Suggested solutions

DUNMAN HIGH SCHOOL
Preliminary Examination 2018
Year 6

H2 CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

INSTRUCTIONS TO CANDIDATES

1 Write your **name**, **index number** and **class** on this cover page.

2 Write in dark blue or black pen.

3 You may use an HB pencil for any diagrams or graphs.

4 Do not use staples, paper clips, glue or correction fluid.

5 Answer **all** questions in the spaces provided on the Question Paper.

The number of marks is given in brackets [ ] at the end of each question or part question.

You are advised to show all workings in calculations.

You are reminded of the need for good English and clear presentation in your answers.

For Examiner's Use	
Question No.	**Marks**
1	**13**
2	**12**
3	**25**
4	**10**
5	**15**
Total	**75**

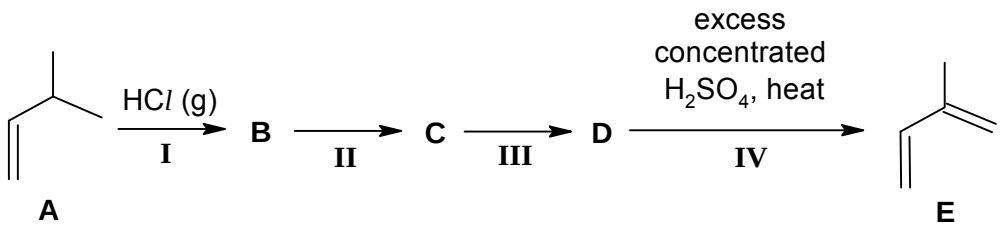
This question paper consists of **18** printed pages and **0** blank page.

[Turn over

Answer **all** questions in the spaces provided.

1 Isoprene, **E**, is an organic compound that could be used to synthesise limonene, which is commonly used in fragrances.

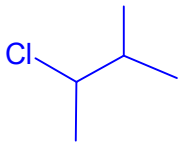
(a) **E** can be synthesised from 3–methylbut–1–ene, **A**, in a 4–step process as follows.

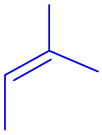


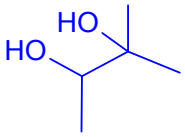
(i) **B** is a major product of step **I**.

Draw the structures of compounds **B**, **C** and **D**.

[3]

B : 

C : 

D : 

(ii) Suggest the reagents and conditions for steps **II** and **III**.

[2]

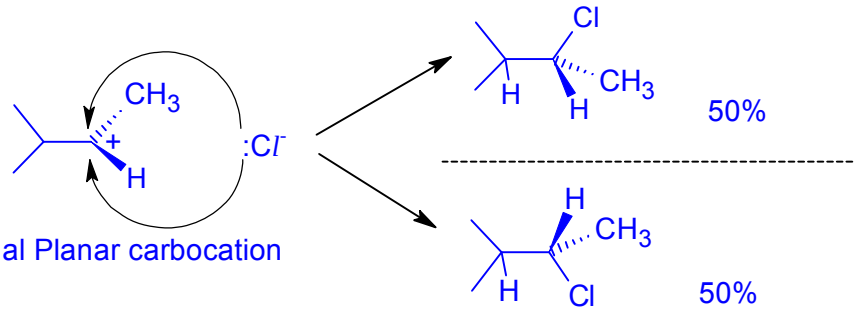
step **II** : alcoholic NaOH heat under reflux

step **III** : cold alkaline $KMnO_4$

(iii) Predict, with reasoning, whether the mixture of products formed in step **I** is optically active.

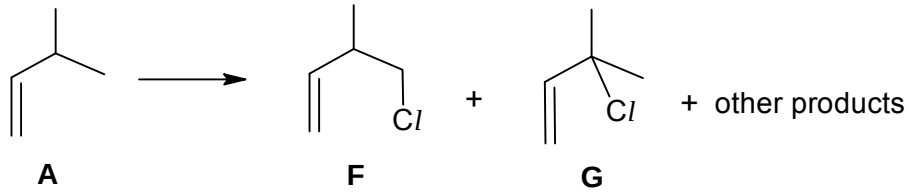
[2]

The reaction mixture in **B** is **not optically active**. During electrophilic addition, a **trigonal planar carbocation** is formed. Cl^- has a **50% chance** each of **attacking the carbocation from the top or bottom of the plane**. Hence, resulting in a **racemic mixture** formed.



Trigonal Planar carbocation

(b) The following reaction shows an alternative route to form intermediates for the synthesis of isoprene, **E**.



A **F** **G**

(i) State the reagents and conditions used to form **F** and **G** from **A**.

[1]

Limited Cl_2, uv

(ii) Predict the ratio in which **F** and **G** will be formed.

[1]

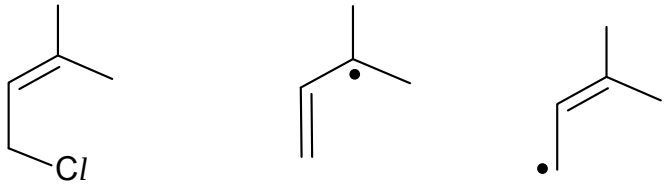
F : **G**
6 : 1

(iii) **Z** was one of the other products formed in the reaction in **(b)**. It was suggested that the radical, •**G**, is involved in the formation of **Z**.

The mechanism of •**G** converting to **Z** is thought to involve 2 steps.

1. Delocalisation of unpaired electron forming •**Z**.
2. •**Z** reacts with Cl_2 to form **Z** and a radical.

The structures of **Z**, •**G** and •**Z** are as follows.

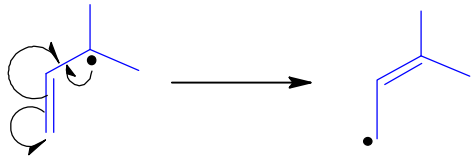


Z •**G** •**Z**

Use the information above to draw out the mechanism for the conversion of •**G** to **Z**. You are advised to use skeletal or structural formula for all species, so that it is clear which bonds are broken and which are formed. Indicate any unpaired electrons by a dot (•). Use curly half-arrows to indicate the movement of unpaired electrons.

[2]

1.



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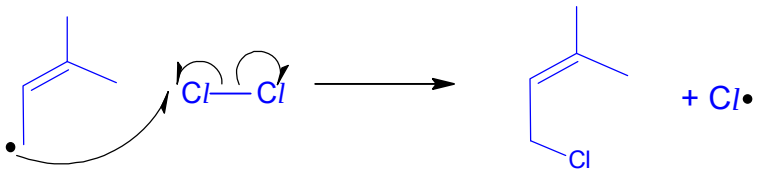


(iv) Describe a chemical test that could distinguish between **A** and **F**. State reagents, conditions and observations clearly in your test.

Add 1 cm^3 of **A** and **F** each into separate test tubes. Add **NaOH (aq)** into both test tubes and **heat**, **followed by** adding excess **HNO_3 (aq)** then add **$AgNO_3$ (aq)**.

F : **White ppt** of AgC*l* seen
A : **no white ppt** seen

[Total: 13]

2 **(a)** Fig 2.1 shows a bar chart of the third ionisation energy (3rd IE) of nine consecutive elements (**J** to **R**) in Periods 2 and 3 of the Periodic Table.

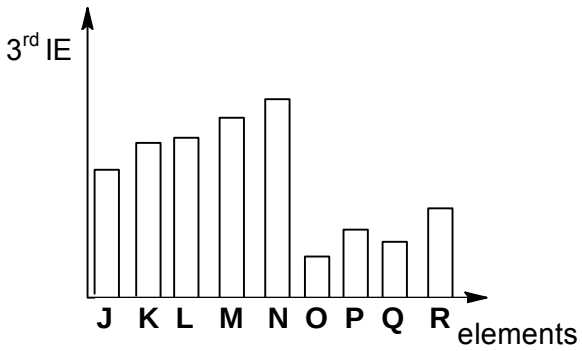


Fig 2.1

(i) Write an equation for the third ionisation energy of element **J**.

[1]

$J^{2+}(g) \rightarrow J^{3+}(g) + e^-$

(ii) Identify element **N**.

[1]

Mg

(iii) Using your answers in **(a)(i)**, **(a)(ii)** and the electronic configurations of the species involved, explain the following features of Fig 2.1.

1. The significantly higher 3rd IE of **N** compared to **O**.

Electronic configuration: **N^{2+} ($1s^2 2s^2 2p^6$)**; **O^{2+} ([Ne]$3s^1$)**

The 3rd ionisation energy of **N** involves the removal of a **2p** electron

The 3rd ionisation energy of **O** involves the removal of a **3s** electron

A **significantly larger amount of energy** is required to remove the **2p** electron in **N^{2+}** which is much more strongly held by the nucleus as it is found in an **inner quantum shell** compared to **3s** electron in **O^{2+}**.

Hence 3rd ionisation energy of **N** is significantly higher than that of **O.**

2. The lower 3rd IE of **Q** than **P**.

[4]

Electronic configuration: **P^{2+} ([Ne]$3s^2$)**; **Q^{2+} ([Ne]$3s^2 3p^1$)**

The 3rd ionisation energy of P involves the removal of a **3s** electron

The 3rd ionisation energy of Q involves the removal of a **3p** electron

Smaller amount of energy is required to remove the **3p** electron in **Q^{2+}** which is of **higher energy** than **3s** electron in **P^{2+}**. (The 3p electron also experiences increased screening effect provided by the filled 3s subshell.)

Hence 3rd ionisation energy of **Q** is lower than that of **P**

(b) Fig 2.2 shows another bar chart of the logarithm of all the ionisation energies, log (IE), of an element **S** against the number of electrons removed.

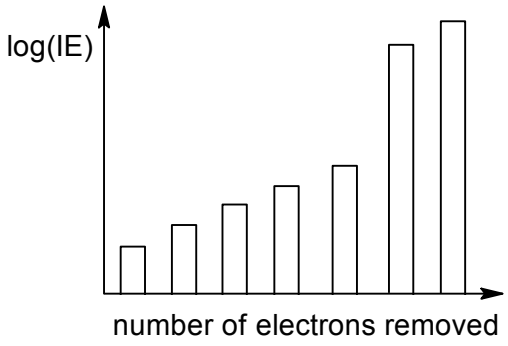


Fig 2.2

(i) Explain the general trend shown in Fig 2.2.

[2]

In an atom of **S**,

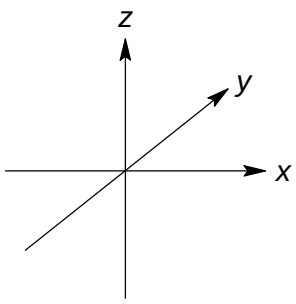
Number of protons unchanged ⇒ **nuclear charge unchanged**

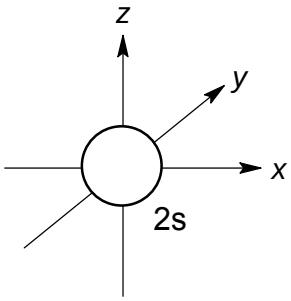
As electrons are removed from the atom, the **increasingly positively charged ion** holds the remaining electrons **more strongly** hence **more energy** is required to remove the remaining electrons resulting in higher I.E

Thus, successive I.E shows an increasing trend.

(ii) On the axes provided, draw and label the orbital which the fifth electron is removed from.

[1]





(c) The Periodic Table shows helium placed at the top of Group 18.

(i) Suggest why the element helium could be placed at the top of Group 2.

[1]

Helium has **2 valence electrons** like all other Group 2 elements.

(ii) Suggest why the element helium is not placed at the top of Group 2, by comparing **one** physical property. Explain your answer.

[2]

Helium atoms are held by **weak instantaneous dipole induced dipole interactions** while within group 2 elements exist **strong electrostatic forces of attraction between cations and a sea of delocalised electrons**.

Hence, helium has **low melting/boiling point** and it **exist as a gas** while group 2 elements has **high melting/boiling point and exist as a solid** at room temperature. Include energy

OR

Hence, **helium** is a **non-conductor of electricity** due to (**absence of mobile/delocalised electrons**) while **group 2 elements** are **good conductor** of **electricity** due to (**presence of delocalised electrons)**.

[Total: 12]

3 The ions of transition elements form *complexes* by reacting with *ligands*.

(a) **(i)** State what is meant by the terms:

Complex

Ligand

[2]

A complex is formed when a **metal ion or atom** forms dative covalent or **coordinate bonds** with **surrounding ion or molecules**.

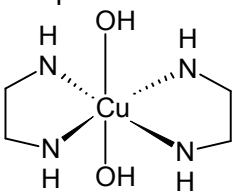
A ligand is a neutral molecule or an anion containing at least one atom with a **lone pair of electrons that can be donated** into **low lying vacant orbital of metal atom/ion to form a coordinate bond**.

(ii) Two of the complexes formed by copper are $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$ and $CuCl_4^{2-}$. Draw three–dimensional diagrams of their structures in the boxes below and name their shapes.

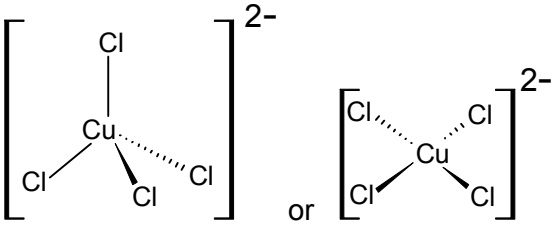
$Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$	$CuCl_4^{2-}$
Shape:	Shape:

[3]

$Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$
Shape: octahedral



$CuCl_4^{2-}$
Shape: tetrahedral or square planar

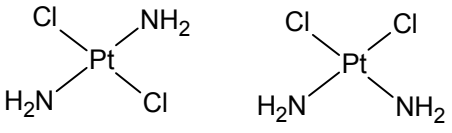


(iii) State the oxidation number of Cu in $Cu(H_2NCH_2CH_2NH_2)_2(OH)_2$.

[1]

+2

(iv) Platinum forms square–planar complexes, in which all four ligands lie on the same plane as the Pt atom. There are two isomeric complexes with the formula $Pt(NH_3)_2Cl_2$. Suggest the structures of the two isomers.



By comparison with a similar type of isomerism in organic chemistry, suggest the type of isomerism shown here and label the isomers above.

Type of isomerism: Cis-trans isomerism

[4]

(b) Copper forms two series of compounds, one containing copper(II) ions and the other containing copper(I) ions.

(i) Complete the electronic configuration of these species.

Cu [Ar]……

Cu(I) [Ar]……

[2]

Cu [Ar] $3d^{10}$ $4s^1$
Cu(I) [Ar] $3d^{10}$

(ii) Explain why the following statements are true.

Copper metal is a better electrical conductor than calcium metal.

Copper(II) salts are generally coloured.

[3]

Copper metal are better electrical conductor because both **4s and 3d valence electrons are available for delocalisation**. This increases the number of mobile charge carriers which in turn increases the conductivity of copper metal.

In the presence of ligands, the **degenerate d orbitals are split into two groups of orbital with different energies**. When white light shines on the complex, a d electron **undergoes d-d transition and is promoted to a higher energy partially filled or empty d orbital**. During the transition, the **d electron absorbs a quantum/photon of light of certain wavelength** from the visible region of the electromagnetic spectrum. The **colour observed is the colour of transmitted light** which is a mixture of remaining wavelengths that have not been absorbed. This colour is the complementary colour of the absorbed light.

(c) Copper(I) oxide and copper(II) oxide can both be used in the ceramic industry to give blue, green or red tints to glasses, glazes and enamels.

The table lists the $\Delta H_f^{\ominus}$ values for some compounds.

Compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
Cu_2O (s)	–168.6
CuO (s)	–157.3
$Cu(NO_3)_2$ (s)	–302.9
NO_2 (g)	+33.2

(i) Copper(II) oxide can be produced in a pure form by heating copper(II) nitrate. Use suitable $\Delta H_f^{\ominus}$ values from the table to calculate the $\Delta H_r^{\ominus}$ for this reaction.

$Cu(NO_3)_2$ (s) $\rightarrow$ CuO (s) + $2NO_2$ (g) + $\frac{1}{2}O_2$(g)

[1]

$\Delta H^{\ominus}_r$ = –157.3 + 2(33.2) + 0 – (–302.9)
= +212 kJ mol^{-1}

(ii) Copper(I) oxide can be produced from copper(II) oxide.

$$2CuO\ (s) \rightleftharpoons Cu_2O\ (s) + \tfrac{1}{2}O_2(g) \quad \text{reaction 1}$$

Suggest whether a low or high temperature would favour the production of copper(I) oxide. Explain your reasoning with appropriate calculation.

[2]

$\Delta H^{\ominus}_r = -168.6 - 2(-157.3)$
$= +146\ kJ\ mol^{-1}$

Since the production of copper(I) oxide from copper(II) oxide is an **endothermic process**, it will be favoured by **high temperature** as predicted by **Le Chatelier's Principle**. The equilibrium will **shift to the right** to counter the high temperature.

(iii) For reaction 1, $\Delta S^{\ominus} = +93.6\ J\ K^{-1}\ mol^{-1}$. Use this value and your answer in **(c)(ii)** to calculate $\Delta G^{\ominus}$.

[1]

$\Delta G^{\ominus} = 146 - (298)(0.0936)$
$= +118.1\ kJ\ mol^{-1}$
$= +118\ kJ\ mol^{-1}$

(iv) Write the expression of the equilibrium constant, K_c, for reaction 1. State the units.

[2]

$K_c = [O_2]^{1/2}$
Units: $mol^{\frac{1}{2}}\ dm^{-\frac{3}{2}}$

(v) For any reaction, $\Delta G^{\ominus}$ and the equilibrium constant, K_c, are related according to the equation,

$$\Delta G^{\ominus} = -2.303RT \log K_c$$

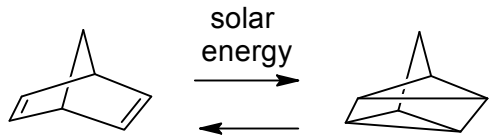
Use this equation to calculate a value of K_c for reaction 1.

[1]

$\log K_c = \frac{-118.1 \times 10^3}{(2.303)(8.31)(298)} = -20.71$

$K_c = 1.95 \times 10^{-21}$

(d) In 1977, Kutal *et al*. conducted a detailed investigation into the photoassisted (solar energy) isomerisation of norbornadiene to quadricyclene.



norbornadiene quadricyclene

In the presence of copper(I) salts as a catalyst, the isomerisation was reversible with the release of approximately 1.08 kJ of energy per gram of quadricyclene.

(i) State the type of isomerism that has occurred when norbornadiene is converted to quadricyclene.

[1]

Functional group isomerism

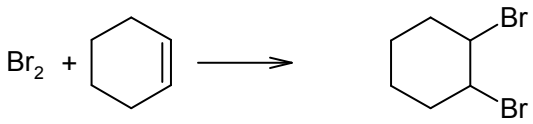
(ii) Based on the above given information, suggest a possible practical use of this norbornadiene–quadricyclene interconversion system. Explain how this system can work to fulfil that practical use.

[2]

This system can potentially work as a solar energy storage system. Norbornadiene is first irradiated with solar energy and converted to quadricyclene. Energy can be released when quadricyclene is reacted with copper(I) salts. This means that solar energy can be stored in the covalent bonds of quadricyclene.

[Total: 25]

4 (a) Cyclohexene can react with Br_2 to form 1,2–dibromocyclohexane as shown below.



cyclohexene 1,2–dibromocyclohexane

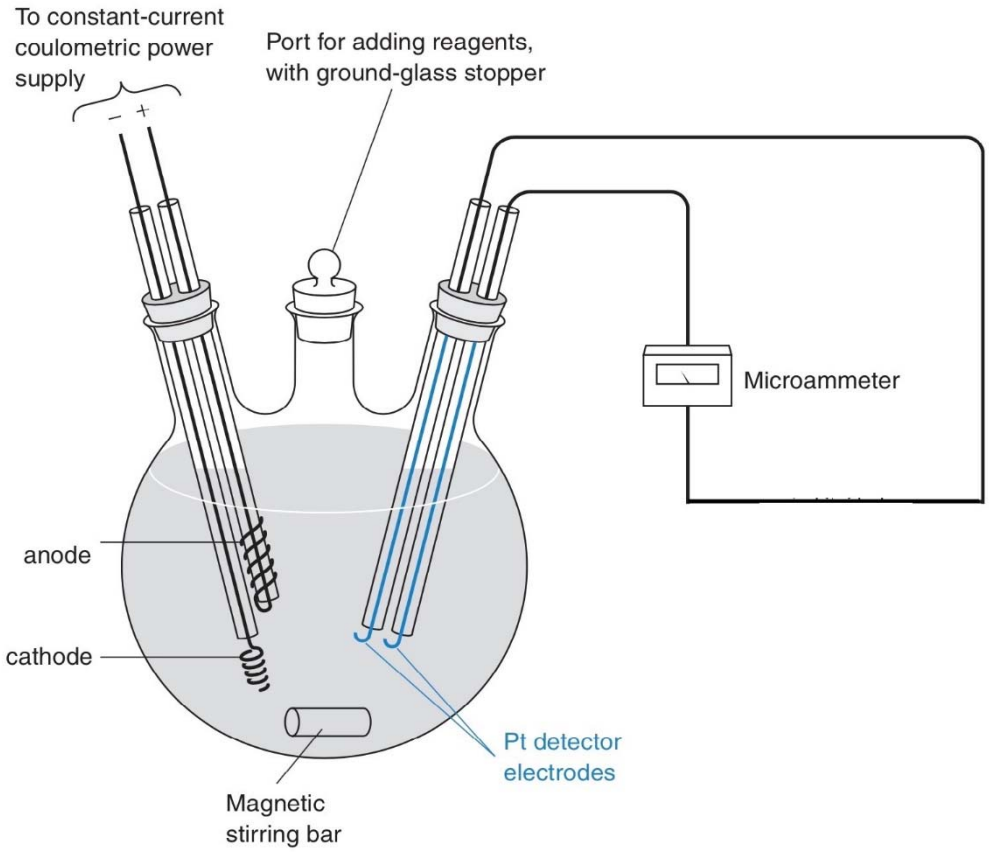
An experiment was carried out where the cyclohexene was titrated with the Br_2 generated by the oxidation of Br^- in the electrolytic cell:

$$2Br^- \rightarrow Br_2 + 2e^-$$

The experiment was carried out at a constant current as shown in the figure below.

The initial solution contains an unknown quantity of cyclohexene and a large amount of Br^- dissolved in a suitable inert solvent that does not participate in the reaction.

The figure below consists of electrolytic and galvanic cells shown on the left–hand and right–hand sides respectively.



Br_2 generated from electrolysis, reacts with the cyclohexene. At the end–point, all the cyclohexene has reacted and the concentration of Br_2 suddenly rises, signalling the end of the reaction.

(i) State whether Br_2 is generated at the cathode or anode of the electrolytic cell. [1]

Anode

(ii) The rise in the concentration of Br_2 is detected by measuring the current between the two Pt detector electrodes in the galvanic cell using the microammeter. The detector current flows by virtue of the reactions:

$$\text{Detector anode: } 2Br^- \rightarrow Br_2 + 2e^-$$

$$\text{Detector cathode: } Br_2 + 2e^- \rightarrow 2Br^-$$

Suggest why there is no current detected before equivalence point is reached.
[1]

Both Br_2 and Br^- must be present for the detector half–reactions to occur.

Prior to the equivalence point, there is Br^- but **no Br_2 is present for reduction at the detector cathode** as any Br_2 formed would have reacted with cyclohexene.

In an experiment, 2 cm^3 of 0.600 x 10^{-3} g cm^{-3} cyclohexene is to be titrated.

(iii) Calculate the amount, in moles, of the cyclohexene used.
[1]

mass of cyclohexene = 2 x 0.600 x 10^{-3}
= 1.20 x 10^{-3} g

number of moles of cyclohexene = $\frac{1.20 \times 10^{-3}}{82.0}$
= **1.46 x 10^{-5} mol**

(iv) The experiment was carried out with a constant current of 5 x 10^{-3} A for the electrolytic cell. Determine the time taken for complete titration.
[2]

$2e^- \equiv Br_2 \equiv$ 

number of moles of e^- = 1.4634 x 10^{-5} x 2
= 2.9268 x 10^{-5} mol

time taken = $\frac{nF}{I}$
= $\frac{2.9268 \times 10^{-5} \times 96500}{5 \times 10^{-3}}$
= **595 s**

(b) Br atoms introduced artificially by industrial activities raise concerns of ozone destruction.

One method that is used to determine the concentration of ozone in the ozone layer is to pass air through alkaline potassium iodide and to measure the amount of iodine liberated.

The following reaction takes place.

$$O_3 + H_2O + 2I^- \rightarrow O_2 + I_2 + 2OH^-$$

The iodine liberated is measured using a platinum electrode immersed in alkaline potassium iodide solution against a standard silver/silver chloride reference electrode. The e.m.f. of the system, in volts, is given by the equation.

$E = 0.32 + 0.029 \log_{10} [I_2]$, where $[I_2]$ is expressed in mol dm^{-3}.

To determine ozone in the atmosphere, a light–weight balloon containing the electrochemical cell was released into the atmosphere. The data collected was then transmitted to the ground station for further processing.

A sample of air was passed through 10 cm^3 of alkaline potassium iodide. The pressure of this sample of air was found to be 0.24 atm measured at room temperature. The potential of the platinum electrode immersed into this solution against the standard silver/silver chloride electrode was 0.21 V.

(i) Calculate the concentration of iodine liberated.

[1]

$0.21 = 0.32 + 0.029 \log_{10} [I_2]$

$[I_2] =$ **1.61×10^{-4} mol dm^{-3}**

(ii) Hence, calculate the volume of ozone present in this sample of air.

[2]

number of moles of $O_3 = 1.6103 \times 10^{-4} \times \frac{10}{1000}$

$= 1.6103 \times 10^{-6}$ mol

$pV = nRT$

$V = \frac{nRT}{p}$

$= \frac{(1.6103 \times 10^{-6})(8.31)(293)}{0.24 \times 101325}$

$=$ **1.61×10^{-7} m^3**

(c) Halogens form binary compounds with hydrogen known as hydrogen halides. State and explain how the thermal stability of hydrogen halides varies down the Group.

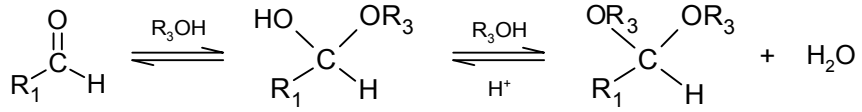
[2]

Thermal stability of hydrogen halides **decreases** down the group.

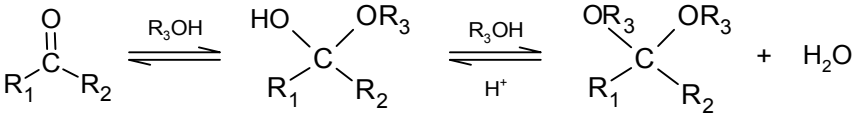
Down the group,
bond energy **decreases** [BE (H–F) > BE (H–C*l*) > BE (H–Br) > BE (H–I)],
covalent bond strength also **decreases** [H–F > H–C*l* > H–Br > H–I].
Hence, thermal stability **decreases** [H–F > H–C*l* > H–Br > H–I].

[Total: 10]

5 (a) Nucleophilic addition of an alcohol to aldehydes and ketones yield hemiacetals. The reaction is slow and reversible under neutral conditions. Upon further reaction with alcohols in the presence of acids as catalyst, hemiacetals can form acetals.

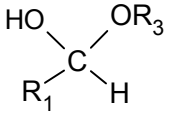


aldehyde hemiacetal acetal



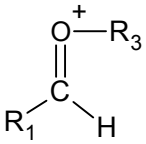
ketone hemiacetal acetal

The acid-catalysed acetal formation from the hemiacetal shown below, involves 4 steps.



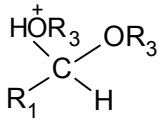
hemiacetal

1. Protonation of the hydroxyl group of the hemiacetal.
2. Loss of water leads to an unstable and highly reactive oxonium ion.



oxonium ion

3. Nucleophilic attack of alcohol, R_3OH, on the oxonium ion to give

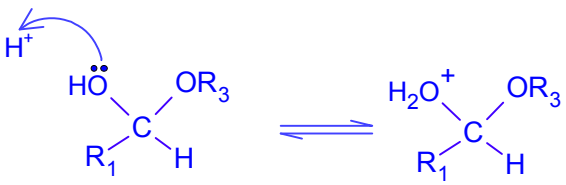


4. Loss of a proton to give the acetal.

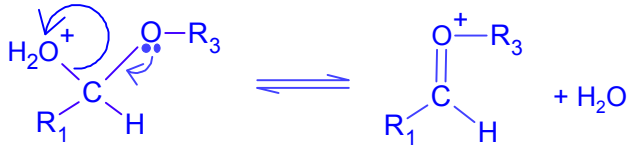
(i) Draw the mechanism as described above, showing clearly the flow of electrons.

[4]

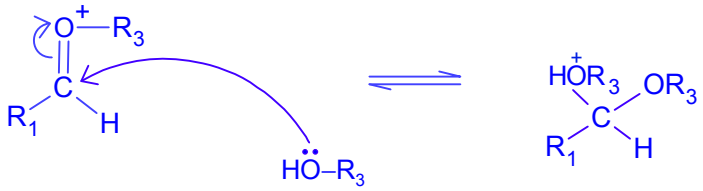
Step 1:



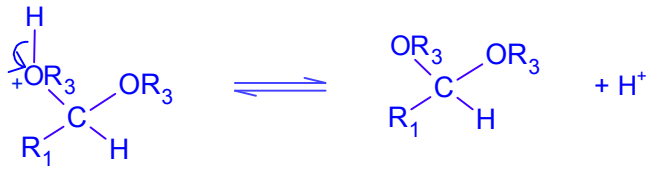
Step 2:



Step 3:



Step 4:



(ii) State the purpose of removing water from the reaction mixture.

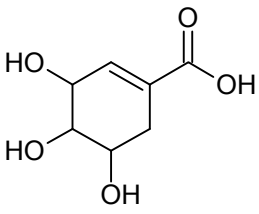
[1]

By Le Chatelier's Principle, removal of water shifts the position of equilibrium to the right, hence **increasing the yield**.

OR

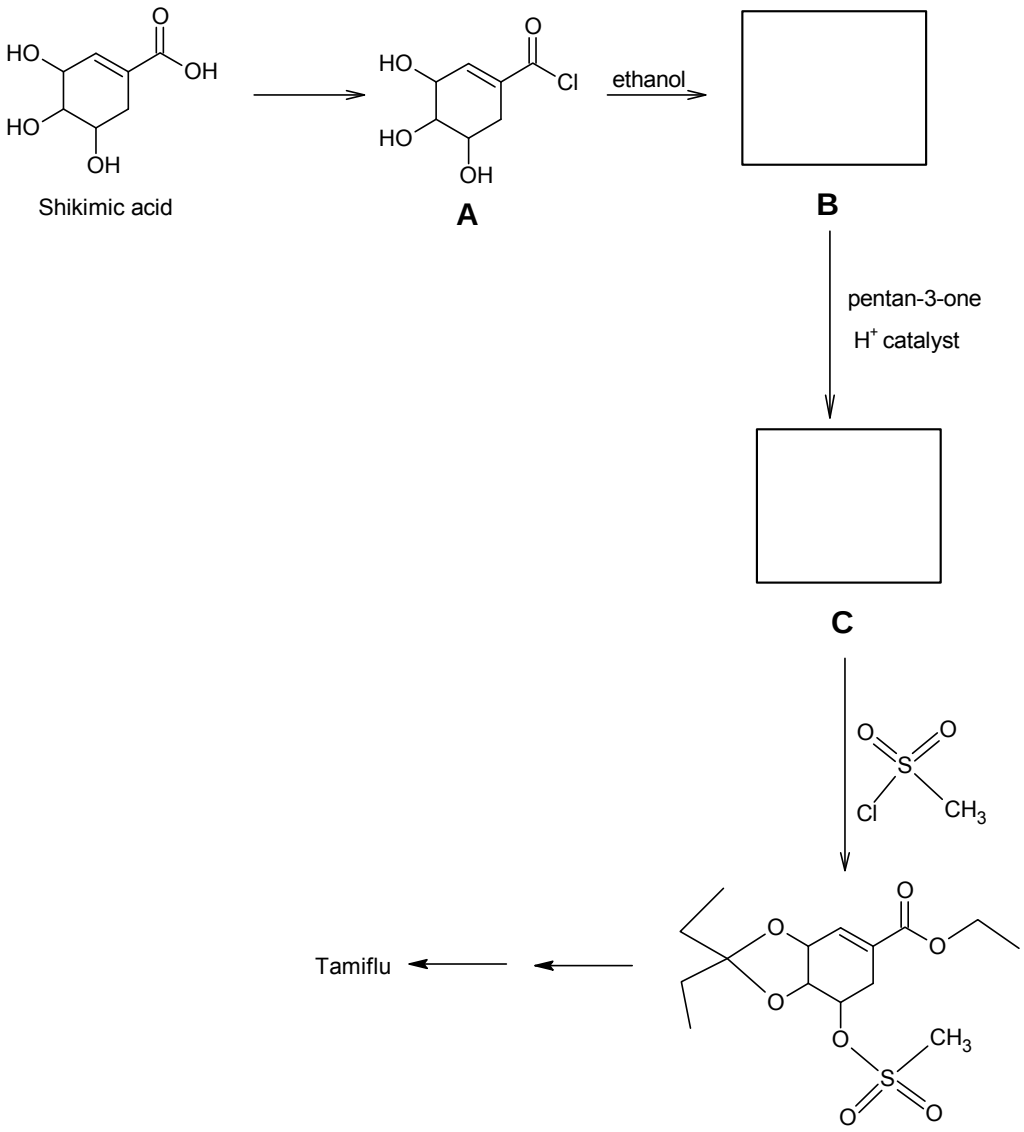
Water is a competing nucleophile to the alcohol, hence other **side products may be formed**.

(b) Tamiflu is the anti-influenza drug currently being used to treat 'Bird–flu'. It can be synthesised from Shikimic acid, which occurs naturally in star anise.



Shikimic acid

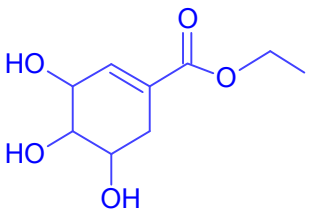
Part of the synthetic route is shown below. Formation of acetals between selected –OH groups of Shikimic acid and ketones helps to control which of the –OH groups reacts to synthesise **C** from **B**.



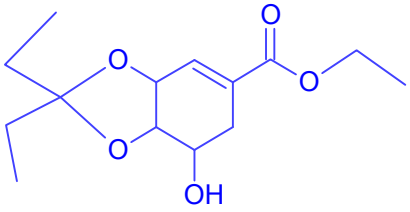
(i) Draw the structures of **B** and **C** in the boxes provided above.

[2]

B



C



(ii) Explain why **B** was formed from **A** instead of Shikimic acid directly.

[1]

A (acid chloride) is **more reactive** than Shikimic acid.

Using **A** will give a better yield as the reaction is irreversible compared to reversible reaction when Shikimic acid is used. The reaction also requires milder conditions (doing–away with heating and use of catalyst).

(c) Like Shikimic acid, methanoic acid occurs naturally in ants. It is a weak acid and dissociates according to the equation shown.

$$HCOOH\ (aq) \rightleftharpoons HCOO^-\ (aq) + H^+\ (aq) \qquad K_a = 1.60 \times 10^{-4}\ mol\ dm^{-3}$$

(i) Explain what is meant by the term pK_a as applied to methanoic acid.

[2]

$pK_a = -\lg K_a$

$K_a = \frac{[HCOO^-][H^+]}{[HCOOH]}$

A flask contains 0.0100 mol of methanoic acid dissolved in 250 cm^3 of water.

(ii) Calculate the pH of this solution.

[2]

$[HCOOH] = \frac{0.0100}{0.250}$

$= 0.0400\ mol\ dm^{-3}$

$[H^+] = \sqrt{(0.0400)(1.60 \times 10^{-4})}$

$= 2.5298 \times 10^{-3}\ mol\ dm^{-3}$

$pH = -\lg (2.5298 \times 10^{-3})$

$= \mathbf{2.60}$

(iii) Hence, calculate the degree of dissociation, α, of methanoic acid in this solution.

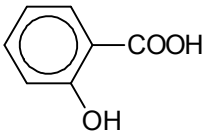
[1]

$\alpha = \frac{[H^+]}{[HCOOH]}$

$= \frac{[2.5298 \times 10^{-3}]}{[0.0400]}$

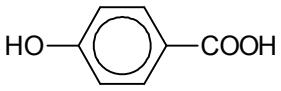
$= \mathbf{0.0632}$

(d) Salicylic acid occurs naturally in plants.



salicylic acid

pK_{a1} = 2.97



isomer of salicylic acid

pK_{a1} = 4.54

Explain why salicylic acid is more acidic than its isomer.

[2]

The conjugate base formed from the dissociation of salicylic acid is stabilised by hydrogen bonds between the –OH and $–COO^-$ groups.

The conjugate base formed from the dissociation of the isomer **cannot form such a bond as the –OH and $–COO^-$ groups are too far apart**.

Hence the conjugate base formed from the dissociation of salicylic acid is **stabilised to a greater extent** compared to that of the isomer. The position of the dissociation equilibrium lies more to the right and salicylic acid is a stronger acid than the isomer.

[Total: 15]