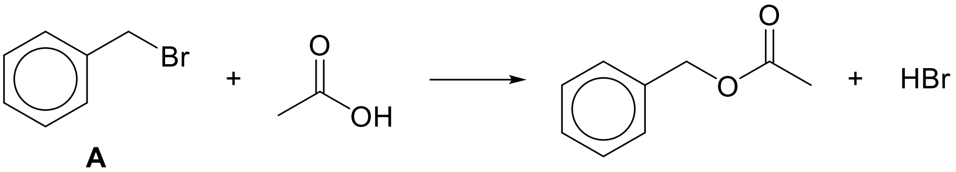
EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2023
General Certificate of Education Advanced Level
Higher 2

Paper 3 Suggested Solutions with Marker's comments

Section A

1 **(a)** Solvolysis is a reaction in which the solvent is one of the reagents and is also present in great excess of that required for the reaction. Usually, the electron-rich solvent molecule substitutes an atom or group in the reactant molecule.

One example of solvolysis is the reaction of compound **A**, $C_6H_5CH_2Br$, with ethanoic acid as the solvent.



This reaction happens *via* an S_N1 mechanism.

(i) Describe the mechanism for the reaction between compound **A** with ethanoic acid. Show relevant lone pairs of electrons, dipoles and curly arrows. [4]

(ii) Explain why this reaction mainly proceeds *via* the S_N1 mechanism. [1]

(iii) Given that the enthalpy change of the reaction is endothermic, draw a labelled reaction pathway diagram for the reaction involving compound **A** and ethanoic acid. [2]

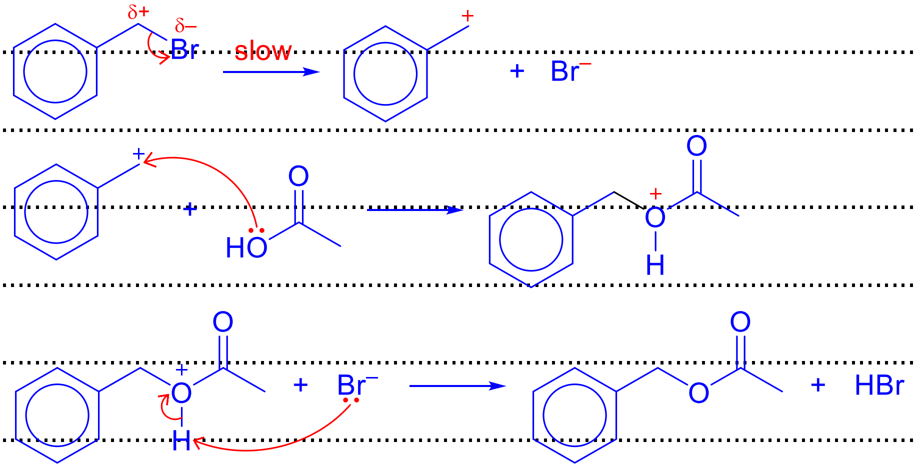
Another reaction was carried out using $C_6H_5CHBrCH_3$ with ethanol as the solvent, in the presence of trace amount of sodium hydroxide. This reaction undergoes the same mechanism as the reaction between compound **A** and ethanoic acid.

(iv) Predict the major organic product formed from the reaction of optically pure $C_6H_5CHBrCH_3$ with ethanol, and comment on the optical activity of the product formed. Briefly explain your answer. [3]

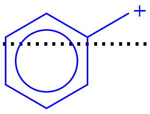
(v) By-products are formed during the preparation of many organic compounds. This usually occurs because the reagents can react in more than one way.

Suggest a possible by-product, in full structural formula, that can be formed from the above reaction. [1]

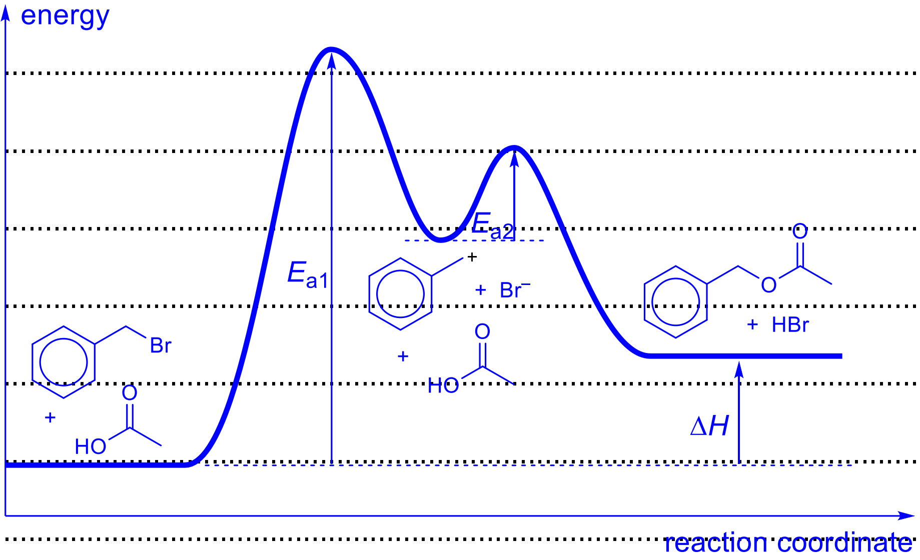
(i)



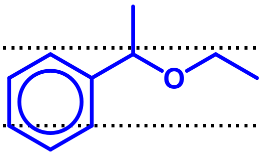
partial charges, slow step, correct carbocation
all correct arrows and lone pairs of electrons
deprotonation and formation of HBr

(ii) Heterolytic fission of C-Br bond in (bromomethylbenzene) forms a **stable benzylic carbocation intermediate**,  , which is stabilised by the **delocalisation of the positive charge into the benzene ring**

(iii)

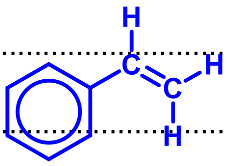


(iv)



The carbocation is **trigonal planar about the positively charge C**, thus the ethanol nucleophile can **attack from either side of the plane with equal probability**, leading to formation of **an equimolar mixture of two enantiomeric products**.

(v)



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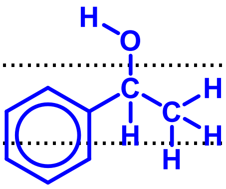


Comments:

(i) is generally well attempted as students showed some understanding of S_N1 mechanism.

(ii) is poorly done. Many students were not able to provide the correct answer.

(iii) is poorly done. While students were able to draw the overall shape of an energy profile diagram, many lose marks due to insufficient labelling.

(iv) is poorly done. Some students showed a lack of understanding of the context of the question i.e. solvolysis. In addition, while students showed knowledge of the properties of S_N1 mechanism, many students were rather vague in their answers and used the wrong terminology.

(v) is generally well attempted.

- **Question analysis and references (where applicable)**

(i) is testing on application of S_N1 mechanism when the nucleophile is a carboxylic acid. Students should also keep in mind that once the bond is formed between O of the acid with C of compound A, there should also be a deprotonation step to remove the H+ bonded to O of the carboxylic acid functional group.

(ii) Students should answer why S_N1 is occurring and not explain why S_N2 will not occur. Students should answer directly to the question of why S_N1 proceeds.

(iii) A reaction pathway diagram is an energy profile diagram. Given that it is an endothermic reaction and with a slow step (S_N1), students should keep in mind the number of peaks in the diagram.

(iv) The starting material has changed. Apply solvolysis (the same mechanism) to the reaction between $C_6H_5CHBrCH_3$ and ethanol to derive the product.

(v) Given that $C_6H_5CHBrCH_3$ and ethanol are reacted in the presence of trace amount of NaOH, NaOH can serve as base (elimination) or a competition nucleophile (nucleophilic substitution).

- **Common mistakes:**

(i) – did not show the removal of H^+ after the protonated produce is formed from the second step.

– Br^- formed at the end of slow step extracted H^+ from the acid. This will not occur as Br^- is not a strong enough base to cause the dissociation of carboxylic acid.

– Showing the simultaneous breaking of C-Br and the attacking of the ethanoic acid nucleophile at the α-carbon.

– Drawing S_N2 even when the question has specified S_N1.

– Did not balance the equation with formation of HBr.

(ii) – Steric hindrance due to the bulky benzene ring is the most common mistake. While benzene is considered a bulky group, it is a planar molecule. As such, when bonded to the α-carbon, it does not effectively block the approach of the nucleophile. Groups such as $(CH_3)_3C–$ are "better" bulky groups.

– Students who were able to correct identify stability of carbocation as the main factor, has the following common errors:

⇒ many stated benzene as electron donating group / electron rich group, thus dispersing the positive charge on C. The formal is incorrect as benzene is neither electron donating nor electron withdrawing. The later is incorrect as the answer is incomplete. Students need to make reference to the delocalisation of the positive charge to be awarded marks.

⇒ Some students also mentioned that benzene is electron rich and thus repels nucleophiles. While this is not wrong, this point should be used to explain why the nucleophilic attack does not occur to benzene.

⇒ Stating that the electron pair from the C^+ delocalises into the benzene. This would actually intensify the positive charge and make the carbocation less stable.

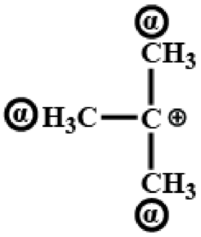
(iii) – Missing out ethanoic acid as one of the intermediates.
– Drawing a straight line parallel to the x-axis for the intermediates. The intermediate stage should be a point, not a duration.
– Did not draw the x-axis or labelled the x-axis incorrectly as time, reaction, energy or rate.
– Not labelling the diagram fully. E_{a1} and E_{a2} are often missing or incorrectly labelled.
– Not reading the question and drawing an exothermic diagram.
– Drew energy cycle instead.

(iv) – Did not read the question carefully. Both starting reactants have changed. Some students are answering the question using compound A and ethanol.
– Using -OH as the nucleophile to form $C_6H_5CH(OH)CH_3$ stating that -OH is a stronger nucleophile than ethanol. While this is true, do note that the context of the question is solvolysis, where the solvent is the nucleophile. Even though ethanol is a weaker nucleophile, in the presence of excess ethanol (as it is the solvent), the major product formed would be an ether. In addition, -OH group is only present in trace amount, even if -OH group has reacted to form the alcohol, the product would not be the major product.
– In terms of explaining racemic mixture, common errors are:

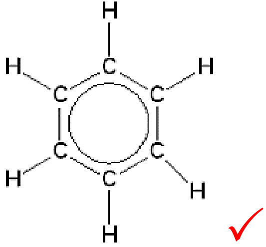
⇒ the carbocation is planar. Note that the shape about the positively charged carbon is trigonal planar, the entire carbocation is not.

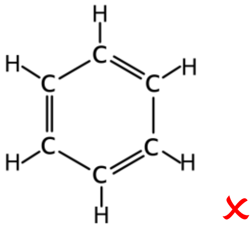
⇒ the carbon which is sp^2 hybridised in trigonal planar in shape. Note that the entire carbocation is made up of 7 sp^2 carbons (6 in the benzene, 1 that is positively charged), thus it is unclear which carbon is being referred to.

⇒ α-carbon of carbocation. This refers to the C directly bonded to the positively charged carbon. For example, in the diagram below, there are 3 α-carbons (marked with "α") present in the carbocation.



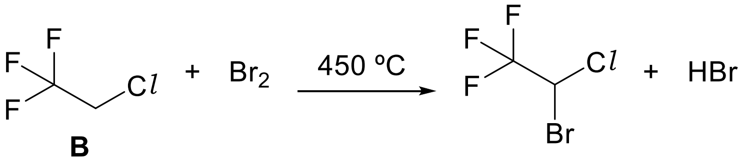
(v) – Did not draw full structural formula (also known as displayed formula). O-H bond has to be shown. However, there is no need to draw all bonds of a benzene ring. However, if it is to be drawn, students should draw the diagram on the left and not the one on the right.





(b) One of the possible methods to produce compound **A** is free radical substitution. This method can also be used to produce halothane, $CF_3CHBrCl$, a general anaesthetic.

(i) Halothane is formed from compound **B** via the following reaction.



With reference to data from the *Data Booklet*, calculate the enthalpy change of the above reaction. [1]

(ii) Suggest why the reaction can be carried out in the absence of uv light. [1]

(iii) Suggest a simple chemical test to distinguish compound **A** from compound **B**. [2]

In free radical reactions of organic compounds, side products such as hydrogen halides are often formed.

(iv) Explain why HF is less volatile than HBr. [2]

(v) With reference to data from the *Data Booklet*, explain the relative stability of HC*l* and HI when subjected to heat. [2]

(i) ΔH_r = ΣBE(bond broken) – ΣBE(bond formed)

= [BE(C–H) + BE(Br–Br)] – [BE(C–Br) + BE(H–Br)]

= (410 + 193) – (280 + 366) = –43 kJ mol^{-1}

(ii) Heat supplied (450 °C) is sufficient to break the Br–Br bond to generate Br radical, thus initiating free radical substitution.

(iii) To both compounds **A** and **B**, add ethanolic $AgNO_3$ and heat.

Compound **A** will produce **white ppt of AgC*l*** while compound **B** will produce **cream ppt of AgBr**.

(iv) Both HF and HBr have **simple** molecular structures.

HF forms intermolecular hydrogen bonding while HBr forms **intermolecular permanent dipole-permanent dipole interaction**.

Thus, more energy is required to overcome the **stronger hydrogen bonding** in HF than the **weaker permanent dipole – permanent dipole interaction** in HI.

(v) I has a **larger atomic size (0.133 nm)** than C*l* **(0.099 nm)**, thus the **extent of orbital overlap** between H and I is **smaller** than that of H and C*l*. Thus, **HI is less stable** to heat than HCl.

or **Bond strength** and bond energy **is weaker** for H–I (**299 kJ mol^{-1}**) than H–C*l* (**431 kJ mol^{-1}**).

Thus, **HI is less stable** to heat than HC*l* as H-I bond is weak.

[Total: 19]

Comments:

- **(i) and (v)** was generally well attempted.
  (iii) and **(iv)** was badly answered, with may answers suggesting a lack of understanding of the question/lack of concept.
  Many answers to **(ii)** showed a clear lack of understanding of the question.

- **Question analysis**
  - **(i)** Bond breaking is endothermic, while bond forming is exothermic. To find enthalpy change of the reaction, consider the bonds that must be broken and the bonds that must be formed. Avoid counting all bonds that are the same on both sides of the equation.
  - **(ii)** Consider what uv light is required for. Since the question stem says that it's a free radical substitution reaction, the uv light would have been required for homolytic fission of Br-Br to generate the Br• radicals. Without uv light, what other sources of energy are there that provides the energy required for homolytic fission to occur?
  - **(iii)** **A** is a bromoalkane attached to a benzene ring, while **B** is a chloroalkane. What reagents and conditions can use to displace the halogen atoms to form halide ions and then test for it?
  - **(iv)** Lower volatility means lower boiling point. What type of compounds are HF and HBr? How to explain why HF has a higher boiling point than HBr?
  - **(v)** The covalent bonds in HX are broken when heated. How do we explain the relative ease of breaking the covalent bonds?

- **Common mistakes:**

(i) - Due to the skeletal formula shown, many omitted the C-H bond that would need to be broken in the reactant before a new C-Br bond can be formed. It should be noted that the number of bonds broken should be the same as the number of bonds formed in this case since the total number of molecules in the reactants and products did not change.

- A number of answers simply used the formula "BE bonds formed in products – BE bonds broken in reactants" without realising that bond breaking is endothermic, while bond forming is exothermic. These ended up with an incorrect overall endothermic reaction instead.

(ii) - Many realised the presence of heat supplied would be sufficient, but failed to elaborate why heat is required for the reaction to occur. Some tried describing the formation of electrophiles/nucleophiles from Br_2, completely ignoring the information given that a FRS had taken place.

- Some thought that the exothermic reaction would produce heat for the reaction to occur, not realising that if the initiation step cannot occur, the reaction would not be able to take place and hence no heat would be given out from the reaction.

(iii) - Many incorrect reagents and conditions were suggested. These include:-
  - neutral $FeCl_3$ (no phenol)
  - Br_2(aq) (no phenol in A, neither would benzene react)
  - Br_2(aq) with $FeBr_3$ / $AlBr_3$ (the water will destroy the Lewis acid catalyst)

- Some correctly suggested using $KMnO_4$(aq), H_2SO_4(aq), heat to distinguish **A** and **B**, but chose to focus on the less important observations such as formation of white ppt or stating white fumes observed instead of the main observation of purple $KMnO_4$ decolourising.

- Answers that realised that the halide ions needed to be freed from the halogen compound often lacked the proper conditions such as heat, or omitted the use of an appropriate nucleophile to substitute the halogen atom i.e. only using $AgNO_3$(*aq*) instead of $AgNO_3$ in ethanol. Some who chose to heat the compound with NaOH(aq) first did not specify an order for addition of excess HNO_3 followed by $AgNO_3$(aq).

(iv) - Majority incorrect thought that the covalent bonds were broken when volatility of substances was related to its boiling point.

- Few described the structures of the compounds. It was also very common for pd-pd to be identified as the main IMF present in HF.

(v) Few thought that ions were found in the H-X compounds and incorrectly quoted ionic radius instead of atomic radius.

2 This question deals with the chemistry of iron and its compounds.

(a) When iron metal is exposed to water and air, it undergoes a series of redox processes, forming rust, which contains mainly a hydrated form of iron(III) oxide.

Rusting occurs in 2 steps. In the first step, iron is initially oxidised to iron(II) ions by oxygen in the air.

equation 1 $2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

(i) State the relationship between the standard Gibbs free energy change, $\Delta G^\ominus$, and standard cell potential, $E^\ominus_{cell}$. Use this relationship to calculate $\Delta G^\ominus$ for the reaction in equation 1 and show that this step occurs spontaneously. [3]

(ii) A method of preventing corrosion is galvanisation, in which iron is coated with a thin layer of zinc.

Explain, with the help of relevant $E^\ominus$ values, how galvanisation helps to prevent the corrosion of iron. [2]

(i) $\boldsymbol{\Delta G^\ominus = -nFE^\ominus}$

$E^\ominus_{cell} = +1.23 - (-0.44) = \underline{\mathbf{+1.67\ V}}$

For the reaction given, 4 moles of electrons are involved per mole of O_2,

$\boldsymbol{\Delta G^\ominus = -nFE^\ominus_{cell} = -(4)(96500)(+1.67)}$

$= -644620\ J\ mol^{-1} = \underline{\mathbf{-645\ kJ\ mol^{-1}}}$

Since **$\Delta G^\ominus$ is negative**, this step occurs spontaneously.

(ii) $Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76\ V$

$Fe^{2+} + 2e^- \rightleftharpoons Fe$ $E^\ominus = -0.44\ V$

Since **$E^\ominus(Zn^{2+}|Zn)$ is more negative (or less positive) than $E^\ominus(Fe^{2+}|Fe)$**, **Zn is more readily oxidised than iron**. Hence, zinc will be oxidised instead of iron.

Comments:

- This question pertains to Electrochemistry Part 1 (Electrochemical cell)

- **Question analysis and references (where applicable)**
  A similar question has been covered in 2022 Nov/III/1(e)(v) where the relationship between the standard Gibbs free energy change, $\Delta G^\ominus$, and standard cell potential, $E^\ominus_{\text{cell}}$ has been asked. Hence, it is important for students to not only recognize their inverse relationship but rather know the equation of $\boldsymbol{\Delta G^\ominus = -nFE^\ominus}$. Students are reminded that it is important to include the correct units of $\Delta G^\ominus$ upon calculating its value.

  Galvanisation has also been covered in secondary chemistry as a viable method to delay rusting of iron since zinc in this context acts as the sacrificial metal that would be preferentially oxidsed over iron.

- **Common mistakes:**
  Several students cannot recall the equation of $\Delta G^\ominus = -nFE^\ominus$ and merely conclude that the reaction occurs spontaneously based on the positive $E^\ominus_{\text{cell}}$. However, this is not acceptable as the conclusion of spontaneity of the reaction is supposed to be based on the calculated value of $\Delta G^\ominus$ as the question asked for the calculation of $\Delta G^\ominus$ before showing that this reaction occurs spontaneously.

  A few students calculated $E^\ominus_{\text{cell}}$ wrongly when they multiply the $E^\ominus(\text{Fe}^{2+}|\text{ Fe})$ by 2 to compute the $E^\ominus_{\text{cell.}}$ They failed to recognize that $E^\ominus$ values are intrinsic properties similar to concentration that do not change with quantity. Values of n (which refers to the amount of electrons being transferred) are commonly mistook to be either 2 or 8 as well.

  In terms of explaining the galvanization process, candidates are reminded to compare the relative ease of zinc being oxidized as compared to iron. Zinc having a feasible reaction with oxygen and water alone would not suffice as reason for its use in galvanization.

(b) When carbon steel corrodes in an environment that contains carbon dioxide and calcium ions, a product mixture of $FeCO_3$ and $CaCO_3$ is obtained.

The thermal decomposition of anhydrous metal carbonates, $CaCO_3$ and $FeCO_3$ was investigated. A pure 1.0 g sample of each carbonate was separately heated using the set-up in Fig. 2.1.

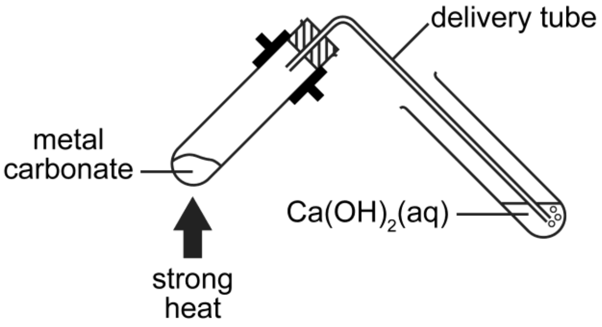


Fig. 2.1

The following observations were noted during the experiment.

carbonate	observations
$CaCO_3$	• white solid remains white • white ppt observed with $Ca(OH)_2$(aq) after some time.
$FeCO_3$	• greenish brown solid turns black. • white ppt observed in $Ca(OH)_2$(aq) after some time.

(i) Write a balanced equation, with state symbols, for the formation of the white precipitate in $Ca(OH)_2$(aq). [1]

(ii) With the aid of suitable data from the *Data Booklet,* explain the relative ease of decomposition of these two carbonates. [3]

(i) $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$

(ii) ionic radius of Fe^{2+} = 0.061 nm; ionic radius of Ca^{2+} = 0.099nm

Fe^{2+} is **smaller** than Ca^{2+} and has a **higher charge density** and **polarising power.**

Hence it **distorts the electron cloud of the CO_3^{2-} anion**, and **weakens** the carbon-oxygen **bond within the anion to a greater extent**, resulting in $FeCO_3$ requiring less energy for thermal decomposition and **$FeCO_3$ decomposes more readily** than $CaCO_3$.

Comments:
This pertains to Periodic Table (Group 2).

- **Question analysis and references (where applicable)**
  A similar question has been covered in 2019 Nov/II/1(b)(i) where the thermal stability of group 2 carbonates were compared with transition metal containing carbonates. This concept is covered in Periodic Table (Group 2). It is important to understand that ease of decomposition of Group 2 carbonates depends on the ease of breaking C-O covalent bond in carbonate anion after the latter has been weakened due to polarising of electron cloud of the carbonate anion by the Group 2 cation.

- **Common mistakes:**
  Many students gave the equation for the thermal decomposition of the carbonates rather than the reaction of how limewater ($Ca(OH)_2$) reacts with carbon dioxide (not oxygen) evolved to give white ppt of $CaCO_3$(not CaO).

  Several students misquoted the wrong data such as electrode potential values, atomic radii from Data Booklet. Many students quoted the correct ionic radii but attributed thermal stability erroneously to magnitudes of lattice energies (or strength of ionic bonds) or covalent character in ionic bonds.

(c) Fig. 2.2 shows an electrolytic cell which is used to prepare potassium ferrate(VI), K_2FeO_4, a powerful oxidising agent.

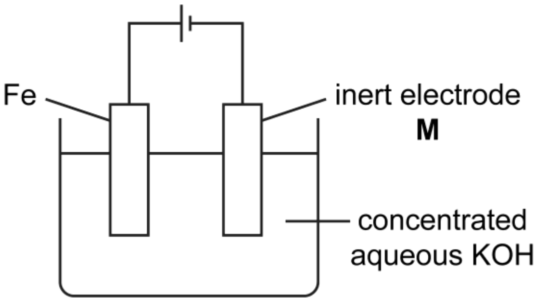


Fig. 2.2

(i) During the reaction, hydrogen gas is evolved at inert electrode **M** while the iron electrode is oxidised to ferrate(VI) ion as shown in the half equation below.

$$Fe(s) + 8OH^-(aq) \rightarrow FeO_4^{2-}(aq) + 4H_2O(l) + 6e^-$$

Construct the overall reaction occurring in the electrolytic cell, showing your working. [1]

(ii) 0.28 g of Fe was consumed when a current of 0.98 A was drawn from the battery for 50 minutes. By calculating the total electrical charge transferred, determine a value for the Avogadro's constant. [2]

(i) Reduction: $\mathbf{2H_2O(l) + 2e^- \rightarrow 2OH^-(aq) + H_2(g)}$ **(×3)**

Oxidation: $Fe(s) + 8OH^-(aq) \rightarrow FeO_4^{2-}(aq) + 4H_2O(l) + 6e^-$ **(×1)**

Overall: $\mathbf{Fe(s) + 2OH^-(aq) + 2H_2O(l) \rightarrow FeO_4^{2-}(aq) + 3H_2(g)}$

or $Fe(s) + 2KOH(aq) + 2H_2O(l) \rightarrow K_2FeO_4(aq) + 3H_2(g)$

(ii) amount of Fe consumed = $0.280 / 55.8 = 5.018 \times 10^{-3}$ mol

amt of electrons used in consuming Fe = $6 \times 5.018 \times 10^{-3}$

= 3.011×10^{-2} mol

total charge drawn = $0.98 \times 50 \times 60$ = **2940 C**

total number of electrons in 2940 C = $2940 \div (1.60 \times 10^{-19}) = 1.8375 \times 10^{22}$

Avogadro's constant = $(1.8375 \times 10^{22}) \div (3.011 \times 10^{-2})$ = $\mathbf{6.10 \times 10^{23}}$

Comments:

- This question pertains to Electrolysis and Redox.

- **Question analysis and references (where applicable)**

This question test on whether students are aware of the alkaline medium of the electrolyte in terms of selection of the appropriate reduction half equation in the construction of the overall redox equation.

In addition, students are tested on whether they know how to derive the experimental Avogadro's constant from the given experimental data in this electrolysis experiment.

- **Common mistakes:**

Many students failed to recognise the alkaline medium of the electrolyte and misquoted $2H^+ + 2e^- \rightleftharpoons H_2$ as the reduction. Students are reminded to check their equation and that H^+ and OH^- are not likely to co-exist in the same redox equation. Reversible arrows are not allowed in the overall equation as well.

Many students failed to compute the experimental value of Avogadro's constant as they are fixated on the value of Faraday's constant being 96500 rather than the amount of electrical charge carried by 1 mol of electrons.

(d) Fig. 2.3 shows some reactions involving potassium ferrate(VI).

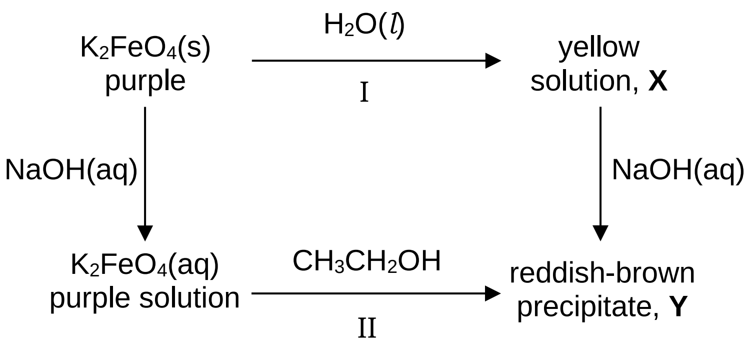


Fig. 2.3

Precipitate **Y** and the complex ion in solution **X** both contain iron, oxygen and hydrogen. The oxidation number of iron in **X** is the same as that in **Y**.

(i) Suggest the formula of the precipitate **Y** and the complex ion in solution **X**. [2]

(ii) Explain why solution **X** is yellow in colour. [3]

(iii) Vigorous effervescence of a colourless gas is observed in step I.
Suggest the identity of the gas evolved in this step. [1]

(iv) Given that step II also produces **Z**, C_2H_4O, state the role of K_2FeO_4 in step II. Hence, suggest the structure of **Z**. [2]

(i) **X**: **$[Fe(H_2O)_6]^{3+}$**

Y: **$Fe(OH)_3$**

(ii) The presence of water **ligands split** the **partially filled 3d-orbitals** of Fe^{3+} into two different sets, resulting in a **small energy gap** between them. **Visible light** that has a wavelength which corresponds to the energy gap is **absorbed to promote a 3d-electron from an orbital of lower energy to an orbital of higher energy**. The **colour observed** (yellow) is **complementary** to the colour of the visible light which is **absorbed** (violet).

(iii) oxygen gas

(iv) oxidising agent

Z is **CH_3CHO**

Comments:

- This question pertains to Transition metals, redox and inorganic QA

- **Question analysis and references (where applicable)**

Colours of iron(iii) hydroxide and aqueous iron(iii) ion containing solutions were already observed in 2023 EJC Prelims Paper 4 Qn3. As for the explanation on why solution X is coloured is a common A-level question that has been covered extensively such as in 2020 Nov/III/1(b)(i).

- **Common mistakes:**

  Many students gave the erroneous explanation of how orbitals (rather than electrons in the lower energy orbitals) are being promoted to higher energy during d-d transition. Students were also penalised for citing either only 1 orbital is or subshell**s** are being split into 2 different energy levels upon approach of ligands. Merely citing ligand exchange causing change in colour is also not acceptable as the question did not ask for explanation on any colour change but rather why a solution is yellow coloured.

  Several students mistook the gas evolved to be hydrogen as they did not see that water is being oxidised to oxygen while Fe is being reduced (from oxidation number of +6 to +3). Similarly, many students failed to recognise the role of K_2FeO_4 being oxidizing agent as Fe is being reduced (from oxidation number of +6 to +3) hence Z is a oxidation product from ethanol that cotains only 1 but not 2 oxygen atoms. Thus Z cannot possibly be ethanoic acid.

(e) The pentane-2,4-dionate ion, $[CH_3COCHCOCH_3]^-$, is a bidentate ligand and is commonly known as acetylacetonate ($acac^-$).

(i) Explain the meaning of the term *bidentate ligand*. [1]

(ii) Fe^{3+} reacts with $acac^-$ ligands to form a chiral complex, $[Fe(acac)_3]$, which exists as a pair of enantiomers. Complete Fig. 2.4 to show the two enantiomeric complexes, illustrating the stereochemical relationship between them.

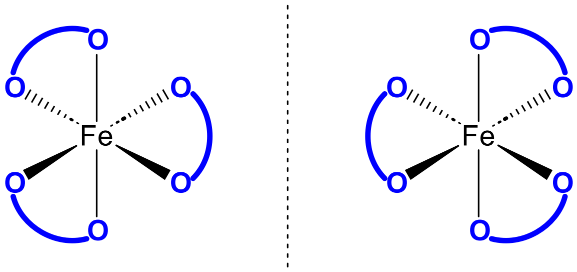


Fig. 2.4

You may use O⌒O to represent the $acac^-$ ligand. [2]

(i) A molecule or an ion with two donor atoms, each of which has at least one electron pair for donation, which can form two coordinate bonds with a central metal atom or ion simultaneously

[Total: 23]

Comments:

- The question pertains to Transition Metals.

- **Question analysis and references (where applicable)**
  A similar question has been covered in 2021 Nov/III/6(c) on effect on plane polarised light due to enantiomerism of cobalt containing complexes.

- **Common mistakes:**
  Many students gave the structure of an enantiomer that cannot exist where the ligand has to form 2 coordinate bonds with the 2 atoms at the axial positions (since the ligand is not long enough). Also, students have to show clearly that the coordinate bonds are formed using the oxygen atoms being the electron pair donor. Merely stating $acac^-$ is not acceptable.

3 **(a)** Aqueous bromine reacts with methanoic acid to produce carbon dioxide gas, as shown in the equation below.

$$Br_2(aq) + HCO_2H(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$$

20 cm^3 of 0.25 mol dm^{-3} of aqueous bromine was reacted with 20 cm^3 of 3 mol dm^{-3} methanoic acid. The reaction was monitored by measuring the volume of carbon dioxide gas over time, at room temperature as shown in Fig. 3.1.

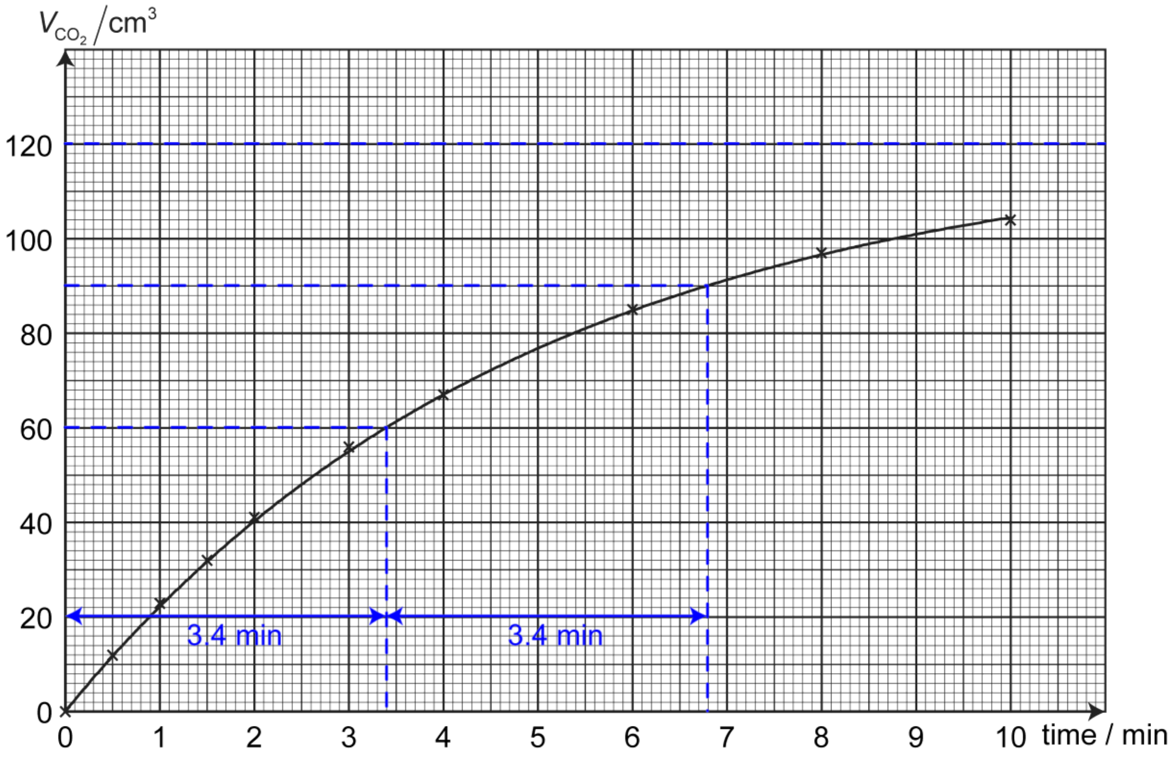


Fig. 3.1

(i) Prove that the order of reaction with respect to Br_2 is one, showing your working clearly on Fig. 3.1. [2]

(ii) Given the order of reaction with respect to HCO_2H is one, calculate the value of the rate constant *k*, stating its units clearly. [1]

(iii) Explain, with the aid of a labelled Maxwell-Boltzmann distribution diagram, the effect on the rate constant, *k*, when temperature of the reaction was increased. [3]

(iv) Apart from measuring the volume of CO_2 gas produced, there are other methods to monitor the rate of reaction between aqueous bromine and methanoic acid.

Outline another experiment to monitor the progress of reaction over time. [2]

(i) amt of Br_2 (aq) = amt of CO_2 produced = $\frac{20}{1000}\times 0.25 = 0.005$ mol

maximum volume of CO_2 = 0.005 × 24 = 0.12 dm^3 = **120 cm^3**

Since ***$t_{½}$* is constant at 3.4 min**, the **order of reaction wrt Br_2 is one**.

(including at least 2 correct depictions of constant $t_{½}$ on Fig. 3.1).

Comments:

- Not well done. Many students are still not familiar with the approach to determine the order of reaction using a product-time graph.
- **Question analysis and references (where applicable).**
  A similar question has been assessed in your 2022 EJC Promotional Examination Paper 2 Q2.

  An improvement from last year, quite a number of students knew that they needed to **determine half-life at the ½, ¾ and 7/8 mark and so on for the product time graph**. However, many students failed to first determine the **maximum volume of CO_2 formed (using mol ratio)** from the reaction before applying the approach.

  It is important to note that merely reading off the highest point on the graph (in Fig 3.1) at 104cm^3 does not depict the maximum volume of the product CO_2 formed.

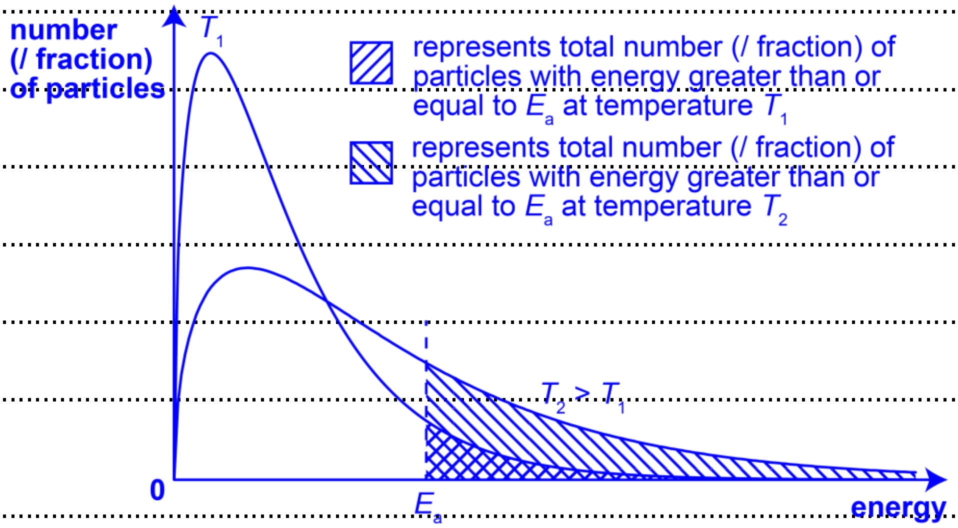
(ii) rate = $k'[Br_2]$, where $k' = k[HCO_2H]$

$$t_{½} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[HCO_2H]}$$

$$k = \frac{\ln 2}{t_{½}[HCO_2H]} = \frac{\ln 2}{3.4 \times 1.5} = \mathbf{0.136\ mol^{-1}\ dm^3\ min^{-1}}$$

Comments:

- Not well done. Many candidates had no idea how to do this because they tried to use the given rate equation to solve for k by finding the gradient at t=0. However, this method does not work as the rate determined using the gradient would have units of cm^3 min^{-1}, which is not consistent with the units for [Br_2] and [HCOOH] which are in mol dm^{-3}, hence they cannot be equated together.
- Many students were not able to apply the formula: **$t_{1/2}$ = ln2/k to** determine the value of k. Other students who attempted to apply the formula did not consider that k in the equation should be k' = k[HCOOH] since this is a pseudo first-order reaction (since [HCOOH] >> [Br_2]).



When temperature is increased, the **average kinetic energy of particles increases,** this results in **increase in frequency of collisions**.

In addition, the **number of particles with energy greater than or equals to activation energy, E_a, increases**.

Together, both results in an **increase in the frequency of effective collisions**, and **hence an increase in the rate constant**

Comments:
Not well done by most students despite this being a recall question.

Question analysis and references (where applicable):

- Pls study Chemical Kinetics lecture notes pg 46 to 48).

Common mistakes:

- **In drawing of the Boltzmann curve**, many students clearly did not display understanding of what the diagram represented, showing incorrect labelling of axes, incorrect shape of graphs, and lack of legend, and incorrect 'height' of peak to represent rxn at higher T.
- Note that the area under the graph represents the number/proportion of particles, and the number/proportion stays the same even if temperate changes, so the curves should not end at the same point. In addition, the shape of the graph should not look like a 'standard deviation graph', as fewer proportion/number of particles posses higher energies (i.e., the shape of graph should show that it tapers off near the end).

- In the explanation, most students miss the key word ‘average’ to describe how the overall K.E. has increased.
  In addition, students are penalised for stating ‘rate’ or ‘number’ of effective colliisions, as it is the ‘**frequency’** (no. of collisions per unit time) that increases.

(iv) Using a **colorimeter, measure the colour intensity of the orange Br_2 solution at regular time intervals**. The **decrease in the colour intensity of the orange solution is directly proportional to the decrease in $[Br_2]$.**

or

Measure the **change in the electrical conductivity** of the reacting mixture at **regular time intervals**. As the **concentration of ions in the solutions increase and thus electrical conductivity increases over time** due to the Br^- and H^+ ions formed, the rate of reaction can be determined.

Comments:

This question requiring students to propose alternative methods to monitor the progress of this reaction: $Br_2(aq) + HCO_2H(aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)$.

Question analysis and references (where applicable):

- Refer to Chemical Kinetics lecture notes Section 5 (pg 24 to 38).

Common mistakes:

- Some students attempted to use ‘clock’ method or the ‘continuous’ method as the alternative approach to monitor the progress.
  - However, as the question asked for ‘progress’ of reaction, the ‘continuous’ method of doing ‘sample → quench → titrate’ does not seek to monitor ‘**progress’** of reaction. Likewise, the ‘clock’ method of varying concentration of Br_2 is not suitable as the ‘**progress’** of the reaction cannot be determined.
- Otherwise, students who managed to propose appropriate approaches did not clearly state how and why the observations/data collected would change (e.g., increase or decrease) as reaction ‘progressed’, and hence could not be awarded the full credit.

(b) Both silver iodide and silver iodate(V) are sparingly soluble salts.

salt	K_{sp}	$\Delta G^\ominus$ / kJ mol^{-1}
silver iodide, AgI	8.52×10^{-17}	+91.5
silver iodate(V), $AgIO_3$	**–**	+42.7

(i) The value of the solubility product, K_{sp}, is related to the standard Gibbs free energy change, $\Delta G^\ominus$, by the mathematical expression shown, where R is the molar gas constant and T is the temperature measured in K.

$$K_{sp} = 10^{-\frac{\Delta G^\ominus}{2.3RT}}$$

Write the expression for the solubility product, K_{sp}, of $AgIO_3$, and calculate its value at 25 °C, stating its units. [2]

(ii) An aqueous solution of silver nitrate was added to a mixture containing 0.001 mol dm^{-3} each of sodium iodide and sodium iodate(V).

Calculate the concentration of iodide ions in the solution when the first trace of silver iodate(V) appears. [2]

(iii) Silver ions and thiosulfate ions react to form a soluble complex, $[Ag(S_2O_3)_2]^{3-}$.

Explain, with the aid of equations, how the solubility of silver iodide would be affected when solid sodium thiosulfate is added to an aqueous solution of silver iodide. [2]

(i) $K_{sp} = [Ag^+][IO_3^-]$ $\underline{\text{mol}^2\ \text{dm}^{-6}}$

$$K_{sp} = 10^{-\frac{\Delta G^\ominus}{2.3RT}} = 10^{-\frac{42.7\times1000}{2.3\times8.31\times298}}$$

$$= \underline{3.18\times10^{-8}\ \text{mol}^2\ \text{dm}^{-6}}$$

Comments:

- Most students were able to write the Ksp expression and determine its corresponding unit correctly.
- Quite number of students calculated the incorrect value as they did not convert $\Delta G^\ominus$ to Joules – note that applying values into equations require students to take note of consistency of units (and their respective powers).

(ii) Assuming the volume of silver nitrate added is negligible,

min. $[Ag^+]$ before AgI ppt $= (8.52 \times 10^{-17})/0.001$

$= 8.52 \times 10^{-14}$ mol dm^{-3}

min. $[Ag^+]$ before $AgIO_3$ ppt $= (3.18 \times 10^{-8})/0.001$

$= 3.18 \times 10^{-5}$ mol dm^{-3}

$[I^-]$ before first trace of $AgIO_3$ appears $= (8.52 \times 10^{-17})/(3.18 \times 10^{-5})$

= **2.68×10^{-12} mol dm^{-3}**

Comments:

- Many students were able to deduce that **AgI precipitates first, followed by $AgIO_3$** based on their respective K_{sp} values.

(iii) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$ **------------------------------------ (1)**

$Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq)$ **---------------- (2)**

When sodium thiosulfate is added, the **position of equilibrium of (2) shifts to the right** to form complex $[Ag(S_2O_3)_2]^{3-}$, and **$[Ag^+]$ decreases.**

Hence, the **equilibrium position of (1) shifts to the right** to produce more Ag^+, so the **solubility of AgI increases.**

Comments:

Generally well done.

- Most students are able to recognise that the [Ag+] decreases, resulting in the position of equilibrium of (1) to shift to the right, hence increasing the solubility of AgI.
- The concept of ‘common ion effect’ will also be applicable for a different context.

(c) When aqueous silver nitrate was shaken with excess aqueous potassium bromide, a pale cream solid **X** was observed.

This solid **X** readily dissolves in excess aqueous sodium cyanide, NaCN, forming a colourless solution of a complex anion. When more aqueous silver nitrate was added to the colourless solution, a white solid **Y**, was formed with the following composition by mass:

Ag: 80.6%; C: 8.96%; N: 10.5%

(i) Identify solid **X**. [1]

(ii) Given **Y** has a molecular mass of 268 and is an ionic compound containing one cation and one complex anion, deduce the formula of **Y** and suggest the formulae of its cation and anion. [3]

(i) **Silver bromide (or AgBr)**

(ii) In 100 g of **Y**,

	Ag	**C**	**N**
mass / g	80.6	8.96	10.5
amount / mol	$\frac{80.6}{107.9} = 0.747$	$\frac{8.96}{12.0} = 0.747$	$\frac{10.5}{14.0} = 0.750$
mole ratio	1	1	1

The empirical formula of **Y** is AgCN.

Let $(AgCN)_n$ be the formula of **Y**.

$$(107.9 + 12.0 + 14.0)n = 268$$

$$n = 2$$

The formula of **Y** is **$Ag_2C_2N_2$**

Y consists of the cation **Ag^+** and the anion **$[Ag(CN)_2]^-$**.

[Total: 18]

Comments:

- This question is about silver halides formation and determination of molecular formula from composition by mass

- **Question analysis and references (where applicable)**

  (i) Most students are able to identify correctly the silver bromide precipitate as **X**, based on the colour of ppt given.

  (ii) Based on the composition by mass, it is recommended for students to derive the **empirical formula** followed by **molecular formula** as shown in the solutions above. Working that does not demonstrate understanding of the assumptions and correct usage of information eg %mass, A_r and M_r will not be awarded marks.

  Using the hint in the question that **Y** has only **<u>one cation and one anion</u>**, the **Ag^+** cation can be easily deduced. The anion will have a **single negative charge, containing one Ag, two C and two N.** Hence the likely anion is a silver cyanide complex, **$[Ag(CN)_2]^-$** since Ag^+ and CN^- are present in the reaction.

- **Common mistakes:**

  (i) Some students stated wrongly that silver cyanide was the precipitate, despite the information clearly stating the reactants involved. Students are reminded to read question carefully.

Section B

Answer **one** question from this section.

4 Phenol can be used to synthesise drugs such as paracetamol as shown in Fig. 4.1.

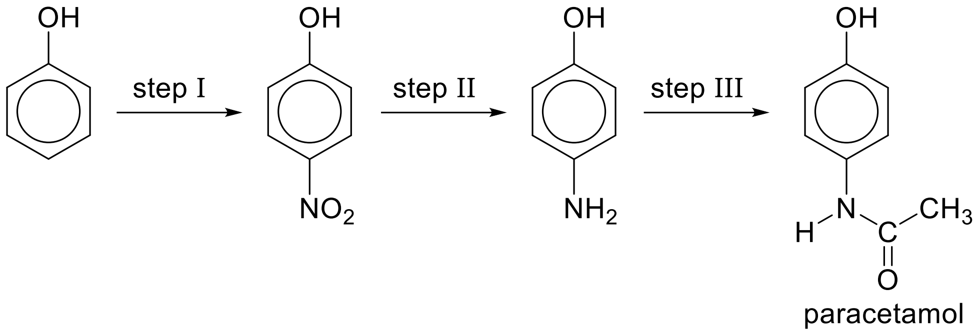


Fig. 4.1

(a) **(i)** State the reagents and conditions for each of steps I and II in Fig. 4.1 [2]

(ii) Predict whether the reagents and conditions used will be different from what you have suggested in **(a)(i)** if methylbenzene is nitrated instead of phenol. Explain your answer clearly. [1]

(i) step I: **dilute HNO_3, r.t.**

step II: **Sn, conc. HC*l*, heat**

(ii) The reagents and conditions used will be **different**. The methyl group is **less activating** as compared to the phenol group. Hence, **harsher** conditions of concentrated HNO_3, concentrated H_2SO_4, heat is needed.

Comments:

- Generally well done, although the expectation was for more students to get full marks for these very straight-forward parts.
- **Question analysis and references (where applicable)**
  (a)(i) is a common question often seen in tutorial; **(a)(ii)** assesses a basic concept in the topic of arenes.
- **Common mistakes:**
  (a)(i)
  - Quite a number of students were confused about the different reagents and conditions required for nitration of benzene, methylbenzene and phenol. Many students wrote that con HNO_3, con H_2SO_4 and 55 ^oC is required for step I.
  - Quite a few students forgot to indicate that HNO_3 is dilute by writing either “dilute” or “HNO_3(aq)”. Others were confused about how to indicate that an acid

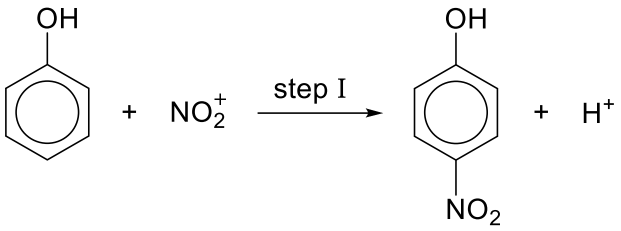
is strong and wrote "con $HCl(aq)$". Do note that for a concentrated acid, there is usually little to no water present. Hence, "(aq)" should not be used as the medium is no longer aqueous.

- Many students used wrong reducing agents such as H_2 with nickel catalyst and $LiAlH_4$ for step II.

(a)(ii)

- Some students mistakenly believed that since both $-CH_3$ and $-OH$ groups are electron-donating and hence the reagents and conditions used will be the same.
- Many students mere stated that $-OH$ is an activating group (with many details about the delocalisation of the lone pair of electrons on O into the benzene ring), without comparing with $-CH_3$.
- A few students thought that $-OH$ is an electron-withdrawing group. Do remember that the information about whether a group is activating or deactivating is in the Data Booklet.

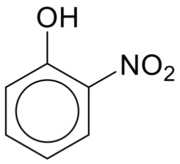
(b) The species that reacts directly with phenol to form 4-nitrophenol in step I is NO_2^+.



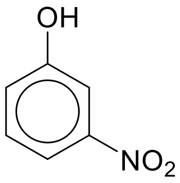
(i) Draw a dot-and-cross diagram showing the bonding in NO_2^+. [1]

(ii) Describe the mechanism for the reaction of phenol with NO_2^+ using curly arrow notation. [3]

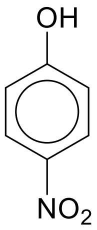
A mixture of three isomers **X**, **Y** and **Z** can be formed in step I.



X



Y

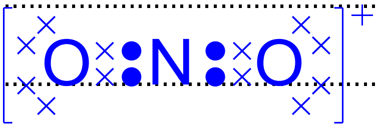


Z

(iii) Suggest why the concentration of **Z** formed is higher than that of **X** and **Y**. [2]

(iv) The boiling point of **X** is lower than that of **Z**. Explain the difference with the aid of clearly labelled diagrams. [3]

(i)



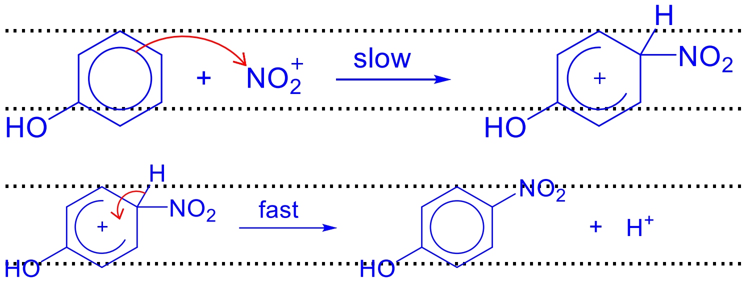
Comments:

- Generally well done.

- **Question analysis and references (where applicable)**
  The exact same dot-and-cross diagram was explained in the lectures for Chemical Bonding in JC1.

- **Common mistakes:**
  - Some students forgot to account for the positive charge. Others used the wrong atom as the central atom. A number of students forgot to include the lone pairs on oxygen atom.
  - A small number of students showed nitrogen atom forming one double bond to an oxygen atom, and a dative bond to the other oxygen atom. While credit was given in this paper as this bonding resembles that of the $-NO_2$ group on nitrophenol, it is not preferred as the central nitrogen atom will be electron-deficient (only 6 electrons).

(ii) Type of mechanism: **Electrophilic substitution**

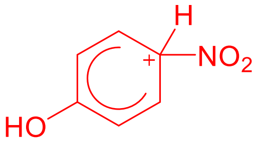


Comments:

- It was apparent that most students have put in the effort to remember the mechanism, but many did not score the full marks because of carelessness and imprecision.

- **Question analysis and references (where applicable)**
  This is a standard mechanism question.

- **Common mistakes:**
  - Many students lost marks unnecessarily because they forgot to:
    - state the type of reaction
    - show clearly and accurately where each arrow starts and ends
    - state that the first step is the slow step
    - ensure that the second step is balanced by including H^+ in the product
  - Some students were penalised for not showing the delocalisation of charge in the arenium ion accurately.

    The arenium ion was often drawn like this:  which makes it seem like the positive charge is till on the carbon atom that $-NO_2$ is bonded to.

(iii) As the phenol group is **2,4-directing**, the **electron density at C-3/C-5 is the lowest**/the **arenium intermediates leading to X and Z are more stable/formed faster than Y**. Hence **concentrations of X and Z formed are higher than that of Y**. A higher concentration of **Z** is formed as the **attack at the 4-position occurs faster** than at the 2-position as there is **less steric hindrance** at 4-position which is **further** away from the −OH group.

Comments:

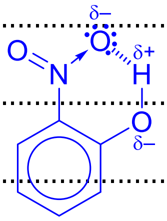
- Not well done. Most students gave incomplete and/or confused answers.

- **Question analysis and references (where applicable)**
  Similar to 'A' Level 2021 P3 Q4(d) and 'A' Level 2018 P2 Q4(b).

- **Common mistakes:**
  - Many students merely stated that the phenol group is 2,4-directing to explain why concentration of Y formed is the lowest, without going on to relate it to either the electron density at the various positions on the benzene ring or the stability of the arenium intermediates.
  - Many students merely stated that there is steric hindrance when $-NO_2$ is substituted at C-2, without comparison with the substitution at C-4.
  - Terms such as "steric hindrance", "steric repulsion" and "steric strain" were used too loosely, and often, inaccurately. While benefit of doubt was given to many students, do clarify what the different terms mean and what they apply to.

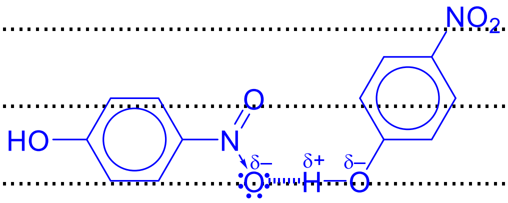
(iv) **X can form intramolecular hydrogen bonds** while **Z** cannot. Hence, the **intermolecular hydrogen bonding between X is less extensive** as compared to that in **Z**, which requires **less energy** to overcome. Hence, **X** has a lower boiling point than **Z**.

For **X**:



intramolecular hydrogen bonding

For **Z**:

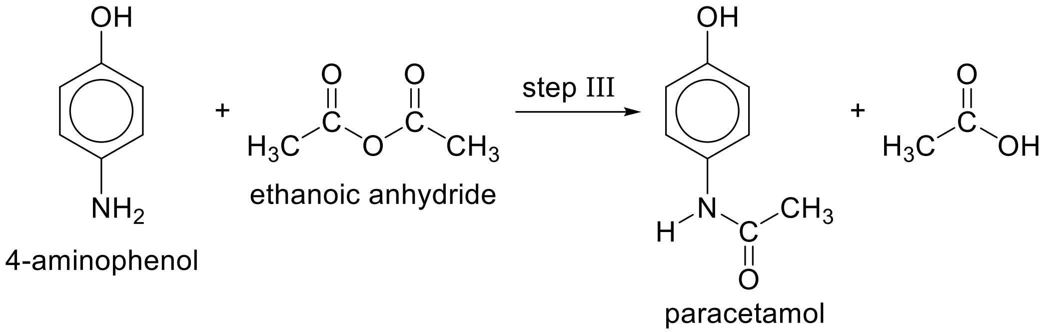


intermolecular hydrogen bonding

Comments:

- Most students were able to relate the question to concepts of inter and intramolecular hydrogen bonding.
- **Question analysis and references (where applicable)**
  This exact example was covered the lectures for Chemical Bonding in JC1.
- **Common mistakes:**
  - Many students did not show hydrogen bonding accurately and completely by:
    - Using lone pair of nitrogen atom to form the hydrogen bond when nitrogen in $-NO_2$ does not have a lone pair.
    - Showing the lone pair involved in hydrogen bonding imprecisely: $\text{——}\text{N}\ddot{\text{O}}_2$.
  - Quite a number of students confused extensiveness of hydrogen bonding with strength. In this context, the strength of hydrogen bonds should not differ between X and Z.

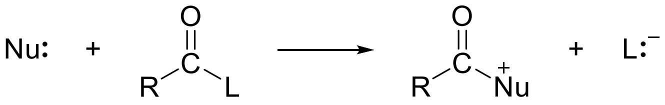
(c) Step III is a nucleophilic acyl substitution involving ethanoic anhydride, $(CH_3CO)_2O$ and the amino group of 4-aminophenol to form an amide.



(i) Phenols can also react with ethanoic anhydride. However, in Step III, 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]

(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.

Explain why step III should be carried out using ethanoic anhydride, $(CH_3CO)_2O$ instead of ethyl ethanoate. [2]

(iii) Suggest a reason why 4-aminophenol is soluble in aqueous ethanoic acid while paracetamol is not. [1]

(i) **N is less electronegative compared to O**/The amino group is a **stronger base** than the hydroxy group, which means that the **lone pair on nitrogen in the amino group is more available for donation** than that on oxygen in the hydroxy group, making the amino group a **stronger nucleophile** hence reacting faster.

(ii) The **negative charge on the leaving group, $CH_3CO_2^-$** is **delocalised over two highly electronegative oxygen atoms**. However, the **negative charge on the leaving group, $CH_3CH_2O^-$** is **intensified by the electron-donating CH_3CH_2– group**. Hence, $CH_3CO_2^-$ is **more stable**, making it a better leaving group.

(iii) 4-aminophenol has a basic **amino** group that **can react with ethanoic acid** to form a soluble salt. Paracetamol has an **amide** group that is neutral, and **does not react with ethanoic acid** to form a soluble salt.

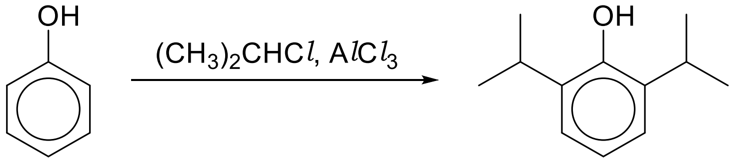
Comments:

- Familiarity of organic reactions (i.e. nucleophilicity and stability) among students who attempted was neither the strongest nor poor. Issues are mainly about phrasing and being careful with what is being asked under time pressure.

- **Question analysis and references (where applicable)**
  - for **(i)**, one needs to realise that between the amino and hydroxy group, which is a better nucleophile. As the context given is that amino group reacts faster, this implies that it is a much better nucleophile. It is now about why is the amino group a better nucleophile, which relates to it being a stronger Lewis base. Explanation behind the strength of bases/ nucleophiles was covered in the nitrogen compounds tutorial.
  - for **(ii)**, one needs to first deduce the structures of the leaving groups. From the leaving groups, which is more stable. One should identify that one is an ethanoate and the other an ethoxide leaving group. Explanation behind the stability of the leaving groups was covered in the carboxylic acid tutorials.
  - for **(iii)**, one needs to realise that the aqueous ethanoic acid solvent used must behave differently from water as a solvent. Given that it is an acid, is there any basic groups present in both compounds? If yes, any reactions? If no, what else could ethanoic acid affect. In this case, it's the difference in basicity of both compounds (or a lack of for paracetamol)

- **Common mistakes:**
  - for **(i)**, some attempted to explain using the amino group being able to protonate/deprotonate, or even the bond energy of O-H vs. N-H. These does not explain why it is a better nucleophile.
  - for **(ii)**, some were not able to identify the leaving groups, which leads to incorrect explanation. Some did not compare both leaving groups clearly, opting to choose one only. Lastly, some of the explanations were not able to explain what happens to the negative charge, and merely talk about the end-results. (i.e. resonance, unstable, etc)
  - for **(iii)**, most go into how the compounds have favourable interactions with the solvent directly without considering any possible reactions first.

(d) Phenol can also form propofol *via* Friedel-Crafts alkylation.



propofol

(i) The first stage of the alkylation involves a reaction between $AlCl_3$ and $(CH_3)_2CHCl$.

$AlCl_3$ behaves an acid in the first stage. Identify the type of acid behaviour and explain why it is possible for $AlCl_3$ to play this role. [2]

(ii) When carrying out Friedel-Crafts alkylation, water cannot be introduced into the reaction mixture. With the aid of appropriate equations, explain why this is so. [2]

(i) $AlCl_3$ is acting as a **Lewis acid**. It **can accept a lone pair** from Cl^- as Al in $AlCl_3$ is **electron deficient** and has an empty orbital.

(ii) $AlCl_3$ **reacts with water**:

$\mathbf{AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(g)}$ *or*

$\mathbf{2AlCl_3(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6HCl(g)}$ *or*

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

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

Without $AlCl_3$, the $(CH_3)_2\overset{+}{C}H$ **electrophile will not be formed**, and the electrophilic substitution reaction will not occur.

[Total: 20]

Comments:

- Time was against most who attempted this part, which proved challenging for most students for an otherwise straightforward question.

- **Question analysis and references (where applicable)**
  - for **(i)**, one needs to know their theories of acid and bases well and understand how to identify which type it is. One that is done, it is about why it can happen.
  - for **(ii)**, one need to know what water does to the reaction. This usually means water does something to the one of the initial reagents, one needs to know which reagent is affected by water. In other words, this is about $AlCl_3$ reacting in water, and how this disables its function as a catalyst and its impact on the reaction.

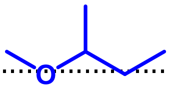
- **Common mistakes:**
  - for **(i)**, some identified wrongly the acid type. Some identified the correct acid type but failed to realise that the Al is electron deficient or has partially filled 3p orbitals. Many attempted to explain via 3d orbitals or expanding the octet structure, which is not the case here.
  - for **(ii)**, many were not clear with what happens to $AlCl_3$ and how this impacts the reaction. Many attempted to say that Al has no more space to accept an addition chloride anion, but this is not right as we want to consider the reactants and catalyst instead.

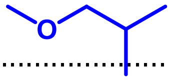
5 This question is about ethers and lactones.

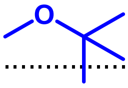
Ethers have the general structure R_1–O–R_2 where R_1 and R_2 are hydrocarbon groups.

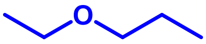
(a) An ether has the molecular formula $C_5H_{12}O$.

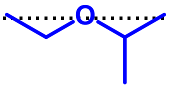
Draw the skeletal formulae for all six constitutional isomers of $C_5H_{12}O$ that contains an ether group. [2]











Comments:

- Most students could only draw five isomers.

- **Question analysis and references (where applicable)**
  This question tests your ability to consider isomerism in a systematic way and is similar to **MYE P2 Q4b** and **2019 A Level P3 Q4(d)(ii)**.

- **Common mistakes:**
  Students tend to miss out 1 of the last 3 isomers of the top row esp. because they tend to repeat the 2nd or 3rd compound of the top row and confused themselves by drawing the C–C bonds in different orientations.
  Start from the longest chain and systematically remove 1 C at the end then try to place that C atom onto next C atom and continue to shift the C.

(b) Diethyl ether, $CH_3CH_2OCH_2CH_3$, is a common solvent used in reduction reactions involving lithium aluminium hydride, $\text{LiA}l\text{H}_4$, which is a source of the hydride ion, H^-.

(i) Suggest, with reasoning, the bond angle and shape around the O atom in diethyl ether. [2]

(ii) Suggest why $\text{LiA}l\text{H}_4$ dissolves well in diethyl ether. [1]

(iii) Apart from its role as a reducing agent, $\text{LiA}l\text{H}_4$ can also act as a strong base.

Water cannot be present in reactions involving $\text{LiA}l\text{H}_4$.
Suggest, with the aid of an equation involving H^-, why this is so. [1]

(iv) $\text{LiA}l\text{H}_4$ is commonly used to reduce many functional groups such as carboxylic acids, esters, and amides. However, it does **not** reduce alkenes.

Suggest why it can reduce the above-mentioned functional groups but not alkenes. [2]

(v) $\text{LiA}l\text{H}_4$ is a stronger reducing agent than $NaBH_4$ and both have similar structure and bonding. Suggest a reason for this difference in reducing strength. [1]

(i) There are **2 bond pairs and 2 lone pairs of electrons around the O atom.** The 4 electron pairs are directed to the corners of a regular tetrahedron. **Lone pair–lone pair repulsion > lone pair–bond pair repulsion > bond pair–bond pair repulsion**.

Hence bond angle is **105º** and shape is **bent**.

(ii) $\text{LiA}l\text{H}_4$ can **form favourable ion-dipole interactions** with diethyl ether which **releases sufficient energy to overcome the ionic bonds in $\text{LiA}l\text{H}_4$ and permanent dipole–permanent dipole interactions in diethyl ether**.

(iii) **H^- reacts (explosively) with H_2O.**

$H^- + H_2O \rightarrow H_2 + OH^-$

(iv) $LiAlH_4$ is a source of H^- and reduces them because the **C atoms of those functional groups are electron-deficient as they are bonded to very electronegative O and/or N atoms** and is **susceptible to nucleophilic attack by H^-** but the **C=C bond in alkenes is electron-rich and repels the H^- nucleophile** resulting in a very high activation energy.

(v) **Al is less electronegative than B** and thus **Al attracts electrons away from H less strongly than B**. This causes the **H of the AlH_4^- ion to be more electron rich and more nucleophilic** thus **AlH_4^- is a better source of H^- ion**.

Comments:

- **(i)** was decently attempted. **(ii)** and **(iii)** were very poorly attempted. **(iv)** and **(v)** were generally well-attempted.

- **Question analysis and references (where applicable)**

  (i) involves a typical VSEPR question on stating and explaining shape and bond angle.
  (ii) involves a fairly typical question on solubility of ionic compound in polar solvent.
  (iii) involves a thinking question using contextual info to deduce what reaction could have occurred and is similar to **2014 A Level P3 Q2(e)(i)**.
  (iv) and **(v)** are typical questions that test on the reducing ability of $LiAlH_4$ and are similar to **2022 A Level P2 Q3(d)** and **2017 A Level P2 Q4(c)(iii)** (which is in the carbonyl compounds tutorial) respectively.

- **Common mistakes:**

(1) For **(i)**, it was disturbing to see that many students failed to count the number of lone pairs on O correctly hence leading to shapes like linear (0 lone pair) or angles like 119° (2 bond pair, 1 lone pair). Please make sure you know how to **count the number of valence electrons and thus number of bond pairs and lone pairs**. Surprisingly, very few discussed the **different strengths of repulsion of electron pairs**.

(2) For **(ii)**, this question is like explaining why $NaCl$ dissolves in water but most failed to recognise that **$LiAlH_4$ is an ionic compound** and/or recognise that **diethyl ether is a polar molecule**.

(3) For **(iii)**, many struggled to come up with the equation, sometimes even giving obviously unbalanced equations or did not use H^- as the reactant as stated in the question. Hints were given that **$LiAlH_4$ acts as a strong base, suggesting that it accepts H^+** and question also said that **water cannot be present, suggesting that it is because water reacts with H^-**.

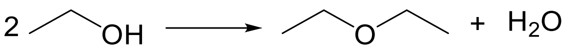
(4) For **(iv)**, **many only attempted to explain why alkenes did not react** and most seemed to know that concept but failed to explain clearly. For example, students mentioned that the alkene is electron-rich but didn't elaborate how that causes the reaction to not take place.

(5) For **(v)**, there were various acceptable arguments that are linked to how AlH_4^- is a better source of H^- e.g. strength of $Al–H$ vs. $B–H$ bond.

There are many ways to synthesise ethers.

(c) **(i)** One such way is when two alcohols react together as shown in equation 1.

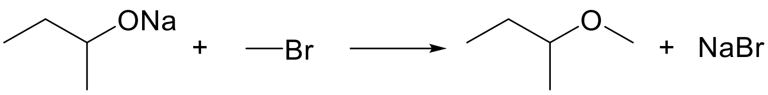
equation 1



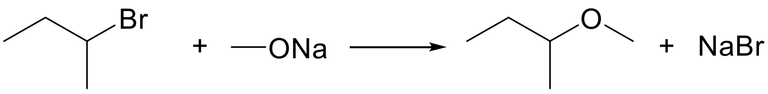
Suggest the type of reaction for the above reaction. [1]

(ii) Another way is the Williamson ether synthesis as shown in equations 2 and 3.

equation 2



equation 3



Given that these reactions occur *via* S_N2 mechanism, explain why the reaction in equation 2 is preferred to form the desired product instead of the reaction in equation 3. [1]

(i) **Condensation**

(ii) The **alkoxide nucleophile attacks a 2° halogenoalkane in the equation 3** which has **2 more alkyl groups at the α-carbon than the halogenoalkane in the equation 2.** The **bulky alkyl groups lead to greater steric hindrance** and S_N2 reaction is more favourable when there **is less steric hindrance** at the α-carbon**.**

Comments:

- **(i)** was generally well-attempted but **(ii)** was generally poorly attempted.

- **Question analysis and references (where applicable)**

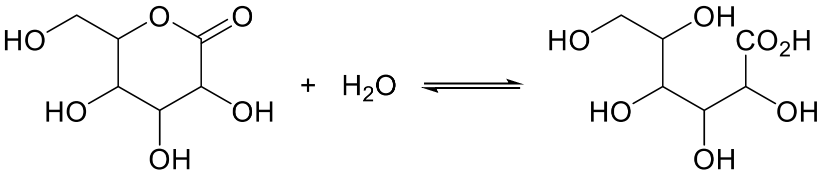
For **(i)**, students had to think about which reaction is most similar to the one shown in the equation and this is very common in A Level questions (e.g. **A Level 2015 P3 Q4(a)**) and for **(ii)**, students had to think about the key concept behind what favours S_N2 reactions which is also very common in A Levels (e.g. **A Level 2020 P3 Q4(a)(i)**).

- **Common mistakes:**

(1) Quite a few students thought it was an **elimination** reaction but that would involve **removing atoms from adjacent atoms** (e.g. RX to form alkene).
(2) Many thought that the nucleophiles were different in the two equations!

Lactones are a class of organic compounds that contain an ester which is inside a ring (*i.e.* they are cyclic esters).

(d) The addition of glucono-delta-lactone, GDL, to soy milk produces a soft form of tofu due to a gradual acidification of the mixture. In aqueous solution the following equilibrium is slowly set up.



GDL gluconic acid

When 2.00 g of GDL (M_r = 178) was dissolved in 100.0 cm^3 water and the solution allowed to reach equilibrium, the concentration of gluconic acid was found to be 0.0670 mol dm^{-3}.

Write an expression for K_c for the equilibrium above, and use the data given to calculate its value. You can assume that $[H_2O]$ = 55.5 mol dm^{-3} throughout. [3]

$$K_c = \frac{[\text{gluconic acid}]}{[\text{GDL}][H_2O]}$$

	GDL	+ H_2O	$\rightleftharpoons$ gluconic acid
initial conc. / mol dm^{-3}	$\frac{2.00}{178} \div \frac{100}{1000} = 0.1124$	55.5	0
change in conc. / mol dm^{-3}	–0.0670	–	+0.0670
eqm conc. / mol dm^{-3}	0.0454	55.5	0.0670

ICE table or relevant working

$$K_c = \frac{[\text{gluconic acid}]}{[\text{GDL}][H_2O]} = \frac{0.0670}{0.0454 \times 55.5}$$

$$= \mathbf{0.0266\ mol^{-1}\ dm^{3}}$$

Comments:

- Generally, this was decently attempted.

- **Question analysis and references (where applicable)**

Students had to do a typical K_c calculation which can be easily solved with ICE table. This question is slightly modified from **A Level 2010 P3 Q2(b)(iv)**.

- **Common mistakes:**

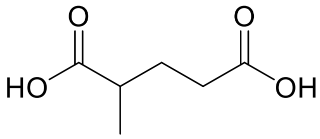
(1) Did not include $[H_2O]$. You need to know that **formation of ester generally involves all species in liquid state thus $[H_2O(l)]$ is to be included**.
(2) **Used the initial [GDL] to calculate K_c instead of equilibrium [GDL]**.
(3) Surprisingly, quite a few misread the 0.0670 as [GDL] instead of gluconic acid.

(e) The Baeyer-Villiger oxidation reaction forms an ester from a ketone with a peroxyacid. An example is shown in equation 4 using peroxyethanoic acid, CH_3CO_3H.

equation 4 $RCOR' + CH_3CO_3H \rightarrow RCO_2R' + CH_3CO_2H$

Ketone **A** was reacted in this way to give **only one** cyclic ester **B**. When heated with HC*l*(aq), **B** gave compound **C** ($C_7H_{14}O_3$).

Compound **C** gave a yellow precipitate when treated with alkaline aqueous iodine and upon acidification, 2-methylpentanedioic acid was formed.



2-methylpentanedioic acid

Compound **C** produced three different alkenes, **D**, **E** and **F** of which two are *cis-trans* isomers, when heated with concentrated H_2SO_4.

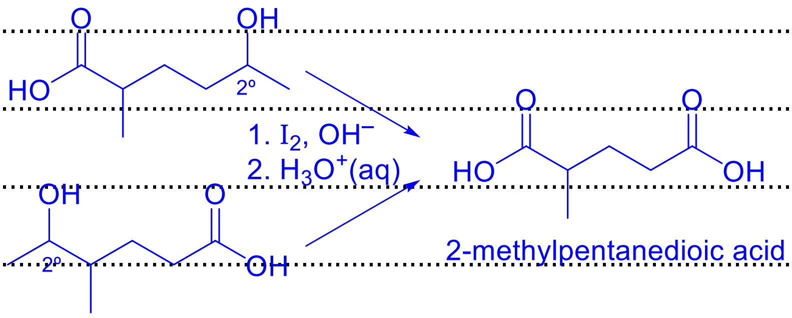
(i) Explain what is meant by *cis-trans isomerism* in alkenes. [1]

(ii) Suggest the structures of **A**, **B**, **C**, **D**, **E**, and **F**. [5]

(i) It is a type of stereoisomerism which arises due to **restricted rotation** in C=C bond and when **each C of the alkene has 2 different substituents** bonded to them.

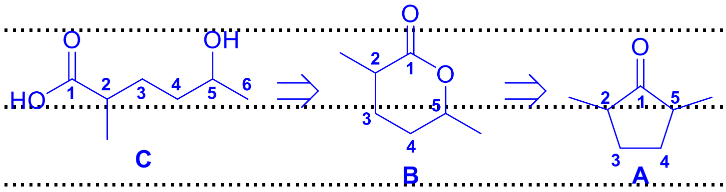
(ii) Since **C** is formed from the acid hydrolysis of lactone **B**, **C** must be a hydroxy acid.

Since **C** gives 2-methylpentanedioic acid upon iodoform reaction, **C** must be either of the two 2° methyl carbinol:

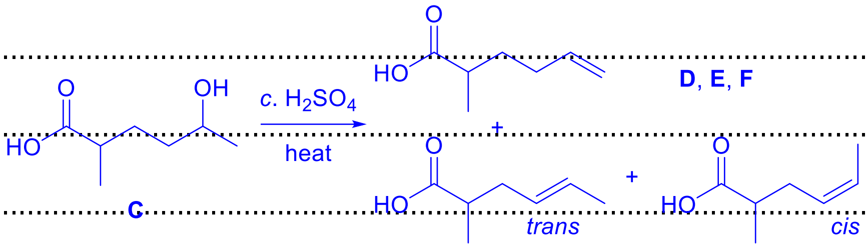


C

Only the first possible **C** will eventually give a cyclic ketone **A** that will give only one cyclic ester **B** due to the symmetry of **A**.



C undergoes elimination to form **D**, **E** and **F**:



Comments:

- Generally, **(i)** was decently attempted and **(ii)** was poorly attempted often probably due to a lack of time.
- **Question analysis and references (where applicable)**
  (i) is just definition of cis-trans isomerism and **(ii)** is a structural elucidation question involving a new reaction introduced in the paragraph and is based on **A Level 2014 P3 Q1(e)**.
- **Common mistakes:**

(1) For **(i)**, many students had vague descriptions that merely tried to show their understanding of how cis and trans isomers are different.

(2) For **(ii)**, usually the problem is in deducing **A** because it was quite straightforward to work backwards from the given molecule to solve **C** and hence **B**, **D**, **E**, **F**. Students had to realise that the ketone must be cyclic and symmetrical since after the oxidation, the ester was also cyclic and there was only 1 ester that could be formed.
Since question did not explicitly ask to explain the reactions, likely marks are awarded solely (or mainly) for drawing the structures.

[Total: 20]

Additional answer space

If you use the following page to complete the answer to any question, the question number must be clearly shown.