ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry 6821

Mark Scheme

2006 examination – June series

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Chemistry AEA

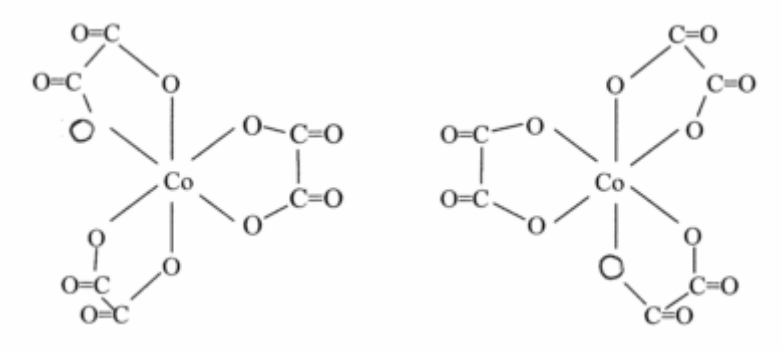
Question 1

(a) $[Co(H_2O)_6]^{2+} + 4Cl^- \rightarrow [CoCl_4]^{2-} + 6H_2O$ (*only*) **1**

(b) $[Co(H_2O)_6]^{2+} + 7NO_2^- + 2H^+ \rightarrow [Co(NO_2)_6]^{3-} + NO + 7H_2O$ **1**

(c) insoluble in water / K^+ salts usually soluble **1**

(d)



ethandioate ligands correctly bonded (1)
3 ligands joined at 90° sites (1)
mirror image (1) **3**
can use for O—O *M2 and M3*

(e)

M1	mix a known amount of the cobalt(III) containing compound with a large excess of a dilute acid	mix the Cobalt (III) compound with the same $[H^+]$ in multiple experiments	
M2	absorption – colorimeter CO_2 - syringe/balance		
M3	single experiment – plot absorption curve	multiple experiments – initial rate outlined	multiple experiments – varying initial concentration of complex – measurement of time for fixed vol. CO_2
M4	describe time to ½ absorption is constant or find gradients at various points then plot [ ] v rate → straight line	check/show that rate $\propto$ [ ]	concentration $\propto$ 1/t

4 marks
Total 10 marks

Question 2

(a) $K_c = [NO]/[N_2]^{0.5}[O_2]^{0.5}$ (1)
let amount of NO formed = x then amount N_2 = amount O_2 = (1-x/2) (1)
$K_c = (x/V)/(1 – x/2)/V = 0.12$ (1)
$x = 0.12-0.06x$ $x = 0.12/1.06 = 0.11(3)$ (1)
% yield = $(0.113/2) \times 100 = 5.7\%$ *(mark conseq. on M4)* (1) **5**
(if K_C is wrong lose M3 and M4)
(if $K_C = [NO]^2 / [N_2][O_2]$ lose M3 and then 4 unless K_C^2 allow full marks)
(if moles wrong but in terms of 'x' lose M4 other wise lose M3 and M4)

(b) $2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$ (1)

(or correct 'dot and cross' diagram) (1)
unpaired electron/free radical (*tied to single electron in M2)* (1) **3**
(not extra free electron)

(c) (i) $K_a = [H^+][HSO_3^-]/[H_2SO_3]$ or $[H^+]_2 / [H_2SO_3]$ (1)
$[H^+] = 10^{-pH} = 0.029$ (mol dm^{-3})(= $[HSO_3^-]$) (1)
$[H_2SO_3] = 0.1- 0.029 = 0.071$ (mol dm^{-3}) (1)
$K_a = 0.029^2/0.071 = 1.17 - 1.2 \times 10^{-2}$ (mol dm^{-3}) (1) **4**
(if $[H_2SO_3] = 0.1$ lose M3 $K_a = 8.29 – 8.41 \times 10^{-3}$
(ignore units unless wrong)

(ii) moles of H_2SO_3 used = 20.0 x 0.100/1000 = 0.0020 (1)
moles of OH^- added = 6.00 x 0.200/1000 = 0.0012 (1)
moles of H_2SO_3 remaining = 0.0020-0.0012 = 0.00080 (1)
conseq on M1+M2
moles of HSO_3^- produced = moles OH^- = 0.0012 (1)
$[H^+] = K_a [HSO_3^-]/ [H_2SO_3] = 1.20 \times 10^{-2} \times 0.00080/0.0012$
$= 7.8 - 8.00 \times 10^{-3}$ mol dm^{-3} *(conseq on K_a value)* (1)
pH = -Log (8.00×10^{-3}) = 2.10 – 2.11 (*conseq on $[H^+]$)* (1) **6**
(if $K_a = 8.29 - 8.41 \times 10^{-3}$ $[H^+] = 5.53 – 5.61 \times 10^{-3}$ pH = 2.25 – 2.26)
(if moles H_2SO_3 used = 0.1 lose M5 and M6)
(if 0.029 assume $[HSO_3^-]=[H^+]$ max 3)

(iii) $[HSO_3^-] = 0.1 \times 20/30 = 0.067$ (1)
$K_a = [H^+][SO^{2-}_3]/[HSO_3^-] = [H^+]^2/[HSO_3^-]$ or $[H^+] = \sqrt{(K_a [HSO_3^-])}$ (1)
$[H^+] = \sqrt{(6.20 \times 10^{-8} \times 0.067)} = 6.45 \times 10^{-5}$ mol dm^{-3}
pH = 4.19 (1) **3**
(if $HSO_3^- = 0.1$ allow M2 and M3 otherwise CE=0
$[H^+] = 7.87 \times 10^{-5}$ pH = 4.10)
(penalise pH with 1 d.p. once only)

(d) (i) orders (+ reason) w.r.t O_2 = 0 + $[O_2]$ halved – rate unchanged (1)
HSO_3^- = 2 + $[HSO_3^-] \times 3$ – rate × 9 (1)
H^+ = $[H^+]$ at pH 5.0 ×4 that at pH 5.6 (1)
2 + Rate down × 4 due to $\underline{[HSO_3^-]} \times 0.5$
Change in rate $\underline{\times 16}$ due to $[H^+] \times 4$ (1)

H^+ ions are catalysts (1)
O_2 must be involved in a fast reaction step/ not in rds (1) **6**

(ii) ` rate = $k[H^+]^2[HSO_3^-]^2$ *(conseq on (i)-if not CE)* (1)
$k = 4 \times 10^6$ mol^{-3} dm^9 s^{-1} answer (1) units (1) **3**

Total 30

Question 3

(a) (i) one H_2O **loses** H^+, so (BL) acid, (1)
another H_2O **gains** H^+, so (BL) base. (1) **2**
(*if both processes but no BL links 1 max)*

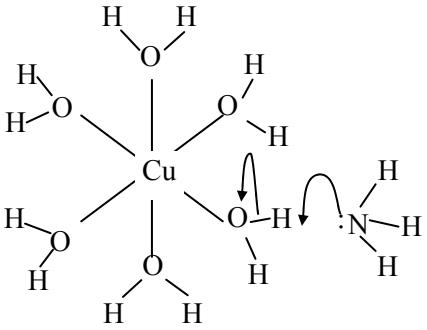
(ii) $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ (1)

$CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$ (1)

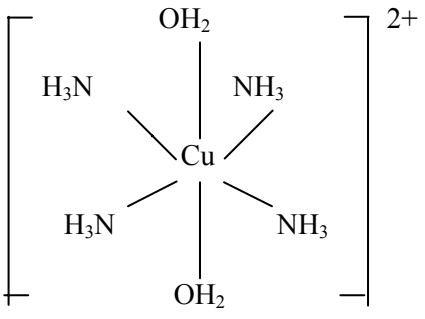
(allow →for 2nd equation)

NH_3 more basic/better lone pair donor/proton acceptor than H_2O (1)
Equilibrium in ammonia is further to right than in water / ethanoic acid completely dissociates (1) **4**

(b) (i) $[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(H_2O)_4(OH)_2] + 2NH_4^+$ (1)



Curly arrow <u>from N</u> of ammonia molecule to H of co-ordinately bonded water (1)
(lone pair need not be shown)
Curly arrow from O–H bond to O atom (1)



Structure = octahedral diagram with water molecules in the axial positions. (1)
Role NH_3 in formation of ppt = BL <u>and</u> L base, as proton removed from water molecule by lone pair donation (1)
Role NH_3 in formation of dk blue complex = Lewis base, as ligand (replacement reaction) or explained (1) **6**

(ii) Lewis base = SO_3^{2-} ; donates lone pair to $\underline{SO}^{2+}$ (1)
$SOCl_2 + Na_2SO_3 \rightarrow 2NaCl + 2SO_2$ (1)
White precipitate = NaCl (1) **3**

(c) (i) **With H_2S**
$SO_3^{2-} + 6H^+ + 4e^- \rightarrow S + 3H_2O$ (1)
$H_2S \rightarrow S + 2H^+ + 2e^-$ (1)

Oxidation state/number of S from +4 → 0 (1)
SO_3^{2-} oxidising agent (1)
$2H_2S + SO_3^{2-} + 2H^+ \rightarrow 3S + 3H_2O$ electrons must not be included (1) **5**

(ii) **With $KMnO_4$**
SO_4^{2-} formed (1)
$SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^-$ (1)
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ (1)

SO_3^{2-} because oxidation state/number of S from +4 → +6 (1)
$2MnO_4^- + 3SO_3^{2-} + H_2O \rightarrow 2MnO_2 + 3SO_4^{2-} + 2OH^-$ (1) **5**

(d) moles of $KMnO_4 = 22.35/1000 \times 0.0200 = 4.47 \times 10^{-4}$ mol (1)
moles of SO_3^{2-} in 25.0 cm^3 = $4.47 \times 10^{-4} \times \underline{5/2}$ mol (1)
total moles of SO_3^{2-} in original sample = $4.47 \times 10^{-4} \times 5/2 \times \underline{250/25} = 0.0112$ mol (1)
$M_r(M_2SO_3) = 1.05 / 0.0112 = 93.75$ *(conseq if M1, M2 or M3 = 0)* (1)
$A_r(M) = [93.96-(32.1+16 \times 3)] / 2 = 6.93$ ∴ **M** = Lithium/Li (*conseq on M4*) (1) **5**

OR

For M4 calculate mass M→0.155g

M5 $\underline{0.155}$ → 6.93
0.02235

Total 30

Question 4

(a) (i) $C_8H_{18} + 12.5O_2 \rightarrow 8CO_2 + 9H_2O$ **1**

(molecular formula only)

(ii) $Pb(C_2H_5)_4 + C_2H_4Br_2 + 16O_2 \rightarrow PbBr_2 + 10CO_2 + 12H_2O$

Formulae (1) balancing(1) **2**

(b) CO (1)

NO_x (1)

$2CO + 2NO \rightarrow 2CO_2 + N_2$ (1) **3**

(ignore unburnt hydrocarbons)

(c) (i) 2 (1)

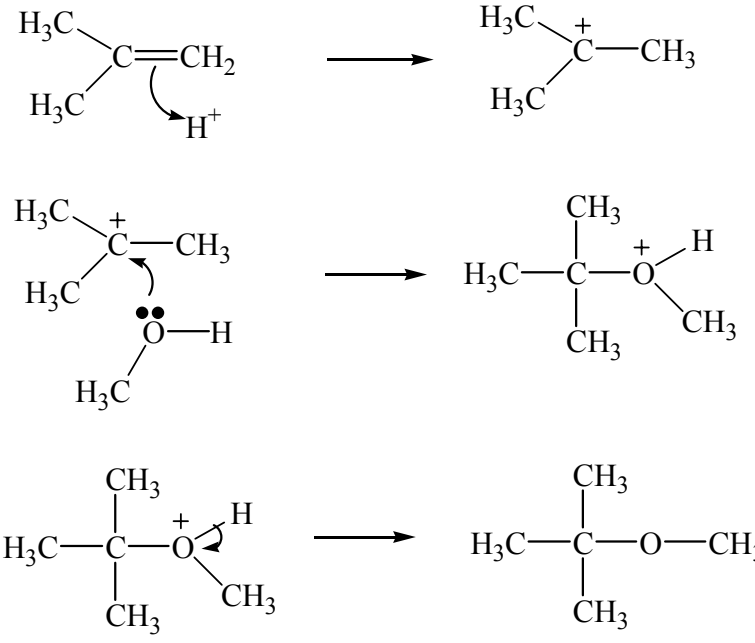
9:3 or 3: 1 (1) **2**

(ii) MTBE has dipole-dipole / van der Waals' imf and alcohols (also) have hydrogen bonding (1)

hydrogen bonding stronger than the other imf (1)

therefore less energy needed to overcome imf in MTBE (1) **3**

(iii)

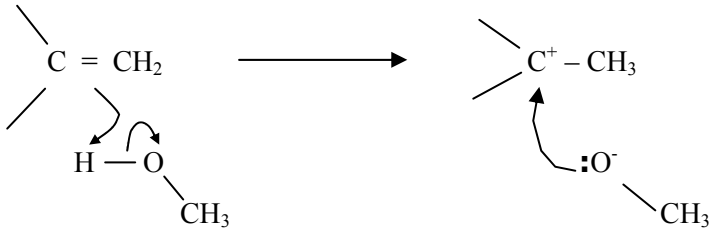


(2 max if wrong alkene used)

n.b. lone pair need not be shown *Each step (1) x 3* **3**

(allow simultaneous deprotonation of methanol in step 2)

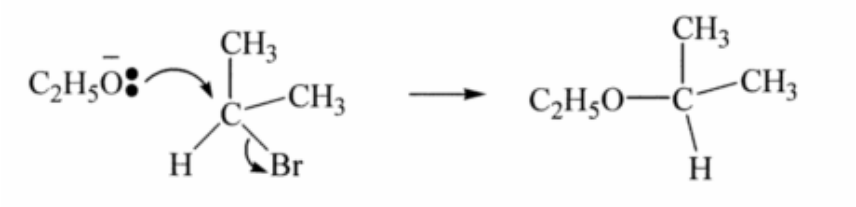
IF



(allow 1)

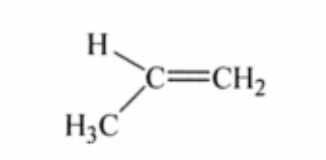
(d) (i) $2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$ (1) **1**

(ii) $C_2H_5ONa + BrCH(CH_3)_2 \rightarrow CH_3CH_2OCH(CH_3)_2 + NaBr$ (1)
nucleophilic substitution (1)
(pernalise –O-Na once)
(penalise wrong bromoalkane once)



(*accept either S_n1 or S_n2 approach)*
each curly arrow (1) x 2 *(n.b lone pair on ethoxide ion not necessary}* (2) **4**

(iii) Elimination (1)

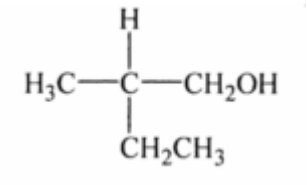


(1)

$CH_3CH{=}CH_2$ (1)

CH_3CH_2OH (1) **3**

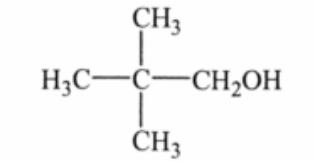
(e) **A**



or $CH_3CH_2CH(CH_3)CH_2OH$ (1)

B $CH_3CH(OH)CH_2CH_2CH_3$ or $CH_3CH(OH)CH(CH_3)_2$ (1)

C



or $(CH_3)_3CCH_2OH$ (1)

X **(**$CH_3)_3CCH_2OCH_2C(CH_3)_3$ *conseq on error in C (if alcohol)* (1)

D $CH_3CH_2CH(OH)CH_2CH_3$ (1)

Y $CH_3CH_2COCH_2CH_3$ *(only)* (1)

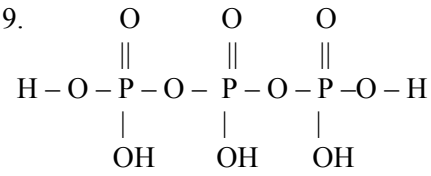
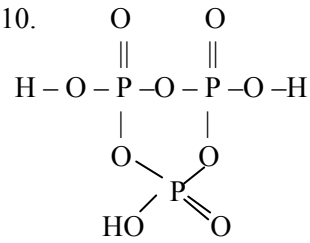
E $CH_3CH_2CH_2CH_2CH_2OH$ (1)

Z $CH_3CH_2CH_2CH=CH_2$ (1) **8**

(allow $CH_3CH=CHCH_2CH_3$ *if* ***E*** *given as* $CH_3\ CH_2CH(OH)CH_2CH_3$*)*

Total 30 marks

Question 5

(a)	1.	Both covalently bonded	(1)	
	2.	SiO_2 is macromolecular	(1)	
	3.	strong covalent bonds must be broken	(1)	
	4.	P_4O_6 is simple molecular	(1)	
	5.	weaker intermolecular/van der Waals' forces broken	(1)	**5**
	1&2.	overall equation for the hydrolysis each chloride	(2)	
	3.	both reactions involve the hydrolysis of a covalent chloride	(1)	
	4.	donation of lone pair/coordination of oxygen of water molecule	(1)	
	5.	using vacant 3d orbital on silicon/phosphorus atom/ to Si or P atom	(1)	
	6.	formation of HCl / H^+ which cause solution to be acidic	(1)	
	7.	step repeated 3/2 times to (initially) form $Si(OH)_4/P(OH)_3$ *(accept either $Si(OH)_4$ or SiO_2 / $P(OH)_3$ or H_3PO_3)*	(1)	**7**
	1.	polarity of the OH (and PO) bonds shown on structure or described	(1)	
	2.	(extensive) hydrogen bonding (occurs between molecules)	(1)	
	3.	forming a (sufficiently) large 3-D network/structure for it to be solid at room temperature	(1)	
	4.	hydrogen bonding persists in concentrated solution causing it to be viscous	(1)	
	5.	as the solution becomes dilute, acid molecules/phosphate ions separated by water molecules	(1)	
	6.	hydrogen bonding between phosphoric acid molecules and water	(1)	
	7.	when phosphoric acid molecules condense water is eliminated	(1)	
	8.	P – O – P links are formed	(1)	
	9.		(1)	
	10.		(1)	**10**
			17 max	
QWC		correct use of technical language in at least one section	(1)	
		written sentences and all three sections attempted	(1)	
		answers presented in a logical form in not less than two sections	(1)	
				Total 20

(b)	1.	each double bond will undergo addition reaction with Br_2	(1)	
	2.	$CH_3(CH)_4COOH + 2Br_2 \rightarrow CH_3(CHBr)_4COOH$	(1)	
	3.	make solution of known mass/volume of acid *(if comparison with mono-ene must be equivalent moles)*	(1)	
	4.	titrated with solution Br_2	(1)	
	5.	until solution just remains brown	(1)	
	6.	calculate number of moles of each reactant	(1)	
	7.	will be in the ratio 1(acid) : 2	(1)	**7**
	1.	restricted/no rotation of C=C	(1)	
	2.	due to sideways overlap of the p orbitals/due to π bond	(1)	
	3.	each C atom of the double bond attached to two different atoms/group of atoms	(1)	
	4.	each double bond in this acid will have 2 geometric isomers / 4 isomers	(1)	
	5-8.	each isomer drawn $4 \times$ (1) *(duplicates cancels)*	(4)	**8**
	1.	acid partially ionised - equilibrium equation	(1)	
	2.	ionisation suppressed by full ionisation of salt	(1)	
	3.	equation for total ionisation of salt	(1)	
	4.	therefore large reservoirs of undissociated acid and anion	(1)	
	5.	effect of addition of H^+ ions – words/equation	(1)	
	6.	therefore H^+ conc. Only rises small amount therefore pH almost constant	(1)	
	7.	effect of addition of OH^- ions – words/equation	(1)	
	8.	therefore H^+ conc. only falls small amount therefore pH almost constant *(allow little change in pH of system provided only small amounts acid/alkali added)* (*if M6 and M8 not given)*	(1) (1)	**8**
			17max	
QWC		correct use of technical language in at least one section	(1)	
		written in sentences and all three sections considered	(1)	
		answers presented in logical form in not less than two sections	(1)	

Total 20 marks