AQA

ASSESSMENT and QUALIFICATIONS ALLIANCE

Mark scheme January 2003

GCE

Chemistry

Unit CHM4

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SECTION A

Answer **all** questions in the spaces provided.

1 (a) The initial rate of the reaction between substances **P** and **Q** was measured in a series of experiments and the following rate equation was deduced.

$$\text{rate} = k[\mathbf{P}]^2[\mathbf{Q}]$$

(i) Complete the table of data below for the reaction between **P** and **Q**.

Experiment	Initial [**P**] / mol dm^{-3}	Initial [**Q**] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.20	0.30	4.8×10^{-3}
2	0.10	0.10	$0.4(0) \times 10^{-3}$ (1)
3	0.40	0.15 (1)	9.6×10^{-3}
4	0.28 (1)	0.60	19.2×10^{-3}

(ii) Using the data from experiment 1, calculate a value for the rate constant, k, and deduce its units.

$k = \dfrac{4.8 \times 10^{-3}}{(0.20)^2 \times (0.30)} = 0.4(0)$ (1)

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

(1)

(6 marks)

(b) What change in the reaction conditions would cause the value of the rate constant to change?

(change in) temperature (1)

(1 mark)

7

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2 Nitrogen dioxide dissociates according to the following equation.

$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

When 21.3 g of nitrogen dioxide were heated to a constant temperature, T, in a flask of volume 11.5 dm^3, an equilibrium mixture was formed which contained 7.04 g of oxygen.

(a) (i) Calculate the number of moles of oxygen present in this equilibrium mixture and deduce the number of moles of nitrogen monoxide also present in this equilibrium mixture.

Number of moles of O_2 at equilibrium $\frac{7.04}{32} = 0.22$ (1)

Number of moles of NO at equilibrium 0.44 (1)
(or 2 x mol of oxygen)

(ii) Calculate the number of moles in the original 21.3 g of nitrogen dioxide and hence calculate the number of moles of nitrogen dioxide present in this equilibrium mixture.

Original number of moles of NO_2 $\frac{21.3}{46} = 0.46(3)$ (1)

Number of moles of NO_2 at equilibrium

$0.46(3) - 0.44 = 0.02(3)$ (1)

(or consequential on mol NO above)

(4 marks)

(b) Write an expression for the equilibrium constant, K_c, for this reaction. Calculate the value of this constant at temperature T and give its units.

Expression for K_c $K_c = \frac{[NO]^2[O_2]}{[NO_2]}$ (1)

Calculation $K_c = \frac{\left(\frac{0.44}{11.5}\right)^2 \times \left(\frac{0.22}{11.5}\right)}{\left(\frac{0.023}{11.5}\right)^2} = 7.0(0)\ mol\ dm^{-3}$

(1) (1) (1)

[if mol NO_2 = 0.02 ; K_c = 9.26 (9.3)]

or conseq on values from (a)

(4 marks)

If vol missed, score only K_c and units

If K_c wrong : max 2 for correct use of vol and conseq units.

If K_c wrong and no vol : max 1 for conseq units.

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(c) The total number of moles of gas in the flask is 0.683. Use the ideal gas equation to determine the temperature T at which the total pressure in the flask is 3.30×10^5 Pa. (The gas constant $R = 8.31\ J\ K^{-1}\ mol^{-1}$)

$pV = nRT$ (1)

$T = \frac{pV}{nR} = \frac{(3.30 \times 10^5) \times (11.5 \times 10^{-3})}{0.683 \times 8.31}$ (1)

$= 669\ K$ (1)

(3 marks)

(d) State the effect on the equilibrium yield of oxygen and on the value of K_c when the same mass of nitrogen dioxide is heated to the same temperature T, but in a different flask of greater volume.

Yield of oxygen increased (1)

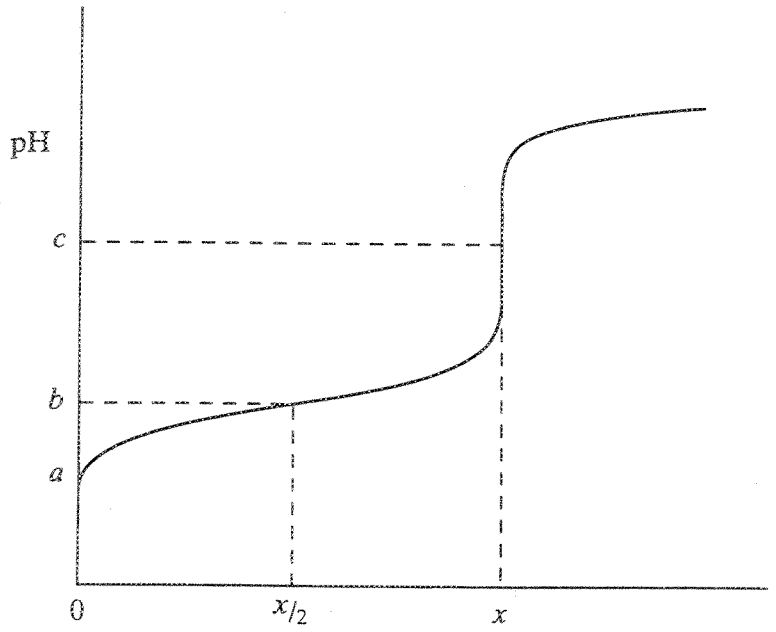
Value of K_c no effect (1)

(2 marks)

13

TURN OVER FOR THE NEXT QUESTION

3 The sketch below shows the change in pH when a 0.200 mol dm^{-3} solution of sodium hydroxide is added from a burette to 25.0 cm^3 of a 0.150 mol dm^{-3} solution of the weak acid HA at 25 °C.



(a) The volume of sodium hydroxide solution added at the equivalence point is x cm^3. Calculate the value of x.

moles HA = $\frac{25}{10^3} \times 0.150 = 3.75 \times 10^{-3}$ (1)

$\therefore$ vol. NaOH = $\frac{3.75 \times 10^{-3}}{0.20} = 1.875 \times 10^{-2}$ dm^3 (1)

or 18.75 cm^3

(2 marks)

(b) (i) Define the term pH.

$pH = -\log_{10}[H^+]$ (1)

(ii) The pH at the equivalence point is c. Suggest a value for c.

Value above 7 but below 11 (1)

(iii) Identify a suitable indicator for detecting the equivalence point of the titration.

phenol red / thymol blue / phenolphthalein / thymolphthalein / (1)

[i.e. indicator with $7 < pK_{in} < 11$]

(3 marks)

(c) The value of K_a for the weak acid HA at 25 °C is 2.75×10^{-5} mol dm^{-3}.

(i) Explain the term *weak* as applied to the acid HA.

only slightly dissociated/ionised (1) NOT not fully dissociated/ionised

(ii) Write an expression for K_a for the acid HA.

$K_a = \frac{[H^+][A^-]}{[HA]}$ (1) NOT $\frac{[H^+]^2}{[HA]}$

(iii) Calculate the pH of the 0.150 mol dm^{-3} solution of acid HA before any sodium hydroxide is added, i.e. the pH at point *a*.

For weak acid alone :

$K_a = \frac{[H^+]^2}{[HA]}$ (1) $\therefore [H^+] = \sqrt{(2.75 \times 10^{-5}) \times 0.15}$

$= 2.03 \times 10^{-3}$ (1)

$\therefore$ pH = 2.69 (1)

[pH should be given to 2 decimal places
penalize answer to 1 dp once in question]

(5 marks)

(d) Calculate the pH of the solution formed when $x/2$ cm^3 of the 0.200 mol dm^{-3} solution of sodium hydroxide are added to 25.0 cm^3 of the 0.150 mol dm^{-3} solution of HA, i.e. the pH at point *b*.

moles OH^- added $= 1.875 \times 10^{-3}$ = moles A^- = moles HA left } (1)

or $[A^-] = [HA]$

$\therefore K_a = [H^+]$ or pH = pKa (1)

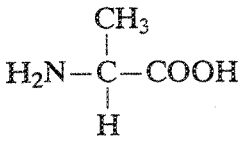
$\therefore$ pH = 4.56 (1)

(3 marks)

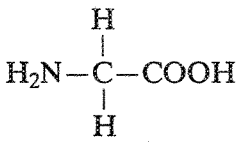
13

TURN OVER FOR THE NEXT QUESTION

4 The structures of the amino acids *alanine* and *glycine* are shown below.



alanine



glycine

(a) Give the systematic name for *alanine*.

2-aminopropanoic acid (1)

(1 mark)

(b) *Alanine* exists as a pair of stereoisomers.

(i) Explain the meaning of the term *stereoisomers*.

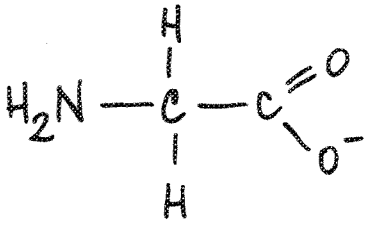
[molecules with same structure / structural formula (1)
but with bonds / atoms / groups arranged differently in space / 3D (1)

(ii) State how you could distinguish between the stereoisomers.

[(plane) polarised light (1)
rotated (equally) in opposite directions (1)

(4 marks)

(c) Give the structural formula of the species formed by *glycine* at pH 14.



(1)

[allow $H_2NCH_2COO^-$]

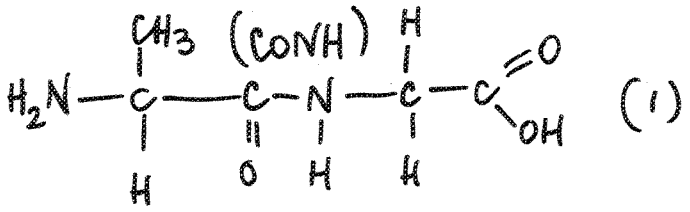
[penalize:
NH_2- } once per
$OH-$ } paper but CH_3- is allowed]

(1 mark)

(d) When two amino acids react together, a dipeptide is formed. Give the structural formulae of the **two** dipeptides which are formed when *alanine* and *glycine* react together.

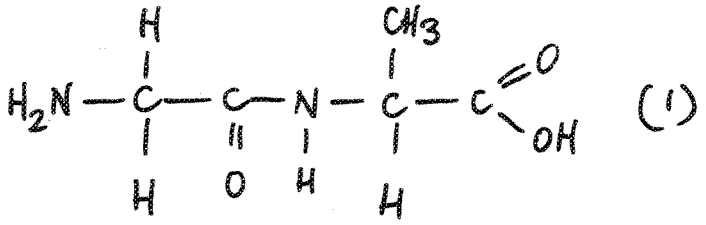
Not anhydrides ; not repeating units.

Dipeptide 1



(1)

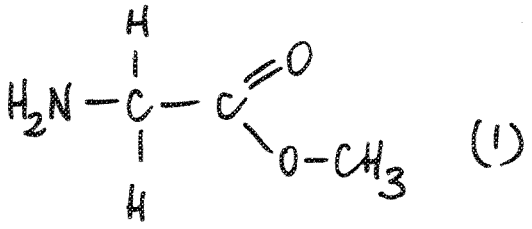
Dipeptide 2



(1)

(2 marks)

(e) Give the structural formula of the organic compound formed when *glycine* reacts with methanol in the presence of a small amount of concentrated sulphuric acid.



(1)

or $H_2NCH_2COOCH_3$

(1 mark)

9

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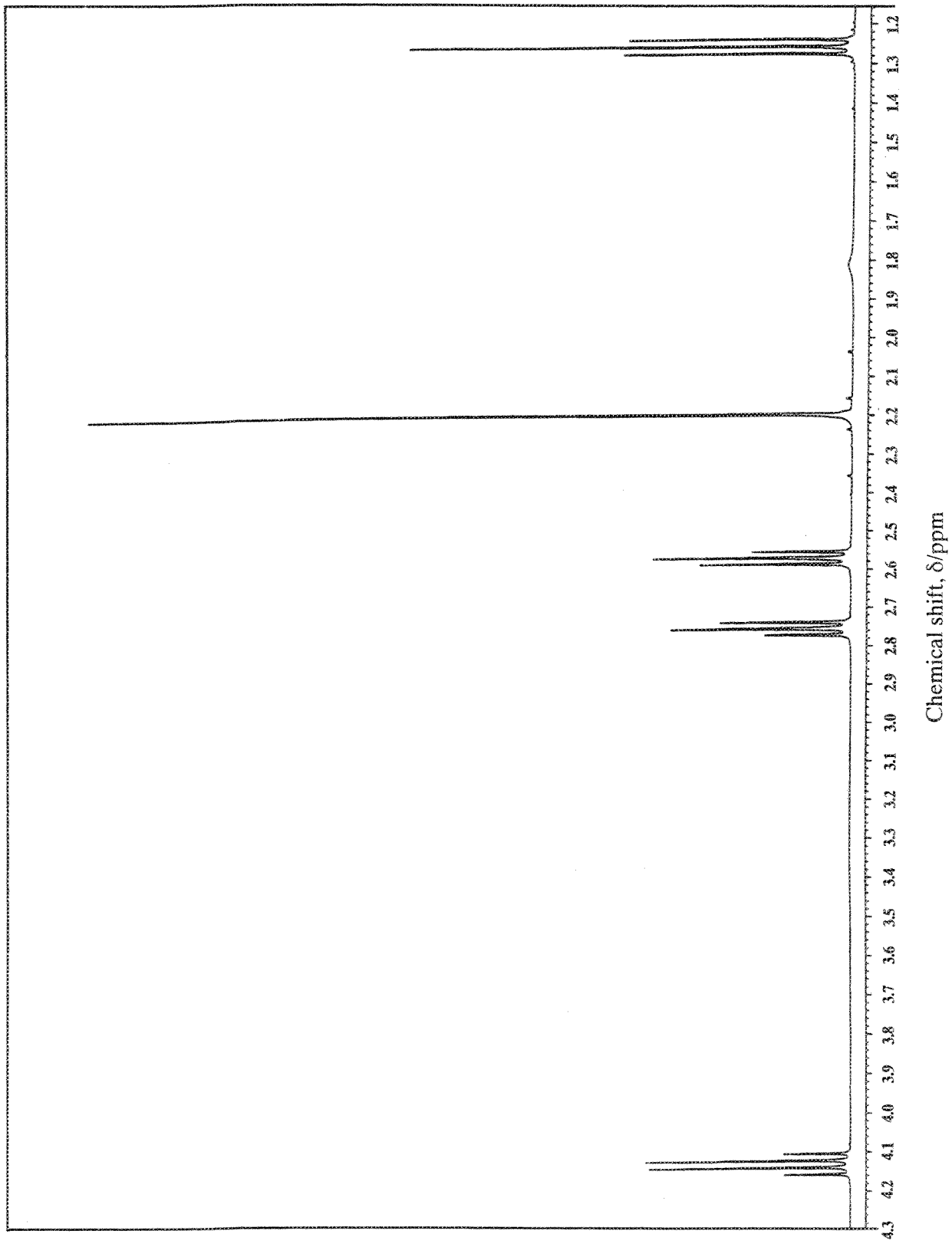
5 The proton n.m.r. spectrum of compound **X** is shown below.



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Compound **X**, $C_7H_{12}O_3$, contains both a ketone and an ester functional group. The measured integration trace for the peaks in the n.m.r. spectrum of **X** gives the ratio shown in the table below.

Chemical shift, δ/ppm	4.13	2.76	2.57	2.20	1.26
Integration ratio	0.8	0.8	0.8	1.2	1.2

Refer to the spectrum, the information given above and the data on the reverse of the Periodic Table provided to answer the following questions.

(a) How many different types of proton are present in compound **X**?

5 (1)

(1 mark)

(b) What is the whole-number ratio of each type of proton in compound **X**?

2 : 2 : 2 : 3 : 3 (1) any order but not multiples *(1 mark)*

(c) Draw the part of the structure of **X** which can be deduced from the presence of the peak at δ2.20.

$CH_3-\overset{\overset{O}{\|}}{C}-(R)$ (1)

(1 mark)

(d) The peaks at δ4.13 and δ1.26 arise from the presence of an alkyl group. Identify the group and explain the splitting pattern.

Alkyl group CH_3CH_2 or C_2H_5 or ethyl (1)

Explanation δ4·13 (quartet) : CH_2 peak split by CH_3 / next to CH_3 (1)

δ 1·26 (triplet) CH_3 peak split by CH_2 / next to CH_2 (1)

(3 marks)

(e) Draw the part of the structure of **X** which can be deduced from the splitting of the peaks at δ2.76 and δ2.57.

CH_2CH_2 (1)

(1 mark)

(f) Deduce the structure of compound **X**. (must be $C_7H_{12}O_3$)

$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_3$ (2)

allow (1) for

$CH_3COCH_2CH_2OCOCH_2CH_3$

or

$CH_3COOCH_2CH_2COCH_2CH_3$

(2 marks)

9

Turn over ▶

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6 (a) Methylamine is a weak Brønsted–Lowry base and can be used in aqueous solution with one other substance to prepare a basic buffer.

(i) Explain the term *Brønsted–Lowry base* and write an equation for the reaction of methylamine with water to produce an alkaline solution.

Brønsted–Lowry base H^+ or proton acceptor (1)

Equation $CH_3NH_2 + H_2O \rightleftharpoons CH_3\overset{+}{N}H_3 + OH^-$ (1)

(ii) Suggest a substance that could be added to aqueous methylamine to produce a basic buffer.

name or formula CH_3NH_3Cl or HCl (1)
or any ammonium compound or any strong acid

(iii) Explain how the buffer solution in part (a)(ii) is able to resist a change in pH when a small amount of sodium hydroxide is added.

(extra) OH^- reacts with $CH_3\overset{+}{N}H_3$
or reaction/equilibrium moves to left } any 2
or ratio $\frac{\text{salt}}{\text{base}}$ remains almost constant

(5 marks)

(b) Explain why methylamine is a stronger base than ammonia.

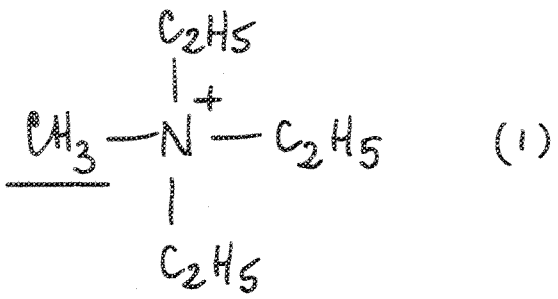
lone pair (on N accepts H^+) (1)
CH_3 { increases electron density (on N)
donates/pushes electrons (1)
has positive inductive effect

(2 marks)

(c) A cation is formed when methylamine reacts with a large excess of bromoethane. Name the mechanism involved in the reaction and draw the structure of the cation formed.

Name of mechanism nucleophilic substitution (1)

Structure



(1)

(2 marks)

9

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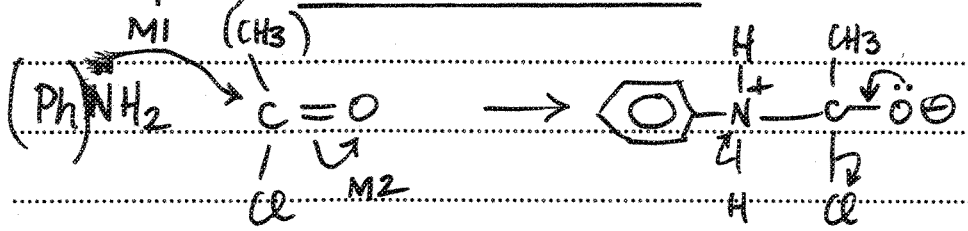
Question 7

(a) CH_3COCl or $(CH_3CO)_2O$ (1) [$AlCl_3$ or H_2O or cH_2SO_4 loses this mark]

[CH_3COOH loses reagent and M3, M4 = max 3]

(nucleophilic) addition–elimination (1)



M3 : structure

M4 : 3 correct arrows

(Allow M1 for attack on $CH_3-\overset{+}{C}=O$) (penalize e⁻ removing H^+) [6]

(b) conc HNO_3 (1) (HNO_3/H_2SO_4 scores 1)

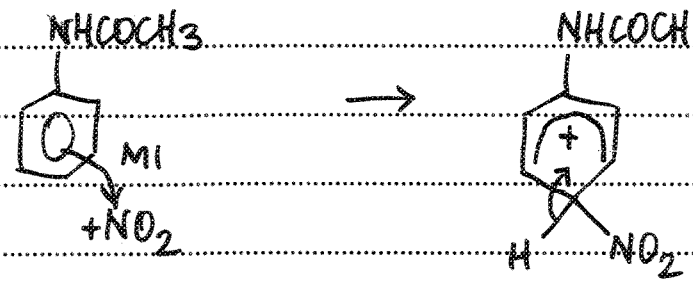
conc H_2SO_4 (1)

$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^-$ (2)

(or H_2SO_4) (or $H_2O + HSO_4^-$)

} any 2

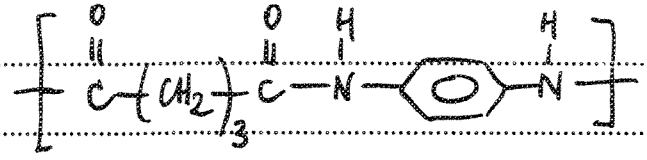
electrophilic substitution (1)



M2 : structure

M3 : arrow [6]

(c) Sn/HCl or Ni/H_2 (1) (NOT $LiAlH_4$ $NaBH_4$)



(1) (1) [3]

[TOTAL 15]

Question 8 part (a) for each section:

A totally wrong reagent scores zero
An incomplete reagent such as silver nitrate for Tollens, loses the reagent mark, but can get both observation marks.
A wrong reagent such as $[Ag(NH_3)_2]^{2+}$ or bromide water loses the reagent mark and the next mark "gained", i.e. can only score 1/3 if both observations correct.

If two tests given and results given correctly for both compounds in both tests then full marks
If one test on A and a different test on B with only these results given

- if both results correct then score 2/3
- if either result wrong then score 1/3
- if either test would not work as a distinction, then score 0/3

If the candidate says A = ketone (or C = benzene), lose this mark.

If the candidate omits the letters when referring to the pair of compounds,
e.g. says alkene decolourises/alkane no reaction penalise one mark only.

(a)(i) penalise observations which just say *colour change occurs* or only state starting colour

Tollens	[1]	Fehlings/Benedicts	[1]	Brady's or 2,4-dnph	[1]	sodium	[1]
No reaction A	[1]	no reaction A	[1]	no reaction A	[1]	bubbles or hydrogen A	[1]
silver or mirror or grey or ppt B	[1]	red or ppt B	[1]	(yellow/orange) xtals or ppt	[1]	no reaction B	[1]
(not silver solution)		not red solution		not yellow/orange solution			

Carboxylic acid/H_2SO_4	[1]	Schiff's	[1]	iodoform or I_2/NaOH	[1]	PCl_5	[1]
(sweet) smell A	[1]	no reaction A	[1]	yellow (ppt) A	[1]	(misty) fumes A	[1]
no reaction B	[1]	goes pink B	[1]	no reaction B	[1]	no reaction B	[1]

(a)(ii)

Bromine(water)	[1]	$KMnO_4$	[1]	$KMnO_4$/ H_2SO_4	[1]		[1]
no reaction C	[1]	no reaction C	[1]	no reaction C	[1]		[1]
decolourised D	[1]	goes brown D	[1]	goes colourless D	[1]		[1]
not clear not discolour(is)ed							

(a)(iii) not just smell for E

an identified (hydrogen)carbonate	[1]	correct metal	[1]	UI or stated indicator	[1]	PCl_5	[1]
no reaction E	[1]	no reaction E	[1]	no change E	[1]	(misty) fumes E	[1]
bubbles or CO_2 F	[1]	bubbles or H_2 F	[1]	red or correct colour F	[1]	no reaction F	[1]

note MAX 8

Question 8(b)

F has absorption at 2500 – 3000 cm^{-1} (due to COOH) [1]

NB Qu asks "How fingerprinting is used" i.e. no marks for simply stating that the fingerprint region is unique.
compare with (spectrum of) known compound or database [1]
(exact) match [1]

[3 marks]

Question 8(c)

major peak $[CH_3CO]^+$ [1]
m/z 43 [1]

$CH_3COOCH_3^{+\cdot} \longrightarrow CH_3CO^+ + OCH_3^{\cdot}$
[1 for molecular ion] [1 for correct other fragment]

Alternative
major peak $[CH_3]^+$ [1]
m/z 15 [1]

$CH_3COOCH_3^{+\cdot} \longrightarrow CH_3^+ + CH_3COO^{\cdot}$ or $COOCH_3^{\cdot}$ or $C_2H_3O_2^{\cdot}$
or $C_3H_6O_2^{+\cdot}$ [1] [1 for radical]

If major peak wrong but possible e.g. CH_3COO^+ m/z = 59
no marks so far, but can score up to 2 for

$CH_3COOCH_3^{+\cdot} \longrightarrow CH_3COO^+$ or $^+COOCH_3 + CH_3^{\cdot}$
[1] [1 for correct other fragment]

[4 marks]

[TOTAL 15 marks]