2.7 Organic Chemistry: 2-hour Pack

AQA 7405 · Calculator allowed · about 120 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 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 1 is 11 marks)

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2 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 2 is 9 marks)

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3 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 3 is 12 marks)

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4 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 4 is 9 marks)

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5 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 5 is 12 marks)

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6 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 6 is 8 marks)

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7 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 7 is 8 marks)

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8 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 8 is 9 marks)

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9 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 9 is 10 marks)

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Mark scheme · 2.7 Organic Chemistry: 2-hour Pack

Question 1

(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 2

(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%

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Question 3

(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 4

(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.

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Question 5

(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 6

(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 7

(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

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Question 8

(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 9

(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.

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