accept Fehling's/Benedict's solution: propanal gives a brick-red precipitate, propanone no change **B1**

(b) Answer: Warm with Tollens' reagent: propanal gives a silver mirror, propanone shows no reaction.

(c) confirms the presence of a carbonyl group (C=O) **B1**

(c) both aldehydes and ketones contain a C=O carbonyl group, so both give the same positive (orange precipitate) result, so the test does not distinguish between them oe **B1**

(c) Answer: Confirms a carbonyl group (C=O) is present; both aldehydes and ketones contain C=O, so both give a positive result and the test cannot distinguish them.

(d) propan-1-ol does not contain a carbonyl group (C=O), so it cannot react with 2,4-DNP or be oxidised by Tollens' reagent in the same way as an aldehyde **B1**

(d) propan-1-ol is not sufficiently acidic (it is a much weaker acid than a carboxylic acid) to react with/release CO_2 from sodium carbonate oe **B1**

(d) Answer: Propan-1-ol has no C=O group, so it does not react with 2,4-DNP or Tollens'; it is not acidic enough to react with sodium carbonate.

Question 4

(a) correct formulae with a reversible arrow: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ **M1**

(a) all state symbols correct: (l), (l), (l), (l) cao **A1**

(a) Answer: $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

(b) acts as a catalyst cao **B1**

(b) Answer: Acts as a catalyst.

(c) moles ethanoic acid = 6.00/60.0 = 0.100 mol **M1**

(c) theoretical moles ester = 0.100 mol (1:1 ratio); theoretical mass = 0.100 x 88.0 = 8.80 g **M1**

(c) % yield = (6.60/8.80) x 100 **M1**

(c) 75.0% cao **A1**

(c) Answer: 75.0%

(d) sum of Mr of reactants = 60.0 + 46.0 = 106.0 **M1**

(d) atom economy = (Mr of desired product / sum of Mr of reactants) x 100 = (88.0/106.0) x 100 **M1**

(d) 83.0% (3 s.f.) cao **A1**

(d) Answer: 83.0%

(e) the reaction of ethanoyl chloride with ethanol produces steamy/misty white fumes of HCl gas (a vigorous, exothermic reaction), unlike the acid + alcohol reaction **B1**

(e) nucleophilic addition-elimination cao **B1**

(e) Answer: Misty white fumes of HCl are produced (vigorous reaction), unlike with ethanoic acid; mechanism is nucleophilic addition-elimination.

Question 5

(a) moles CO_2 = 1.76/44 = 0.0400 mol (= moles of C) **M1**

(a) moles H_2O = 0.720/18 = 0.0400 mol, so moles of H = 0.0800 mol **M1**

(a) mass of C + mass of H = (0.0400 x 12) + (0.0800 x 1) = 0.480 + 0.0800 = 0.560 g, equal to the sample mass, confirming no oxygen is present **M1**

(a) mole ratio C:H = 0.0400:0.0800 = 1:2, empirical formula CH_2 (empirical mass = 14) **M1**

(a) 56/14 = 4, so molecular formula = C_4H_8 cao **A1**

(a) Answer: C_4H_8

(b) there must be restricted rotation about the C=C double bond, and each carbon of the double bond must be attached to two different groups oe **B1**

(b) in but-1-ene, CH_2=$CHCH_2CH_3$, the C1 carbon of the double bond is attached to two hydrogen atoms (the same group twice) **B1**

(b) so but-1-ene cannot exist as two distinguishable geometric (E/Z) forms oe **B1**

(b) Answer: E/Z isomerism requires restricted rotation about C=C and two different groups on each double-bond carbon; in but-1-ene, C1 has two identical H atoms, so no E/Z isomerism is possible.

(c) H^+ (from HBr) adds to the terminal (CH_2=) carbon of propene, with the electron pair of the C=C π bond forming the new C-H bond **M1**

(c) this forms a secondary carbocation intermediate (positive charge on the central carbon), with Br^- released as a free ion **M1**

(c) Br^- then uses a lone pair to bond to the positively charged carbon, forming 2-bromopropane, $CH_3CHBrCH_3$ cao **A1**

(c) Answer: 2-bromopropane ($CH_3CHBrCH_3$) forms via a secondary carbocation intermediate.

(d) the secondary carbocation (leading to 2-bromopropane) is more stable than the primary carbocation (leading to 1-bromopropane) **B1**

(d) because alkyl groups are electron-donating (positive inductive effect), and there are more alkyl groups adjacent to the secondary carbocation, better stabilising/dispersing the positive charge oe **B1**

(d) Answer: The secondary carbocation is more stable than the primary one because more electron-donating alkyl groups disperse the positive charge, so it forms preferentially, giving 2-bromopropane as the major product.

Question 6

(a) 1-iodobutane reacts fastest (precipitate forms first), then 1-bromobutane, then 1-chlorobutane (slowest) cao **B1**

(a) the C-I bond has the lowest bond enthalpy (is the weakest) of the three carbon-halogen bonds; C-Cl has the highest bond enthalpy (strongest) **B1**

(a) the weaker the C-X bond, the more easily it is broken, so the faster the nucleophilic substitution by water occurs oe **B1**

(a) Answer: Rate: iodide > bromide > chloride, because the C-I bond has the lowest bond enthalpy (weakest bond) and the C-Cl bond has the highest bond enthalpy (strongest bond).

(b) aqueous NaOH (or KOH), warmed **B1**

(b) nucleophilic substitution cao **B1**

(b) Answer: Aqueous NaOH (or KOH), warmed; nucleophilic substitution.

(c) NaOH (or KOH) dissolved in ethanol, heated under reflux **B1**

(c) elimination cao **B1**

(c) Answer: NaOH (or KOH) in ethanol, heated under reflux; elimination.

Question 7

(a) NaBr and H_2SO_4 react together to generate hydrogen bromide, HBr, in situ: NaBr + H_2SO_4 -> $NaHSO_4$ + HBr **B1**

(a) the HBr formed then reacts with butan-1-ol, providing the Br^- nucleophile/substituting group oe **B1**

(a) Answer: NaBr + H_2SO_4 -> $NaHSO_4$ + HBr; the HBr generated reacts with the alcohol.

(b) correct formulae, C_4H_9OH and HBr as reactants, C_4H_9Br and H_2O as products **M1**

(b) C_4H_9OH + HBr -> C_4H_9Br + H_2O, correctly balanced cao **A1**

(b) Answer: C_4H_9OH + HBr -> C_4H_9Br + H_2O

(c) reflux uses a vertical condenser that continuously condenses and returns evaporated volatile reactants and products (butan-1-ol, HBr, 1-bromobutane) to the flask **B1**

(c) this allows prolonged heating (to increase the rate/extent of reaction) without the loss of volatile substances oe **B1**

(c) Answer: Reflux returns evaporated volatile substances to the flask via the condenser, allowing prolonged heating without losing reactants or product.

(d) the crude product mixture is distilled, collecting the fraction with a boiling point close to that of 1-bromobutane (removes the least volatile/non-volatile impurities) **B1**

(d) the distillate is shaken with water in a separating funnel and the layers allowed to separate; the lower, organic (1-bromobutane) layer is run off and retained, as 1-bromobutane is denser than water **B1**

(d) the organic layer is then washed with sodium hydrogencarbonate solution to neutralise/remove acidic impurities (H_2SO_4/HBr), venting gas pressure (CO_2) regularly by inverting and opening the tap **B1**

(d) washed again with water to remove any remaining aqueous/hydrogencarbonate impurities **B1**

(d) dried using an anhydrous drying agent (e.g. anhydrous calcium chloride or magnesium sulfate) to remove residual traces of water, then decanted/filtered from the drying agent **B1**

(d) the dried liquid is redistilled, collecting only the fraction that boils at the correct literature temperature (close to 101°C), discarding the first and last fractions to ensure purity **B1**

(d) Answer: Distil crude product; separate organic layer in a separating funnel; wash with $NaHCO_3$(aq) then water; dry with anhydrous $CaCl_2$ or $MgSO_4$; redistil, collecting only the correct boiling-point fraction.

(e) moles butan-1-ol = 7.40/74.0 = 0.100 mol **M1**

(e) theoretical moles of 1-bromobutane = 0.100 mol (1:1 stoichiometry); theoretical mass = 0.100 x 137.0 = 13.7 g **M1**

(e) % yield = (9.13/13.7) x 100 **M1**

(e) 66.6% (3 s.f.) cao **A1**

(e) Answer: 66.6%

(f) a valid reason, e.g. some butan-1-ol undergoes a competing elimination side reaction with concentrated H_2SO_4 to form but-1-ene instead of substitution **B1**

(f) a further linked/alternative valid point, e.g. some product is inevitably lost during transfers between apparatus and during purification steps (distillation, separating funnel, drying) oe **B1**

(f) Answer: For example: some butan-1-ol undergoes elimination (side reaction) to form but-1-ene instead of substitution; and/or product is lost during transfers and purification steps.

(g) measure the boiling point of the product during (re)distillation using a thermometer **B1**

(g) compare to the known (data book) boiling point of 1-bromobutane (about 101°C); a pure sample boils over a narrow (1-2°C) range at the correct value, an impure sample boils over a wider range/at the wrong temperature oe **B1**

(g) Answer: Measure the boiling point during distillation and compare to the literature value (about 101°C); a pure sample boils over a narrow range at this temperature.

(h) a valid precaution, e.g. wear eye protection/gloves, and/or carry out the heating and distillation steps in a fume cupboard **B1**

(h) linked reason, e.g. concentrated H_2SO_4 is corrosive, and HBr/1-bromobutane vapours are toxic/irritant and should not be inhaled oe **B1**

(h) Answer: For example: work in a fume cupboard, because HBr and 1-bromobutane vapours are toxic/irritant, and wear eye protection because concentrated H_2SO_4 is corrosive.

Question 8

(a) orange solution turns green ($Cr_2O_7^{2-}$ is reduced to Cr^{3+}) **B1**

(a) butan-2-ol is oxidised to butanone, a ketone **B1**

(a) because butan-2-ol is a secondary alcohol (the carbon bonded to -OH is attached to only one hydrogen and two other carbon-containing groups), so only one oxidation step is possible oe **B1**

(a) Answer: Orange to green colour change; butanone (a ketone) forms, because butan-2-ol is a secondary alcohol.

(b) butan-1-ol is heated with a limited/controlled amount of acidified potassium dichromate(VI), using distillation apparatus (not reflux) **B1**

(b) butanal (the aldehyde) has a lower boiling point than butan-1-ol and is distilled off/removed from the reaction mixture as soon as it forms **B1**

(b) this limits its contact time with the oxidising agent, preventing/reducing further oxidation to butanoic acid oe **B1**

(b) Answer: Heat with a limited amount of acidified dichromate using distillation (not reflux); the aldehyde distils off as it forms, limiting further oxidation to the carboxylic acid.

(c) elimination (via a carbocation intermediate) **B1**

(c) concentrated sulfuric acid (or aluminium oxide/Al_2O_3 catalyst) cao **B1**

(c) Answer: Elimination (via a carbocation intermediate); catalysed by concentrated H_2SO_4 (or Al_2O_3).

(d) but-1-ene, CH_2=$CHCH_2CH_3$ **B1**

(d) but-2-ene, CH_3CH=$CHCH_3$ **B1**

(d) a mixture forms because an H^+ ion can be lost from either of the two different carbon atoms adjacent to the (original C-OH) carbocation carbon, giving two different alkenes oe **B1**

(d) Answer: but-1-ene (CH_2=$CHCH_2CH_3$) and but-2-ene (CH_3CH=$CHCH_3$); a mixture forms because H^+ can be lost from either neighbouring carbon of the carbocation intermediate.

Question 9

(a) H^+ (from HBr) adds to the CH carbon of the double bond (the carbon bonded to only one methyl group and one H), with the electron pair of the C=C π bond forming the new C-H bond **M1**

(a) this forms a tertiary carbocation intermediate (positive charge on the carbon bonded to two methyl groups), with Br^- released as a free ion **M1**

(a) Br^- then uses a lone pair to bond to the positively charged carbon, forming 2-bromo-2-methylbutane, $CH_3C(Br)(CH_3)CH_2CH_3$ cao **A1**

(a) Answer: 2-bromo-2-methylbutane forms via a tertiary carbocation intermediate.

(b) the tertiary carbocation (leading to 2-bromo-2-methylbutane) is more stable than the secondary carbocation that would lead to 2-bromo-3-methylbutane **B1**

(b) because alkyl groups are electron-donating (positive inductive effect), and the tertiary carbocation has more alkyl groups adjacent to the positive carbon, better dispersing/stabilising the positive charge oe **B1**

(b) Answer: The tertiary carbocation is more stable than the secondary one, because more electron-donating alkyl groups disperse the positive charge, so it forms preferentially, giving 2-bromo-2-methylbutane as the major product.

(c) moles 2-methylbut-2-ene = 7.00/70.0 = 0.100 mol **M1**

(c) theoretical moles of product = 0.100 mol (1:1 stoichiometry); theoretical mass = 0.100 x 151.0 = 15.1 g **M1**

(c) % yield = (11.6/15.1) x 100 **M1**

(c) 76.8% (3 s.f.) cao **A1**

(c) Answer: 76.8%

Question 10

(a) correct formulae with a reversible arrow: $CH_3COOH + (CH_3)_2CHCH_2CH_2OH \rightleftharpoons CH_3COOCH_2CH_2CH(CH_3)_2 + H_2O$ **M1**

(a) all state symbols correct: (l), (l), (l), (l) cao **A1**

(a) Answer: $CH_3COOH(l) + (CH_3)_2CHCH_2CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_2CH(CH_3)_2(l) + H_2O(l)$

(b) acts as a catalyst **B1**

(b) reflux uses a vertical condenser that continuously condenses and returns evaporated volatile substances to the flask, allowing prolonged heating (to increase the rate/extent of reaction) without loss of volatile reactants or product oe **B1**

(b) Answer: Catalyst; reflux returns evaporated volatile substances to the flask, allowing prolonged heating without losing reactants or product.

(c) upper layer **B1**

(c) the ester is less dense than the aqueous layer, and the two liquids are immiscible (esters do not hydrogen-bond appreciably with water), so the ester floats on top oe **B1**

(c) Answer: Upper layer, because the ester is less dense than water and the two liquids are immiscible.

(d) moles 3-methylbutan-1-ol = 4.40/88.0 = 0.0500 mol **M1**

(d) theoretical moles of ester = 0.0500 mol (1:1 ratio); theoretical mass = 0.0500 x 130.0 = 6.50 g **M1**

(d) % yield = (4.81/6.50) x 100 **M1**

(d) 74.0% cao **A1**

(d) Answer: 74.0%

(e) % uncertainty = (0.005/4.40) x 100 **M1**

(e) 0.114% (3 s.f.) cao **A1**

(e) Answer: 0.114%

Question 11

(a) the carbonyl carbon of butanone is delta+ (electrophilic), because oxygen is more electronegative and withdraws electron density from the C=O bond **M1**

(a) the CN^- ion (nucleophile) uses a lone pair to attack the delta+ carbonyl carbon, and the C=O π bond breaks heterolytically with both electrons moving onto the oxygen **M1**

(a) this forms a negatively charged (alkoxide, O-) intermediate **A1**

(a) the intermediate is then protonated (by H^+ from the dilute H_2SO_4) to give the neutral hydroxynitrile product, 2-hydroxy-2-methylbutanenitrile cao **A1**

(a) Answer: CN^- attacks the delta+ carbonyl carbon, forming an alkoxide intermediate, which is then protonated to give 2-hydroxy-2-methylbutanenitrile.

(b) a carbon atom bonded to four different atoms or groups **B1**

(b) the chiral carbon is C2 (the original carbonyl carbon of butanone), now bonded to -OH, -CN, $-CH_3$ and $-CH_2CH_3$ cao **B1**

(b) Answer: A carbon bonded to four different groups; here, C2, bonded to OH, CN, CH_3 and CH_2CH_3.

(c) butanone is a planar molecule around the trigonal planar carbonyl carbon **B1**

(c) the CN^- nucleophile can attack the delta+ carbon from either face (side) of this planar group with equal probability, producing equal amounts of both enantiomers (a 50:50/racemic mixture) **B1**

(c) a racemic mixture has no net effect on plane-polarised light (it is optically inactive), because the equal and opposite rotations caused by each enantiomer cancel out oe **B1**

(c) Answer: The planar carbonyl carbon can be attacked from either face with equal probability, giving equal amounts of both enantiomers (racemic mixture); this mixture does not rotate plane-polarised light, as the equal and opposite rotations cancel.

Question 12

(a) order (weakest to strongest): phenylamine < ammonia < ethylamine cao **B1**

(a) in ethylamine, the ethyl (alkyl) group is electron-donating (positive inductive effect), increasing the electron density on the nitrogen and making the lone pair more available, so ethylamine is a stronger base than ammonia **B1**

(a) in phenylamine, the nitrogen lone pair is partially delocalised into (overlaps with) the aromatic ring's π electron system **B1**

(a) this reduces the availability of the lone pair to bond with a proton (H^+), making phenylamine a weaker base than ammonia oe **B1**

(a) Answer: phenylamine < ammonia < ethylamine (increasing base strength), because alkyl groups increase lone pair availability (stronger base) while the aromatic ring delocalises the lone pair in phenylamine (weaker base).

(b) $CH_3CH(NH_3^+)COO^-$ cao **B1**

(b) the acidic -COOH group donates (transfers) a proton **B1**

(b) to the basic $-NH_2$ group within the same molecule (an intramolecular acid-base/proton-transfer reaction), forming $-COO^-$ and $-NH_3^+$ oe **B1**

(b) Answer: $CH_3CH(NH_3^+)COO^-$; formed by intramolecular proton transfer from the -COOH group to the $-NH_2$ group.

(c) overall positive charge (a cation), $CH_3CH(NH_3^+)COOH$ **B1**

(c) in excess H^+ (acidic conditions), the $-COO^-$ group becomes protonated to -COOH, leaving the $-NH_3^+$ group as the only charged group oe **B1**

(c) Answer: Overall positive charge; in acidic solution the $-COO^-$ group is protonated to -COOH, leaving only the positively charged $-NH_3^+$ group.

(d) condensation reaction **B1**

(d) peptide (amide) bond, -CONH- **B1**

(d) water, H_2O, is released cao **B1**

(d) Answer: Condensation reaction; forms a peptide (amide) bond, -CONH-; releases H_2O.

Question 13

(a) the broad absorption at 2500-3300 cm-1 is due to the O-H bond of the carboxylic acid group (hydrogen-bonded, giving a very broad peak), present only in R **B1**

(a) the sharp peaks at 1710 cm-1 and 1740 cm-1 are both due to C=O stretching, present in both a carboxylic acid and an ester **B1**

(a) S (an ester) has no O-H bond, so shows no absorption in the 2500-3300 cm-1 region **B1**

(a) spectrum 1 (broad O-H, C=O at 1710) = R (butanoic acid); spectrum 2 (no O-H, C=O at 1740) = S (methyl propanoate) cao **B1**

(a) Answer: Spectrum 1 = R (butanoic acid); Spectrum 2 = S (methyl propanoate).

(b) loss of *OH (mass 17): 88 - 71 = 17 **B1**

(b) fragment = $CH_3CH_2CH_2CO^+$ (the acylium ion), m/z = 71 cao **B1**

(b) Answer: Loss of *OH (17); fragment = $CH_3CH_2CH_2CO^+$ (m/z = 71).

(c) loss of C_2H_5* (ethyl radical, mass 29): 88 - 59 = 29 **B1**

(c) fragment = $+C(=O)OCH_3$ (the methoxycarbonyl cation), m/z = 59 cao **B1**

(c) Answer: Loss of C_2H_5* (29); fragment = $+C(=O)OCH_3$ (m/z = 59).

Question 14

(a) X-ray diffraction shows all six carbon-carbon bond lengths in benzene are equal (about 0.139 nm), intermediate between a C-C single bond (0.154 nm) and a C=C double bond (0.134 nm); the Kekule structure predicts two different, alternating bond lengths **B1**

(a) the enthalpy of hydrogenation of benzene (about -208 kJ/mol) is much less exothermic than three times the enthalpy of hydrogenation of cyclohexene (3 x -120 = -360 kJ/mol); benzene is about 152 kJ/mol more thermodynamically stable than the Kekule structure predicts **B1**

(a) this evidence suggests the six p-orbital electrons are delocalised, forming a ring of electron density above and below the plane of the carbon atoms **B1**

(a) rather than being fixed as three alternating, localised C=C double bonds as the Kekule model proposes oe **B1**

(a) Answer: All C-C bonds are equal length (0.139 nm) and benzene's hydrogenation enthalpy is about 152 kJ/mol less exothermic than predicted for the Kekule structure, showing the π electrons are delocalised around the ring rather than fixed as alternating double bonds.

(b) correct species: NO_2^+, H_3O^+ and HSO_4^- **M1**

(b) $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ cao **A1**

(b) Answer: $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$

(c) NO_2^+ (the electrophile) attacks the delocalised π electron ring system of benzene, forming a new bond to one ring carbon **M1**

(c) this forms a positively charged intermediate (arenium ion/ σ complex), in which the delocalisation is disrupted (retained over only the other five carbons) **M1**

(c) HSO_4^- acts as a base and removes/accepts an H^+ from the carbon bonded to the NO_2 group **A1**

(c) this restores full delocalisation (aromaticity) of the ring and regenerates H_2SO_4, forming nitrobenzene cao **A1**

(c) Answer: NO_2^+ attacks the ring, forming a positively charged arenium ion intermediate; HSO_4^- removes an H^+ from this intermediate, restoring the aromatic ring and regenerating H_2SO_4.

Question 15

(a) the 1H signal at 9.75 ppm (integration 1H) is characteristic of an aldehyde -CHO proton **B1**

(a) the integration ratio 1:2:2:3 across four signals matches four different proton environments, consistent with a straight-chain -$CH_2CH_2CH_3$ group attached to CHO **B1**

(a) P is butanal, $CH_3CH_2CH_2CHO$ cao **A1**

(a) Answer: P is butanal, $CH_3CH_2CH_2CHO$.

(b) no signal beyond 3.5 ppm rules out an aldehyde proton, so the carbonyl is a ketone; the integration ratio 3:2:3 (two CH_3 environments plus one CH_2) matches Q = butan-2-one, $CH_3COCH_2CH_3$ cao **B1**

(b) Answer: Q is butan-2-one, $CH_3COCH_2CH_3$.

(c) moles butan-2-one = 1.44/72.0 = 0.0200 mol **M1**

(c) moles $NaBH_4$ available = 0.400/37.8 = 0.0106 mol (3 s.f.); moles $NaBH_4$ needed = 0.0200/4 = 0.00500 mol, which is less than 0.0106 mol available, confirming $NaBH_4$ is in excess **M1**

(c) moles butan-2-ol formed = 0.0200 mol (1:1 conversion, since butan-2-one is the limiting reagent) **M1**

(c) mass = 0.0200 x 74.0 = 1.48 g cao **A1**

(c) Answer: 1.48 g

Question 16

(a) recognise the 1:1:1:1 stoichiometry, so the change in each reactant = -0.667 mol and the change in each product = +0.667 mol **M1**

(a) equilibrium ethanoic acid = 1.00 - 0.667 = 0.333 mol; equilibrium propan-1-ol = 1.00 - 0.667 = 0.333 mol **M1**

(a) equilibrium water = 0.667 mol cao **A1**

(a) Answer: Ethanoic acid = 0.333 mol; propan-1-ol = 0.333 mol; water = 0.667 mol.

(b) Kc = $[CH_3COOC_3H_7][H_2O] / [CH_3COOH][C_3H_7OH]$ **M1**

(b) substitute concentrations (= moles, since the vessel volume is 1.00 dm3): (0.667 x 0.667) / (0.333 x 0.333) **M1**

(b) Kc = 4.01 (3 s.f.) cao **A1**

(b) no units, since the powers of concentration (mol dm-3) in the numerator and denominator are equal and cancel oe **B1**

(b) Answer: Kc = 4.01, no units

(c) Kc would decrease **B1**

(c) by Le Chatelier's principle, increasing the temperature favours the endothermic (reverse) direction, shifting the equilibrium position back towards the reactants and reducing the proportion of products at equilibrium, so Kc decreases oe **B1**

(c) Answer: Kc would decrease, because increasing temperature favours the endothermic reverse reaction (Le Chatelier's principle), shifting the equilibrium position towards the reactants.

Question 17

(a) Br_2 -> 2Br* (or Br_2 -> Br* + Br*) **B1**

(a) homolytic fission, each bromine atom keeping one electron from the shared pair, initiated by UV light **B1**

(a) Answer: Br_2 -> 2Br*, by homolytic fission initiated by UV light.

(b) identify bond broken = C-H (+413 kJ/mol) and bond formed = H-Br (+366 kJ/mol) **M1**

(b) enthalpy change = bonds broken - bonds formed = 413 - 366 **M1**

(b) +47 kJ/mol (endothermic) cao **A1**

(b) Answer: +47 kJ/mol

(c) correct species: C_2H_5Br formed and Br* regenerated **M1**

(c) C_2H_5* + Br_2 -> C_2H_5Br + Br* cao **A1**

(c) Answer: C_2H_5* + Br_2 -> C_2H_5Br + Br*

(d) any valid radical-radical combination other than Br* + Br* -> Br_2, e.g. C_2H_5* + Br* -> C_2H_5Br, or C_2H_5* + C_2H_5* -> C_4H_{10} cao **B1**

(d) Answer: C_2H_5* + Br* -> C_2H_5Br (or C_2H_5* + C_2H_5* -> C_4H_{10})

(e) the equivalent first propagation step for chlorine, C_2H_6 + Cl* -> C_2H_5* + HCl, breaks the same C-H bond (413) but forms the stronger H-Cl bond (432), so this step is exothermic for chlorine but endothermic for bromine (as calculated in part b) **B1**

(e) the less favourable (more endothermic) propagation step for bromine has a higher activation energy, making this rate-determining step slower for bromine, so the overall chain reaction proceeds more slowly with bromine than with chlorine, even though bromine's initiation step is easier oe **B1**

(e) Answer: The rate-determining propagation step is exothermic for chlorine (bonds broken 413, bonds formed 432, so -19 kJ/mol) but endothermic for bromine (+47 kJ/mol), giving bromine's propagation step a higher activation energy and a slower overall reaction, despite its easier initiation step.

Question 18

(a) the half-life (time for the concentration to halve) is constant at 300 s throughout the data: 0.0500 to 0.0250 in 300 s, 0.0250 to 0.0125 in the next 300 s, and 0.0125 to 0.00625 in the next 300 s **B1**

(a) a constant half-life, independent of concentration, is characteristic of a first-order reaction, consistent with an SN1 mechanism in which only the halogenoalkane appears in the rate-determining step **B1**

(a) Answer: The half-life is constant at 300 s throughout, which is characteristic of a first-order reaction.

(b) k = ln2 / 300 **M1**

(b) ln2 = 0.6931 **M1**

(b) k = 2.31 x 10^{-3} s-1 cao **A1**

(b) Answer: 2.31 x 10^{-3} s-1

(c) rate = 2.31 x 10^{-3} x 0.0500 **M1**

(c) 1.16 x 10^{-4} mol dm-3 s-1 cao **A1**

(c) Answer: 1.16 x 10^{-4} mol dm-3 s-1

Question 19

Level 3 A full and accurate comparison: correctly describes the one-step mechanism for 1-bromobutane (OH^- attacks the delta+ carbon from the side opposite the leaving Br^-, in a single step, with the rate depending on the concentrations of both the halogenoalkane and OH^-), correctly describes the two-step mechanism for 2-bromo-2-methylpropane (slow ionisation to form a carbocation intermediate, then fast attack by OH^-, with the rate depending only on the concentration of the halogenoalkane), and clearly explains, using both steric hindrance (from the three methyl groups on the tertiary carbon) and carbocation stability (tertiary more stable than primary), why each halogenoalkane reacts by its particular route. **5-6**

Level 2 A moderate comparison: describes the general difference between the two mechanisms (one-step versus two-step via an intermediate) with some correct detail, and refers to either steric hindrance or carbocation stability as a reason for the difference, but the explanation is incomplete, has minor errors, or omits how the rate depends on reactant concentrations for one or both halogenoalkanes. **3-4**

Level 1 Basic comments: states that the two halogenoalkanes react by different mechanisms or at different rates, with little or no correct mechanistic or kinetic detail, and no reference to steric hindrance or carbocation stability. **1-2**

Indicative content:

- 1-bromobutane is a primary halogenoalkane; OH^- is not sterically hindered from approaching the delta+ carbon, and attacks from the side opposite (backside relative) to the leaving Br^- in a single, concerted step
- this gives a rate equation of rate = k[1-bromobutane][OH^-], i.e. the reaction is second order overall (first order in each reactant)
- 2-bromo-2-methylpropane is a tertiary halogenoalkane; the three bulky methyl groups create steric hindrance that prevents OH^- from approaching the carbon closely enough for a one-step attack
- instead the C-Br bond breaks first, by heterolytic fission, in a slow step to form a tertiary carbocation intermediate and Br^-
- the tertiary carbocation is relatively stable because the three surrounding alkyl groups donate electron density (positive inductive effect), dispersing the positive charge enough for the carbocation to exist as a discrete intermediate
- OH^- then rapidly attacks the planar carbocation in a fast second step
- this gives a rate equation of rate = k[2-bromo-2-methylpropane] only, independent of [OH^-], so the reaction is first order overall
- a primary carbocation, which would be needed for 1-bromobutane to react by the same two-step route, is too unstable (too little alkyl stabilisation) to form readily, so 1-bromobutane instead reacts by the single-step route
- overall, the mechanism followed is governed by a balance of steric hindrance (favouring the one-step route for less hindered, primary substrates) and carbocation stability (favouring the two-step route for more substituted, tertiary substrates)