EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2020
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	1	9	–			INDEX NUMBER		

CHEMISTRY

9729/02

Paper 2 Structured Questions

02 September 2020
2 hours

Candidates answer on the Question Paper

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group, index number on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
Paper 2	
1	/ 12
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5	/ 17
Total	/ 75

This document consists of **21** printed pages and **1** blank page.

For Examiner's Use

1 (a) Nitrogen can form a few hydrides such as NH_3 and N_2H_4.

The boiling points of these two hydrides are given in Table 1.1.

Table 1.1

compound	boiling point / ºC
NH_3	−33
N_2H_4	114

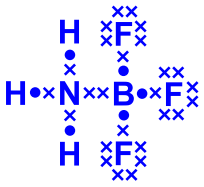
Provide **two** explanations for why N_2H_4 has a higher boiling point than NH_3.

N_2H_4 can form an **average of two hydrogen bonds per molecule** while NH_3 can only form **one**. More energy is required to break the **more extensive hydrogen bonds between N_2H_4**, hence it has a higher boiling point. N_2H_4 also has **more electrons**, which gives rise to a **larger and more polarisable electron cloud**, and hence **stronger intermolecular instantaneous dipole-induced dipole interactions** than in NH_3. Hence, more energy is required to overcome the intermolecular forces of attraction between N_2H_4 than C_2H_4

..... [2]

(b) When NH_3 is reacted with BF_3 in the gaseous phase, a white solid of NH_3BF_3 is formed.

(i) Draw a dot-and-cross diagram to show the bonding within NH_3BF_3 and state the shape about the nitrogen atom.



shape ..... **tetrahedral** .....

[2]

(ii) State the type of reaction that NH_3 has undergone with BF_3, and explain why it is possible.

Lewis acid-base reaction. **N atom** on NH_3 has a **lone pair** which can be **donated** to the **electron-deficient B atom** on BF_3 which has an **empty 2p orbital to achieve a stable noble gas configuration**. [2]

(c) Both NH_3 and PH_3 have trigonal pyramidal shape, but the bond angles in NH_3 are 107º while those in PH_3 are 94º. By considering the electronegativities of the central atoms, suggest why this is so.

Nitrogen is more electronegative than phosphorus, and **draws the electron density of its bond pairs closer to itself** than phosphorus does. The **bond pairs in NH_3 are closer to the central atom**, leading to **greater bond pair-bond pair repulsion**.

Hence, NH_3 has a larger bond angle than PH_3.

..... [2]

For Examiner's Use

(d) Table 1.2 shows the successive ionisation energies of an element **A**.

Table 1.2

ionisation energies / kJ mol^{-1}	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
element **A**	945	1794	2735	4839	6056	11690	14180	17370	20550	23830

(i) Explain why the successive ionisation energies of an element always increase.

As electrons are removed, **number of electrons decrease** while **nuclear charge remains the same**. Hence, there are **stronger electrostatic forces of attraction between the nucleus and the remaining electrons** and more energy is required for subsequent removal of electrons. [1]

(ii) Is element **A** likely to be from the same group as nitrogen? Explain your answer clearly.

There is a **significant increase** in the values of the **5th and 6th ionisation energies**. This means that the **6th electron is removed** from an **inner principal quantum shell** which is **closer to the nucleus**, and hence experiences stronger electrostatic forces of attraction. This means that there are **5 valence electrons** in element **A**, which puts it in **Group 15**, the same group as nitrogen. [2]

(iii) State and explain how the first ionisation energy of element **A** will compare to that of the element to its right in the periodic table.

Element **A** will have a **higher** first ionisation energy as the electron to be removed from element **A** is **unpaired** while that removed from the element to its right in the periodic table is **paired**. Less energy is required to remove the electron from the latter due to **inter-electron repulsion between the paired electrons in the same orbital**. [1]

[Total: 12]

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2 One widely recognised free radical in the atmosphere that drives ozone depletion is the hydroxyl radical, HO•. The hydroxyl radicals can react with HC*l* molecules existing in the atmosphere to produce chlorine atoms, which may then play a role in catalysing ozone decomposition.

$$[HO\bullet] + HCl \longrightarrow \text{water} + Cl \text{ atom}$$

To study the kinetics of the rate of reaction of hydroxyl radicals with a large excess of HC*l*, [HO•] was measured at regular time intervals at 300 K. The results are shown in Table 2.1.

Table 2.1

time / ms	0.0	1.0	2.0	3.0	4.0	5.0	6.0
[HO•(g)] / × 10^{-9} mol dm^{-3}	10.0	6.8	4.5	3.0	2.1	1.4	0.9

(a) Plot the graph of [HO•] against time on the grid in Fig. 2.1, and use the graph to show that the reaction is first order with respect to hydroxyl radicals.

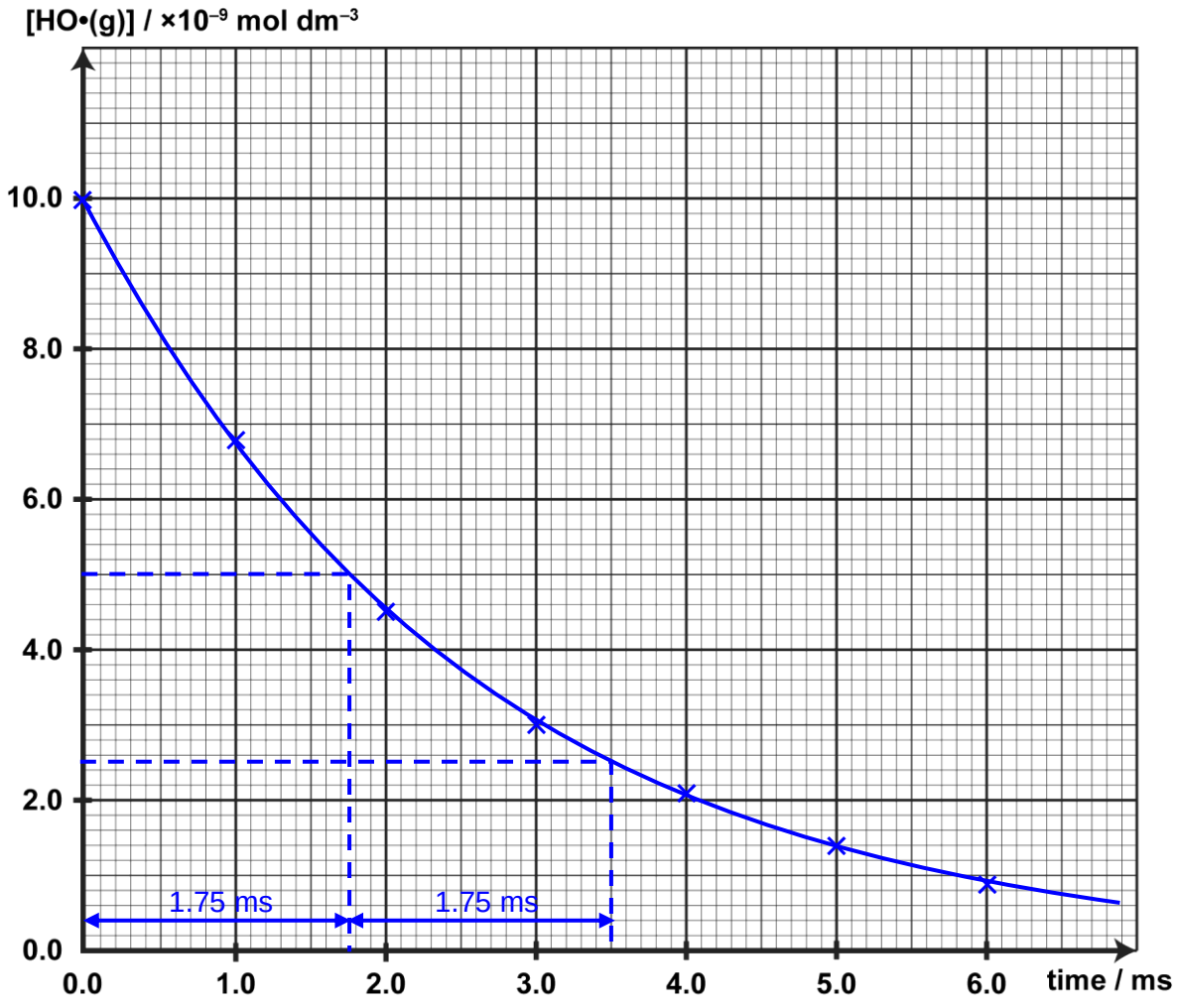

Fig. 2.1

explanation: Since the **half-life of the reaction** between hydroxyl radicals with hydrogen chloride is **relatively constant** at **1.75 ms**, the order of the reaction is first order with respect to hydroxyl radicals. [4]

(b) Table 2.2 shows how the half-life changes when the reaction was conducted at 300 K using different concentrations of HC*l*.

Table 2.2

[HC*l* (g)] / mol dm^{-3}	1.6×10^{-6}	2.8×10^{-6}
half-life / ms	2.2	1.3

(i) Explain why a large excess HC*l* was used in the reaction.

The concentration of HC*l* was used in large excess so that the concentration of hydrogen chloride **does not change significantly** throughout the reaction. In turn, this allows for the study of the order of reaction with respect to the concentration of the hydroxyl radicals. [1]

(ii) State what is meant by the term *half-life*.

The half-life of a reaction is the **time taken for the concentration of the reactant to reach half its initial concentration.**

[1]

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(iii) Using the data in Table 2.2, determine the order of the reaction with respect to HC*l*.

Since the reaction is 1st order w.r.t to HO•, thus $t_{\frac{1}{2}} = \frac{\ln 2}{k[HCl(g)]^m}$ where m is the order of reaction with respect to HC*l*(g).

Therefore,

$$(t_{\frac{1}{2}})_1 \times [HCl(g)]_1^m = (t_{\frac{1}{2}})_2 \times [HCl(g)]_2^m$$

$$2.2 \times (1.6 \times 10^{-6})^m = 1.3 \times (2.8 \times 10^{-6})^m$$

$$\frac{2.2}{1.3} = \frac{(2.8 \times 10^{-6})^m}{(1.6 \times 10^{-6})^m}$$

$$\lg \frac{2.2}{1.3} = m \lg \frac{(2.8 \times 10^{-6})}{(1.6 \times 10^{-6})}$$

$$m = 1$$

[3]

(iv) Hence, construct a rate equation for the reaction between the hydroxyl radicals and HC*l*.

rate = *k*[HO•][HC*l*] ..... [1]

(c) Suggest how the value of the rate constant would change when the reaction is carried out at a higher temperature of 350 K.

According to the Arrhenius equation where $k = Ae^{-\frac{E_a}{RT}}$, ($e^{-\frac{E_a}{RT}}$ describes the probability of successful collisions), the **rate constant would increase at a higher temperature OR** Since there would be **a greater number of reactants particles with energy greater than or equal to E_a at higher temperatures**, the rate constant **increases**. ..... [1]

(d) The reaction between hydroxyl radicals and HF is slower than that with HC*l* of the same concentration. Explain why this is the case.

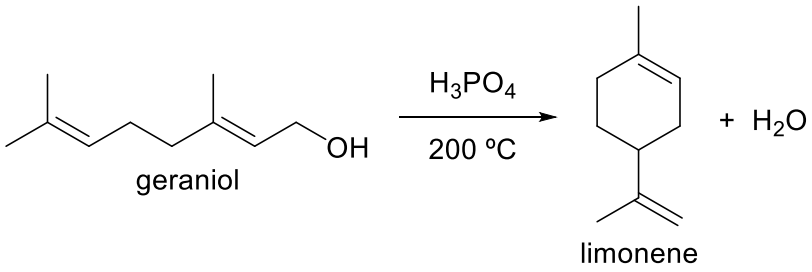
The **bond dissociation energy of HF is higher than of HC*l***, hence the rate constant for the reaction is smaller in magnitude (due to the increase in activation energy and the overall rate of reaction decreases. ..... [1]

[Total: 12]

For Examiner's Use

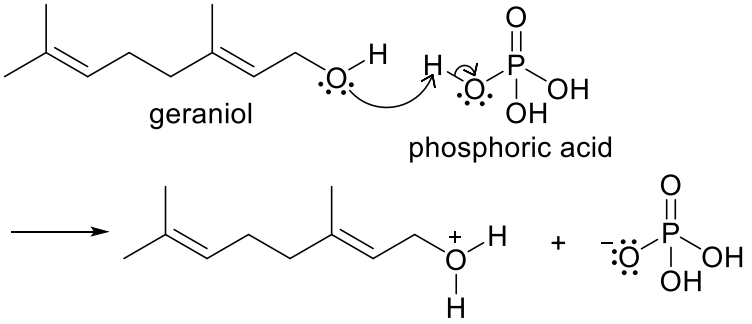
3 Geraniol ($C_{10}H_{18}O$) appears as a clear to pale-yellow oil that has a rose-like scent and is commonly used in perfumes.

On treatment with phosphoric acid, H_3PO_4 at 200 ºC, geraniol dehydrates to give limonene, $C_{10}H_{16}$.



(a) The dehydration reaction can be broken into the following steps:

Step 1: Geraniol, a primary alcohol, is protonated by phosphoric acid.



Step 2: The C–O bond breaks to form a water molecule. At the same time, the carbon atom is attacked by an electron-rich double bond leading to the formation of a carbocation with a six-membered ring.

Step 3: The positively charged carbon in the carbocation accepts a transfer of electrons from a C–H bond. This step also involves $H_2PO_4^-$ acting as a Brønsted base.

(i) Complete Fig. 3.1 to show the mechanism for the conversion of protonated geraniol to limonene.
In your answer show any relevant charges, dipoles or lone pairs of electrons you consider to be important in this mechanism.

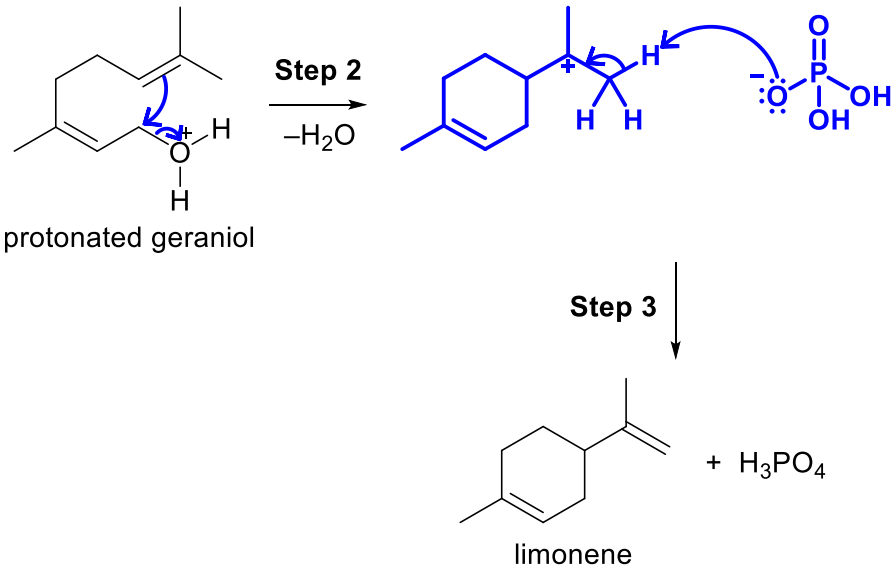


Fig. 3.1

[3]

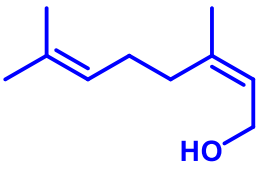
(b) Nerol is a stereoisomer of geraniol.

(i) Explain what is meant by the term *stereoisomers*.

Stereoisomers are compounds with the **same molecular and structural formula**, but differ from one another in the **spatial arrangement of the atoms**.

..... [1]

(ii) Suggest a structure for nerol and state the type of steroisomerism displayed.



type of stereoisomerism: .....***cis-trans* isomerism**.....

[2]

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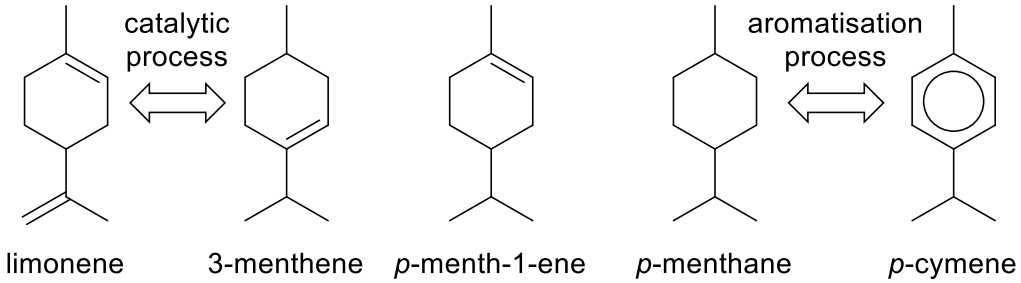
(c) Limonene is also found in the oil of citrus fruit peel and is used as a food flavouring in food manufacturing. It can undergo a network of catalytic transformation and final aromatisation step to form *p*-cymene which is also widely used as an intermediate in the synthesis of fine chemicals for flavourings, fragrances, perfumes.



(i) Describe one simple chemical test you could carry out to distinguish limonene from *p*-menth-1-ene.

test: **Add acidified $KMnO_4$ and heat**

observation: Limonene **will decolourise $KMnO_4$ and evolve CO_2(g) which gives a white ppt with $Ca(OH)_2$,** while *p*-menth-1-ene **only decolourises $KMnO_4$** without any effervescence.

[2]

(ii) Explain why *p*-menthane is generally unreactive towards reagents such as dry hydrogen chloride whereas *p*-menth-1-ene reacts readily with dry hydrogen chloride.

Absence of **electron-rich** or **poor regions** in *p*-menthane. Hence *p*-menthane does not react with both nucleophiles and electrophiles. *p*-Menth-1-ene possesses an **electron-rich** double bond and hence readily react with electrophiles such as hydrogen chloride. [1]

(iii) When *p*-menth-1-ene is added to BrC*l* in an inert solvent at room temperature in the dark, there is a reaction that decolourises the golden-brown BrC*l*. Describe the mechanism of this reaction, showing curly arrows, charges, dipoles and any relevant lone pairs.

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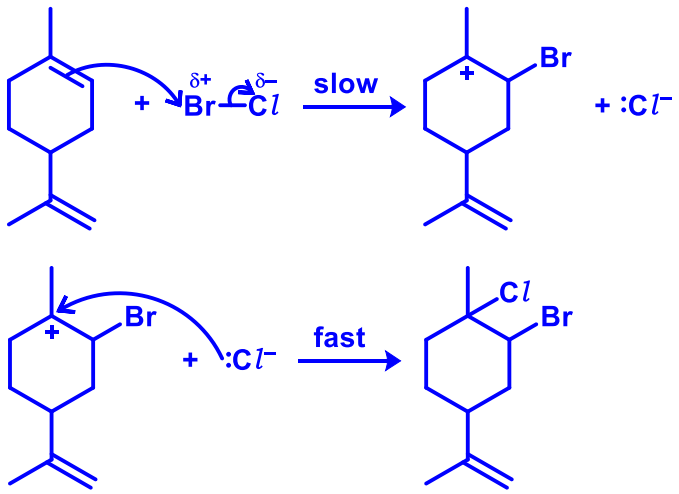
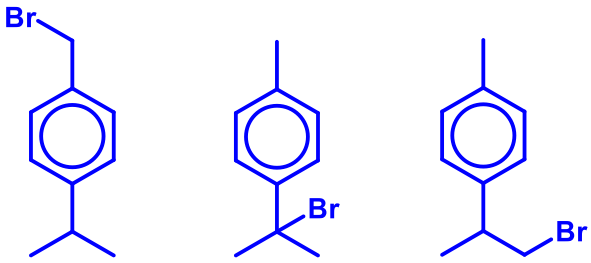
Electrophilic addition



[3]

(iv) When *p*-cymene is treated with a small quantity of bromine in the presence of ultraviolet light, a mixture of monobrominated products are formed.

Draw the possible monobrominated products from the reaction and state the approximate ratio in which they are formed.



3 : 1 : 6

[3]

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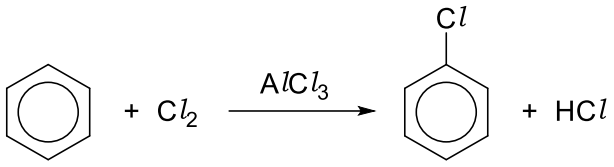
(d) Aluminium chloride is used as a catalyst in electrophilic substitution reactions.



Aluminium chloride reacts in a similar way with an acyl chloride, producing a carbocation that can then attack a benzene ring.

Compound **C**, $C_{14}H_{10}O$, can be produced via the synthesis route shown in Fig. 3.2. Methylbenzene is reacted to form benzyl chloride and benzoyl chloride, which are then reacted together in the presence of aluminium chloride to form compound **C**.

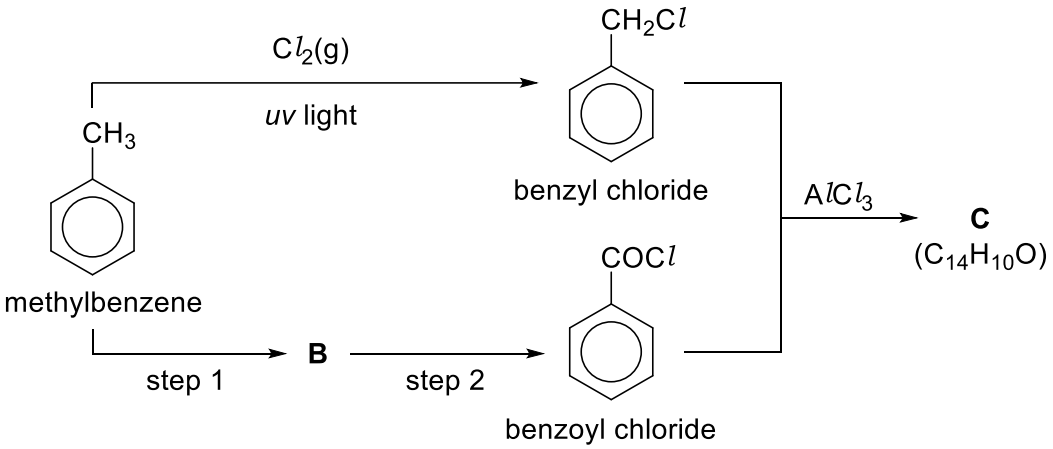
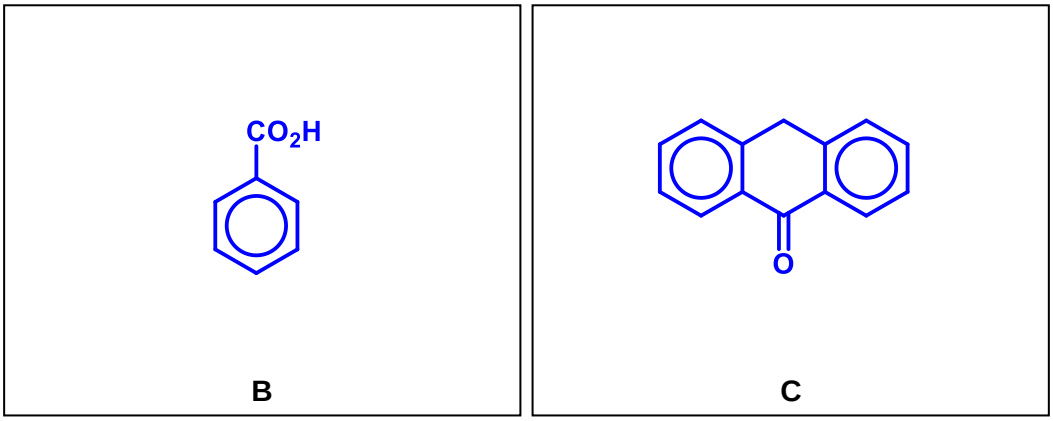


Fig. 3.2

Suggest reagents and conditions for steps 1 and 2, and the structures of compounds **B** and **C**.

step 1: $KMnO_4$, dilute H_2SO_4, heat

step 2: PCl_5, r.t.



[3]

[Total: 18]

4 (a) Nitrogen is an important element found in natural and synthetic organic compounds.

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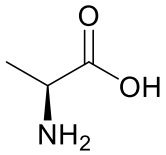
Alanine is a natural-occurring α-amino acid that is used in the biosynthesis of proteins. Its structure is as follows.



alanine

Amino acids can exist as zwitterions. In the synthesis of alanine in the laboratory, the resulting zwitterion of alanine can be obtained from 2-hydroxypropanoic acid.

Complete the synthesis route in Fig. 4.1. by drawing the structures of the intermediates and stating the reagents and conditions for steps **I**, **II** and **III**.

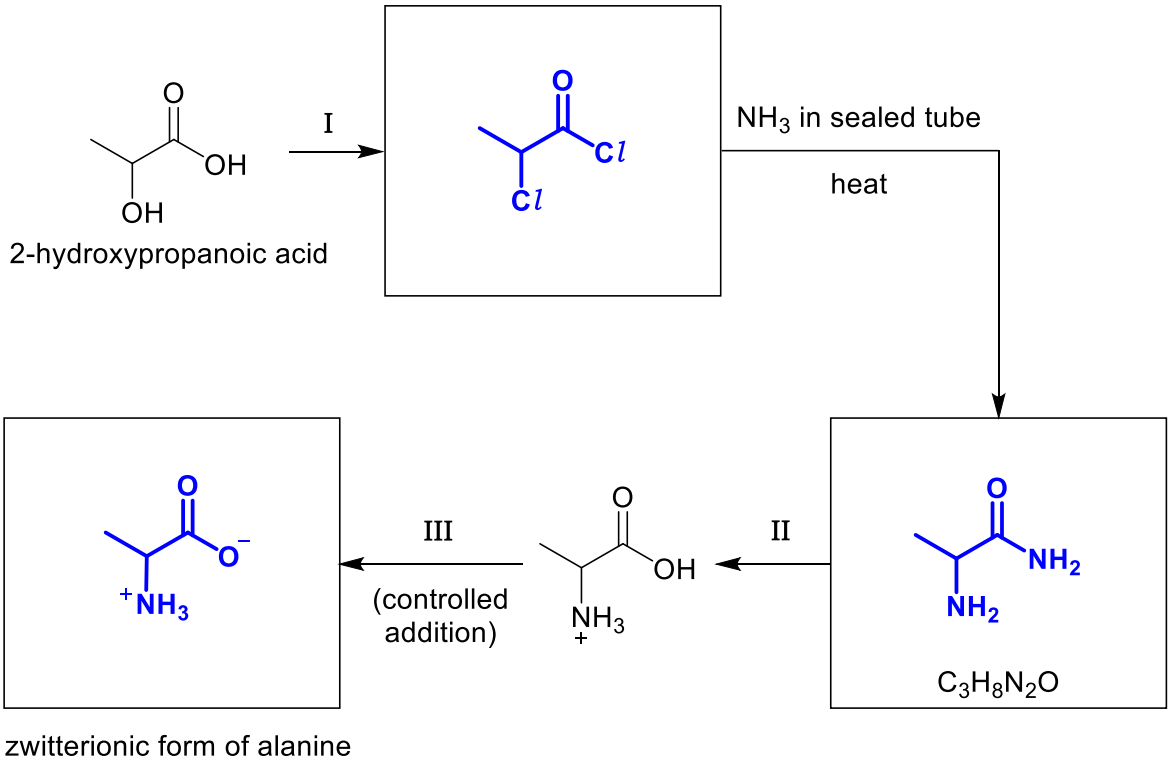


Fig. 4.1

I: PCl_5 r.t. or PCl_3 / $SOCl_2$, heat

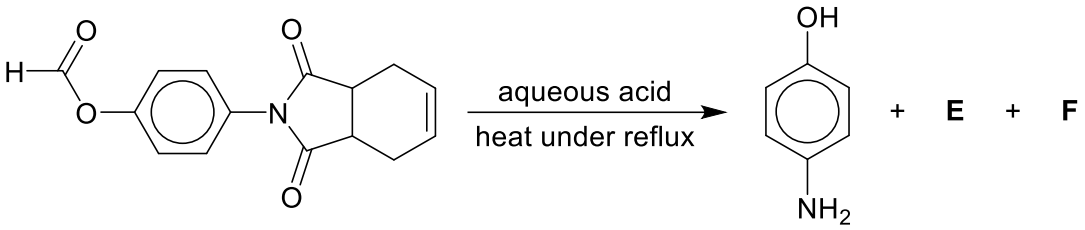
II: $HCl(aq)$ or $H_2SO_4(aq)$, heat

III: $NaOH(aq)$ / Na_2CO_3 / $NaHCO_3$, r.t.

[6]

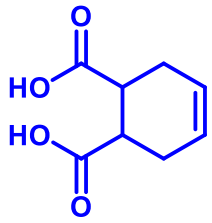
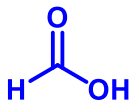
(b) Phenylamine and its analogues are organic nitrogen compounds with unique properties.

When compound **D** is heated under reflux with aqueous acid, 4-aminophenol together with cyclic compound **E** and non-cyclic compound **F** are formed.



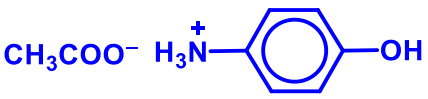
D 4-aminophenol

(i) Draw the structural formulae of compounds **E** and **F** in the boxes below:

	
cyclic compound **E**	non-cyclic compound **F**

[2]

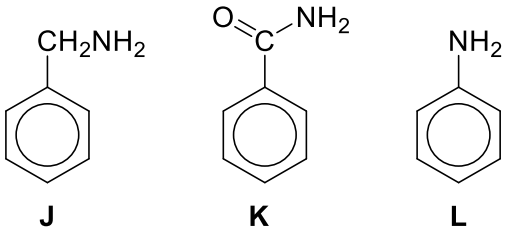
(ii) 4-Aminophenol can react with ethanoic acid at room temperature to produce compound **G** ($C_8H_{11}O_3N$). Suggest a structure for compound **G**, and state the type of reaction undergone.



type of reaction: ……**acid–base reaction**……

[2]

(c) The following organic nitrogen compounds were found in unlabelled bottles inside the chemistry laboratory.



J **K** **L**

(i) You are to distinguish between the above three compounds **J**, **K**, and **L**, using **only two** chemical tests. Fill in the reagents and conditions to be used and the observations to be made in Table 4.1.

Table 4.1

reagents and conditions	observations		
	J	**K**	**L**
Br_2(aq), r.t.	Orange solution not decolourised no white ppt or fumes formed	Orange solution not decolourised no white ppt or fumes formed	Orange solution decolourise white ppt formed white fumes formed
NaOH(aq), heat	No gas evolved	Pungent gas evolved turned damp red litmus paper blue	No gas evolved
$KMnO_4$(aq), H_2SO_4(aq), heat	Purple $KMnO_4$ decolourised White ppt formed	Purple $KMnO_4$ not decolourised White ppt formed	Purple $KMnO_4$ not decolourised No white ppt formed
CH_3COCl, r.t.	white fumes of HCl observed	no white fumes formed	white fumes of HCl observed

[4]

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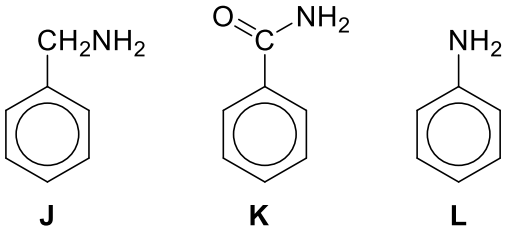
(ii) The compounds in **(c)(i)** show varying degrees of basicity. Account for the relative degrees in basicity of the three compounds, **J**, **K** and **L**.



J **K** **L**

The strength of the base depends on the **availability of lone pair of electrons on N to bond with H^+** (or to be protonated). Thus **basicity of J > L > K**

Compound **K** (amide): **lone pair of electrons on N** is **delocalised** into the neighbouring **carbonyl group** with δ+ C and highly electronegative O due to overlap of p orbital of N with π cloud of C=O. Hence, the lone pair is **not** (readily) **available** for donation/protonation, and the amide is **neutral**.

Compound **L** (phenylamine): **lone pair** of electron **delocalised into the benzene** ring, making it **less readily available for donation**.

Compound **J** (primary amine): **alkyl group is electron donating**, which **increases** the **electron density** around N. The **lone pair of electrons is more available for donation**, increased basic strength, hence **most basic** of the three.

[2]

[Total: 16]

5 Table 5.1 and Table 5.2 show some physical properties of the Group 1 and Group 13 elements, respectively.

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Table 5.1

element	radius / nm		$\Delta H_f^{\ominus}(M(g))$ / kJ mol^{-1}	$\Delta H_f^{\ominus}(M^+(aq))$ / kJ mol^{-1}	$\Delta G_f^{\ominus}(M^+(aq))$ / kJ mol^{-1}
	metallic	ionic (M^+)			
Li	0.152	0.076	+162	–278.5	–293.3
Na	0.186	0.102	+108	–240.3	–261.9
K	0.227	0.138	+89.6	–252.1	–283.3
Rb	0.248	0.152	+82.0	–251.1	–284.0
Cs	0.265	0.167	+78.2	–258.0	–292.0

Table 5.2

element	ionisation energy / kJ mol^{-1}				$\Delta H_f^{\ominus}(M^{3+}(aq))$ / kJ mol^{-1}	$\Delta G_f^{\ominus}(M^{3+}(aq))$ / kJ mol^{-1}
	first	second	third	fourth		
A*l*	577	1820	2740	11600	–528.4	–485.3
Ga	577	1980	2960	6190	–211.7	–159.0
In	558	1821	2706	5350	–105.0	–98.0
T*l*	589	1971	2878	4934	+196.6	+214.6

The lighter Group 13 metals form compounds in the +3 oxidation state predominantly, although T*l* tends to form compounds in the +1 oxidation state.

(a) What does the $\Delta G_f^{\ominus}(M^{3+}(aq))$ data in Table 5.2 suggest about the stability of the $M^{3+}(aq)$ ions formed?

$\Delta G_f^{\ominus}(M^{3+}(aq))$ becomes **increasingly positive** down the Group 13 metals, suggesting **decreasing stability of the +3 oxidation state** in aqueous solution.

.....

..... [1]

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(b) From Table 5.1, it can be seen that $\Delta G_f^{\ominus}\left(M^+(aq)\right)$ is more negative than the corresponding $\Delta H_f^{\ominus}\left(M^+(aq)\right)$ for the Group 1 metals.

(i) What does this suggest about the sign of $\Delta S_f^{\ominus}\left(M^+(aq)\right)$ for the Group 1 metals?

Since $\Delta G_f^{\ominus} = \Delta H_f^{\ominus} - T\Delta S_f^{\ominus}$,

$\Delta S_f^{\ominus}\left(M^+(aq)\right)$ is **positive** for the Group 1 elements. [1]

(ii) Suggest a reason for the sign of $\Delta S_f^{\ominus}\left(M^+(aq)\right)$ in **(b)(i)**.

Formation of the **mobile aqueous ions** from the **crystalline**/regular metal **lattice** results in an **increase in the disorderliness**, and hence entropy, *i.e.* $\Delta S_f^{\ominus}$ is positive, and thus $\Delta G_f^{\ominus}$ will be more negative than $\Delta H_f^{\ominus}$.

[1]

(iii) However, from Table 5.2, $\Delta G_f^{\ominus}\left(M^{3+}(aq)\right)$ is significantly less negative than $\Delta H_f^{\ominus}\left(M^{3+}(aq)\right)$ for the tripositive Group 13 cations, especially A*l* and Ga. Suggest a possible reason in terms of structure and bonding.

Due to the **high charge density** of the tripositive cations, the attraction of the M^{3+} ions for the polar **hydrated water molecules** is very strong. As a result, the water molecules are **highly organised around the M^{3+} ion**, leading to a **loss in entropy** when these are formed from the **crystalline metal lattice**.

[1]

For Examiner's Use

(c) An energy cycle relating the standard enthalpy change of formation of $M^+(aq)$ to three other energy terms, **I**, **II** and **III**, is shown in Fig. 5.1.

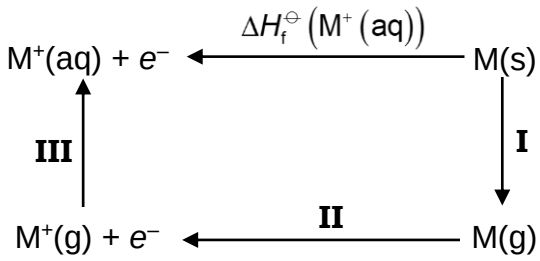

Fig. 5.1

(i) Name the three energy terms.

I : enthalpy change of **atomisation** / enthalpy change of **formation of M(g)**

II : **first ionisation energy**

III : standard enthalpy change of **hydration** of M^+

[3]

(ii) Explain the following trends down the Group 1 elements:

- energy term **II** becomes less endothermic

  First ionisation energy becomes less endothermic (from +519 kJ mol^{-1} for Li to +376 kJ mol^{-1} for Cs). This is due to the **increase in metallic radius** from Li to Cs, hence the electron removed is further away from the nucleus.

- energy term **III** becomes less exothermic

  Enthalpy change of hydration becomes less exothermic from Li^+ to Cs^+ due to the **increase in ionic radius** (of 0.076 nm for Li^+ to 0.167 nm for Cs^+), hence the charge density of the M^+ ion decreases, leading to **weaker ion-dipole interactions**.

[2]

For Examiner's Use

(iii) Using Fig. 5.1, data from Table 5.1, and your answer to **(c)(ii)**, account for the relatively invariant $\Delta H_f^{\ominus}\left(M^+(aq)\right)$ from K to Cs.

$\Delta H_f^{\ominus}\left(M^+(aq)\right)$ is given by the **sum of the enthalpy changes for I, II and III** (application of Hess law)

The **enthalpy change for I**, $\Delta H_f^{\ominus}\left(M(g)\right)$, is relatively **invariant from K to Cs**, while the **trend for II and III** in **(b)(ii) offsets each other**.

Hence, $\Delta H_f^{\ominus}\left(M^+(aq)\right)$ remains relatively invariant from K to Cs.

..... [2]

(d) The standard electrode potentials for rubidium and caesium are not available in the *Data Booklet*.

Using suitable data from Table 5.1, calculate a value for $E^{\ominus}\left(Rb^+|Rb\right)$.

$\Delta G_f^{\ominus}\left(M^+(aq)\right)$ refers to the process: $M(s) \rightarrow M^+(aq) + e^-$

Hence, $\Delta G^{\ominus}$ for the reduction of $M^+(aq)$ to M(s) is $-\Delta G_f^{\ominus}\left(M^+(aq)\right)$

$\Delta G^{\ominus} = -nFE^{\ominus}$, where $n = 1$ in this case,

$$E^{\ominus} = -\frac{\Delta G^{\ominus}}{nF} = -\frac{-\left(-284.0\times10^3\right)}{1\times96500}$$

$$= \mathbf{-2.94\ V}$$

[2]

The valence electronic configuration of the Group 13 elements take the form $ns^2\ np^1$, hence allowing for both the +1 and +3 oxidation states.

The monochlorides and trichlorides are known for all four Group 13 metals, but A*l*C*l* only occurs as short-lived diatomic molecules in the gas phase, disproportionating to give A*l*C*l*$_3$, while T*l*C*l* is the stable chloride of T*l*.

Table 5.3

MC*l*	$\Delta H_f^\ominus(\mathrm{MC}l(s))$ / kJ mol^{-1}	MC*l*$_3$	$\Delta H_f^\ominus(\mathrm{MC}l_3(s))$ / kJ mol^{-1}
A*l*C*l*	–188	A*l*C*l*$_3$	–704
T*l*C*l*	–204	T*l*C*l*$_3$	–315

(e) Based on the information given, and using the data given in Table 5.3, show by calculation why A*l*C*l* undergoes disproportionation, but not T*l*C*l*.

$\mathrm{MC}l(s) \rightarrow \frac{2}{3}\mathrm{M}(s) + \frac{1}{3}\mathrm{MC}l_3(s)$

$\Delta H_{disprop}(\mathrm{MC}l) = \frac{1}{3}\Delta H_f^\ominus(\mathrm{MC}l_3(s)) - \Delta H_f^\ominus(\mathrm{MC}l(s))$

$\Delta H_{disprop}(\mathrm{AlCl}) = \frac{1}{3}(-704) - (-188) = -46.7\ \mathrm{kJ\ mol^{-1}} < 0$, hence spontaneous

$\Delta H_{disprop}(\mathrm{TlCl}) = \frac{1}{3}(-315) - (-204) = +99\ \mathrm{kJ\ mol^{-1}} > 0$, hence non-spontaneous

..... [2]

This occurrence of an oxidation state which is 2 less than the group valency, as exemplified by T*l*, is sometimes referred to as the "inert-pair effect".

(f) However, the term "inert-pair effect" is somewhat inaccurate since it implies that the energy required to involve the valence ns^2 electron pair in bonding increases in the sequence A*l* < Ga < In < T*l*.

Using appropriate data from Table 5.2, justify why the term "inert-pair effect" is inaccurate.

Removal of the ns^2 electron pair involves the **second and third ionisation energy**.

In increasing order of ease of removal of the ns^2 electron pair is

In (**4527** kJ mol^{-1}) < A*l* (**4560** kJ mol^{-1}) < T*l* (**4849** kJ mol^{-1}) < Ga (**4940** kJ mol^{-1})

instead. ..... [2]

[Total: 17]

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