Version 1.0

ASSESSMENT and QUALIFICATIONS ALLIANCE

General Certificate of Education

Chemistry 5421

CHM4 Further Physical and Organic Chemistry

Mark Scheme

2005 examination - June series

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

It must be stressed that a mark scheme is a working document, in many cases further developed and expanded on the basis of candidates' reactions to a particular paper. Assumptions about future mark schemes on the basis of one year's document should be avoided; whilst the guiding principles of assessment remain constant, details will change, depending on the content of a particular examination paper.

Question 1

(a) propyl methanoate; 1

$HCOOC_3H_7 + OH^- \rightarrow HCOO^- + C_3H_7OH$

OR

$HCOOC_3H_7 + NaOH \rightarrow HCOONa + C_3H_7OH$; 1

order wrt A = 1; 1

order wrt NaOH = 1; 1

Initial rate in Exp 4 = 2.4×10^{-3}; 1

(b) (i) r(ate) = k[A]

OR

r(ate) = k[A][NaOH]^0; 1

(*penalise missing [ ] but mark on)*

(penalise missing [ ] once per paper)

(if wrong order, allow only units mark conseq on their rate eqs)

(penalise k_a or k_w etc)

(ii) $k = \frac{9.0 \times 10^{-3}}{0.02}$; 1

$= 0.45$; 1

s^{-1}; 1

(iii) (large) excess of OH^- or [OH^-] is large/high; 1

[OH^-] is (effectively) constant

OR

[A] is the limiting factor; 1

(d) (i) CH_2OH
|
$CHOH$
|
CH_2OH; 1

propan(e)-1,2,3-triol

OR

1,2,3-propan(e)triol

OR

Glycerol; 1

(ii) $CH_3(CH_2)_{16}COONa$ or $C_{17}H_{35}COONa$ or $C_{18}H_{35}O_2Na$; 1

(*ignore 3 in front of formula but not if indicating trimer)*

(not just anion and penalise Na shown as covalently bonded)

soap – allow with detergent but not detergent alone; 1

Total 15

Question 2

(a) (i) B; 1
C; 1
A; 1

(ii) cresolphthalein

OR

thymolphthalein; 1

(b) (i) $-\log[H^+]$; 1

(ii) $[H^+] = 1.259 \times 10^{-12}$ (or 1.26 or 1.3) *OR* pOH = 14 - pH; 1

$[OH^-] = \dfrac{10^{-14}}{1.258\times10^{-12}}$ *OR* = 2.10; 1

$= 7.9(4) \times 10^{-3}$; 1

(if $[H^+]$ is wrong allow 1 for $[OH^-] = K_w/[H^+]$ or as numbers)

(c) (i) $K_a = [H^+]^2/[CH_3CH_2COOH]$

OR

$[H^+]^2/[HA]$

OR

$[H^+] = [A^-]$ etc; 1

$[H^+] = \sqrt{1.35 \times 10^{-5}} \times 0.117$ or expression without numbers; 1

$= 1.257 \times 10^{-3}$

pH = 2.90; 1

(ii) $K_a = [H^+]$

OR

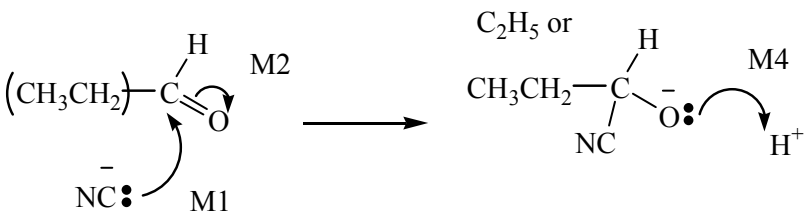
$pK_a = pH$; 1

pH = 4.87; 1
(penalise 1dp once)

Total 13

Question 3

(a) necleophilic addition; 1



M3 structure ; 4

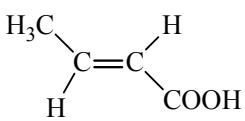
(be lenient on position of charge on CN^-)

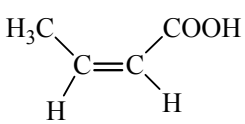
(M2 not allowed independent of M1, but allow M1 for correct attack on C+ if M2 show as independent first.)

(+on C of C=O loses M2 but ignore □+ if correct)

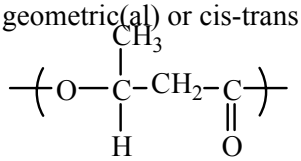
(M4 for arrow and lone pair (only allow for correct M3 or close))

(b) (i) 2-hydroxybutanoic acid 1

(ii)  1

 1

geometric(al) or cis-trans 1

(c) (i)  1

(*one unit only)*

(ignore brackets or n)

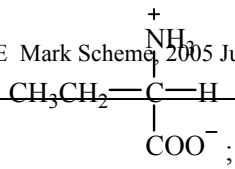
(trailing bonds are needed)

(ii) can be hydrolysed

OR

can be reacted with/attacked by acid/base/nucleophiles/H_2O/OH^-; 1

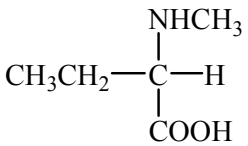
(d) (i)



; 1

(allow $-NH_3^+$)

(ii)



; 1

(or zwitterions product)

(iii) nucleophilic substitution; 1

Total 14

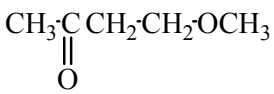
Question 4

(a) (i)  or $RCOCH_3$; 1

(or description in words)
(ignore trailing bonds)

(ii)  or $ROCH_3$; 1
(allow 1 if both (i) and (ii) give CH_3- or H_3C- only)

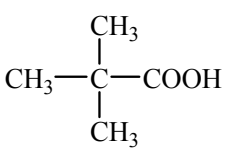
(iii) CH_2CH_2 or two adjacent methylene groups; 1

(iv) 

OR

$CH_3COCH_2CH_2OCH_3$; 1

(b) (i) OH in acids or (carboxylic) acid present 1

(ii)  ; 1

(c)

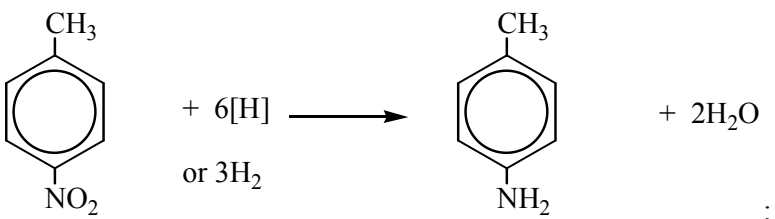
reagent	$K_2Cr_2O_7$ /H^+	$KMnO_4$ /H^+	1
Y	no reaction	no reaction	1
Z	orange to green or turns green	purple to colourless or turns colourless	1

Total 9

Question 5

(a) electrophilic substitution; 1
conc HNO_3; 1
conc H_2SO_4 either or both conc missing scores one for both acids; 1

(b) Sn or Fe/HCl (conc or dil or neither); 1
(ignore extra NaOH)
Sn or Fe/H_2SO_4 (dil or neither)
(not HNO_3 at all)
or H_2/Ni
(not $NaBH_4$/ $LiAlH_4$ or Na/C_2H_5OH)

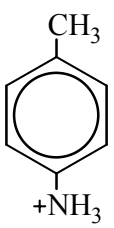


;

1

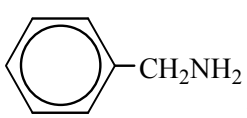
(c) 77 or 92; 1

(d)



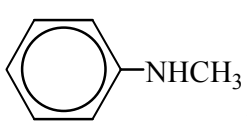
, 1
(allow $-NH_3^+$)

(e) **G**



; 1

H



; 1

Total 9

Question 6

(a) (*must state correct effect on yield or rate to score the reason mark)*

T	effect:	higher temp:	yield greater or shifts equm to right;	1
	effect:	higher temp:	rate increased;	1
	reason:	endothermic *OR* more particles have $E>E_a$ *OR* more successful/productive collisions;		1
P	effect:	higher pressure:	yield less or shifts equm to left;	1
	effect:	higher pressure:	rate increased;	1
	reason:	increase in gas moles L to R *OR* greater collision frequency;		1

(b)

M1 equilibrium moles of CO = 62.8 – 26.2 = 36.6 1

M2 equilibrium moles of H_2 = 146 – 2(26.2) = 93.6 1

M3 total no moles = 36.6 + 93.3 + 26.2 = 156.4 1

M4 partial pressure = mole fraction x total pressure 1

M5 $K_p = \dfrac{p_{CH_3OH}}{p_{CO} \times p^2_{H_2}}$ 1

M6 $= \dfrac{\left(\frac{26.2}{156.4} \times 9.50\right)}{\left(\frac{36.6}{156.4} \times 9.50\right) \times \left(\frac{93.6}{156.4} \times 9.50\right)^2}$

$\dfrac{(0.168 \times 9.50)}{(0.234 \times 9.50) \times (0.598 \times 9.50)^2}$

$= \dfrac{(1.59)}{(2.22) \times (5.69)^2}$ 1

M7 $0.022(1)$ $2.2(1) \times 10^{-8}$ $2.2(1) \times 10^{-14}$ 1

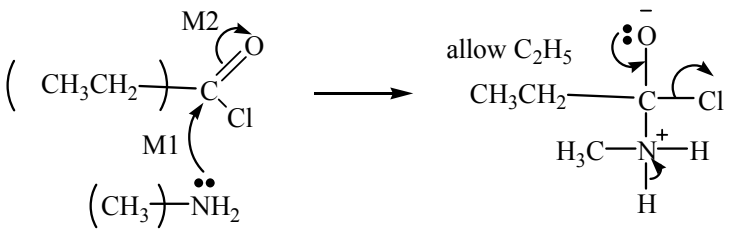
M8 MPa^{-2} kPa^{-2} Pa^{-2} 1

(If no subtraction lose M1, M2 and M3)
(If ×2 missed in M2, lose both M2 and M3)
(If M1 gained but moles of H_2 = 73.2 (i.e. double CO), M2 and M3 lost)
(If M1 gained but mol H_2 = 2(146 – 26.2), M2 and M3 lost)
(If M1 and M2 correct but M3 lost for CE, penalise M6 also)
(M4 can be gained from the numbers in the expression for M6 even if these numbers are wrong)
(If Kp contains [ ] lose M5 but then mark on)
(If chemically wrong expression for Kp, lose M5, M6 and M7 (allow M8 conseq on their K_p))
(If divided by 9.5, or not used 9.5 at all, lose M6 and M7 (and M4))
(If tried to convert to kPa and is factor(s) of 10 out, penalise in M6 and allow M8 for kPa^{-2})

Total 14

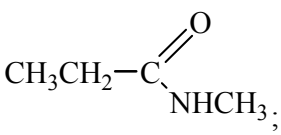
Question 7

(a) (nucleophilic) addition-elimination; 1



4

(M3 for structure)
(M4 for 3 arrows and lone pair)
(M2 not allowed independent of M1, but allow M1 for correct attack on C+ if M2 show as independent first.)
(+on C of C=O loses M2 but ignore □+ if correct)
(Cl⁻ removing H^+ loses M4)

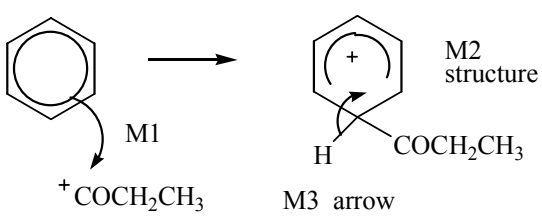


; 1

(If M3 lost above for wrong C chain, do not penalise same error again here)

(b) $CH_3CH_2COCl + AlCl_3 \rightarrow [CH_3CH_2CO]^+ + AlCl_4^-$; 1

(penalise wrong alkyl group once at first error)
(position of + on electrophile can be on O or C or outside [ ])
(penalise wrong curly arrow in the equation or lone pair on $AlCl_3$)



(horseshoe must not extend beyond C2 to C6 but can be smaller)

(+ not too close to C1)

(penalise M2 if CH_3 chain wrong again but allow M1 and M3)

(M3 arrow into hexagon unless Kekule)

(allow M3 arrow independent of M2 structure)

(M1 arrow from within hexagon to C or to + on C)

(don't penalise position of + on C of RCO+) ;
$AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$;
1

(or can be gained in mechanism)

3

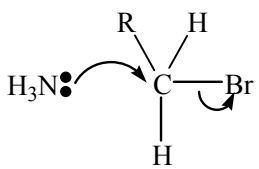
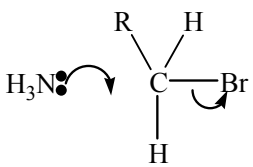
(c)	M1	$CH_3CH_2COCl + H_2O \rightarrow CH_3CH_2COOH + HCl$ *(penalise wrong alkyl group once at first error)*	1
	M2	M_r of $CH_3CH_2COCl = 92.5$ *(if M_r wrong, penalise M2 only)*	1
	M3	moles of $CH_3CH_2COCl = 1.48/92.5 = 0.016$	1
	M4	moles NaOH = $2 \times 0.016 = 0.032$ *(allow for × 2 conseq to wrong no of moles)*	1
	M5	volume of NaOH = $0.032/0.42 =$ $\underline{0.0762\ dm^3}$ or $\underline{76.2\ cm^3}$ *(with correct units)* *(if ×2 missed in M4 lose M5 also)*	1

Total 16

GENERAL ORGANIC POINTS FOR MARKING CHM4

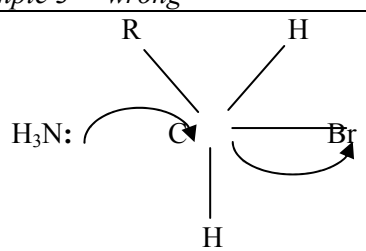
1 Curly arrows

These must show the movement of a pair of electrons,
i.e. from a bond or a lone pair
either to an atom (example 1)
or to the space between two atoms (example 2)

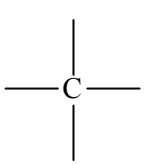
Example 1 - correct	**Example 2 - correct**
	

Curly arrows never start at an atom e.g. the right hand arrow in example 3 is wrong

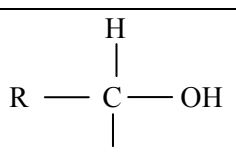
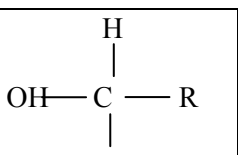
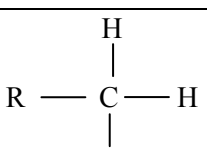
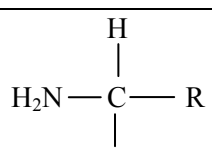
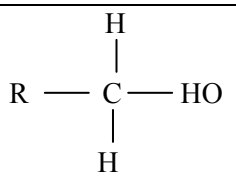
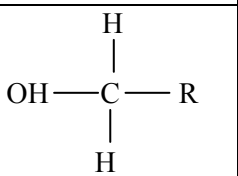
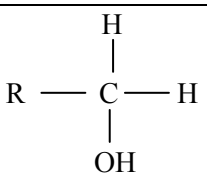
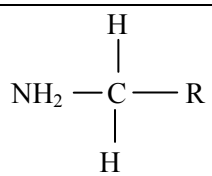
Example 3 wrong



2 Incorrect Structures which are generally penalised once per paper:

a) Sticks, i.e. bonds without (hydrogen) atoms on their ends, e.g. 

b) Incorrectly bonded functional groups e.g.

correct				
wrong				

Alkyl groups, however, can be written in several different ways.
The following alkyl group arrangements are allowed as correct:

CH_3 ——	H_3C ——	—— CH_3	CH_3 |	CH_3 |

c) cyclohexane for benzene **penalised once per paper**