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CHEMISTRY **9701/42**

Paper 4 A Level Structured Questions **May/June 2017**

MARK SCHEME

Maximum Mark: 100

Published

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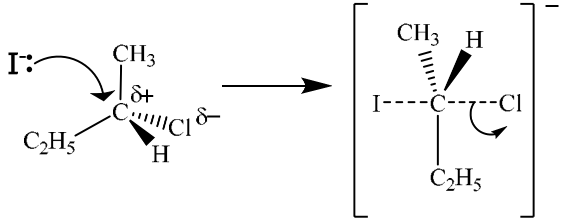
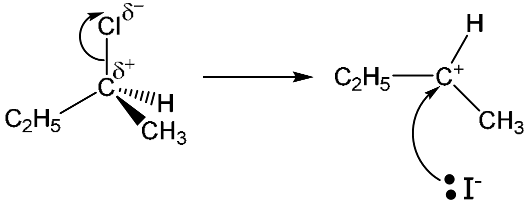
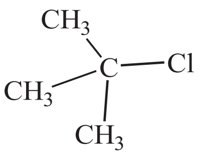
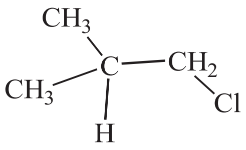
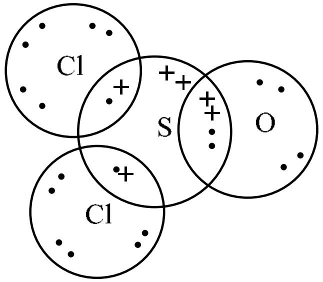
This document consists of **13** printed pages.

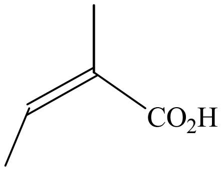
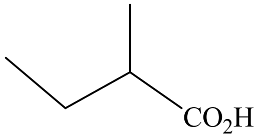
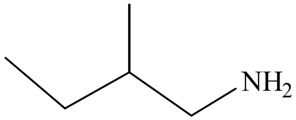
Question	Answer	Marks
1(a)(i)	increases down the group	**1**
	radius / size of (cat)ion/M^{2+} increases	**1**
	less polarisation / distortion of anion / carbonate **ion** / CO_3^{2-}	**1**
1(a)(ii)	Na^+ has smaller ionic charge **and** larger ionic radii OR the **charge density** of the **Na^+** is **lower**	**1**
1(b)(i)	$2KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O$	**1**
1(b)(ii)	$NaHCO_3$ because Na^+ is **smaller** OR charge density Na^+ is **larger**	**1**
1(c)(i)	LE $= \Delta H_f - 2(\Delta H_{at} + IE) - ½(O{=}O) - (EA_1 + EA_2)$ $= -361 - 2(89) - 2(418) - 496/2 - (-141+798)$ $=$ **–2280** (kJ mol^{-1}) correct answer scores [3]	**3** **1** **1** **1**
1(c)(ii)	LE of Na_2O will be **more negative** AND as $Na^{(+)}$ is smaller / larger charge density / smaller radii AND so greater attraction (between the ions) OR (ionic) bonds will be stronger	**1**
	Total:	**10**

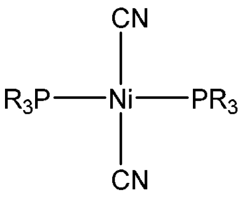
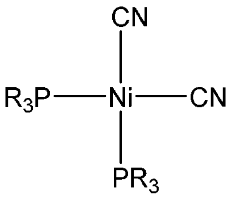
Question	Answer	Marks
2(a)	Add $AgNO_3$ Cl^- gives a white ppt **and** I^- gives a yellow ppt.	1
	Add NH_3(aq); ppt dissolves **and** ppt is insoluble	1
2(b)(i)	conductivity **decreases** during the reaction, AND number of Na^+ / I^- / **ions** are **decreased** / used up (from solution)	1
2(b)(ii)	(Equilibrate) solutions at 40 °C / with a water bath (cannot be after mixing) mix **known volumes and** start the clock / timing clearly mentioned/implied measure conductance / conductivity at regular intervals / every measured time [method A] OR measure the time for conductance to go to zero / a specific value / to be constant [method B] prepare a curve of conductance vs. time [related to method A] OR prepare a curve of conductance vs. concentration [related to method A] OR repeating the experiment at different concentrations [related to method A and B] any 3 points	3
2(c)(i)	[R-Cl]: rate increases by 5 / 3 when concentration increases by 10 / 6 (5 / 3), so order = 1	1
	[I^-]: rate increases by 5 / 3 when concentration increases by 5 / 3, so order = 1	1
2(c)(ii)	rate = $k[I^-][CH_3CH_2CHClCH_3]$ AND units of k = $dm^3\ mol^{-1}\ s^{-1}$	1
2(c)(iii)	relative rate = 5 / 5.3	1

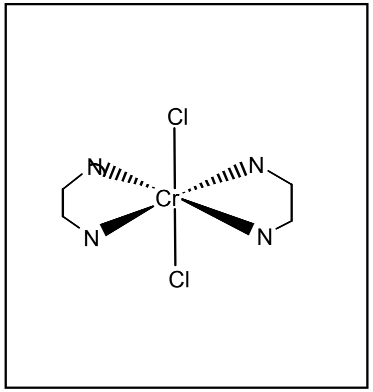
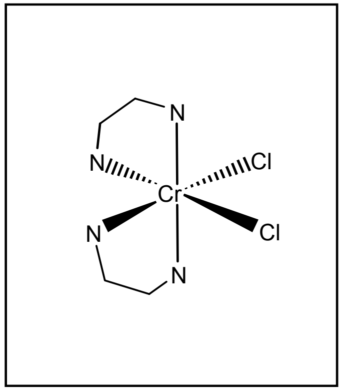
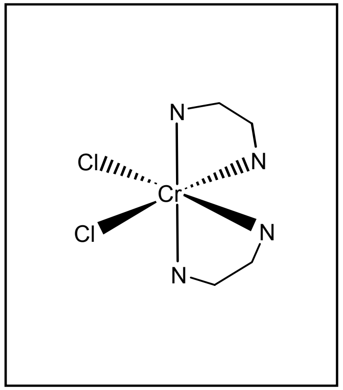
Question	Answer	Marks
2(d)(i)	either S_N1 or S_N2 mechanism S_N2  S_N1 	
	C-C*l* dipole AND C-C*l* curly arrow	**1**
	intermediate cation OR 5-valent transition state (charge essential)	**1**
	I^- with lone pair AND other curly arrow	**1**
2(d)(ii)	If S_N1 in 2(d)(i) **mixture of / two** optical isomers will be formed, AND the intermediate can be formed by the I^- approaching from top or bottom plane If S_N2 in 2(d)(i) **one optical isomer** AND attack always from fixed direction / opposite side	**1**

Question	Answer	Marks
2(e)(i)	**4** peaks	**1**
2(e)(ii)	 	**1 + 1**
	number of peaks = 2 number of peaks = 3	**1**
	Total:	**18**

Question	Answer	Marks
3(a)		
	four shared pairs: S=O and 2 × S-Cl	**1**
	all (9) lone pairs	**1**
3(b)(i)	$NaOH + HCl \longrightarrow NaCl + H_2O$	**1**
	$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$	**1**

Question	Answer	Marks
3(b)(ii)	moles (at start) = 0.5 × 60 / 1000 = 3×10^{-2} AND moles (at end) = 0.5 × 10.8 / 1000 = 5.4×10^{-3}	1
	moles reacted (= (30–5.4) × 10^{-3} =) **2.5×10^{-2}** correct ans. scores [2]	1
3(b)(iii)	moles of RCO_2H = $2.46 \times 10^{-2}/3$ = $8.2–8.3 \times 10^{-3}$ mole	1
3(b)(iv)	$M_r = 1.00 / (8.2 \times 10^{-3}) = 121.95$ (=122)	1
3(b)(v)	$C_7H_6O_2$ OR $C_6H_5CO_2H$	1
3(c)(i)	$LiAlH_4$	1
3(c)(ii)	 angelic acid  **T**  **U**	3
3(c)(iii)	angelic acid: geometrical OR cis-trans compound **T**: optical	1
	Total:	**14**

Question	Answer	Marks
4(a)(i)	$M_r = 52 + 6 \times 18 + 3 \times 35.5 = 266.5$	**1**
4(a)(ii)	1.00g = 1 / 266.5 **OR** 3.75×10^{-3} moles (of complex in 1g) for **A**, n=2 **AND** $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ for **B**, n=1 **AND** $[Cr(H_2O)_5Cl]Cl_2.H_2O$ for **C**, n=0; **AND** $[Cr(H_2O)_6]Cl_3$	**2**
4(b)(i)	Geometric(al) / cis-trans	**1**
4(b)(ii)	 isomer 1  isomer 2	**1**
4(b)(iii)	isomer 2 AND dipoles do not cancel OR CN^- are on the same side of the molecule	**1**
	Total:	**6**

Question	Answer	Marks
5(a)(i)	*bidentate*: (a species that) forms **<u>two</u>** dative bonds / donates **<u>two</u>** lone pairs	**1**
	ligand: a species that uses a **lone pair** to form a **dative** bond to **a metal atom / metal ion**	**1**
5(a)(ii)	   each structure [1] x 3	**3**
5(b)(i)	$K_{stab1} = [Cu(NH_3)_4{}^{2+}]/[Cu^{2+}][NH_3]^4$	**1**
	$K_{stab2} = [Cu(en)_2{}^{2+}]/[Cu^{2+}][en]^2$	**1**
	$mol^{-4}\ dm^{12}$ AND $mol^{-2}\ dm^{6}$	**1**
5(b)(ii)	$K_{eq3} = K_{stab2} / K_{stab1}$	**1**
5(b)(iii)	$K_{eq3} = K_{stab2} / K_{stab1} = 4.4(2) \times 10^6$	**1**
	$mol^2\ dm^{-6}$	**1**
5(c)(i)	(ΔS_{eq1} is negative as) **more / 5** moles of reactants are forming (one mole of) the complex OR (ΔS_{eq2} is positive as) **fewer / 3** moles of reactants are forming (one mole of) the complex	**1**
5(c)(ii)	ΔG_{eq2} = –100 – 298 × 40 / 1000 OR $\Delta G = \Delta H - T\Delta S$ = –112 or –111.9 (kJ mol^{-1}) correct answer [2]	**2** **1** **1**

Question	Answer	Marks
5(c)(iii)	Since (ΔG_{eq2}) is **more** negative (than ΔG_{eq1}) AND equilibrium 2 is more feasible	1
5(c)(iv)	$\Delta H_{(3)} = -8$ (kJ mol^{-1})	1
5(c)(v)	**<u>ligand</u>** exchange / replacement / substitution / displacement	1
	Total:	**17**

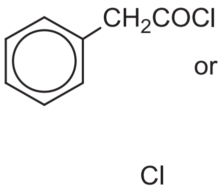
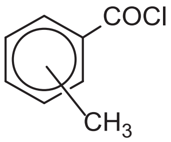
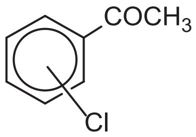
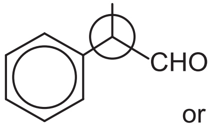
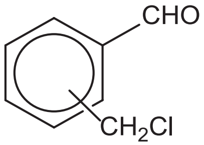
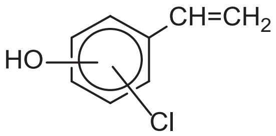
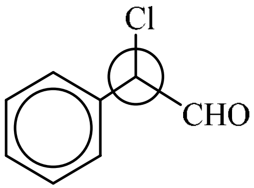
Question	Answer	Marks
6(a)(i)	the lower / smaller the pK_a, the stronger the acid	1
6(a)(ii)	pK_a = –log(K_a) or pK_a = –lg(K_a) or $K_a = 10^{-pka}$	1
6(a)(iii)	(stronger than ethanoic acid because) C*l* is electron-withdrawing	1
	and so stabilises the RCO_2^- anion / conjugate base **or** weakens O-H bond (so H^+ is more easily released)	1
6(b)(i)	$NH_3^+CH_2CO_2^- \longrightarrow NH_2CH_2CO_2^- + H^+$ OR $NH_3^+CH_2CO_2^- + H_2O \longrightarrow NH_2CH_2CO_2^- + H_3O^+$	1
6(b)(ii)	$K_a = 10^{-9.87} = 1.35 \times 10^{-10}$ $[H^+] = \sqrt{(K_a.c)} = 3.67 \times 10^{-6}$	1
	pH = **5.4** (5.43–5.44) min 2sf	1

Question	Answer	Marks
6(b)(iii)	curve starts at 5.4 and continuous	**1**
	vertical portion (end point) at vol added = 10.0 cm^3	**1**
	finishes at pH = 12.5 **at 20 cm^3** (and does not increase in pH)	**1**
	Total:	**10**

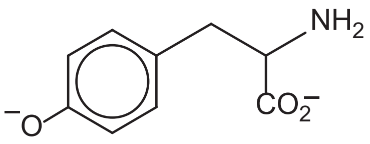
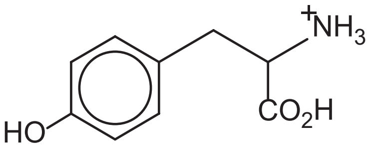
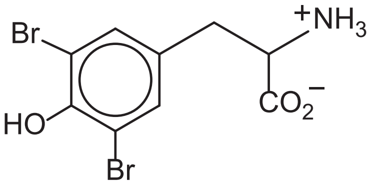
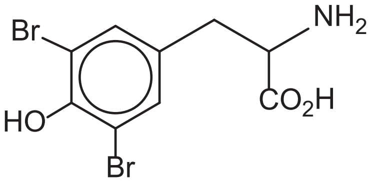
Question	Answer	Marks
7(a)	see table below; 0–1 [0]; 2 [1]; 3 [2]; 4 [3]; 5 [4]; 6–8 [5]	**5**

W	X	Y	Z
acyl chloride / COC*l*	methyl ketone / CH3CO group aryl chloride	aldehyde / CHO chloro(alkane) / RC*l*	Alkene / C=C phenol / C_6H_5OH aryl chloride

0–1 [0]; 2 [1]; 3 [2]; 4 [3]; 5 [4]; 6–8 [5]

Question	Answer	Marks
7(b)(i)	**W**  or  **X** 	**1 + 1**
	Y  or  **Z** 	**1 + 1**
7(b)(ii)	**Y**  OR any chiral atom correctly labelled	**1**
	Total:	**10**

Question	Answer	Marks
8(a)(i)	step 1 electrophilic substitution **ignore** acylation	**1**
	step 2 nucleophilic addition	**1**
8(a)(ii)	hydrolysis	**1**

Question	Answer	Marks
8(a)(iii)	step 1 $ClCH_2CHO$ (**allow** Br, I for Cl)	**1**
	$AlCl_3$	**1**
	step 2 HCN + NaCN	**1**
	step 3 heat in H_3O^+ / heat H^+(aq)	**1**
	step 5 NH_3 under pressure (+ heat) **or** heat NH_3 in a sealed tube	**1**
8(a)(iv)	with NaOH(aq)  [2]	**1 + 1**
	with HCl(aq)  [1]	**1**
	with Br_2(aq)  or  [1]	**1**
8(b)(i)	**P** is tyr	**1**
	tyr is 2– AND it is small / has a small *M*r	**1**

Question	Answer	Marks
8(b)(ii)	*(dipeptide / phe-tyr)* 2– is about double the M_r / mass of (*phe*) *1* OR mass / charge ratios are about the same for each (for dipeptide / phe-tyr and phe)	**1**
	Total:	**15**