EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2021
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME	

CIVICS GROUP	2	0	–			REGISTRATION NUMBER		

CHEMISTRY

9729/02

Paper 2 Structured Questions

16 September 2021
2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not use paper clips, highlighters, glue or correction fluid.
Write your name, civics group, registration 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.
Answer all questions on the **Question Paper**
The number of marks is given in brackets [ ] at the end of each question or part question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

For Examiner's Use	
Paper 2	
1	/ 15
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3	/ 13
4	/ 15
5	/ 20
Total	**/ 75**

This document consists of **19** printed pages and **1** blank page.

1 Nitrosyl chloride, NOCl decomposes at temperatures above 100 °C to form nitrogen monoxide and chlorine as shown in the equation below.

$$2\text{NOC}l(g) \rightarrow 2\text{NO}(g) + \text{C}l_2(g)$$

(a) A sample of NOCl was allowed to decompose at 127 °C and 147 atm. Assuming that NOCl behaves ideally, show that its initial concentration is 4.48 mol dm^{-3}.

$$pV = nRT$$

$$[\text{NOC}l] = \frac{n}{V} = \frac{p}{RT}$$

$$= \frac{147 \times 101325}{8.31 \times (127 + 273)}$$

$$= 4480 \text{ mol m}^{-3}$$

$$= \frac{4480}{1000} \text{ mol dm}^{-3}$$

$$= \underline{\mathbf{4.48 \text{ mol dm}^{-3}}}$$

[2]

(b) A student pointed out that the assumption in **(a)** that NOCl behaves ideally is not valid. Suggest and explain **two** possible reasons why this may be so.

The **pressure** of NOCl is **very high**, causing the **volume of each gas particle becomes more significant relative to the total volume of the gas**.

NOCl has **significant intermolecular forces of attraction** as it is **polar**/has a **relatively large polarizable electron cloud**.

[2]

(c) The change in the concentration of NOC*l* was monitored as the decomposition reaction occurred over time. The data obtained is shown in Fig. 1.1.

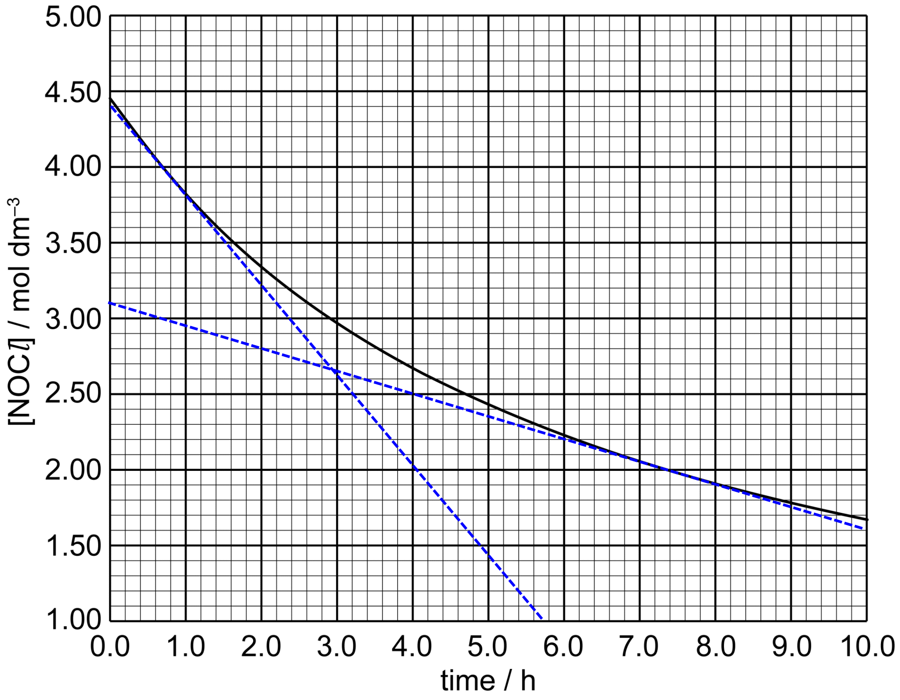


Fig. 1.1

(i) Using Fig. 1.1, show that the reaction is second order with respect to NOC*l*.

$$\text{rate at 4.00 mol dm}^{-3} = \left|\frac{4.40-1.00}{0.0-5.7}\right| = 0.5965 \text{ mol dm}^{-3}\text{ h}^{-1}$$

$$\text{rate at 2.00 mol dm}^{-3} = \left|\frac{3.10-1.60}{0.0-10.0}\right| = 0.1500 \text{ mol dm}^{-3}\text{ h}^{-1}$$

Since the **rate increases** by $\frac{0.596}{0.150} \approx$ **4 times** when **[NOC*l*] doubles**, the reaction is second order with respect to NOC*l*.

[3]

(ii) Given that the rate equation is $\text{rate} = k[\text{NOC}l]^2$, calculate the rate constant of the reaction, stating its units clearly.

$$\text{rate} = k[\text{NOC}l]^2$$

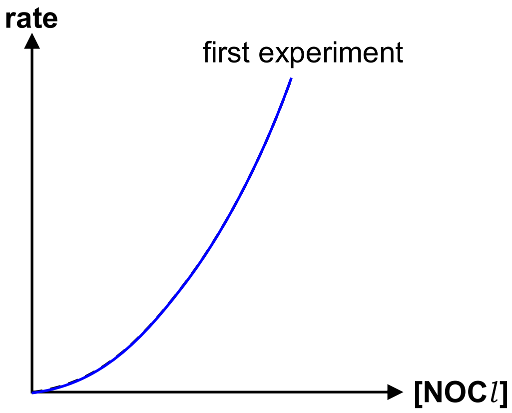
$$0.5965 = k(4.00)^2$$

$$k = \underline{\mathbf{0.0373\ mol^{-1}\ dm^{3}\ h^{-1}}}$$

[2]

(iii) A second experiment was conducted under the same conditions, but using half the initial concentration of NOC*l*.

On the axes provided below, sketch the graph that will be obtained using data from the second experiment, relative to that provided for the first experiment.



[1]

(d) **(i)** Define *half-life*.

Half-life of a reaction is the **time taken** for the **concentration/amount of a reactant to decrease to half its initial value**.

[1]

(ii) The rate equation for the second-order decomposition of NOC*l* can also be represented in the following manner:

$$\frac{1}{[\text{NOC}l]_t} - \frac{1}{[\text{NOC}l]_0} = kt$$

where $[\text{NOC}l]_t$ = concentration of NOC*l* at time, *t*,

$[\text{NOC}l]_0$ = original concentration of NOC*l*, and

k = rate constant

Using this equation, derive an expression for the half-life of the reaction.

$$\frac{1}{[\text{NOC}l]_t} - \frac{1}{[\text{NOC}l]_0} = kt$$

$$\frac{1}{\frac{1}{2}[\text{NOC}l]_0} - \frac{1}{[\text{NOC}l]_0} = kt_{\frac{1}{2}}$$

$$\boldsymbol{t_{\frac{1}{2}} = \frac{1}{k[\text{NOC}l]_0}}$$

[1]

(iii) Hence, state and explain whether the half-life of a second-order reaction will increase or decrease as the reaction proceeds.

Since half-life is **inversely proportional** to the initial reference concentration of the reactant, it will **increase** as the reaction proceeds.

.... [1]

(e) The reverse of the decomposition reaction can also occur such that NOC*l* is formed from NO and C*l*₂.

Given that a possible mechanism for the reaction is as shown below, suggest the rate equation for the reaction.

Step 1: $NO + NO \xrightleftharpoons{\text{fast}} N_2O_2$

Step 2: $Cl_2 + N_2O_2 \xrightarrow{\text{slow}} 2NOCl$

From slow step: rate = $k[Cl_2][N_2O_2]$

However, N_2O_2 is an intermediate.

From Step 1,

$$K_c = \frac{[N_2O_2]}{[NO]^2}$$

$$\begin{aligned} \text{rate} &= k[Cl_2][N_2O_2] \\ &= k[Cl_2]\left(K_c[NO]^2\right) \\ &= k'[Cl_2][NO]^2\text{, where } k' = k \times K_c \end{aligned}$$

[2]

[Total: 15]

2 During the 2000s, researchers looked into creating high-capacity rechargeable batteries for use in energy storage in renewable energy generation. The zinc-cerium battery shown in Fig. 2.1 is one example of such a rechargeable battery involving redox flow.

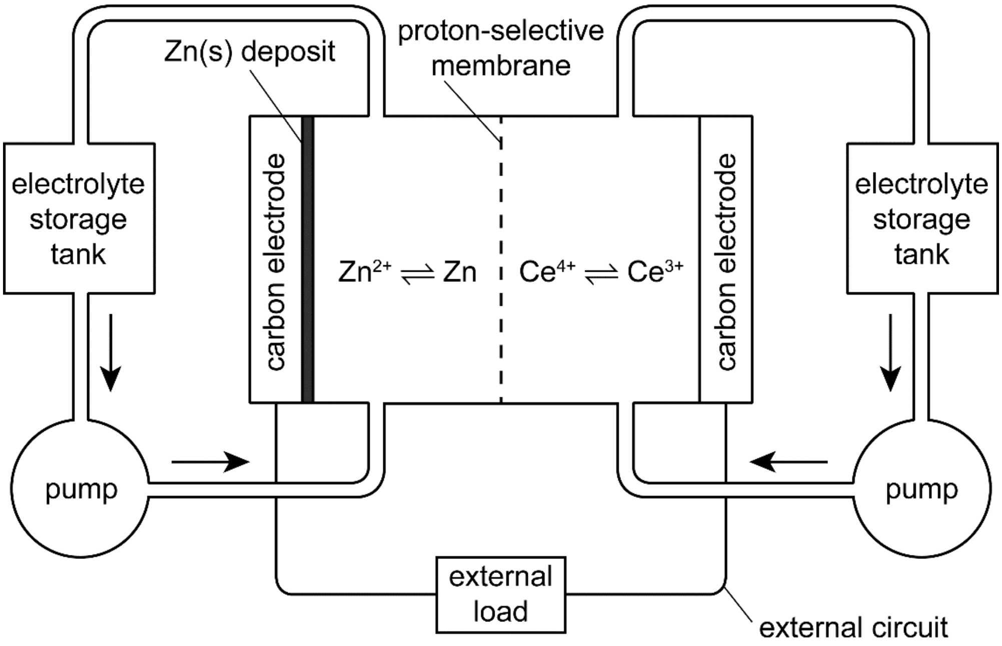


Fig. 2.1

The half-cells are made up of the following:

half-cell	electrolyte	electrode
Zn^{2+}/Zn	$Zn(CH_3SO_3)_2(aq)$, $CH_3SO_3H(aq)$	carbon-based polymer (similar to graphite) with fine Zn metal particles on surface
Ce^{4+}/Ce^{3+}	$Ce(CH_3SO_3)_3(aq)$, $Ce(CH_3SO_3)_4(aq)$, $CH_3SO_3H(aq)$	carbon-based polymer (similar to graphite)

The two electrolytes, consisting of methanesulfonic acid, CH_3SO_3H, and the respective salts, are separated by a proton-selective membrane.

(a) During the discharge process, the Zn^{2+}/Zn half-cell undergoes oxidation.

(i) Identify the polarity of the electrodes for the half-cells during the discharge process.

Zn^{2+}/Zn: ....**negative**.......... Ce^{4+}/Ce^{3+}: ....**positive**.......... [1]

(ii) Draw on Fig. 2.1 the direction of electron flow in the external circuit during the discharge process. [1]

(iii) Write the overall equation for the reaction during the discharge process.

$2Ce^{4+}(aq) + Zn(s) \rightarrow 2Ce^{3+}(aq) + Zn^{2+}(aq)$ .... [1]

(iv) Given that $E^{\ominus}\left(Ce^{4+}\middle|Ce^{3+}\right) = +1.44\ V$, with the aid of the *Data Booklet*, calculate the $E^{\ominus}_{cell}$ for the reaction during the discharge process.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-} \qquad E^{\ominus} = -0.76\ V$$
$$E^{\ominus}_{cell} = +1.44 - (-0.76) = \underline{\mathbf{+2.20\ V}}$$

[1]

(v) Hence, calculate the standard Gibbs free energy in kJ mol^{-1}.

$$\begin{aligned}\Delta G^{\ominus} &= -nFE^{\ominus}_{cell}\\ &= -(2)(96500)(+2.20)\\ &= -424600\ J\ mol^{-1}\\ &= \underline{\mathbf{-425\ kJ\ mol^{-1}}}\ (3\ s.f.)\end{aligned}$$

[1]

(b) Methanesulfonic acid dissociates fully in water. During the discharging process, the Zn^{2+}/Zn half-cell becomes more positive than the Ce^{4+}/Ce^{3+} half-cell over time.

(i) Explain how the proton exchange membrane maintains electrical neutrality.

It allows for **migration** of H^+ ions / **protons from Zn^{2+}/Zn tank to the Ce^{4+}/Ce^{3+} tank** to maintain electrical neutrality. .... [1]

When a high concentration of methanesulfonic acid was used, it was found that cerium(III) methanesulfonate, $Ce(CH_3SO_3)_3$, precipitates out in the electrolyte.

(ii) Suggest the effect on E_{cell} when a higher concentration of methanesulfonic acid was used as the electrolyte. Explain your answer.

With an **increase in the concentration of methanesulfonic acid**, Ce(III) methanesulfonate will precipitate out, **resulting in a decrease in the concentration of $Ce^{3+}(aq)$**. The *E* for the cathode will be **more positive than +1.44 V**, giving in a **more positive E_{cell} compared to** $E^{\ominus}_{cell} = +2.40\ V$.

.... [2]

(c) Although the zinc-cerium battery has potential in renewable energy storage, some side-reactions hinder its application.

During the **charging process**, the electromotive force used is large enough to drive these side-reactions to be thermodynamically feasible.

Using relevant values from the *Data Booklet,* identify one side-reaction during the charging process and explain why it will occur.

Since $E^\ominus(H^+|H_2) = +0.00$ V is **more positive than** $E^\ominus(Zn^{2+}|Zn) = -0.76$ V, **H^+**

can be reduced to **H_2** in the Zn^{2+}/Zn half-cell **.** ***or***

Since $E^\ominus(O_2|H_2O) = +1.23$ V is **less positive than** $E^\ominus(Ce^{4+}|Ce^{3+}) = +1.44$ V,

H_2O can be oxidised to **O_2** in the Ce^{3+}/Ce^{4+} half-cell **.** [2]

(d) Suggest

(i) why the carbon-based polymer can be used as a suitable material for the electrode for the Ce^{3+}/Ce^{4+} half-cell.

The carbon-based polymer is a **good electrical conductor / inert.**

[1]

(ii) why the zinc-cerium battery has a short lifespan, by considering the possible reactions occurring at the Zn^{2+}/Zn half-cell.

The Zn electrode will be **corroded over time by the acidic electrolyte**.

[1]

[Total: 12]

3 Double indicator acid-base titrations are used in scenarios where there is more than one end-point to a titration. Hence, it can also be used to determine the composition of mixtures of acids, as well as the pH of buffer solutions formed from polyprotic acids.

A typical example of a polyprotic acid is carbonic acid, where:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq) \qquad pK_{a1} = 6.36$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq) \qquad pK_{a2} = 10.3$$

(a) Explain why the value of pK_{a2} is higher than that of pK_{a1}.

It is **more difficult to lose a proton** due to the **stronger electrostatic force of attraction** between the **increasing negatively charged anion** and **the proton.**

.... [1]

A buffer solution was prepared by mixing Na_2CO_3 and $NaHCO_3$. To determine the pH of the buffer solution, a double-indicator titration was performed with 25.0 cm^3 of the buffer against 0.200 mol dm^{-3} HCl using phenolphthalein (pK_{In} = 9.3) as an indicator for the first end-point.

After the first end-point was attained, methyl orange (pK_{In} = 3.7) was then added as the second indicator to the same solution to determine the second end-point.
The first end-point occur at 16.90 cm^3. An additional titre volume of 19.20 cm^3 was required to reach the second end point.

The reaction between CO_3^{2-} ions and HCl occurs in two stages, with HCO_3^- as the intermediate product.

$$CO_3^{2-}(aq) + H^+(aq) \rightarrow HCO_3^-(aq)$$

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$

(b) **(i)** Calculate the concentration of CO_3^{2-} present in the buffer solution initially.

$n_{CO_3^{2-}} = n_{HCl}$ reacted at the first end-point

$$= \frac{16.90}{1000} \times 0.200 = 3.38 \times 10^{-3} \text{ mol}$$

$$[CO_3^{2-}] = \frac{3.38 \times 10^{-3}}{\frac{25.0}{1000}}$$

$$= 0.1352$$

$$\approx \mathbf{0.135\ mol\ dm^{-3}}$$

[1]

(ii) Hence or otherwise, calculate the volume of hydrochloric acid used to fully react with the HCO_3^- present in the buffer solution initially.

n_{HCl} required to react with CO_3^{2-} at the second end-point

$$= 2n_{CO_3^{2-}} = 2 \times 0.1352 \times \frac{25}{1000}$$

$$= 6.76 \times 10^{-3} \text{ mol}$$

volume of HCl required to react with CO_3^{2-} $= \frac{6.76 \times 10^{-3}}{0.200}$

$= 0.0338 \text{ dm}^3$

$= 33.80 \text{ cm}^3$

volume of HCl required to react with HCO_3^- $= 36.10 - 33.80$

$= \underline{\mathbf{2.30\ cm^3}}$

Alternatively, 19.20 – 16.90 = 2.30 cm^3

[1]

(iii) Using your answer to **(b)(ii)**, calculate the concentration of HCO_3^- present in the buffer solution.

$$n_{HCO_3^-} = n_{HCl} = \frac{2.30}{1000} \times 0.200 = 4.60 \times 10^{-4} \text{ mol}$$

$$[HCO_3^-] = \frac{4.60 \times 10^{-4}}{\frac{25.0}{1000}} = \underline{\mathbf{0.0184\ mol\ dm^{-3}}}$$

[1]

(iv) Hence, calculate the initial pH of the buffer solution.

$$\text{pH} = \text{p}K_{a2} + \lg\frac{[CO_3^{2-}]}{[HCO_3^-]}$$

$$= 10.3 + \lg\frac{0.1352}{0.0184}$$

$$= \underline{\mathbf{11.2}}$$

[1]

(v) Calculate the pH of the mixture attained at the second equivalence point.

At the second equivalence point, the solution comprises H_2CO_3 only

$$n_{H_2CO_3} = n_{CO_3^{2-}} + n_{HCO_3^-} = 3.38 \times 10^{-3} + 4.60 \times 10^{-4}$$

$$= 3.84 \times 10^{-3} \text{ mol}$$

$$[H_2CO_3] = \frac{3.84 \times 10^{-3}}{\frac{25.0 + 36.10}{1000}} = 0.06284 \text{ mol dm}^{-3}$$

$$[H^+] = \sqrt{K_{a1} \times [H_2CO_3]}$$

$$= \sqrt{10^{-6.36} \times 0.06284}$$

$$= 1.656 \times 10^{-4} \text{ mol dm}^{-3}$$

[3]

$$\text{pH} = -\lg(1.656 \times 10^{-4})$$

$$= \underline{\mathbf{3.78}}$$

For Examiner's Use

(vi) By considering the initial concentrations of Na_2CO_3 and $NaHCO_3$, calculate the volume of HC*l* to be added to 25.0 cm^3 of the buffer to produce a resultant mixture with a pH of 10.3.

Since pH = pK_{a2} = 10.3

$$[CO_3^{2-}] = [HCO_3^-] = \frac{0.1352 + 0.0184}{2}$$

$$= 0.0768 \text{ mol dm}^{-3}$$

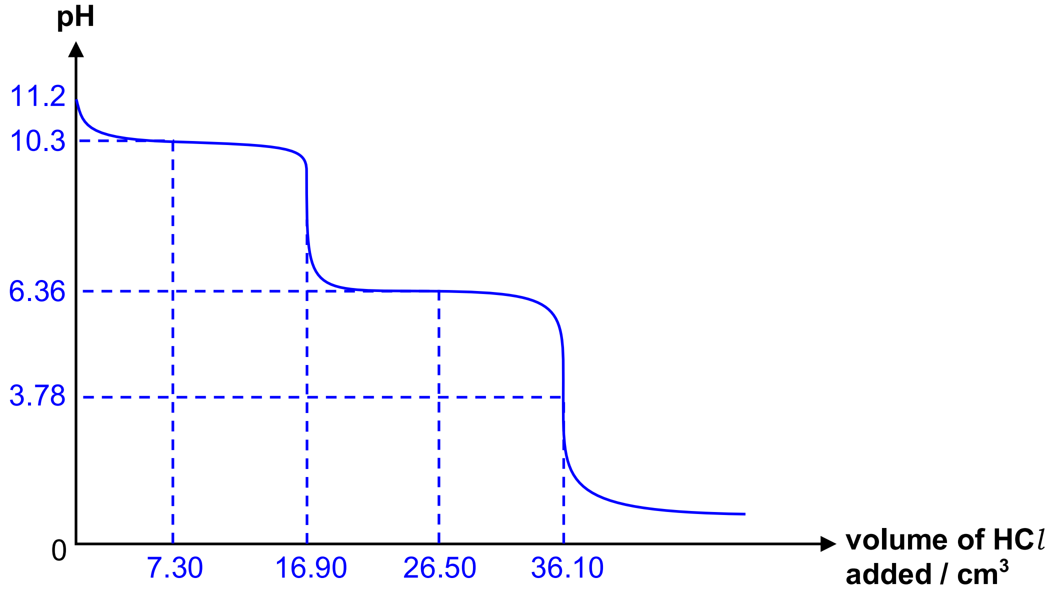
$$\text{volume of HC}l\text{ added} = \frac{(0.1352 - 0.0768) \times \frac{25.0}{1000}}{0.200}$$

$$= 7.30 \times 10^{-3} \text{ dm}^3$$

$$= \underline{\mathbf{7.30\ cm^3}}$$

[2]

(c) Using the information provided in the question as well as your answers from **(b)(iv)** – **(b)(vi)**, sketch a graph to show the pH changes that occur when 50.00 cm^3 of 0.200 mol dm^{-3} HC*l* is added to 25.0 cm^3 of the initial buffer solution.



[2]

(d) Explain why ethanoic acid cannot be used in place of hydrochloric acid for this titration.

Ethanoic acid is a weak acid and there will be **no sharp increase of pH** that is typically found along with the end-point, hence there is no indicator that can be used to produce a distinct colour change to identify the end-point. ....

.... [1]

[Total: 13]

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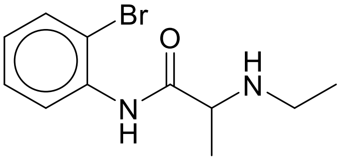
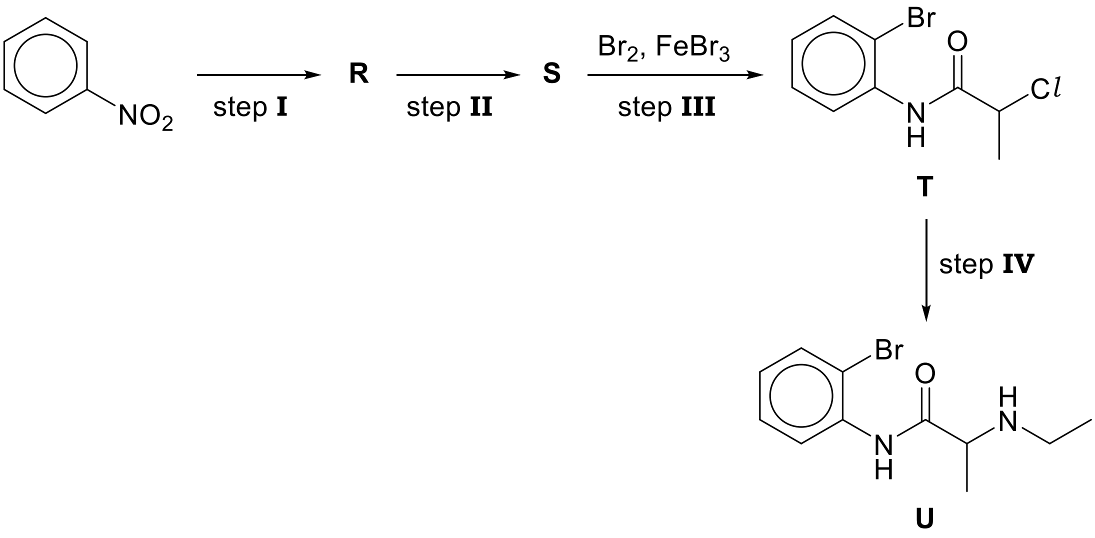
4 Compound **U** was developed in the drug discovery process for an anaesthetic.

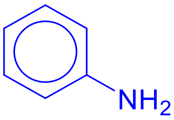
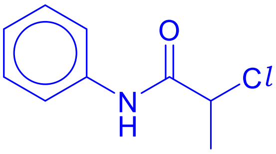


U

(a) The following synthetic scheme shows the synthesis of compound **U**.



(i) Draw the structures of the organic compounds **R** and **S**.

 **R**	 **S**

[2]

(ii) State the reagents and conditions for steps **I**, **II** and **IV**.

step **I**: **Sn, conc. HC*l*, heat** followed by NaOH at rt

step **II**: **C*l*COCH(CH$_3$)C*l***, r.t.

step **IV**: **CH$_3$CH$_2$NH$_2$** in ethanol, **heat** in sealed tube

[3]

(iii) Suggest why bromination cannot be carried out in step **I**.

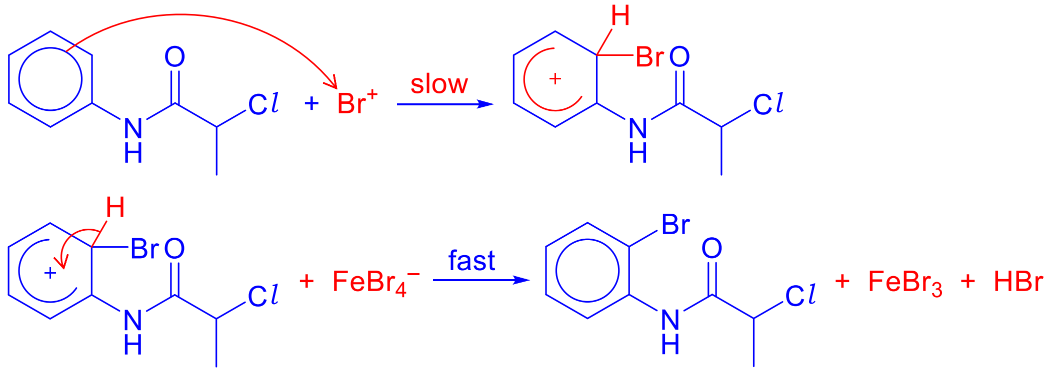
Bromination cannot be carried out in step **I** as the NO_2 group in nitrobenzene is **3-directing**, hence the Br^+ electrophile will not be directed at the 2-position to form the product.

[1]

(iv) Describe the mechanism for the reaction in step **III**.

Type of mechanism: **Electrophilic substitution**

$FeBr_3 + Br_2 \rightleftharpoons Br^+ + FeBr_4^-$

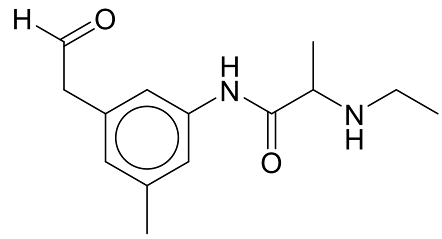


[3]

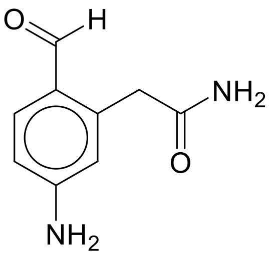
For Examiner's Use

(b) During the process of drug discovery, the following four compounds, **W** to **Z**, were also developed.

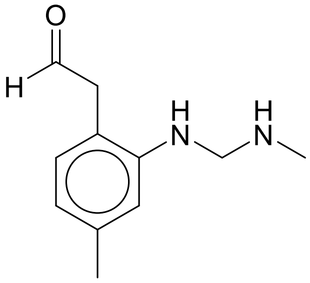
W:



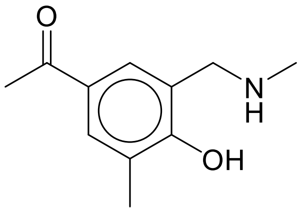
X:



Y:



Z:



Describe three simple chemical tests that could be carried out in sequence to distinguish between compounds **W**, **X**, **Y** and **Z**. State the expected observations for each test.

Test 1: Add **Tollens' reagent** to separate samples of the 4 compounds.

Observations: **No ppt will be observed for Y, silver mirror for W, X and Z.**

Test 2: Add **Fehling's solution** to separate samples of **W**, **X** and **Z**.

Observations: **Brick-red ppt will be observed for W, no brick-red ppt for X and Z.**

Test 3: Add **neutral iron(III) chloride** to separate samples of compounds **X** and **Z**.

Observations: **Violet colouration will be observed for Z, no violet colouration for X.**

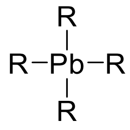
[6]

[Total: 15]

For Examiner's Use

5 Organometallic chemistry is the study of compounds containing, and reactions involving, metal–carbon bonds. In addition, other bonds such as metal–nitrogen and metal–halogen bonds, are also of interest.

Common examples of organometallic compounds are

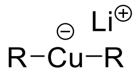


PbR_4

organolead

$R-Mg-X$

organomagnesium (Grignard reagents)



$R-Cu^{\ominus}-R\ Li^{\oplus}$

organocuprate (Gilman reagents)

where R = alkyl groups; X = C*l*, Br or I

(a) Tetraethyllead, $(C_2H_5)_4Pb$, is an example of an organolead compound, that for much of the 20th century was the chief antiknock agent for automotive gasoline, or petrol.

(i) State and explain the shape of the tetraethyllead molecule.

Since there are only **4 Pb–C** σ **bond pairs and no lone pairs** around the central Pb atom, tetraethyllead will be **tetrahedral** in shape. [2]

In the car engine, tetraethyllead burns to deposit solid lead and lead(II) oxide, PbO, which destroy the engine. Hence, lead scavengers such as 1,2-dibromoethane and 1,2-dichloroethane are used in conjunction with tetraethyllead, forming gaseous lead(II) bromide and lead(II) chloride in the engine instead.

(ii) Explain why $PbCl_2$ and $PbBr_2$ are more volatile than PbO.

Due to the much **larger anionic radius and lower anionic charge** of Cl^- and Br^- compared to O^{2-}, **less energy is required to overcome the weaker ionic bonds** in $PbCl_2$ and $PbBr_2$ leading to **lower boiling points** compared to PbO.

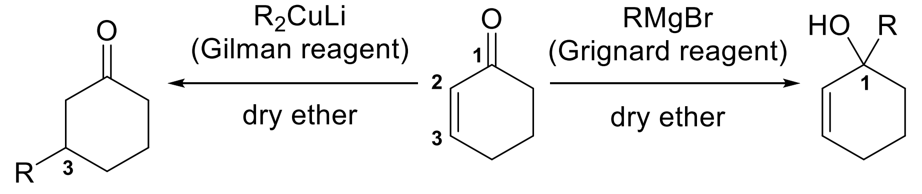
[2]

Organometallic compounds tend to act as carbon-based nucleophiles.

(b) With reference to the bonding in organometallic compounds, suggest why they tend to act as carbon-based nucleophiles.

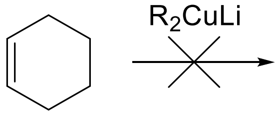
Carbon is **more electronegative** than the metals. Hence the **metal–carbon bond** is polarised in such a way that the **carbon carries the partial negative (δ–) charge**, hence rendering the carbon nucleophilic / Lewis basic. [1]

Both Gilman reagents and Grignard reagents act as carbon-based nucleophiles, adding across double bonds. However, the addition product with cyclohex-2-en-1-one differs for the two reagents.



3-alkylcyclohexan-1-one cyclohex-2-en-1-one 1-alkylcyclohex-2-en-1-ol

Nonetheless, Gilman reagent does not react with cyclohexene.

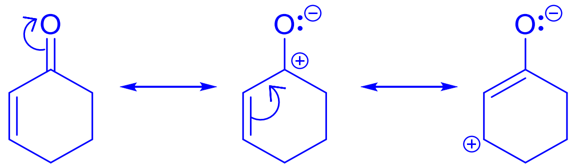


no addition reaction

(c) **(i)** Explain why Gilman reagent does not react with cyclohexene.

The carbon-based **nucleophile** of Gilman reagent is **repelled** by the **electron-rich π-electron cloud** of the **C=C**, hence R_2CuLi does not add across C=C. ....[1]

(ii) With the aid of a suitable diagram, explain why Gilman reagent reacts with carbon-3 of cyclohex-2-en-1-one but not carbon-2, using the concept of electronegativity and delocalisation in your answer.



Due to the **much higher electronegativity** of **oxygen** compared to carbon, and the **delocalisation of the π-electrons** of **C=C** into the **C=O** shown above, **carbon-3** will attain a **partial positive (δ+) charge**, while **carbon-2** is **neutral**. Hence, the carbon-based **nucleophile** of Gilman reagent will attack carbon-3, but not carbon-2.

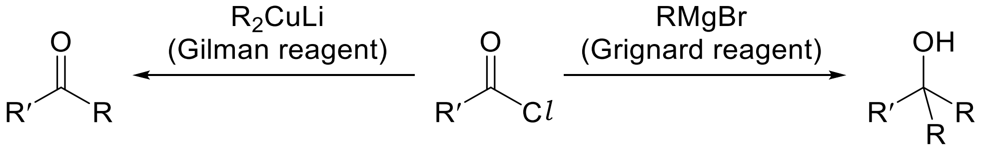
..........[2]

(iii) With reference to the structure of the cyclohex-2-en-1-one and the relative polarity of the metal–carbon bonds, suggest why Gilman reagent reacts preferentially with carbon-3 of cyclohex-2-en-1-one but Grignard reagent reacts with carbon-1, the carbonyl carbon.

As carbon-3 is **further away from the electronegative oxygen** than carbon-1, the **partial positive (δ+) charge on carbon-3 is lesser than that one carbon-1**. Since magnesium is **less electronegative / more electropositive** than copper, the **carbon atom** in the **Mg–C** bond has a **larger partial negative (δ–) charge** than that in Cu–C. Hence, the more nucleophilic R group in Grignard reagent favours the more electrophilic carbon-1, while the less nucleophilic R group in Gilman reagent favours the less electrophilic carbon-3.

.... [2]

Another reaction where Gilman reagents and Grignard reagents give different product is in their reaction with acyl chlorides.



Gilman reagents react with acyl chloride to give ketones, while Grignard reagents react to give tertiary alcohols.

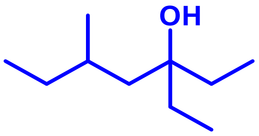
(d) **(i)** State the type of reaction undergone by the acyl chloride with Gilman reagent.

Nucleophilic (acyl) substitution [1]

(ii) The reaction with Grignard reagents involves another type of reaction. State this second type of reaction.

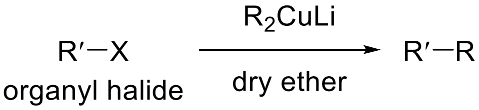
Nucleophilic addition [1]

(iii) Draw the skeletal formula of the product obtained when 3-methylpentanoyl chloride reacts with the Grignard reagent, CH_3CH_2MgBr.



[1]

Gilman reagents are also effective nucleophiles for substitution reactions with organyl halides, in what is known as the Corey-House synthesis, as shown below. Grignard reagents, on the other hand, perform very poorly in this reaction.



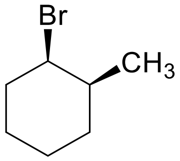
where R = methyl, 1°, 2°, 3° alkyl, aryl, alkenyl
R′ = methyl, 1°, cyclic 2° alkyl, aryl, alkenyl
X = Br or I

(e) **(i)** What evidence suggest an S_N2-type mechanism in the Corey-House synthesis?

Only **methyl**, **primary** and cyclic secondary alkyl halide reacts in the Corey-House synthesis, but **not tertiary halide**.

..........[1]

(ii) The S_N2-type mechanism in the Corey-House synthesis can be established by using the following cyclic secondary bromide as an organyl halide substrate.

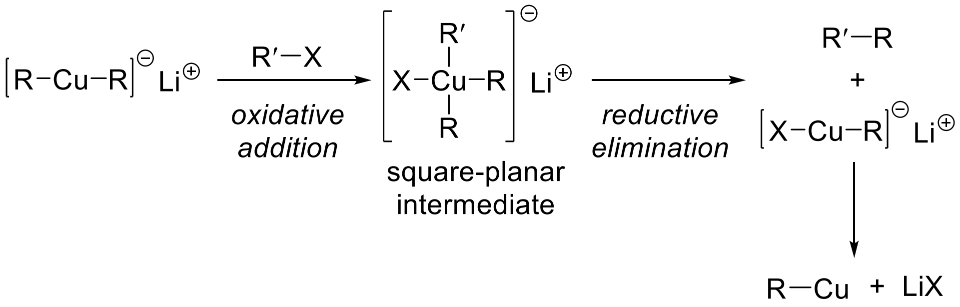


State the observation which will confirm a S_N2-type mechanism.

An **inversion of configuration** will be observed about the C–Br **α-carbon**.

..........[1]

The Corey-House synthesis is believed to proceed via first *oxidative addition* of the organyl halide to give a square planar copper-containing intermediate, which then undergoes *reductive elimination* to provide the product, R′–R.



(f) **(i)** State the oxidation state of copper in

- the square-planar intermediate: **+3**
- $[X–Cu–R]^-$: **+1**

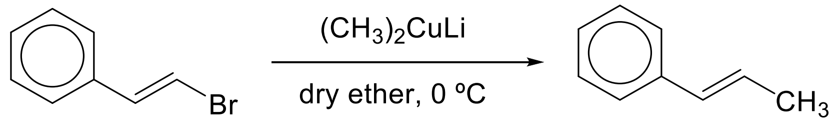
[2]

(ii) With reference to **(f)(i)**, suggest why the second step is known as *reductive elimination*.

The second step involves the **lost of two alkyl groups** from the Cu centre, with **decrease in oxidation state** of the Cu centre by 2 units.

[2]

Unlike the reaction of organyl halides with aqueous sodium hydroxide, where aryl and alkenyl halides are unreactive, alkenyl and aryl bromide and iodide reacts readily with Gilman reagents. For example,



an alkenyl bromide

(g) Explain why alkenyl halides are unreactive towards aqueous sodium hydroxide.

The **lone pair of electrons** on the halogen is **delocalised into the C=C**, imparting **partial double bond character** to the C–Br bond, **strengthening the bond**, making substitution difficult.

[1]

[Total: 20]

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