Section A

Answer **all** questions from this section.

1 Ethanoic acid, CH_3COOH, is a common precursor used in industries to synthesise more complex compounds.

(a) Ethanoic acid has a K_a value of 1.74×10^{-5}.

(i) Calculate the pH of 0.200 mol dm^{-3} ethanoic acid to 1 decimal place. [1]

$[H^+] = -\log_{10}\sqrt{(0.200 \times 1.74 \times 10^{-5})} = \underline{\mathbf{2.7}}$ **[1]**

Marker's Comments

- Almost all candidates could do this calculation, but some candidates ignored the instructions for 1 d.p.

(ii) Write the K_a expression for ethanoic acid. [1]

$\mathbf{K_a = [H^+] \times [CH_3COO^-] / [CH_3COOH]}$ **[1]**

Marker's Comments

- Almost all candidates scored this mark.

(b) An aliquot of 25.0 cm^3 of 0.200 mol dm^{-3} of ethanoic acid is titrated with 25.0 cm^3 of 0.200 mol dm^{-3} NaOH solution.

(i) Explain, with the aid of a chemical equation, why the pH at equivalence point is alkaline. [2]

$\mathbf{CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-}$ **[1]**

At 25.0 cm^3 of NaOH, the ethanoic acid is completely neutralised into **ethanoate** ions, which then undergoes **salt hydrolysis** to form an alkaline solution. **[1]**

Marker's Comments

- The question specifically asked for a singular chemical equation, but some candidates wrote multiple equations. They need to be aware there is a possibility that actual A-Level markers may only credit the first equation and ignore subsequent answers, so as to not credit candidates who are regurgitating without discernment.
- About half of the candidates wrote equation for the neutralisation instead, $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$. Hence they need to read the question carefully to know what it wants.

(ii) A buffer was formed during this titration. Write a chemical equation to show how the buffer solution resists pH change when a small amount of NaOH is added. [1]

$\mathbf{CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O}$ (single arrow) **[1]**

Marker's Comments

- This question only asked for chemical equation and no explanation was required. Nonetheless, many candidates gave lengthy explanations for zero additional credit.
- The question asked for change that happened, so the reversible arrow was rejected.

(iii) By using the K_a value from **(a)**, calculate the pH of the solution to 2 decimal places when 15.0 cm^3 of NaOH was added. [3]

Initial amount of ethanoic acid = 25.0/1000 × 0.200 = 0.00500 mol
Amount of NaOH in 15.0 cm^3 = 15.0/1000 × 0.200 = 0.00300 mol **[1]**

After neutralisation, amt of ethanoate formed
= amt of NaOH added = 0.00300 mol
After neutralisation, amt of ethanoic acid remaining
= 0.00500–0.00300 = 0.00200 mol **[1]**

New total volume = 25.0 + 15.0 = 40.0 cm^3 = 0.0400 dm^3

$$pH = pK_a + \log_{10}\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$= 4.76 + \log_{10}\left(\frac{0.00300/0.0400}{0.00200/0.0400}\right)$$

= 4.76 + 0.18 = 4.94 **[1]**

Alternative:
pH = pKa + $\log_{10}$[(15.0) / (25.0 – 15.0)]
= 4.76 + 0.18
= **4.94** **[3]**

Marker's Comments

- Most candidates' errors arose from misunderstanding the context, or focusing on single components without realising that this is a buffer solution.

(c) A sample of industrial waste contains only hydrochloric acid and ethanoic acid. 50.0 cm^3 of the industrial waste was collected in a volumetric flask and topped up to 250 cm^3. A 25.0 cm^3 sample of the resultant solution was then titrated using 0.200 mol dm^{-3} NaOH solution, giving two equivalence points at 12.40 cm^3 and 23.55 cm^3. The first equivalence point is for the neutralisation reaction with HC*l*.

(i) Both hydrochloric acid and ethanoic acid are Brønsted-Lowry acids. Define the term *Brønsted-Lowry acid.* [1]

A Brønsted-Lowry acid is a **H^+ donor**. **[1]**

Marker's Comments

- Almost all candidates scored this mark.

(ii) Calculate the concentration of hydrochloric acid present in the 50.0 cm^3 sample of industrial waste. [3]

amount of NaOH reacted with HCl = 12.40/1000 × 0.200 = **0.00248 mol** **[1]**
amount of HC*l* in 25.0 cm^3 = 0.00248 mol
amount of HC*l* in 250 cm^3 = 0.00248 × 250/25.0 = **0.0248 mol** **[1]**
amount of HC*l* in 50 cm^3 of industrial waste = 0.0248 mol
[HC*l*] in 50 cm^3 of industrial waste = 0.0248 ÷ (50.0/1000) = **0.496 mol dm^{-3}** **[1]**

Marker's Comments

- Some candidates were confused by the context, leading to wrong procedure or simply confusing dilution and extracting aliquots. Otherwise, many candidates scored full marks.

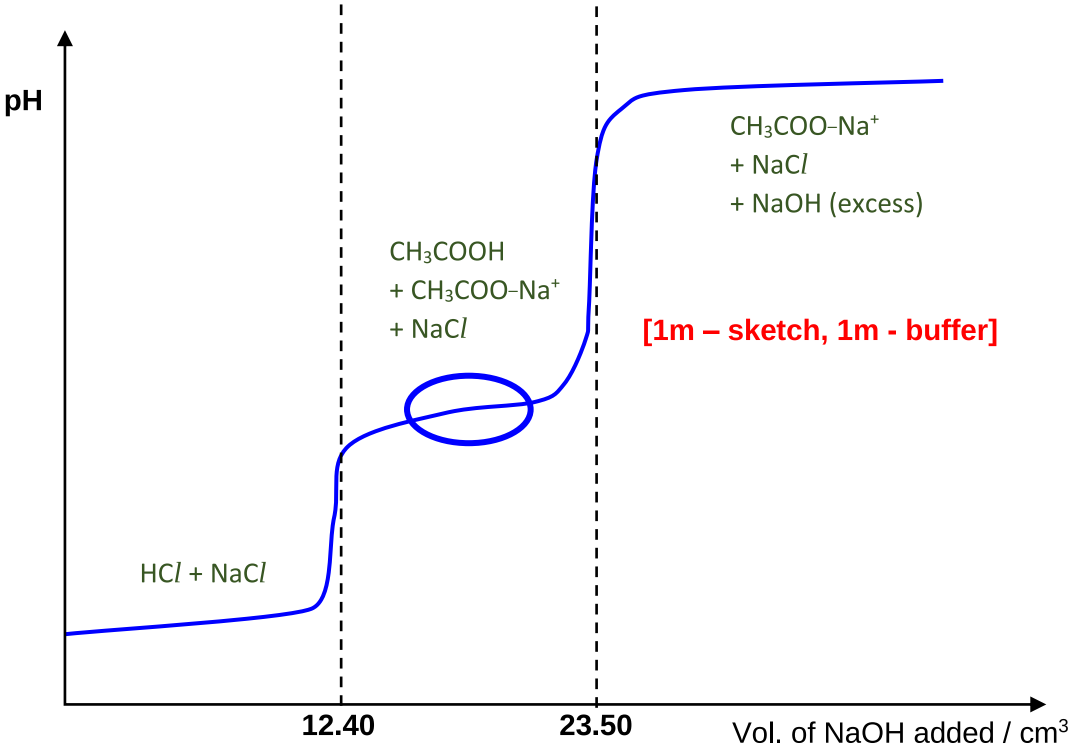
(iii) Hence, calculate an approximate value for the pH of the industrial waste. Give your answer to 1 decimal place. [1]

pH = $-\log_{10}0.496$ = **0.3** **[1] e.c.f.**

Marker's Comments

- Most candidates recognised correctly that the contribution from the weak acid could be ignored.

(iv) Sketch the shape of the titration curve and circle the portion that represents a buffer solution. No numerical pH values are needed. [2]



[1m – sketch, 1m - buffer]

Marker's Comments

- Most candidates correctly derived the shape of the titration curve (1st mark), but the buffer zone (2nd mark) was derived with less success. Some candidates showed clear evidence of analysing the species present at each point on the horizontal axis, and these tend to lead to correct answers.

[Total: 15]

[Turn over

2 Cobalt is a critical component in lithium-ion batteries, which are essential for powering electric vehicles and portable electronics due to their high energy density and reliability.

(a) The following sequence of reactions in Fig. 2.1 involves cobalt and its complexes.

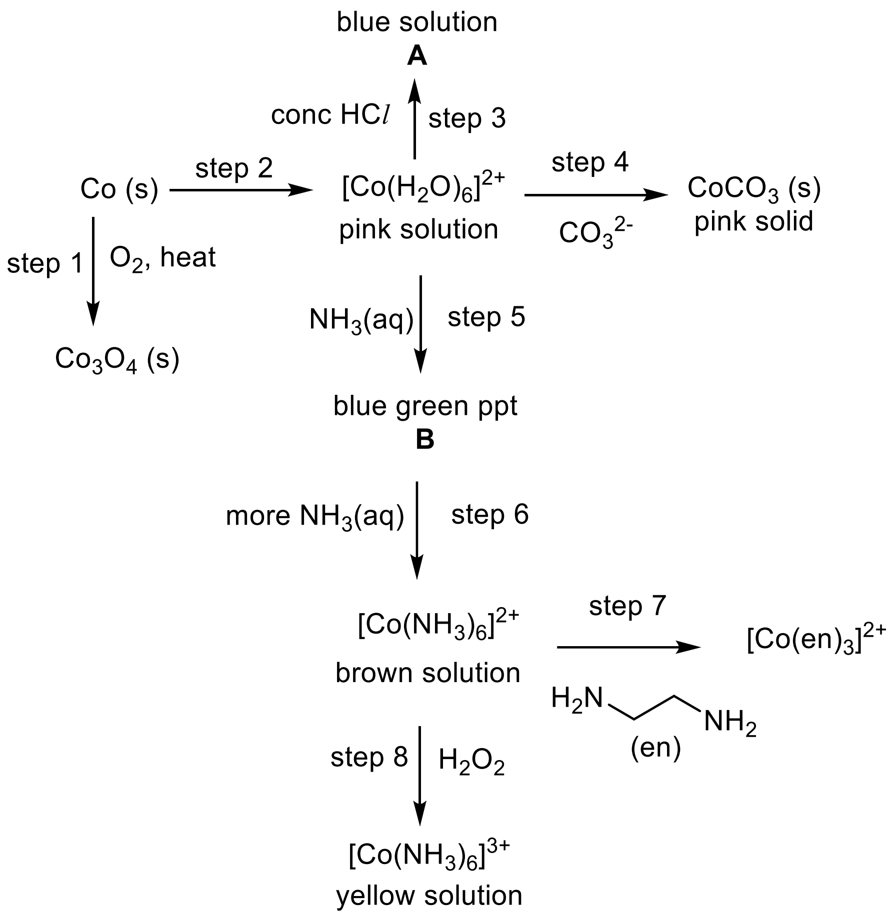


Fig. 2.1

(i) State the type of reaction that occurred in step 3 and the role of H_2O_2 in step 8. [2]

Step 3: **Ligand exchange [1]**

role of H_2O_2 in Step 8: **oxidising agent [1]**

(ii) Given that complex **A** is square planar in shape, suggest the identities of complexes **A** and **B.** [2]

A – $[CoCl_4]^{2-}$ [1]

B – $Co(OH)_2$ [1]

Marker's Comments

- Candidates should apply their knowledge of copper chemistry to identify compounds A and B. They must recognize that the overall charge of a ppt is zero.

(iii) When solutions of $[Co(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ are each mixed with sodium carbonate solution, different reactions occur. $[Fe(H_2O)_6]^{3+}$ produces effervescence of CO_2 but not $[Co(H_2O)_6]^{2+}$.

Explain why $[Fe(H_2O)_6]^{3+}$ results in the evolution of carbon dioxide gas when reacted with carbonate ions. [2]

Fe^{3+} has a **higher charge density** ✓ than Co^{2+}, which allows it to **polarise water molecules** ✓and **weaken the O–H bond**. ✓This results in the **breaking of the O–H bond**, ✓ **making the solution acidic**. ✓ The acidity neutralizes the carbonate, producing effervescence of CO_2. **2 -3 ✓ - [1], 4-5 ✓ - [2],**

Marker's Comments

- A weaker response attempts to explain the evolution of CO_2 using the thermal stability of carbonate. Candidates should present their answers clearly and avoid generalizing that the entire complex has a higher charge density.

(b) Co_3O_4, also known as cobalt tetroxide, is a black ionic compound that contains both Co^{2+} and Co^{3+} ions.

(i) Suggest the ratio of the two different cobalt ions in Co_3O_4. [1]

Co^{2+} and Co^{3+} ratio is **1:2** **[1]** ($4O^{2-} = -8$, so in order to balance the charge, it must be 2 Co^{3+} and 1 Co^{2+})

Cobalt tetroxide can be reduced to cobalt oxide at 900 °C.

$$Co_3O_4(s) \rightleftharpoons 3CoO(s) + \tfrac{1}{2}O_2(g) \qquad \Delta H^\ominus_{rxn}\,1$$

Some relevant thermochemical data is listed in the Table 2.1 below.

enthalpy change	value / kJ mol^{-1}
$\Delta H^\ominus_{at}$ Co(s)	+426
$\Delta H^\ominus_f$ O^{2-}(g)	+850
Lattice energy of CoO(s)	–3910
$\Delta H^\ominus_f$ Co_3O_4(s)	–910

(ii) Using the data given in Table 2.1 and relevant information from the *Data Booklet*, show that the standard enthalpy change of formation of CoO, $\Delta H^\ominus_f$ CoO, is –237 kJ mol^{-1}. [3]

F = A + I + L

$\Delta H^\ominus_f$ CoO = $\Delta H^\ominus_{at}$ Co(s) + 1st and 2nd IE of Co + $\Delta H^\ominus_f$ O^{2-}(g) + LE of CoO

= 426 + 757 + 1640 **[1]** + 850 –3910 **[1]** = **–237 kJ mol^{-1}** **[1]**

Marker's Comments

- To use the F = A + I + L formula, candidates need to understand that the enthalpy of formation $\Delta H^\ominus_f$ O^{2-} involves the atomization of O (g) and the 1st and 2nd electron affinities of O (g). They should also refer to the Data Booklet for the 1st and 2nd IE of Co.

(iii) Hence, determine the enthalpy change of reaction, $\Delta H^\ominus_{rxn}$ 1. [1]

$\Delta H^\ominus_{rxn}$ 1 $= \sum \Delta H_f$ product – $\sum \Delta H_f$ reactants = 3 x –237 – (–910)

= +199 kJ mol^{-1} [1]

Marker's Comments

- Surprisingly, many candidates struggled with this, often making the following errors:
    1. Forgetting the formula (formation of products minus formation of reactants).
    2. Ignoring stoichiometric ratios.
    3. Using the bond energy (BE) of oxygen in their calculations.
    4. Failing to consider the sign and units of their answers (no marks will be deducted for these mistakes).

(c) Cobalt oxide exhibits behaviour like aluminium oxide in its chemical properties and reactions, displaying both acidic and basic characteristics depending on the reaction environment.

(i) In your laboratory, you have three unidentified substances: magnesium oxide, silicon oxide and aluminium oxide. Describe a method to identify each substance based on their reactions with acids and bases. Provide relevant chemical equations for these reactions, describing the differences in their observable behaviours. [4]

For MgO it will **dissolve in acid** to form salt and water. ✓

$MgO + 2HCl \rightarrow MgCl_2 + H_2O$ ✓

For SiO_2, it will **dissolve in concentrated base** to form salt and water. ✓

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$ ✓

For Al_2O_3, it will **dissolve in both acids and bases** to form salt and water. ✓

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$ ✓✓

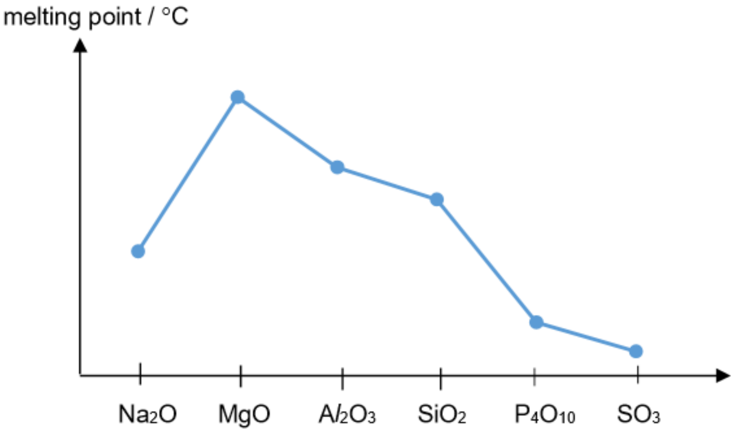
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ ✓✓

1-2 ✓ - [1], 3-4 ✓ - [2], 5-6 ✓ - [3], 7-9 ✓ - [4]

Marker's Comments

- Balancing equations proved to be challenging. Additionally, candidates should avoid using "react" as a type of observation. When dealing with silicon dioxide, they need to understand that concentrated base is required to dissolve it.

(ii) Draw a melting point trend graph for period 3 oxides. Explain why MgO has a higher melting point than Na_2O. [3]



[1]

lattice energy $| \propto \frac{q_+ \times q_-}{r_+ + r_-}$

Mg^{2+} has a **higher ionic charge** ✓and **smaller ionic radius** ✓than Na^+. **Ionic** bonds in MgO are stronger than that in Na_2O and require **more energy** to break. ✓ **. 1-2 ✓ - [1], 3-4 ✓ - [2],**

(d) **(i)** Describe the trend observed in the decomposition temperatures of Group 2 carbonates. [2]

(ii) Use relevant information from the Data Booklet, suggest which carbonate in Group 2 has a thermal decomposition temperature similar to that of $CoCO_3$. [1]

- ✓ **Charge density and polarising power** of the cation **decreases** as ionic charge remains the same while size of cation (NOT atom) increases.
- ✓ **Less distortion of the anion electron cloud**
- ✓ This **weakens the C–O bond within the anion to a smaller extent.**
- ✓ **More energy is required to decompose** CO_3^{2-}
- ✓ Hence, Group 2 carbonates become more thermally stable and have **higher decomposition temperature** down the group. **2-3 ✓ [1]; 4-5 ✓ [2]**

$MgCO_3$ (similar charge density due **SAME** ionic radius (Data Booklet) and charge) **[1]**

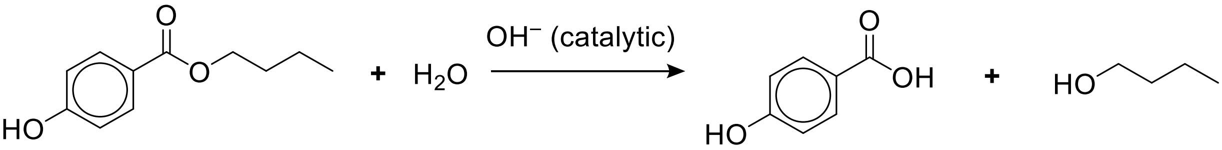
[Total: 21]

Marker's Comments

- Candidates are reminded to do their bookwork and score well for the above type of questions.

3 **(a)** Butylparaben (BP) is a member of the parabens family of organic compounds. Direct exposure to elevated levels of parabens is known to be harmful for human health.

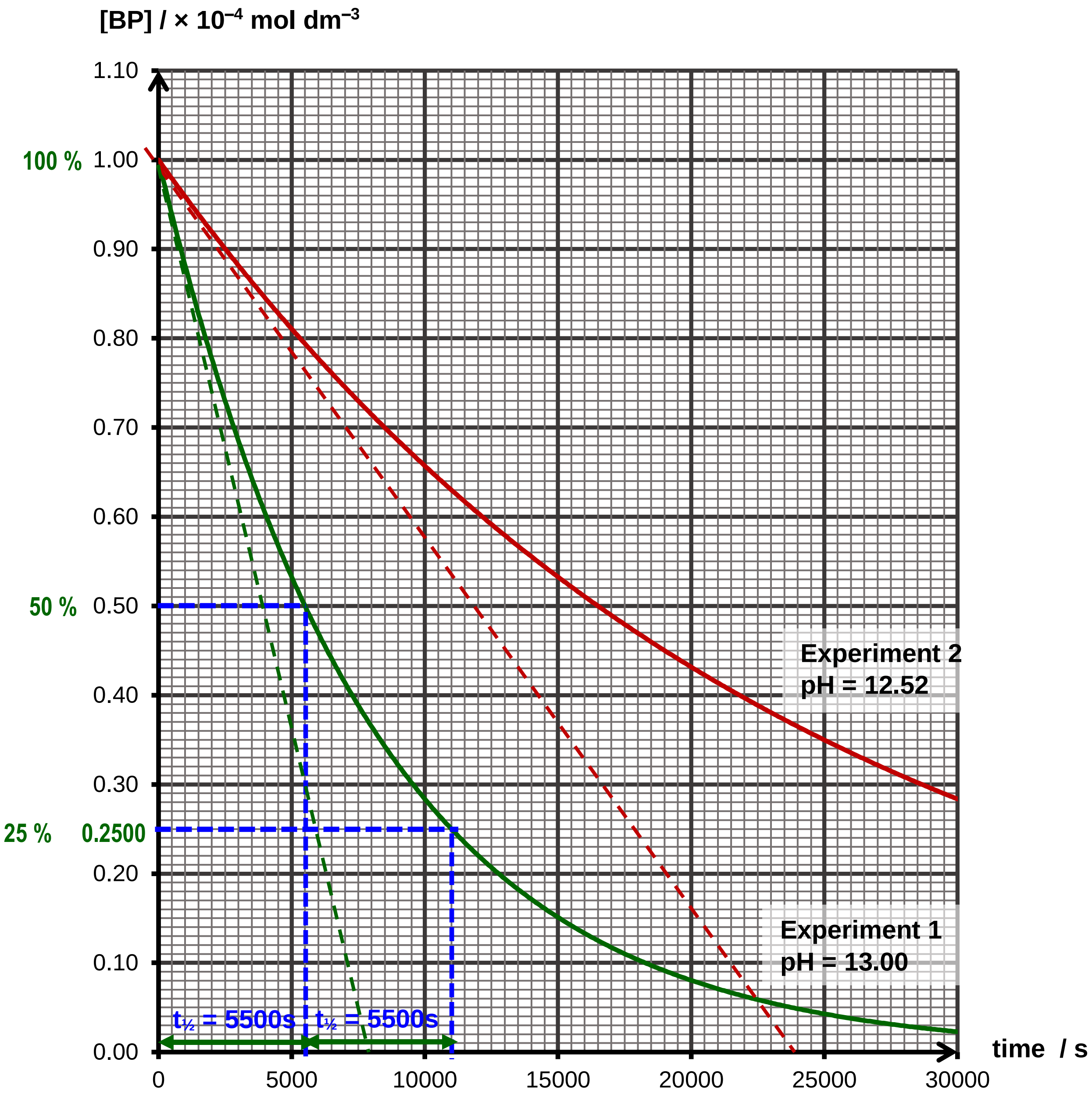
The kinetics of the hydrolysis of BP is investigated.



butylparaben (BP)

Two experiments at different pH levels were used to study the kinetics of the reaction. The pH of the reaction mixture was maintained throughout each experiment.

An [BP]–time graph was plotted using the results obtained from the experiments.



(i) Suggest why the pH of the reaction mixture was maintained throughout each experiment. [1]

To ensure that the **[OH⁻] remains constant throughout the course of the experiment** so that the **order of reaction with respect to BP can be determined more easily.** [1]

Markers' Comments

- This question was not well attempted. Many candidates did not fully understand the intent of the question behind the experimental design to keep pH constant and hence [OH⁻] constant.
- Some candidates wrongly accounted for [H⁺] which is not relevant in the context of this question – basic hydrolysis of BP ester.

(ii) Using the graph provided, show that the reaction is first order with respect to BP and first order with respect to hydroxide ion. Hence, write the rate equation for this reaction. [4]

[1] for two sets of constructions lines for half-life determination on graph

From the **graph of Experiment 1**, a **constant half-life of 5500 s** [1] is observed.
Order of reaction w.r.t. [BP] = 1

Experiment 1, pH = 13.00, pOH = 1.00 ➔ **$[OH^-] = 10^{-1.00} = 1.00 \times 10^{-1}$ mol dm^{-3}**

Initial Rate of Expt 1 = $\left|\dfrac{(1.00-0.00)\times10^{-4}}{0-8000}\right|$ = **1.25×10^{-8} mol dm^{-3} s^{-1}**

Experiment 2, pH = 12.52, pOH = 1.48 ➔ **$[OH^-] = 10^{-1.48} = 3.31 \times 10^{-2}$ mol dm^{-3}**

Initial Rate of Expt 2 = $\left|\dfrac{(1.00-0.00)\times10^{-4}}{0-24000}\right|$ = **4.17×10^{-9} mol dm^{-3} s^{-1}**

From the graphs, **when [OH⁻] increases** $\dfrac{1.00\times10^{-1}}{3.31\times10^{-2}}$ = = ~ **3 times,**

rate of reaction increases $\dfrac{1.25\times10^{-8}}{4.17\times10^{-9}}$ = **~ 3 times.** **(indicated by tripling of the magnitude of the gradient)**;

[1] for reasoning and correlating to the gradient of the two graphs at t =0 (initial rate); also allow for comparison of $t_{½}$ between the two experiments (Expt 1: $t_{½}$ = 5 500 s; Expt 2: $t_{½}$ = 16 500 s)

Order of reaction w.r.t. OH⁻ = 1

Rate = *k* [BP] [OH⁻] [1]

Markers' Comments

- This question was generally well attempted. Some candidates also failed to read the half-life of the reaction from the scale of the graph accurately.
- Some candidates struggled to systematically determine the order of reaction w.r.t. [OH⁻]. These candidates failed to compute the change in [OH⁻] based on the pH given as well as the initial rate of reaction which is indicated by the gradient of the tangent of graph at time, t = 0 s.

(iii) Suggest how the half-life for Experiment 1 would change when the initial concentration of BP is increased to 2.00×10^{-4} mol dm^{-3}. Explain your answer. [1]

Rate = k [BP] [OH$^-$]

As [OH$^-$] was used in large excess and kept constant,

Rate = k'[BP] where $k' = k$[OH$^-$] **Concept:** pseudo first order reaction

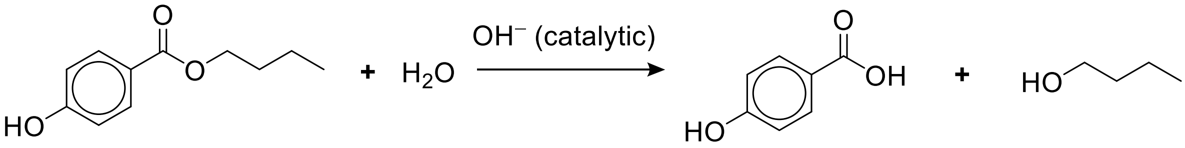
$t_{½}$ = $\frac{\ln 2}{k'} = \frac{\ln 2}{k\,[\text{OH}^-]}$ Hence, it could be seen that $t_{½}$ is **not affected by [BP]**. The half-life of experiment 1 will **remain constant at 5500s**. **[1]**

OR

The reaction is **first order with respect to BP** and hence the **half-life** of the reaction is **independent of [BP]**. The half-life of experiment 1 will **remain constant at 5500 s**. **[1]**

> **Markers' Comments**
> This question was generally poorly attempted. Many candidates did not explain clearly how half-life, $t_{½}$ is independent of [BP] but gave generic motherhood statement that $t_{½}$ is independent of reactants.

The basic hydrolysis of BP follows a nucleophilic acyl substitution mechanism.



butylparaben (BP)

This mechanism occurs via three steps.

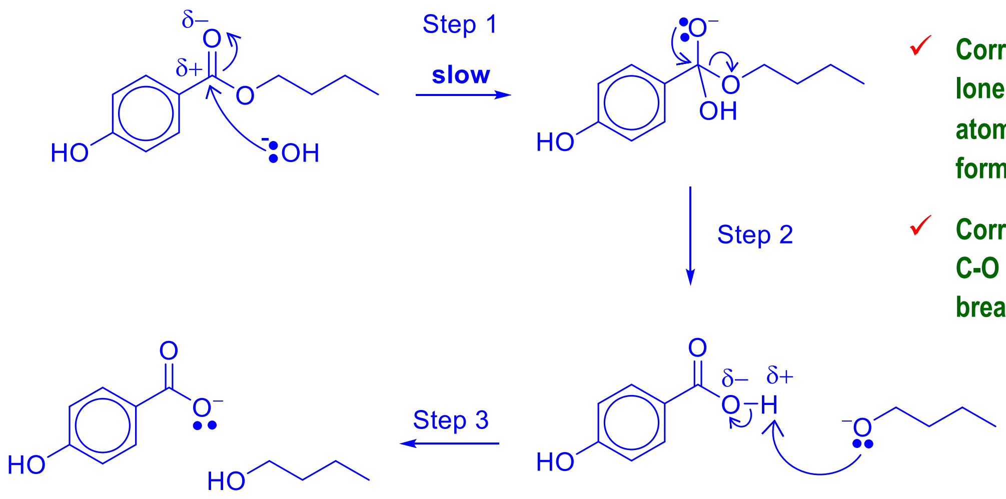
Step 1: The hydroxide ion attacks the carbonyl carbon of the ester to form a tetrahedral intermediate.

Step 2: This is followed by the removal of an alkoxide ion, RO$^-$, from the tetrahedral intermediate to give a carboxylic acid.

Step 3: The carboxylic acid is then quickly deprotonated by the alkoxide to give a carboxylate salt.

(iv) Draw the mechanism. In your answer, you should show all relevant charges, dipoles, and lone pairs; and show the movement of electrons by curly arrows. [3]

- ✓ Correct arrow pushing from lone pair on O atom of OH^- to δ^+ C atom (bond forming)
- ✓ Correct arrow pushing from C-O bond to O atom (bond breaking)
- ✓ Correct dipoles on C=O bond
- ✓ Indicate slow step



- ✓ Correct tetrahedral intermediate structure
- ✓ Correct arrow pushing from lone pair on O atom to carbon atom / C–O bond (bond forming)
- ✓ Correct arrow pushing from C-O bond to O atom (bond breaking)

- ✓ Correct alkoxide ion and carboxylic acid formed.
- ✓ Correct arrow pushing from lone pair on O atom of alkoxide to H atom of COOH (bond forming)
- ✓ Correct dipoles on H-O bond
- ✓ Correct arrow pushing from O-H bond to C atom (bond breaking)
- ✓ Correct products (carboxylate and alcohol)

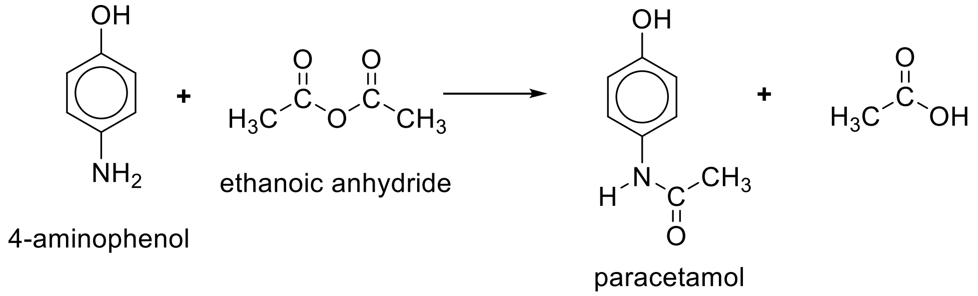
10 – 12 ✓	[3]
6 – 9 ✓	[2]
3 – 5 ✓	[1]

Markers' Comments

- This question was generally well attempted. Many candidates were able to correctly represent bond forming and bond breaking accurately using arrow pushing. That said, many missed out stating the slow step in Step 1, which can be gleamed from the kinetics determined earlier in 3(a) – first order w.r.t. BP and OH^-.

- Weaker responses showed little / no correlation to the information given in the steps of the mechanism, for example some candidates in their responses have demonstrated their lack of understanding of these terms. tetrahedral intermediate, carboxylic acid, alkoxide and carboxylate.

(b) Paracetamol can be synthesised by reacting ethanoic anhydride, $(CH_3CO)_2O$ and the amino group of 4-aminophenol to form an amide via a nucleophilic acyl substitution mechanism.



(i) Phenols can also react with ethanoic anhydride. However, the amino group of 4-aminophenol reacts faster with ethanoic anhydride than the hydroxy group, and the paracetamol product is isolated before the hydroxy group reacts.

Suggest a reason why the amino group reacts faster than the hydroxy group in the reaction between 4-aminophenol and ethanoic anhydride. [1]

Nitrogen is less electronegative than oxygen and hence **it is more likely to donate its lone pair of electrons to form a dative bond**. **[1]**

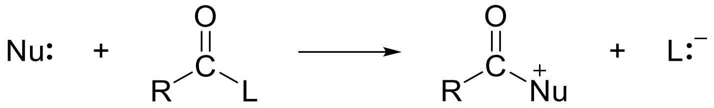
OR The amino group is a **stronger Lewis base** / **a stronger nucleophile** than the hydroxy group. The **lone pair on nitrogen in the amino group is more available for dative bonding** than that on oxygen in the hydroxy group. **[1]**

Hence, the amino group can react faster.

Markers' Comments

This question was generally poorly attempted. Many candidates did not understand the context of the question and failed to identify that both phenol (-OH) and phenylamine ($-NH_2$) are acting as nucleophiles in this reaction. Thus, the approach to this question should be on the relative availability of the lone pair of electrons on O of phenol and N of phenylamine respectively to form a dative bond.

(ii) One of the factors that affect the rate of nucleophilic acyl substitution is the nature of the leaving group, L.

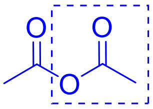


Leaving groups that form more stable anions, L⁻, can be substituted more easily, leading to faster reactions.

Suggest why should the synthesis of paracetamol should be carried out using ethanoic anhydride, $(CH_3CO)_2O$ instead of ethyl ethanoate, $CH_3CO_2CH_2CH_3$. [2]

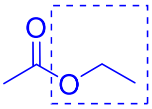
Approach:

Leaving Group for ethanoic anhydride



: CH_3COO^- (carboxylate)

Leaving Group for ethyl ethanoate



: $CH_3CH_2O^-$ (alkoxide)

In using **ethanoic anhydride**, the **negative charge on the leaving group, $CH_3CO_2^-$** (carboxylate) is **delocalised over two highly electronegative oxygen atoms and carbon atom, which disperses the intensity of negative charge to a great extent.** **$CH_3CO_2^-$** is **resonance stabilised.** ✓

In using **ethyl ethanoate**, the **negative charge on the leaving group, $CH_3CH_2O^-$** (alkoxide) is **intensified by the electron-donating $CH_3CH_2^-$ group.** ✓

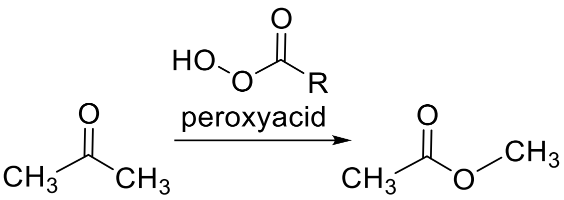
Hence, **$CH_3CO_2^-$** (carboxylate) **is more stable,** ✓ making it a better leaving group, thus **increasing the rate of nucleophilic acyl substitution**.

[2] for 3 ✓; [1] for 2 ✓

Markers' Comments

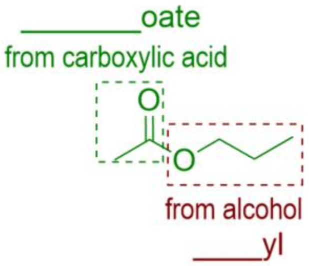
- This question was generally poorly attempted. Many candidates did not understand the context of the question and failed to identify the correct species for the leaving groups.
- Candidates who identified the leaving groups correctly were generally able to explain for the relative stability of the carboxylate and alkoxide anions. However, some candidates did not explain clearly for both anions.

(c) Esters can also be formed via Baeyer-Villiger reactions. A ketone is reacted with a peroxyacid, RCO_3H and this involves inserting an O atom into a C–C bond adjacent to a carbonyl group. For example, methyl ethanoate can be synthesised from propanone.

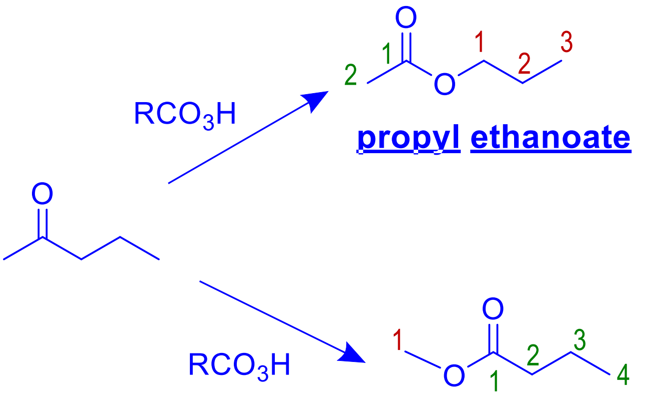


(i) Name an ester that can be formed by reacting pentan-2-one with peroxyacid, RCO_3H. [1]

Concept:



Name of ester: ____**yl** ____**oate**
(alcohol) (carboxylic acid)



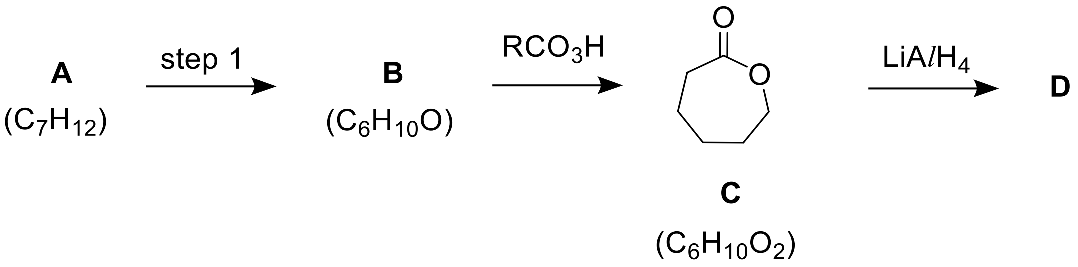
propyl ethanoate

methyl butanoate

[1] for name of ester

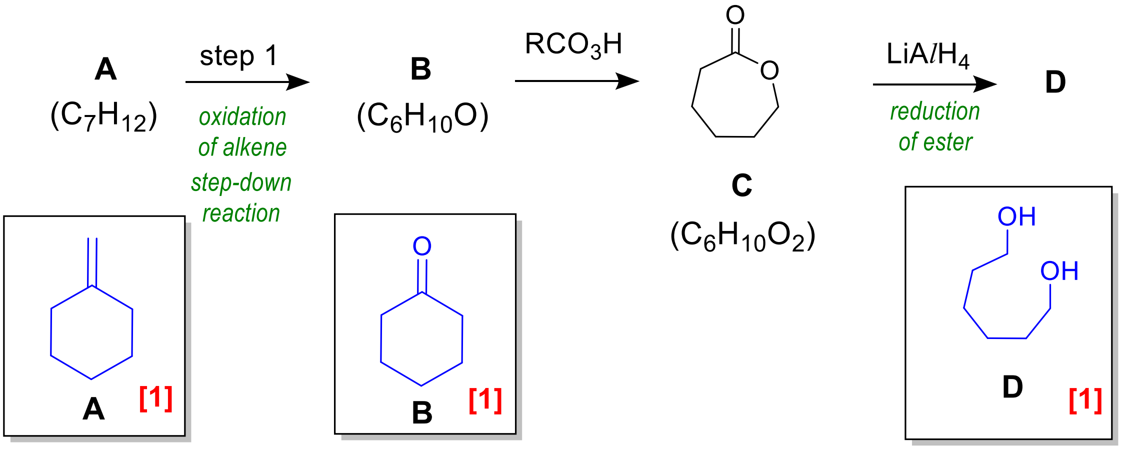
Markers' Comments
This question was generally poorly attempted. Many candidates struggled with the naming nomenclature of ester despite having the correct structure.

(ii) The following reaction scheme involves using Baeyer-Villiger reaction to synthesise a cyclic ester, compound **C**.



State the reagents and conditions required for step **1** and suggest structures for the organic compounds **A**, **B** and **D**. [4]

acidified $KMnO_4$ (aq), heat
$KMnO_4$ (aq), H_2SO_4 (aq), heat [1]



oxidation of alkene

step-down reaction

reduction of ester

must contain ketone in order to form ester in step 2

6 carbon atoms

Markers' Comments
This question was generally poorly attempted. Many candidates struggled with the reduction of ester.

(d) Compound **E** has a molecular formula of $C_6H_9O_3Cl$ and is a ❶ neutral molecule. ❷ Compound **E** reacts with hot sodium hydroxide, followed by acidification to yield two organic compounds, **F** and **G** in a 1:1 ratio.

❸ Compound **F,** $C_2H_2O_3$ gives an observation with Tollens' reagent. ❹It also reacts with hot acidified $KMnO_4$ to form carbon dioxide gas only.

Compound **G** contains 2 chiral carbon atoms and has a molecular formula of $C_4H_{10}O_2$. ❺ Compound **G** gives a negative test with 2,4–dinitrophenylhydrazine but ❻ reacts with hot aluminium oxide to form **only** three isomers with the molecular formula of C_4H_8O. ❼ Only one of the three isomers, **H** exhibits enantiomerism.

Suggest structures for compounds **E**, **F**, **G** and **H**, showing your reasoning clearly.

[7]

❶ **E is a neutral molecule. ➔ ✓ E is not a carboxylic acid nor an acyl chloride.**

❷ ✓ **E undergoes nucleophilic substitution and basic hydrolysis with hot NaOH (aq) (followed by acidification) to form F and G in a 1:1 ratio.**

✓ **E is an ester. OR**
F/G contains alcohol group and G/F contains carboxylic acid.

❸ ✓ **F undergoes oxidation with Tollens' reagent.**

✓ **F contains aldehyde.**

❹ ✓ **F undergoes oxidation with acidified $KMnO_4$ to give CO_2.**

✓ **F contains aldehyde and carboxylic acid.**

✓ **F forms ethanedioic acid and it undergoes further oxidation to form CO_2 only.**

❺ ✓ **G does not undergo condensation with 2,4–DNPH.**

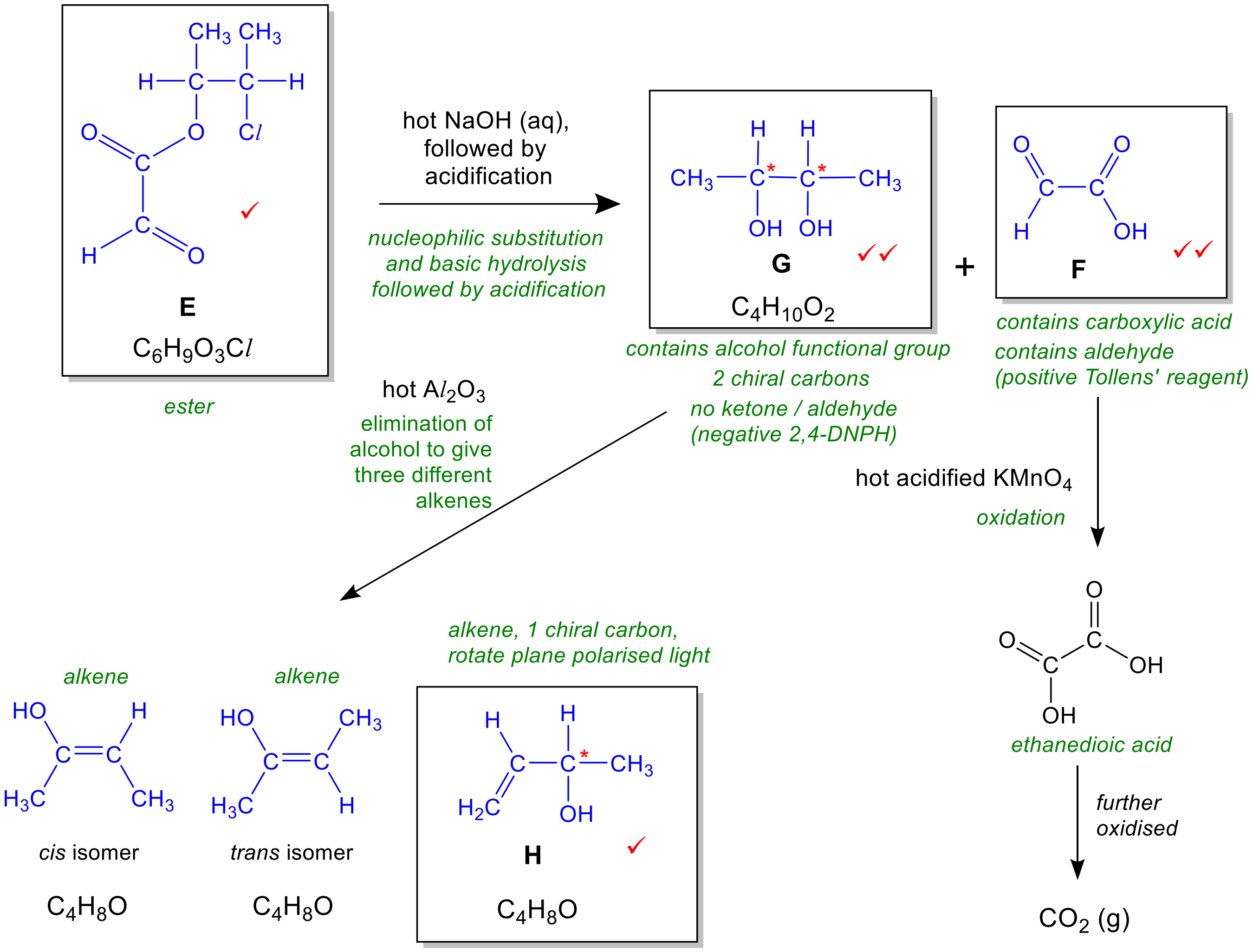
✓ **G does not contain aldehyde or ketone.**

❻ ✓ **G undergoes elimination with hot Al_2O_3.**

✓ **G contains alcohol. OR H contains alkene.**

❼ ✓ **H contains chiral carbon and does not have an internal plane of symmetry.**

[4] for 10 – 13 ✓
[3] for 6 – 9 ✓
[2] for 4 – 5 ✓
[1] for 2 – 3 ✓



ester

nucleophilic substitution and basic hydrolysis followed by acidification

contains alcohol functional group
2 chiral carbons
no ketone / aldehyde
(negative 2,4-DNPH)

contains carboxylic acid
contains aldehyde
(positive Tollens' reagent)

elimination of alcohol to give three different alkenes

oxidation

alkene

alkene

alkene, 1 chiral carbon, rotate plane polarised light

ethanedioic acid

further oxidised

Structure - [1] for every 2 ✓

Markers' Comments

The deductive statements for functional groups and the type of reactions were generally well-attempted.

Common mistakes for FGs include using inappropriate terms / representation

- carbonyl compound ➔ correct version should be aldehyde and ketone
- -COOH ➔ correct version should be carboxylic acid
- -OH ➔ correct version should be alcohol

Many candidates struggled with elucidating the structures of **H** & **E**.

[Total: 24]

[Turn over

Section B

Answer **one** question from this section.

Marker's Comments
- Markers' Comments: 48% of the candidates chose Q4 and 52% chose Q5.
- Candidates scored better for Q4 than Q5, mainly because Q5 has a fair bit of bookwork questions which were not well answered. Hence candidates should choose the questions which they can score more marks in.

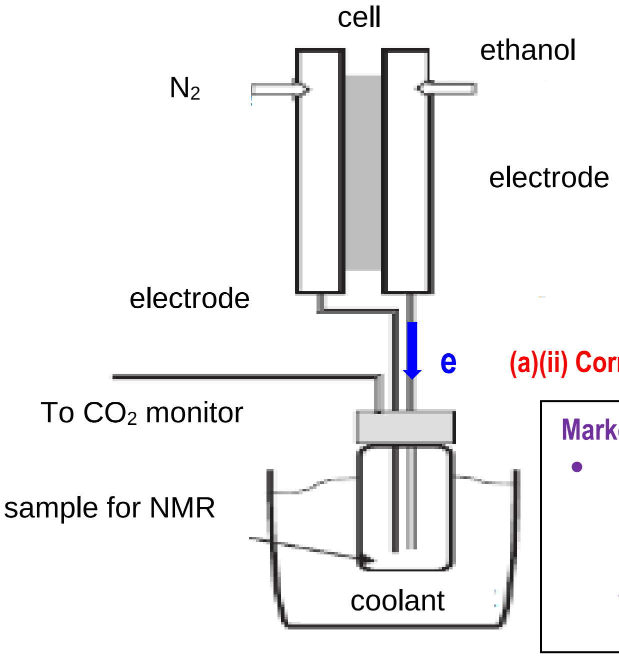
4 Ethanol has numerous important applications across various industries, making it a vital compound in our daily lives.

(a) Ethanol was electrolysed at different voltages in one research experiment. To achieve high energy efficiencies in cells, the yield of carbon dioxide in Equation 1 must be high.

Equation 1: $CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e$

However, in practice, low yields of CO_2 have generally been reported, with the major products being ethanal and ethanoic acid. The three products at the anode, ethanoic acid, ethanal and carbon dioxide, were collected and analysed.

The amounts of ethanol consumed, and products were determined by proton nuclear magnetic resonance (NMR) spectroscopy while CO_2 was measured with a non-dispersive infrared CO_2 monitor.



(a)(ii) Correct direction of electron flow [1]

Marker's Comments
- Candidates need to know that electrons flow from anode (ethanol present) to cathode (nitrogen) and use the wires in Fig.4.1 to indicate the electron flow.

Fig. 4.1

(i) Write the two half-equations, for the reactions involving ethanol occurring at the anode to account for the two major products, ethanoic acid, ethanal.

[2]

$CH_3CH_2OH \rightarrow CH_3CHO + 2e + 2H^+$ [1]

$CH_3CH_2OH + H_2O \rightarrow CH_3CO_2H + 4e + 4H^+$ [1]

Marker's Comments
- Balancing half-equations proved to be challenging. Additionally, candidates need to present the structural formula of aldehydes correct ($C_nH_{2n+1}CHO$), in this case ethanal as CH_3CHO instead of CH_3COH.

(ii) Draw and label the direction of electron flow in the cell on Fig. 4.1. [1]

The percentages of products (ethanoic acid, ethanal and carbon dioxide) using catalyst mounted on a carbon anode, platinum (Pt/C) are shown in Fig. 4.2.

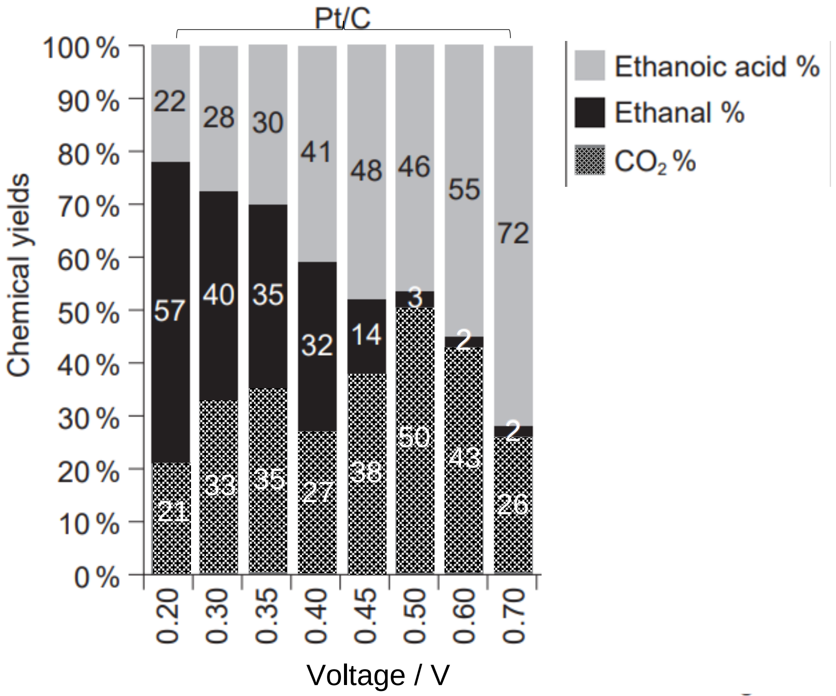


Fig. 4.2

[Source: Product Distributions and Efficiencies for Ethanol Oxidation in a Proton Exchange Membrane Electrolysis Cell, Rakan M. Altarawneh and Peter G. Pickup, Journal of the Electrochemical Society, 2017, volume 164, issue 7, http://jes.ecsdl.org/]

(iii) Describe what happens to the chemical yield of ethanal using Pt/C as a catalyst when the voltage increases. [1]

Yield **decreases** **[1]**

Marker's Comments

- This question was generally well attempted. Many candidates were able to differentiate ethanal using the diagram and observed a decreasing trend in chemical yield.

(iv) With reference to Fig. 4.2 and Equation 1, calculate the rate of reaction of carbon dioxide, in molecules per minute, that produces a current of 1.00 A at 0.50 V using Pt/C as a catalyst. [3]

From Fig. 4.2: 0.50 V will give **50% yield** of CO_2.

Quantity of charge per minute = 1.00 × 60 = 60 C **[1]**

Amount of electrons transferred per minute $= \frac{60}{96500} = 6.218 \times 10^{-4}$ mol

$1CO_2 \equiv 6e^-$

Amount of CO_2 reacted per minute $= \frac{6.218\times10^{-4}}{6} = 1.036 \times 10^{-4}$ mol **[1]**

Rate of reaction of CO_2 (No. of CO_2 molecules reacted per minute, 50% yield)

$= (1.036 \times 10^{-4})(6.02 \times 10^{23})(0.5)$ **[1]**

= **3.12×10^{19} molecules per minute** **[1]**

Marker's Comments

Many candidates found this question challenging, some common errors include,

1. Equating the no.of moles of electron to 12 instead of 6. $1CO_2 \equiv 6e^-$ (Eqn 1)
2. Not understanding the Q = It (t is in s), question asked for per min, hence the time is 60s.
3. Not realising the yield of CO_2 is only 50% (Fig 4.2)
4. Not finding the number of molecules using Avogadro's constant.

(b) Ethanol is also being investigated as a fuel in fuel cells.

The equation for the complete combustion of 1 mol of ethanol is shown below.

$$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

(i) The standard enthalpy change of combustion of ethanol, $\Delta H^\ominus_c$, has a value of –1367 kJ mol^{-1}, and the entropy change for the same process is –140 J mol^{-1} K^{-1}.

Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the combustion of ethanol at 298K.

[1]

$$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus = -1367 - (298)\left(-\frac{140}{1000}\right)$$

$= \underline{-1330 \text{ kJ mol}^{-1}}$ **[1, $\Delta S^\ominus$ into kJ mol^{-1} K^{-1}]**

Marker's Comments

- This question was generally well attempted. Many candidates were able to convert $\Delta S^\ominus$ into kJ mol^{-1} K^{-1} and determine the temperature to be 298K (standard conditions).

(ii) Account for the negative sign of ΔS for the complete combustion reaction of ethanol. [1]

ΔS is negative. There is **a decrease in the number of gaseous molecules from 3 mol to 2 mol**. The system becomes less disordered. Entropy decreases **[1]**

(iii) Hence, comment on the effect of decreasing temperature on the spontaneity of the reaction. State any assumption that must be made for your comment to be valid.

[2]

At lower T, **$|T\Delta S| < |\Delta H|$**

Hence, **$\Delta G < 0$ at lower temperatures.**
As the temperature of the reaction decreases, **$\Delta G^\ominus$ becomes more negative**.

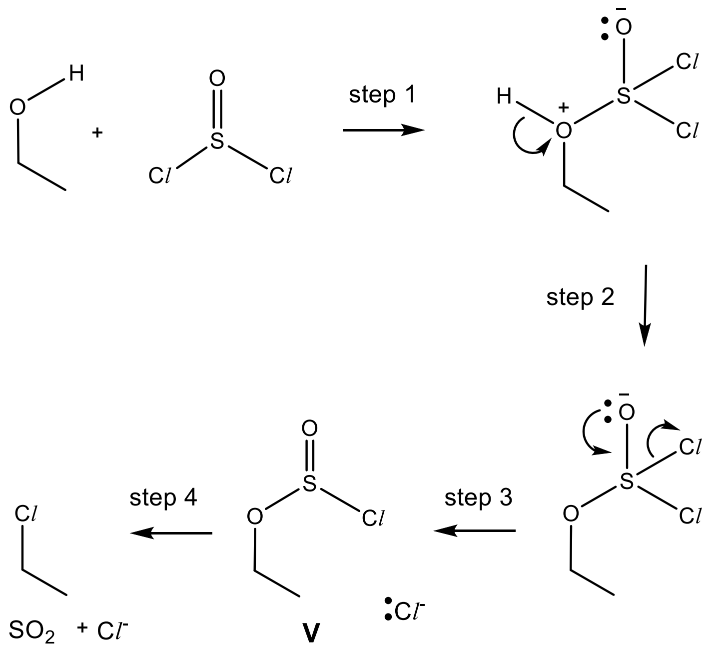
The reaction is **spontaneous at lower temperature**. **[1]**

Assumption is that **$\Delta H^\ominus$ and $\Delta S^\ominus$ remains constant / are unaffected by temperature change**. **[1]**

Marker's Comments

- This question was generally well attempted. Some candidates mistakenly use Le Chatelier's principle to explain not realising there is no equilibrium established when considering the complete combustion of ethanol.
- There were 2 parts to this question, quite a number of candidates did not address the assumption part correctly, spontaneity of reaction is linked to ΔG, the consideration should be in regards to variables in the equation, $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$.

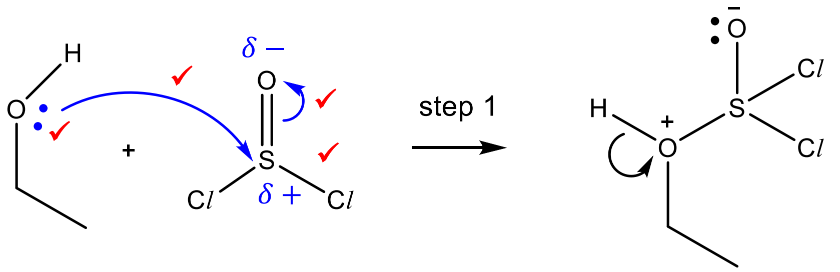
(c) The mechanism for the reaction of ethanol with $SOCl_2$ in the presence of base is shown in Fig. 4.3.



The reaction of **V** with Cl^- ions in step 4 proceeds via an S_N2 mechanism. Sulfur dioxide is a by-product of this reaction.

(i) Complete the mechanism for step 1 on Fig. 4.3 by adding a lone pair, curly arrows and a dipole.

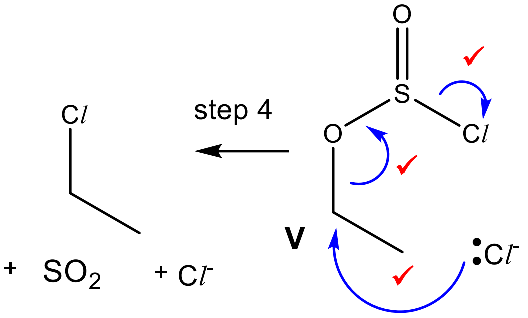
[2]



2 ✓ [1], 4✓ [2]

(ii) Complete the mechanism for step 4 on Fig. 4.3 by adding **three** curly arrows.

[2]



1-2 ✓ [1], 3✓ [2]

Marker's Comments

- This question's format was modelled after a recent A-level question, candidates need to know that a dipole consists of positive δ+ and negative δ- partial charges in a covalent bond, hence the S and O will adopt δ+ and δ- respectively based on their electronegativities.
- Arrows pushing indicate the electron movement, hence arrows start from source of electrons to an area that is electron deficient. Candidates should also get hints from the new compounds formed, indicating new bonds were formed after movement of electrons.

(d) Compound **W** can be used to synthesise compound **Z** by the four–step route shown in Fig. 4.4.

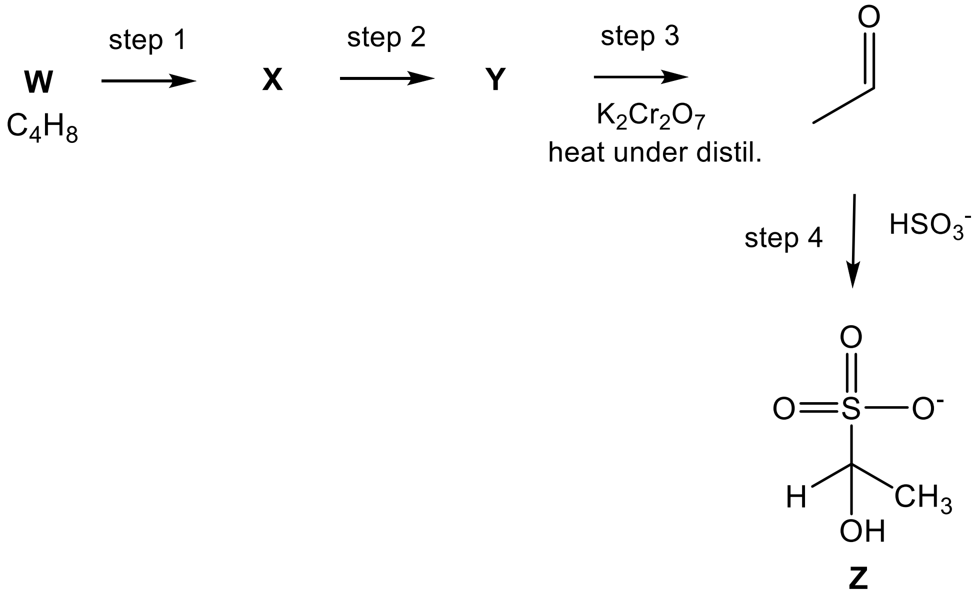
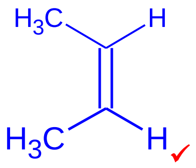
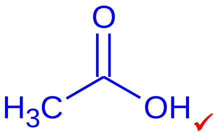


Fig. 4.4

(i) State the reagents and conditions required for each of the step from steps 1–2 and suggest structures for the organic compounds **W**, **X**, and **Y**. [3]

Step 1: **$KMnO_4$ / H_2SO_4(aq), heat** ✓
Step 2: **$LiAlH_4$, dry ether, r.t.p** ✓

W:


X:


Y: **CH_3CH_2OH** **[1]**

[2] – 3 to 4 ✓
[1] – 1 to 2 ✓

Marker's Comments

- To solve this question, candidates need to deduce the structure of Y to be ethanol (2 carbon structure) since it undergone oxidation (heat under distillation) to form ethanal (2 carbon structure).
- Candidates need to have firm foundation of their reagents and conditions for the organic reactions in order to do well.

(ii) Oxygen was accidentally added to **step 4** in Fig. 4.4.

Table 4.1

Electrode reaction	$E^\ominus$/ V
$HSO_3^- + 5H^+ + 4e^- \rightleftharpoons HS^- + 3H_2O$	–0.11
$SO_4^{2-} + 3H^+ + 2e^- \rightleftharpoons HSO_3^- + H_2O$	+0.54

Use data from the *Data Booklet* and Table 4.1 to predict whether a side reaction between oxygen and HSO_3^- can occur. Explain your reasoning.

[2]

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^\ominus = +1.23$ V
$SO_4^{2-} + 3H^+ + 2e^- \rightleftharpoons HSO_3^- + H_2O$ $E^\ominus = +0.54$ V

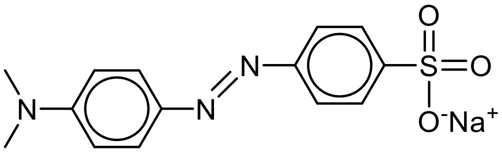
Overall : $2HSO_3^- + O_2 \rightarrow 2SO_4^{2-} + 2H^+$

$E^\ominus_{cell} = E^\ominus_{red} - E^\ominus_{oxid}$
$= +1.23 - (0.54)$ **[1]**
$=$ **+0.69 V > 0** $\Rightarrow$ Reaction is **spontaneous** **[1]**

Marker's Comments

- E_{cell} of the reaction needs to be found to determine whether the reaction is feasible.
- Candidates must consider the $E_{O2/H2O}$ = +1.23V from Data Booklet since oxygen is present in acidic medium (HSO_3^-) and established that oxygen will undergo reduction while HSO_3^- will undergo oxidation meaning HSO_3^- needs to be at the RHS of the standard electrode potential equation, hence E_{oxid} should be +0.54 V and not -0.11 V even though the value is more negative.

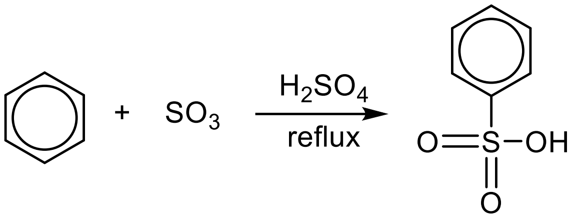
5 **(a)** Methyl orange is an azo dye which is commonly used as a pH indicator in titrations because of its clear and distinct colour change at different pH values and its structure is given below.



methyl orange

A precursor compound used in the synthesis of methyl orange is benzenesulfonic acid, which is produced by heating benzene with fuming sulfuric acid under reflux in **reaction I** shown in Fig. 5.1. Fuming sulfuric acid is a concentrated solution of sulfur trioxide, SO_3, in sulfuric acid, H_2SO_4.

reaction I:

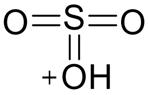


benzenesulfonic acid

Fig. 5.1

Reaction I is an electrophilic substitution reaction which involves the following steps.

- The first step involves the protonation of SO_3 by H_2SO_4 to form HSO_3^+. The structure of HSO_3^+ is shown.



$$O{=}\underset{\overset{||}{+OH}}{S}{=}O$$

- In the second step, benzene reacts with HSO_3^+ to form an intermediate.
- In the last step, the stable benzene ring is restored to form benzenesulfonic acid and H_2SO_4 is regenerated at the end of the reaction.

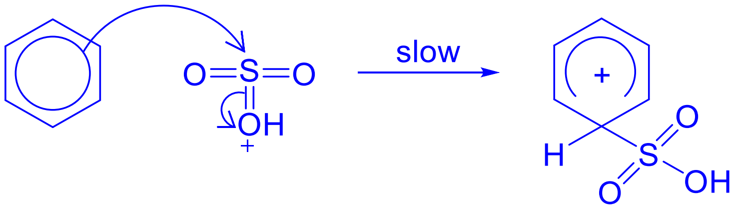
(i) Outline the mechanism occurring in **Reaction I** to form benzenesulfonic acid. Include all relevant charges, lone pairs of electrons and curly arrows.

[3]

Electrophilic substitution

Step 1: $SO_3 + H_2SO_4 \rightleftharpoons HSO_3^+ + HSO_4^-$ **✓ Equation**

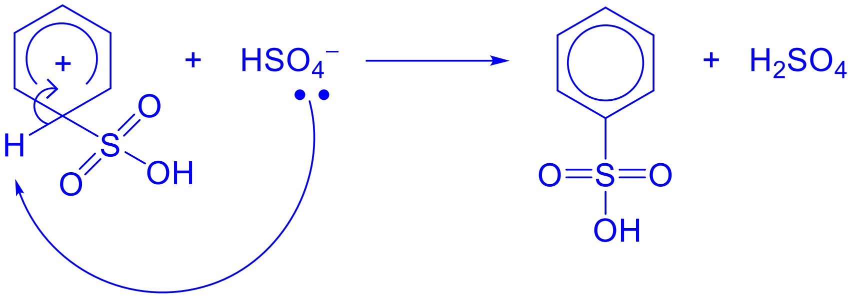
Step 2:



✓ curly arrow from benzene to S in HSO_3^+ **✓ slow** **✓ carbocation intermediate**

✓ curly arrow from double bond to O

Step 3:



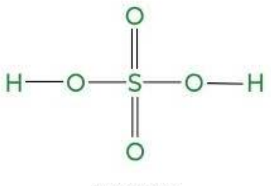
✓ curly arrow from C–H bond to +vely charged ring **✓ both products**

✓ lone pair on O in HSO_4^-

✓ curly arrow from lone pair on O to H

Marker's Comments

- In general, candidates were able to draw this electrophilic substitution mechanism based on the information given in the question as well as their knowledge of the mechanism from the syllabus.
- It is important to take note not to combine steps 2 and 3 together as this will result in the equations not being balanced.
- Several candidates attempted to draw the arrow pushing for step 1 but were not accurate.
- For those who attempted to draw the structure of H_2SO_4, H_2SO_4 looks like this, where the H atoms are bonded to the O atoms



Sulfuric Acid

7 – 9 ✓ [3]

4 – 6 ✓ [2]

2 – 3 ✓ [1]

Diazotization is the process of converting primary aromatic amines into its diazonium salts. Diazonium salts are important synthetic intermediates that can undergo “coupling reactions” to form azo dyes.

Fig. 5.2 shows the reaction scheme of how methyl orange can be formed from a primary aromatic amine.

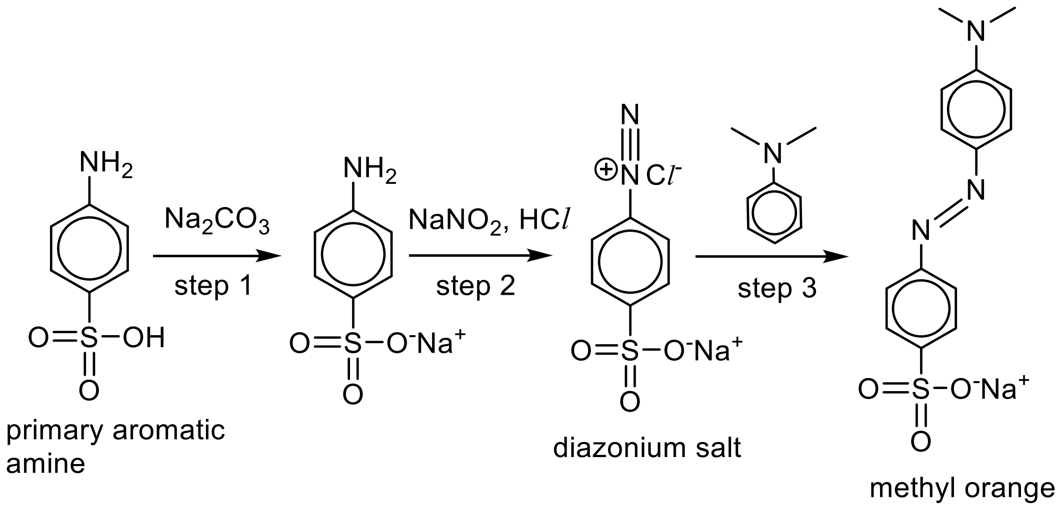


Fig. 5.2

(ii) Suggest the type of reaction for step 1 and step 3. [2]

Step 1: acid – base reaction OR acid – carbonate reaction [1]

Step 3: electrophilic substitution [1]

Marker’s Comments

- Most candidates were able to see that step 1 is an acid-base reaction between sodium carbonate and the benzenesulfonic acid
- For step 3, several candidates mistook this as a condensation reaction. This is an electrophilic substitution reaction as the diazonium ion is acting as an electrophile, reacting with the benzene ring of N,N-dimethylphenylamine and replacing the H atom in a substitution reaction.

(b) When compound **L** is reacted with Cl_2 dissolved in CCl_4, compounds **M** and **N** are two of the products formed, as shown in Fig. 5.3.

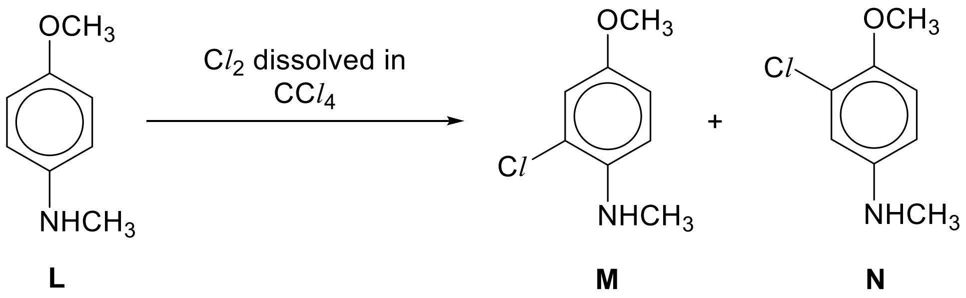


Fig. 5.3

Suggest why compound **M** will be formed in a greater proportion.

[1]

M will be formed in a greater proportion as **–$NHCH_3$ group is more activating** than the –OCH_3 group since **nitrogen is less electronegative than oxygen** **[1]** and **directs** the electrophilic substitution to occur more at the **2–position relative to –$NHCH_3$**. For –$NHCH_3$, the lone pair of electrons on N is more readily delocalised into the benzene ring, **increasing the electron density** of the benzene ring. (or words to the same effect)

Marker's Comments

- This question was not well attempted.
- Both the -$NHCH_3$ and -OCH_3 are activating groups and hence comparison must be made between the two to emphasise that -$NHCH_3$ is more activating because nitrogen is less electronegative than oxygen.

(c) Fig. 5.4 shows the synthesis of compound **Q** from but-2-ene.

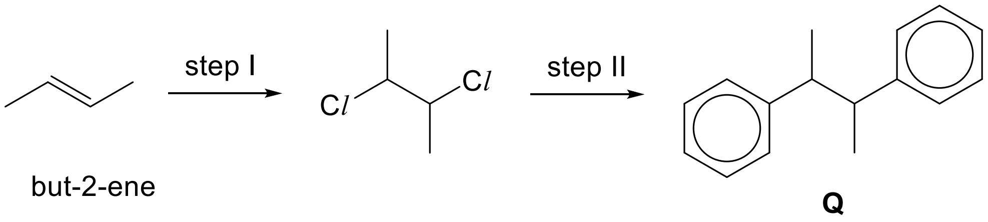


Fig. 5.4

(i) Describe the C=C bond in but-2-ene with reference to the hybridisation of the carbon atoms and orbital overlap.

[2]

$H_3C^{\alpha}C^{\beta}H{=}C^{\beta}HC^{\alpha}H_3$

hybridisation: sp^2 for C^{β}

$C^{\beta}-C^{\beta}$ σ bond is formed by $2sp^2-2sp^2$ head-on orbital overlap

$C^{\beta}-C^{\beta}$ π bond is formed by 2p−2p sideway orbital overlap

[1] for hybridisation / hybridised orbitals

[1] for describing orbital overlap

Marker's Comments

- This question was generally well attempted.
- Candidates need to recognise that the hybrid orbitals are **sp^2** and not sp orbitals.

(ii) Suggest the reagents and conditions required for step II. [1]

(excess) **benzene, $AlCl_3$** (or $FeCl_3$) **[1]**

Marker's Comments

- Many candidates were able to recall the reagents and conditions needed for this electrophilic substitution reaction.

There are three different types of compound **Q** molecules, namely **R**, **S** and **T** molecules.

- molecule **R** has no effect on plane-polarised light
- molecule **S** rotates plane-polarised light by 15° to the left
- molecule **T** rotates plane-polarised light by 15° to the right

(iii) Explain why molecule **R** has no effect on plane-polarised light. [1]

R has a plane of symmetry and the mirror images are superimposable on each other. [1]

OR

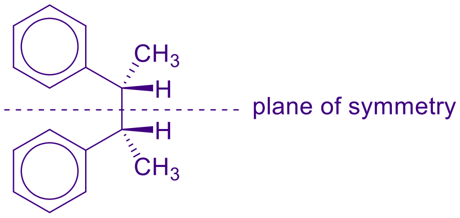
One chiral carbon rotates the plane polarised light to the right and the other chiral carbon rotates the plane polarised light to the left by the same amount, resulting in no net rotation.

OR

R has a **plane of symmetry** and it is optically inactive as the **optical activity of one chiral carbon exactly cancels the optical activity of the other chiral carbon.**

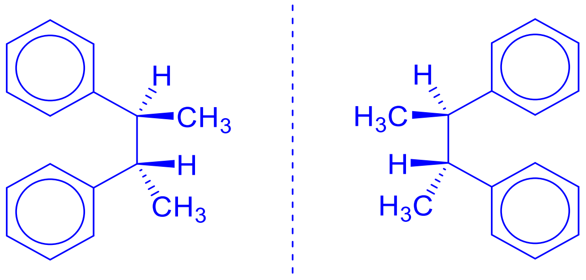
Marker's Comments

- Some candidates were mistaken and thought that there were no chiral C atoms in compound **R**. There are in fact 2 chiral C atoms in **R** and the structure of **R** is this:



(iv) Draw the structures of molecules **S** and **T**.

[1]



Structures of **S** and **T**: **[1]**

Marker's Comments

- **S** and **T** are mirror images of each other. The above is the accurate drawing for **S** and **T**. Most candidates only showed the 3 D shape about 1 chiral C when in fact the 3 D shape should be drawn about the 2 chiral C atoms.

(d) **(i)** Describe the reactions, if any, of the chlorides $NaCl$, $AlCl_3$, and PCl_5, with water. Write equations for all reactions that occur, and suggest the pH of the resulting solutions. Relate the reactivity of these chlorides to their structure and bonding.

[5]

$NaCl$ **dissolves readily** in water to form a neutral solution of **pH 7** . ✓

Hydration: $\mathbf{NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)}$ ✓

$AlCl_3$ **dissolve readily** in water to form an acidic solution of **pH 3** ✓ due to appreciable hydrolysis.

$\mathbf{AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)}$ ✓

$\mathbf{[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)}$ ✓

PCl_5 **reacts** with water (readily hydrolyses in water) to form white fumes (of HCl) to form a strongly acidic solution of **pH 2**. ✓

$\mathbf{PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)}$ ✓

$NaCl$ is **giant ionic with ionic bonds** (Or **electrostatic forces of attraction between oppositely charged ions)** ✓ ; it undergoes **hydration** (only) or **ion-dipole interactions with water**. ✓

$AlCl_3$ and PCl_5 are **simple molecular** and **covalent bonds** ✓ exist between atoms within the molecules; they undergo **hydrolysis**. ✓

State symbols are not required for equations.

Marker's Comments

- This is a standard bookwork question on Periodicity and candidates are expected to do their bookwork well.
- When the questions asked for reactivity, it is referring to the interaction with water in terms of **hydration** or **hydrolysis**.
- Take note that is $AlCl_3$ is simple molecular and not giant ionic.
- Candidates need to make mention that both $AlCl_3$ and PCl_5 are covalent.
- For the reaction involving $AlCl_3$, the following equation is not relevant and applicable here since the question is asking for the **resulting solutions** and for this equation involving limited water, the products will involve the white solid of $Al(OH)_3$ and HCl gas, which is not a solution. Hence the equation was not accepted.
  $AlCl_3(s) + 3\ H_2O\ (l) \rightarrow Al(OH)_3\ (s) + 3\ HCl\ (g)$

10 – 11 ✓ [5]
8 – 9 ✓ [4]
6 – 7 ✓ [3]
4 – 5 ✓ [2]
2 – 3 ✓ [1]

(ii) Table 5.1 gives the melting points, in °C, of the fluorides and chlorides of three elements in Period 3.

Table 5.1

	sodium	magnesium	silicon
fluoride	993	1261	–90
chloride	801	714	–70

Explain the differences in melting points between

- NaC*l* and MgC*l*$_2$ [1]

Both NaC*l* and MgC*l*$_2$ have giant ionic lattice structures.

Mg^{2+} has **higher charge density** (as compared to Na^+) and **polarises C*l*$^-$ anion electron cloud** to some extent, resulting in some **covalent character in the ionic bonding, weakening the ionic bond** **[1]** / electrostatic forces of attraction between Mg^{2+} and C*l*$^-$ ions, less energy required to overcome the bonds in MgC*l*$_2$ and hence lower melting point.

Marker's Comments

- Candidates need to be careful when reading the data of melting point given. Several candidates misread the question thinking that the melting point of MgC*l*$_2$ is higher than that of NaCl and hence answered incorrectly.

- MgF_2 and SiF_4, [2]

MgF_2 has giant ionic lattice structure and SiF_4 has a simple molecular structure. **Larger amount of energy** is required to **overcome the stronger electrostatic force of attraction between oppositely charged ions, Mg^{2+} and F^- ions** **[1]** than the **weaker intermolecular instantaneous dipole-induced dipole attraction** **[1]** in SiF_4. MgF_2 has a higher melting point than SiF_4.

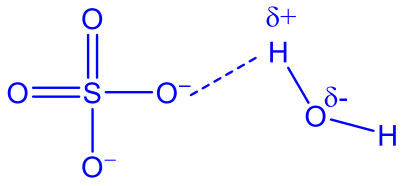
Marker's Comments

- This question was generally quite well done. Candidates need to be careful with usage of proper technical terms to describe structure and bonding.

(iii) Unlike magnesium fluoride which is highly insoluble in water, magnesium sulfate exhibits high solubility in water. When magnesium sulfate dissolves, the anions and cations are each surrounded by water molecules.

Draw a simple diagram to show how a water molecule can be attached to a sulfate anion. Label the diagram to show the type of interaction involved.

[1]



------ ion-dipole interaction

[1] for anion

[Total: 20]

Marker's Comments

- Candidates need to take note to label the diagram clearly with the relevant dipoles on water.
- The ions dissolve in water through ion-dipole interactions, so the main interaction here should be ion-dipole interactions and the anion will form ion-dipole interaction with the delta plus end H atom of H_2O.