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ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry (6421)

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2008 examination - January series

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Question 1

(a) (i) $K_w = [H^+][OH^-]$ if wrong only score in (ii) and (iii) except if $[H_2O] = 1$ * 1

(ii) 2.34×10^{-7} penalise 2.3×10^{-7} i.e. 2 sfs once in the question 1

(iii) 2.34×10^{-7} conseq = (ii) 1

(iv) 5.48 to 5.50 $\times 10^{-14}$ conseq = (ii) × (iii) 1

*if $[H_2O] = 1$ can score for correct answer here

(b) [H+] = $\frac{10^{-14}}{0.136}$ (1) = 7.35×10^{-14} OR pOH = 0.87 1

pH = 13.13 1

Total 6

Question 2

(a) M1 $K_a = \frac{[H^+]^2}{[CH_3CH_2COOH]}$ if wrong, score max 1 for M3 from their $[H^+]$ 1

penalise round brackets once in the qu

M2 $[H^+] = \sqrt{(1.35 \times 10^{-5} \times 0.169)}$ (1) $= 1.51 \times 10^{-3}$ 1

If √ visible can score 2 for 5.64

M3 pH = 2.82 allow 1 for correct pH from their $[H^+]$ 1

(b) (i) $CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COONa + H_2O$ penalise 1
OR $CH_3CH_2COOH + OH^- \rightarrow CH_3CH_2COO^- + H_2O$ covalent Na

(ii) mol propanoic acid = 0.250 – 0.015 = 0.235 penalise rounding to 1
mol propanoate ions = 0.190 + 0.015 = 0.205 2sfs once 1

(iii) M1 $[H^+] = \frac{K_a \times [CH_3CH_2COOH]}{[CH_3CH_2COO^-]}$ correct rearrangement, as here or with their numbers even if x 1

allow $\frac{K_a \times [HA]}{[A^-]}$

M2 = $\frac{(1.35 \times 10^{-5})(0.235)}{0.205}$ insertion of correct numbers here or in Ka expression 1

(= 1.548×10^{-5})

M3 4.81 allow 1 for correct pH from their [H+] 1

Total 9

Question 3

(a) $K_c = \frac{[H_2]^3[C_2H_2]}{[CH_4]^2}$ if round brackets, penalise here but mark on 1
if K_c wrong can score only M1 and conseq units

(b) M1 dividing by volume throughout shown — if moles used instead of conc can score only M3* (+ units M4); can score this in M2 1

M2 $K_c = \frac{(\frac{0.28}{0.25})^3(\frac{0.12}{0.25})}{(\frac{0.44}{0.25})^2}$ 1

$(= \frac{(1.12)^3(0.48)}{(1.76)^2})$

M3 = 0.218 or 0.22 allow 0.217 – 0.22 — * 1.36×10^{-2} if vol not used 1

M4 $mol^2\ dm^{-6}$ 1

(c) to right or to product(s) or forwards 1
Increase 1

(d) to left or to reagent or backwards 1
no effect 1

(e) total no moles = 0.84 — if CE, no second mark 1

$\frac{0.12}{0.84}$ = 0.14(3) — allow $\frac{1}{7}$ 1

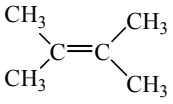
(f) $0.143 \times 2.78 \times 10^4 = 3.97 \times 10^3$ (allow 3.89– 4.00 $\times 10^3$ & 2 sfs i.e. 3.9 – 4.0) 1
conseq on (e) : penalise wrong units

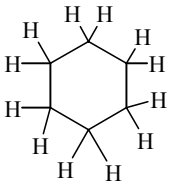
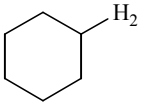
(g) mol H_2 = 2.1 — mark independently 1

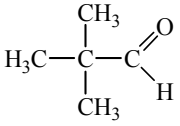
mol C_2H_2 = 0.7 1

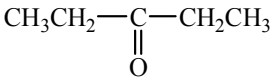
Total 14

Question 4

(a) (i) A  must show C=C 1

B  allow  but NOT  etc 1

(ii) C  or $(CH_3)_3CCHO$ NOT $(CH_3)_3CCOH$ 1

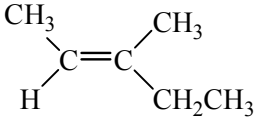
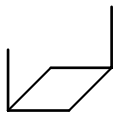
D  allow C_2H_5 and $C_2H_5COC_2H_5$ 1

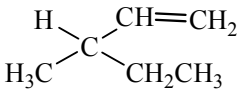
(iii) E CH_3CH_2COOH or $C_2H_5CO_2H$ 1

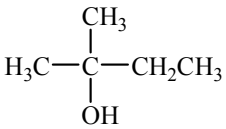
F $HCOOCH_2CH_3$ or $HCO_2CH_2CH_3$ 1

(iv) G $CH_3CH=CHCH_2CH_2CH_3$ $CH_3CH=CHCH(CH_3)_2$

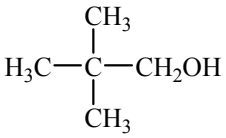
$CH_3CH=CHC_3H_7$ $CH_3CH_2CH=CHCH_2CH_3$ 1

  must show C=C in alkenes

H  allow C_2H_3 or $CHCH_2$ 1

(v) I  or $(CH_3)_2C(OH)C_2H_5$ 1

J or $(CH_3)_3CCH_2OH$ 1

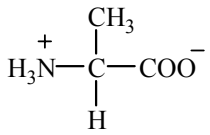


(b) (i) 5 1

(ii) a singlet QWC 1
b triplet QWC 1

Total 13

Question 5

(a) (i)  1

(ii) $H_2N\text{-}CH_2CH_2\text{-}COOH$ not $H_2N\text{-}C_2H_4\text{-}COOH$ 1

(iii) ethan(e)-1,2-diamine allow ethylene diamine or 1,2-diaminoethane but penalise wrong numbers 1

butan(e)(-1,4-)dioic acid NOT dibutanoic acid 1

(b) (i) addition not additional 1

(ii) 3-methylpent-2-ene 1

(c) (i) $HOCH_2CH_2OH$ 1
$HOOCCH_2CH_2COOH$ or $ClOCCH_2CH_2COCl$ 1

(ii) $HOCH_2CH_2COO^-$ allow -COONa but not covalently bonded Na 1

(d) (i) van der Waals allow vdW or London forces or dispersion forces 1

(ii) dipole- dipole QWC Not temporary dipole- induced dipole 1

Total 11

Question 6 **all answers to 3 sfs penalise fewer once**

(a) (i) Expt 2 2.68×10^{-4} 1

Expt 3 $10.7(2) \times 10^{-4}$ 1

Expt 4 2.08×10^{-3} 1

(ii)

k = $\frac{\text{rate}}{[X]^2}$ or $\frac{2.68\times10^{-4}}{(1.20\times10^{-3})^2}$ 1

= 186 1

$mol^{-1}dm^3s^{-1}$ allow $mol^{-1}dm^3$ for misprint 1

(b) increases (exponentially) allow straight line but not  1

Total 7

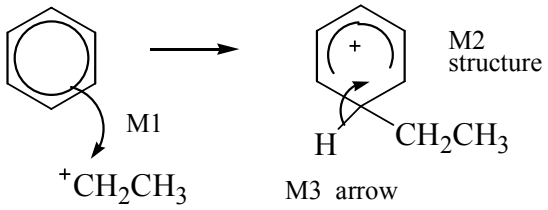
Question 7

(a) $AlCl_3$ or $AlBr_3$ $FeCl_3$ $FeBr_3$ 1

$CH_3CH_2Cl + AlCl_3 \rightarrow CH_3CH_2^+ + AlCl_4^-$ ignore arrows unless wrong e.g. from lp on Al 1

$H^+ + AlCl_4^- \rightarrow AlCl_3 + HCl$ allow words if all reagents and products described correctly 1

electrophilic substitution 1



3

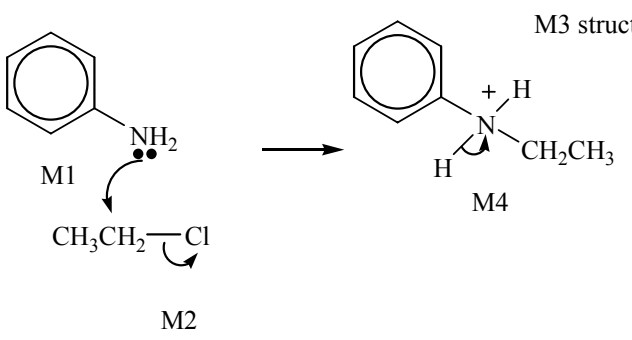
ethylbenzene ignore numbers allow phenylethane 1

phenylethene or poly(phenylethene) or styrene or poly(styrene) 1

or formula or repeating unit

9 marks

(b) nucleophilic substitution 1



Allow SN1

M2 lost if $AlCl_3$ used

M4 lost if Cl^- removes H^+ in mechanism or equation

4

N-ethylphenylamine or 1

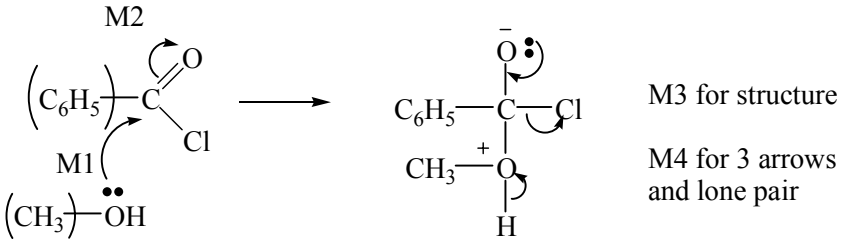
N-phenylethylamine

6 marks

Total 15

Question 8

(a) (nucleophilic) addition-elimination 1



NB *Different from Qu 7b → do not penalise M4 if Cl^- removes H^+* 4

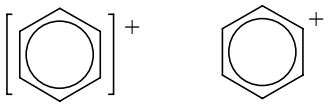
5 marks

NB There are four fragment ions in parts (b) and (c).
If these are written with a negative charge or with a radical dot they are all wrong, but if they are written with no charge at all, penalise the first two without + then allow the rest .

(b)

m/z 105 $C_6H_5\overset{+}{C}O$ or $C_6H_5CO^+$ 1

m/z 77 $C_6H_5^+$ or



but not Wheland horseshoe intermediate 1

$C_6H_5COOCH_3^{+\bullet} \rightarrow C_6H_5CO^+ + {}^{\bullet}OCH_3$ allow dot anywhere 2

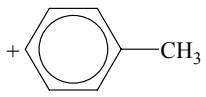
(1) (1) (for balanced equation)

4 marks

(c) *m/z* 43 CH_3CO^+ 1

V is $CH_3COOC_6H_5$ 1

m/z 91 $C_6H_5CH_2^+$ or



1

W is $HCOOCH_2C_6H_5$ $HCOOC_6H_4CH_3$ 1

4 marks

(d)	(i)	OH or acid or (absorption at) 2500-3000 cm^{-1}	1
		(present in acid not in ester)	
	(ii)	use of fingerprint region or (exact match with) known spectrum	1
			2 marks
			Total 15