



General Certificate of Education

Chemistry 6421

**CHM4 Further Physical and Organic
Chemistry**

Mark Scheme

2010 examination - January 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.

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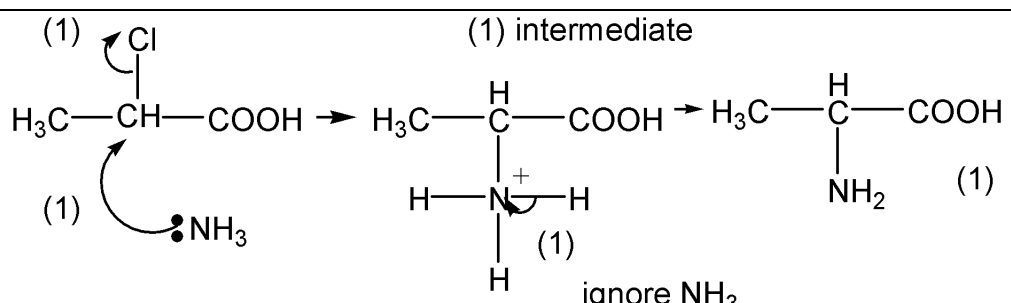
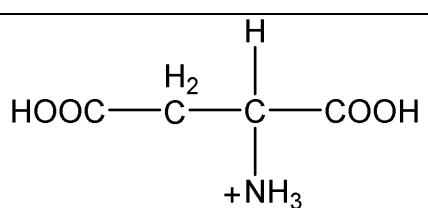
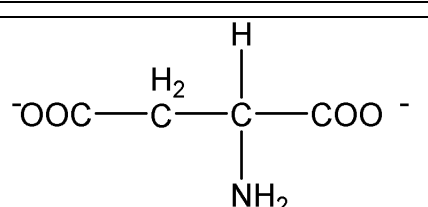
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Question	Part	Sub Part	Marking Guidance	Mark	Comments
1	(a)	(i)	In experiments 1 and 2, when [W] doubled rate doubles	1	Stated or shown numerically
1	(a)	(ii)	2	1	Or shown as $[x]^2$
1	(b)	(i)	$K = \frac{6.20 \times 10^{-5}}{(0.25)^2 \times 0.50}$ $= 1.98 \times 10^{-3}$ $\text{Mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$	1 1 1	Allow 1.9 – 2.0 x 10 ⁻³
1	(b)	(ii)	$\text{Rate} = 1.98 \times 10^{-3} \times 0.35^2 \times 0.10$ $= 2.4(3) \times 10^{-5}$	1	Allow conseq Ignore units

Question	Part	Sub Part	Marking Guidance	Mark	Comments
2	(a)	(i)	$\frac{1.60}{32} = 0.05;$	1	Allow 2*their mol O ₂
			0.10	1	
2	(a)	(ii)	0.125	1	Allow conseq
			$0.125 - 0.10 = 0.025$	1	
2	(b)		$\frac{[\text{NO}]^2 [\text{O}_2]}{[\text{NO}_2]^2};$	1	Penalise $[\text{NO}_2/v]^2$ etc If no use of volume CE lose both marks If eg forget square one o the terms when substituting AE lose 1 but mark conseq Kc correct
			$K_c = \frac{\left[\frac{0.10}{5.0}\right]^2 \times \left[\frac{0.05}{5.0}\right]}{\left[\frac{0.025}{5.0}\right]^2}$	1	
			= 0.16	1	
			Mol dm ⁻³	1	
2	(c)		Increased	1	
			No effect	1	

Question	Part	Sub Part	Marking Guidance	Mark	Comments
3	(a)		Decrease	1	CE if wrong
			Higher pressure gives higher yield / moves to right	1	
			Equilibrium moves to reduce pressure / favours side with fewer moles	1	
3	(b)		Exothermic	1	CE if wrong
			Increase in temperature decreases yield / moves to left	1	
			Equilibrium moves to lower temperature / favours endothermic direction	1	

Question	Part	Sub Part	Marking Guidance	Mark	Comments
4	(a)		$K_a = \frac{[H^+][A^-]}{[HA]}$	1	Allow [HX] or similar
4	(b)		$K_a = \frac{[H^+]^2}{[HA]}$ OR $[H^+] = [A^-]$ $[H^+] = \sqrt{(2.54 \times 10^{-5} \times 0.300)}$ $= 2.76 \times 10^{-3}$ pH = 2.56	1 1 1	Penalise other than 2dp Note 5.12 gets three ticks since only AE is to forget to take the square root
4	(c)	(i)	pH almost unchanged/ (very) small increase/ stays the same OWTTE	1	Must be correct to score rest.
			NaOH reacts with H^+ , then H^+ replaced by more dissociation of HA	1	Must make both points

Question	Part	Sub Part	Marking Guidance	Mark	Comments
5	(a)		2 – chloropropanoic acid	1	
5	(b)		Peak at δ 1.72 doublet CH_3 next to CH (one proton) Peak at δ 4.44 Quartet CH next to CH_3 (three protons)	1 1	
5	(c)		Two triplets;	1	Ignore reference to the COOH proton unless wrong
5	(d)		<p>(1) </p> <p>(1) intermediate</p> <p>(1) ignore NH_3</p>	5	Allow $\text{S}_{\text{N}}1$ alternative mechanism Penalise Cl^- removal of H in final mark
5	(e)	(i)		1	Allow + anywhere on $-\text{NH}_3$
5	(e)	(ii)		1	Allow – anywhere on $-\text{COO}^-$ Penalise covalent O-Na

5	(e)	(iii)	$\begin{array}{ccccccc} & & \text{H} & \text{O} & & \text{H} & \\ & & & & & & \\ \text{HOOC} & - & \text{C} & - & \text{C} & - & \text{N} & - & \text{C} & - & \text{COOH} \\ & & & & & & & & & & \\ & & \text{NH}_2 & & & & \text{CH}_2 & & & & \\ & & & & & & & & & & \\ & & & & & & \text{COOH} & & & & \end{array}$	1	Allow anhydride
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Question	Part	Sub Part	Marking Guidance	Mark	Comments
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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 $[\text{Ag}(\text{NH}_3)_2]^{2+}$ or bromide water loses the reagent mark and the next mark “gained”, i.e. can only score 1/3 if both observations correct.

6	(a)	(i)	Tollens	[1]	Fehlings/ Benedict s	[1]	Brady's of 2,4- dnph	[1]	sodium	[1]	Penalise “Nothing” as an observation once in this question
			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 <u>ppt</u>	[1]	(yellow/orange) <u>xtals or ppt</u>	[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]	

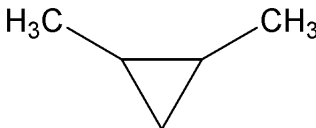
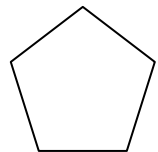
If two tests given and results given correctly for both compounds in both tests then full marks should be awarded.

If one test on A and a different test on B with only these results given

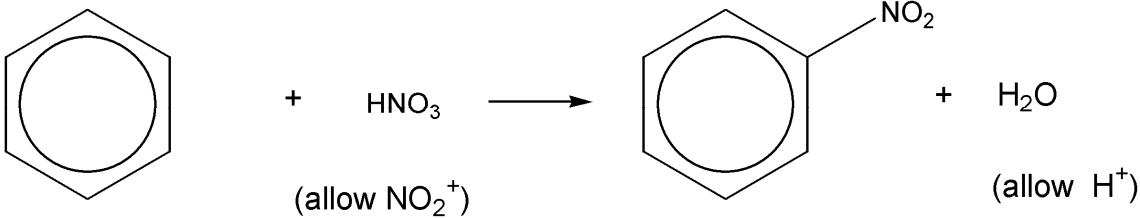
- If both results correct then score 2 marks.
- If either result wrong then score 1 mark.
- If either test would not work as a distinction, then score 0.

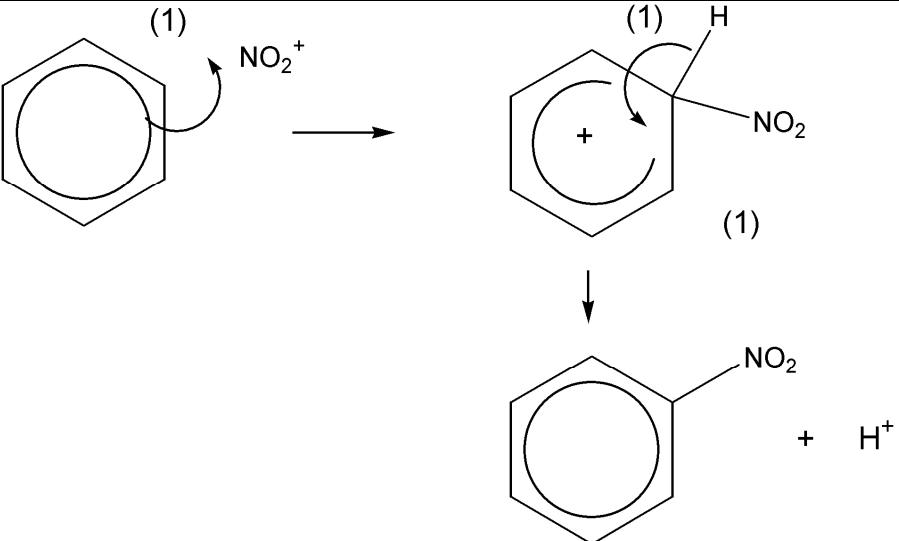
If the candidate omits the letters when referring to the pair of compounds.

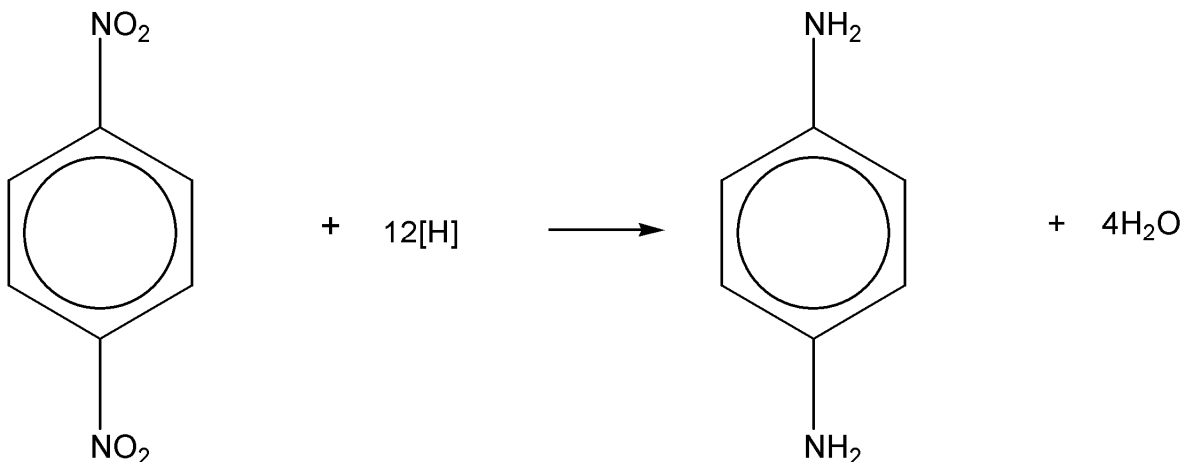
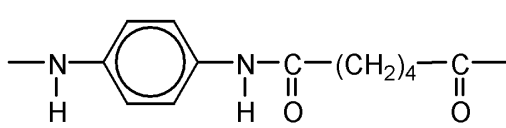
6	(a)	(ii)	An identified (hydrogen) carbonate	[1]	Correct metal	[1]	UI or stated indicator	[1]	PCl ₅	[1]	6 max
			No reaction C	[1]	No reaction C	[1]	No change C	[1]	No reaction C	[1]	
			Bubbles or CO ₂ D	[1]	Bubbles or H ₂ D	[1]	Red or correct colour D	[1]	Misty fumes D	[1]	
6	(b)		Compare with <u>IR spectrum</u> of known compound;							1	
			(Exact) match (dependent on the first mark)							1	

Question	Part	Sub Part	Marking Guidance	Mark	Comments
7	(a)	(i)	2-methylbutan-1-ol	1	
		(ii)	Optical	1	
7	(b)	(i)	Elimination	1	Not nucleophilic nor any other qualification. Not just dehydration.
7	(b)	(ii)	$ \begin{array}{c} \text{CH}_3\text{CH}_2 \\ \\ \text{---C---C---} \\ \quad \quad \\ \text{CH}_3 \quad \quad \text{H}_2 \end{array} $	1	Penalise $-\text{CH}_3\text{CH}_2$ each time
			Addition or radical; i.e. not additional	1	QoL
7	(b)	(iii)	$ \begin{array}{c} \text{CH}_3\text{CH}_2 \quad \quad \text{H} \\ \diagdown \quad \quad / \\ \text{C} = \text{C} \\ / \quad \quad \diagdown \\ \text{H} \quad \quad \quad \text{CH}_3 \end{array} $ or 	1	Allow $\text{C}_2\text{H}_5\text{CH} = \text{CHCH}_3$.
7	(b)	(iv)		1	Not $-\text{H}_2$

8			EXTRA If $\text{CH}_3\text{CH}_2\text{Cl}$ given for ethanoyl chloride		Mark correct mechanisms and names similar to above BUT Max 12 marks
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Question	Part	Sub Part	Marking Guidance	Mark	Comments
9	(a)		<p>Conc HNO₃</p> <p>Conc H₂SO₄</p> <p>$\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$</p> <p><i>(or</i> $\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + \text{H}_2\text{O} + \text{HSO}_4^-$ <i>or</i> $\text{HNO}_3 + \text{H}^+ \rightarrow \text{NO}_2^+ + \text{H}_2\text{O})$</p> <p>  </p> <p>Electrophilic substitution</p>	<p>1</p> <p>1</p> <p>1</p> <p>1</p> <p>1</p>	<p>If both conc missing can score one for both acids. If omitted can score one for reagents in the equation. Ignore temp/reflux etc. Or in two equations.</p>

			3	<p>M1 arrow from within hexagon to N or to + on N. Don't penalise position of + on N or NO₂. Horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1. M3 arrow into hexagon unless Kekule.</p>
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9	(b)	<p>1,4-dinitrobenzene</p> <p>Sn/Fe and HCl (conc or dil or neither)</p> <p>(or Sn/Fe and H₂SO₄ (dil or neither) or H₂/Ni)</p> <div style="text-align: center;">  </div> <p>Lone pair or electron pair on N in S Delocalised into ring Less available(for protonation) than lp in T(dependent on first point)</p>	<p>1</p> <p>1</p> <p>1</p> <p>1</p> <p>1</p> <p>1</p> <p>1</p>	<p>Ignore extra NaH NOT HNO₃ at all NOT NaBH₄/ LiAlH₄ or Na/C₂H₅OH</p> <p>Allow C₆H₄(NO₂)₂ and C₆H₄(NH₂)₂</p> <p>Allow 6H₂ if Ni/H₂ stated as reagents</p> <p>QoL</p>
9	(c)	<div style="text-align: center;">  </div>	1	<p>Allow -NHCO-</p> <p>Do not allow C₄H₈. Ignore [] or n. But must have trailing bonds.</p>