GCE 2004
June Series

ASSESSMENT and QUALIFICATIONS ALLIANCE

Mark Scheme

Chemistry
(Subject Code CHM4)

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CHM 4 Further Physical and Organic Chemistry

SECTION A

Question 1

(a) (i) Experiment 2 2.60×10^{-3} 1
Experiment 3 0.60×10^{-2} 1
Experiment 4 11.4×10^{-2} 1

(ii) $k = \dfrac{10.4 \times 10^{-3}}{(4.80\times10^{-2})(6.60\times10^{-2})^2}$ 1

$= 49.7$ 1
(Allow 49.8 and 50)

$mol^{-2}\,dm^6\,s^{-1}$ 1

(b) No change 1

Total 7

Question 2

(a) $K_a = \dfrac{[H^+][A^-]}{[HA]}$ 1
(All three sets of square brackets needed, penalise missing brackets or missing charge once in the question)
(Don't penalise extra $[H^+]^2/[HA]$)

(b) $K_a = \dfrac{[H^+]^2}{[HA]}$ or $[H^+] = [A^-]$ 1

$[H^+] = \sqrt{(1.45\times10^{-4}) \times 0.25}$ 1

$= 6.02 \times 10^{-3}$ 1

pH = 2.22 1
(must be to 2dp)
(allow 4th mark consequential on their $[H^+]$)

(c) (i) pH (almost) unchanged 1
(Must be correct to score explanation)

H^+ removed by A^- forming HA 1
or acid reacts with salt
or more HA formed

(ii) $[H^+] = 10^{-3.59} = 2.57 \times 10^{-4}$ or 2.6×10^{-4} 1

$[A^-] = \dfrac{K_a[HA]}{[H^+]}$ 1

$= \dfrac{(1.45\times10^{-4}]\times0.25}{2.57\times10^{-4}}$ 1

$= 0.141$ (mol dm^{-3}) 1
(Allow 0.139 to 0.141 and allow 0.14)
(If not used 3.59, to find $[H^+]$ can only score M2 for working)
(If 3.59 used but $[H^+]$ is wrong, can score M2 for correct method and conseq M4)
If wrong method and wrong expression, can only score M1)

(ii) *Alternative scheme for first three marks of part (c)(ii)*
$pH = pK_a - \log\dfrac{[HA]}{[A^-]}$ (1)

$pK_a = 3.84$ (1)

$3.59 = 3.84 - \log\dfrac{0.250}{[A^-]}$ (1)

Total 11

Question 3

(a) 12 (kPa) 1

pp = mole fraction × total pressure **or** mole fraction = 12/104 1

= 0.115 1
(allow 0.12)

(b) 68 (kPa) 1

(c) $K_p = \frac{(pSO_3)^2}{(pSO_2)^2 \times (pO_2)}$ 1
(If K_p wrong, allow consequential units only)
(penalise square brackets in expression but then mark on)

$= \frac{68^2}{24^2 \times 12}$ 1

= 0.669 1
(Allow 0.67)
(A*llow full marks in calculation consequential on their values in (a) and (b))*

kPa^{-1} 1

(d) T_2 1
(Must be correct to score any marks in this section)

Exothermic 1

Reduce T to shift equilibrium to the right 1
or forward reaction favoured by low T
or K_p increases for low T
or low T favours exothermic reaction

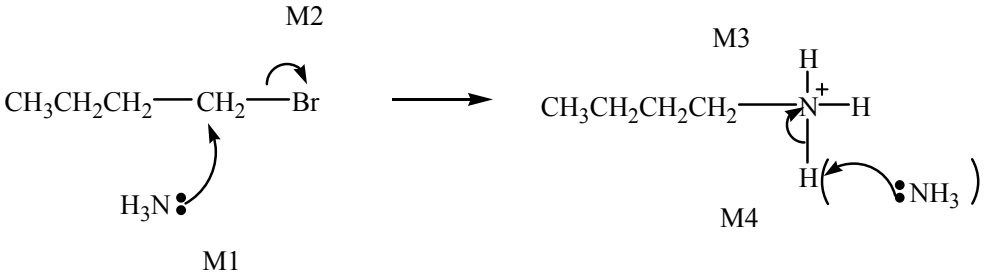
(e) Increase 1

None 1

Total 13

Question 4

(a) Nucleophilic substitution 1



4

M1, M2 and M4 for arrows, M3 for structure of cation
(Allow M2 alone first, i.e. SN1 formation of carbocation)
(Penalise M4 if Br^- used to remove H^+)

(b) Step 1 $CH_3CH_2CH_2CN$ 1

$CH_3CH_2CH_2Br$ + KCN (or CN^-) *(not HCN)* ⟶ $CH_3CH_2CH_2CN$ + KBr balanced (or Br^-) 1

Step 2 $CH_3CH_2CH_2CN + 2H_2$ (or 4[H]) ⟶ $CH_3CH_2CH_2CH_2NH_2$ 1

(c) (i) Lone pair (on N) (in correct context) 1

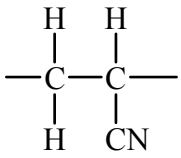
R group increases electron density / donates electrons /pushes electrons / has positive inductive effect 1

(ii) Any strong acid (but not concentrated) 1
or any amine salt or ammonium salt of a strong acid

(d) $CH_3CH_2N(CH_3)_2$ 1

Total 12

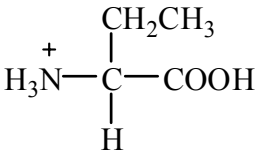
Question 5

(a) (i)  1

(Ignore n or brackets, but trailing bonds are essential)

(ii) Addition or radical 1

(b) (i) 2-aminobutanoic (acid) 1

(ii)  1

(c) (i) $C_3H_4O_2$ 1

(ii)  1

(1,4-)butan(e)dioic (acid) 1
(allow succinic, but not dibutanoic nor butanedicarboxylic acid)

(iii) Can be hydrolysed / can react with acid or base or water / 1
can react with nucleophiles

Total 8

Question 6

(a) Pentan-2-one 1

(b) (i) 1680 – 1750 (cm^{-1}) 1

(ii) 3230 – 3550 or 1000 – 1300 (cm^{-1}) 1

(iii) 4 1

(c)

Reagent	$K_2Cr_2O_7/H^+$	$KMnO_4/H^+$	Na	CH_3COOH/H_2SO_4
with **C**	no reaction	no reaction	no reaction	no reaction
with **D**	goes green	goes colourless	effervescence	smell

1 1 1

(penalise incomplete reagent e.g. $K_2Cr_2O_7$ or $Cr_2O_7^{2-}/H^+$ then mark on)

(d)

Reagent	Tollens	Fehlings or Benedicts
with **E**	silver (mirror)	red ppt or goes red *(not red solution)*

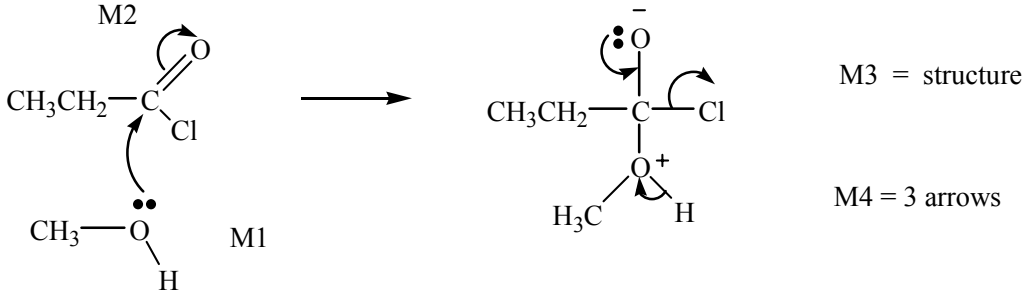
1 1

Total 9

SECTION B

Question 7

X is methyl propanoate 1



M1 for arrow and lone pair, 4
M2 for arrow
addition-elimination 1

Spectrum 2 1
if thinks Spectrum 1 = X can only score for structure of Y
Y is CH_3COOCH_2CH3 1
The two marks for explanation are awarded for discussing one or more of the four peaks (not those for the CH_3 of the ethyl groups) 2
for stated δ values the integration or the splitting should be related to the structure: e.g. structure of **X** shows that
at δ 3.7 – 4.1 (1) spectrum of **X** should have integration 3 / singlet (1)
or
at δ 2.1 – 2.6 (1) spectrum of **X** should have integration 2 / quartet (1)
Spectrum 2 has these
[OR Spectrum 1 has
at 3.7 – 4.1 (1) quartet / integration 2 (1) so not **X**
at 2.1 – 2.6 (1) singlet / integration 3 (1) so not **X**]

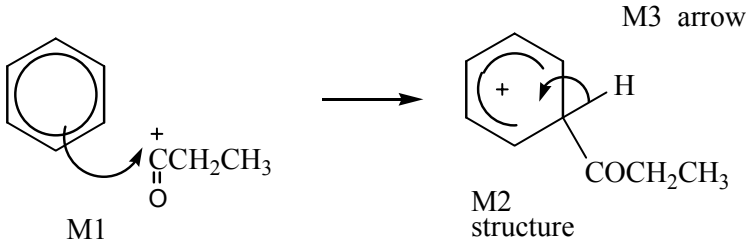
Total 10

Question 8

(a) $[CH_3CH_2CO]^+$ 1

$CH_3CH_2COCl + AlCl_3 \longrightarrow [CH_3CH_2CO]^+ + AlCl_4^-$ 1

(Penalise wrong arrows in the equation or lone pair on Al
In the equation, the position of the + on the electrophile can be on O or C or outside square brackets,
Can score electrophile mark in mechanism if not previously gained)



3

(Arrow for M1 must be to C or to the + on C
penalize + in intermediate if too close to C1 ;
horseshoe should extend from C2 to C6)

(b) *m/z* = 105 $C_6H_5CO^+$ 1

m/z = 77 $C_6H_5^+$ (*not Wheland intermediate)* 1

(Penalise missing + once)
Allow position of + on O or C of CO or outside [ ] for the fragment ion $[C_6H_5CO]^+$
Allow position of + on H or C or outside [ ] for the fragment ion $[C_6H_5]^+$

$[C_6H_5COCH_2CH_3]^{+\cdot} \longrightarrow C_6H_5CO^+ + CH_3CH_2^{\cdot}$

(˙ must be on H or C of CH_2 *or outside bracket)*

[1] for molecular ion [1] for RHS 2

Allow molecular formulae, i.e. $C_9H_{10}O^{+\cdot} \longrightarrow C_7H_5O^+ + C_2H_5^{\cdot}$

(c) Nucleophilic addition 1

1 Q contains asymmetric carbon or chiral centre or are chiral molecules
2 with 4 different groups/atoms attached (stated) *not molecules attached*
3 planar C=O
4 attack from each side
5 equally likely or equal amounts of each isomer formed
6 Racemic mixture or racemate (Q of L)
7 of mirror images or enantiomers or d/l or +/– or R/S or drawn max 6

(d) Conc H_2SO_4 or conc H_3PO_4 or Al_2O_3 or iron oxides Not HCl or HBr 1

Geometrical or cis-trans 1

Double bond or C=C not just π cloud *(stated not just drawn)* 1

2 Different atoms/groups on each C (not molecules) *(stated not just drawn)* 1

Total 20