

CHEMISTRY

9729/03

Paper 3 Free Response Questions

2 hours

READ THESE INSTRUCTIONS FIRST

Write in dark blue or black pen.

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

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

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer **all** questions.

Section B

Answer **one** question.

The use of an approved scientific calculator is expected, where appropriate.

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

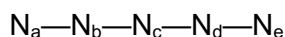
Question	1	2	3	4	5	Total
Marks scored						
Maximum Marks	22	15	23	20	20	80

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Section A: Answer **all** questions.

- 1 Nitrogen, being the most abundant element in our atmosphere, is an element with much research interest and many applications.
- (a) Apart from N_2 , there are a few other poly-nitrogen species that are discovered to be stable enough at room temperature.

One of these poly-nitrogen species is N_5^+ . N_5^+ has 5 nitrogen atoms arranged in a straight-chain. Only the sigma bonds of N_5^+ is shown in the structure below.



Some data is presented in **Table 1.1**.

Bond length of N_a-N_b and N_d-N_e	110 pm
Bond length of N_b-N_c and N_c-N_d	130 pm
Bond angle of $N_a-N_b-N_c$	168°
Bond angle of $N_b-N_c-N_d$	111°

Table 1.1

- (i) State the principles of the Valence Shell Electron Pair Repulsion theory. [2]
- (ii) State the geometry at the atoms N_b , N_c and N_d that most suitably explains the data in **Table 1.1**. [1]
- (iii) By considering your answer in (ii) and data in **Table 1.1**, draw a dot-and-cross diagram of N_5^+ . [2]
- (iv) State the oxidation state of each of the nitrogen atoms N_a to N_e from your dot-and-cross diagram in (iii). [1]

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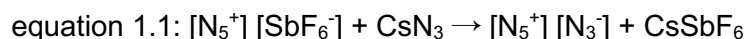
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(b) The azide ion, N_3^- , is another poly-nitrogen species.

The hypothetical salt $[\text{N}_5^+][\text{N}_3^-]$ has been postulated to be unstable at low temperatures.

Some 2.267 mmol of $[\text{N}_5^+][\text{SbF}_6^-]$ was mixed with 2.267 mmol of CsN_3 in SO_2 at $-196\text{ }^\circ\text{C}$. The mixture was warmed to $-64\text{ }^\circ\text{C}$ (the melting point of SO_2), and a violent reaction started to take place which produced yellow flames together with bubbling. After the reaction, 0.8990 g of white solid was obtained at $-64\text{ }^\circ\text{C}$.

Equation 1.1 describes what this experiment was aiming to achieve.



- (i)** Suggest an equation that accounts for the violent reaction. [1]
- (ii)** With reference to your answer in **(i)**, suggest why when the mixture was warmed, the reaction mixture became violent. [1]
- (iii)** State the identity of the white solid, and comment on the amount of white solid obtained after the reaction. [2]
- (iv)** At $-64\text{ }^\circ\text{C}$, the value of K_{sp} of CsN_3 in liquid SO_2 is 9.86. Calculate the minimum volume of SO_2 that needs to be added to dissolve all of the CsN_3 . [2]
- (v)** Explain how the presence of dissolved CsN_3 affects the solubility of CsSbF_6 in liquid SO_2 . [1]

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- (c) Azide salts are highly unstable and decompose to give nitrogen gas. They have a variety of applications. For example, sodium azide is used in airbags.

Electric detonators in the military contain lead(II) azide, $\text{Pb}(\text{N}_3)_2$. When an electric current is passed through lead(II) azide, it decomposes.

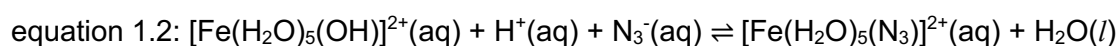
- (i) An electric detonator has a cylindrical aluminium covering that contains the detonating substance. In 1 electric detonator measuring 45.0 mm in length, and 7.00 mm in **diameter**, the detonator carries 0.600 g of lead(II) azide.

A soldier passes a current through the detonator. **Estimate** the pressure inside the cylindrical aluminium covering after all the lead(II) azide has decomposed, and just before the covering is about to break. Assume that the covering is rigid. [3]

Slight amounts of copper present in the electric detonator may lead to the formation of copper(II) azide, $\text{Cu}(\text{N}_3)_2$, over time. Copper(II) azide is much more sensitive than lead(II) azide, so this may lead to premature detonations and is very dangerous to the user.

One way to detect copper(II) azide is through the iron(III) chloride test.

A few drops of aqueous iron(III) chloride is added to the detonator. If a red colouration is seen, copper(II) azide is most likely present. Equation 1.2 represents the reaction taking place.



numerical value of $K_c = 0.5088$

- (ii) Explain why a solution of iron(III) chloride is acidic. [1]

- (iii) Explain why $[\text{Fe}(\text{H}_2\text{O})_5(\text{N}_3)]^{2+}$ has a different colour compared to $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$. [1]

- (iv) 5.00 cm^3 of a buffered solution containing $[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})]^{2+}$ with a concentration of $0.0200 \text{ mol dm}^{-3}$ and pH of 2.72 was dropped onto a detonator suspected to have a contamination of copper(II) azide. Assume that this solution did not contain any azide ions initially. A red colouration was observed. 0.1 cm^3 of this mixture, at equilibrium, was extracted for analysis. It was determined that the concentration of $[\text{Fe}(\text{H}_2\text{O})_5(\text{N}_3)]^{2+}$ is $1.40 \times 10^{-6} \text{ mol dm}^{-3}$.

Calculate the mass of copper(II) azide detected. [4]

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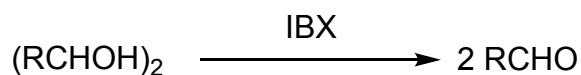
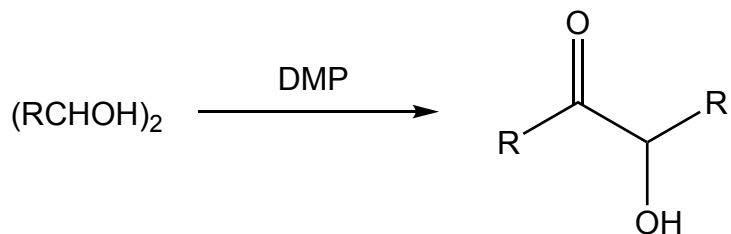
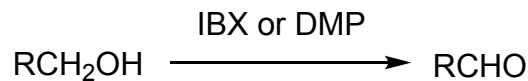
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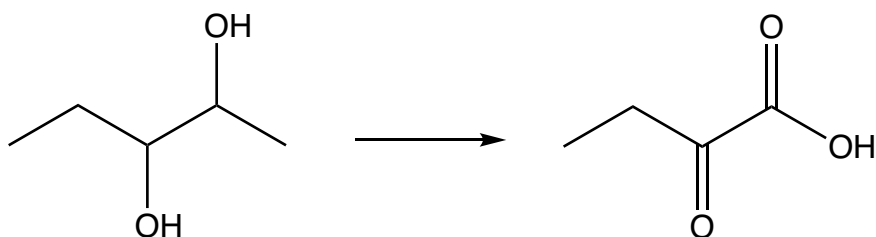
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- (c) Iodine-containing reagents are also employed in oxidation reactions. 2 of these are IBX and DMP. IBX and DMP can oxidise primary and secondary alcohols to aldehydes and ketones respectively.

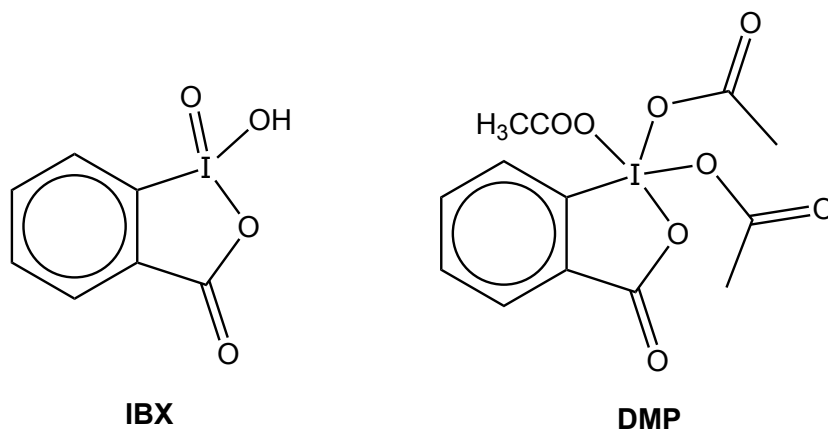
Study the following reactions below:



- (i) Suggest steps using **at least three** different iodine-containing reagents that achieve the conversion below. You can use **either** IBX **or** DMP, but **not** both of them in this question. Draw the intermediates after each step. [5]



- (ii) State the geometry and the oxidation states of the iodine atoms of IBX and DMP. [2]



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- (b) Amino acids with 1 chiral centre undergo a reversible racemisation reaction which reverses the stereochemical configuration of the chiral centre. This is represented by equation 3.1.



The rate constants of the forward and backward reaction are both k .

The concentrations of the R enantiomer, R , and the S enantiomer, S , are governed by the following relationship below.

$$\ln \left(\frac{[\text{S}] + [\text{R}]}{[\text{S}] - [\text{R}]} \right) = 2kt + C$$

At time t after the start of this racemisation, the concentration of R and S are $[\text{R}]$ and $[\text{S}]$ respectively. C is a dimensionless constant.

- (i) Deduce the overall order of reaction of the forward reaction of equation 3.1. [1]
- (ii) State ΔG^\ominus of the forward reaction of equation 3.1. Explain why ΔG^\ominus takes on this value by considering that S and R are enantiomers of each other. [1]
- (iii) Peptides from a dead body found in an Egyptian tomb were hydrolysed for 4 hours. The amino acid arginine was isolated. Arginine has 1 chiral centre. The ratio of the R to the S enantiomer was found to be 0.059 after the hydrolysis. During hydrolysis, racemisation occurs.

Describe the reactants and conditions for this hydrolysis to take place. [1]

- (iv) In the body, only S is present. When a human dies and is preserved, racemisation does not take place.

Show that $C = 0$ if racemisation does not take place during the duration of death. [1]

- (v) Hence, determine the value of the rate constant, k_2 , for this racemisation process during hydrolysis. State its **SI units** and express your answer in SI units. [2]

(The SI unit for time is s, for amount is mol, and for length is m.)

- (vi) Bodies may be preserved by boiling them in water for a period of time. Another body found in an Egyptian tomb was boiled in hot water before storage in the tomb. A bone of this dead body was subjected to hydrolysis as that in (iii). The ratio of the R enantiomer to the S enantiomer of arginine was found to be 0.090 after the hydrolysis.

Only when the body was boiled before the body was stored in the tomb, racemisation took place with a rate constant **value** of $k_1 = 1.417 \times 10^{-6}$. The value of k_1 is given in SI units.

(vi) continues on the next page.

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(c) Boiled dead bodies are hard to distinguish from un-boiled ones on first sight. In order to determine whether a body is boiled or not, a biologist extracts a liver sample from a dead body.

Liver contains the enzyme catalase, which catalyses the decomposition of hydrogen peroxide to water and oxygen gas.

Explain how the biologist would be able to determine whether the body was boiled. Include a brief explanation on why your procedure works. [2]

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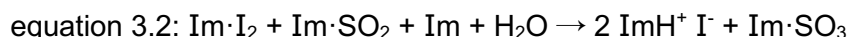
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- (d) Egyptian mummifying was one of the most effective ways in preserving a body back before refrigerators were invented. A dead body had to be dehydrated severely before being wrapped in bandages.

The water content of the body can be measured through a method known as the Karl-Fischer titration.

A 5.203 g sample of human flesh from an Egyptian Mummy was cut. This was placed in a solution of ethanol containing KI, SO₂, and a base, imidazole.

When the solution is electrolysed, iodide ions are oxidised to iodine. Iodine then reacts with water and SO₂ in the presence of imidazole (abbreviated as Im) according to equation 3.2.



When all the water has reacted with I₂, excess I₂ produced by the electrolysis results in electricity being cut off, thereby completing the titration.

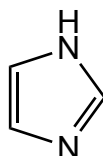
- (i) The sample requires 5.027×10^{-3} moles of electrons to be passed in the electrolysis for the titration to be completed.

Determine the percentage by mass of water in the sample of human flesh. [2]

- (ii) Imidazole behaves as a Lewis Base in equation 3.2.

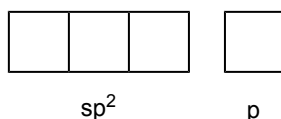
Explain **one other** type of basic behaviour of imidazole in equation 3.2. [1]

- (iii) The structure of imidazole is shown below.



Both of the N atoms are sp² hybridised.

Copy the following electron-in-box diagram and populate the boxes with the appropriate number of electrons for **each** N atom in imidazole. [2]



- (iv) Hence, explain which N atom acts as the stronger Lewis Base, and draw the structure of Im·I₂. [2]

(b) (i) Phenol may **not** be synthesised from chlorobenzene and sodium hydroxide.

Give **two** reasons why this is so.

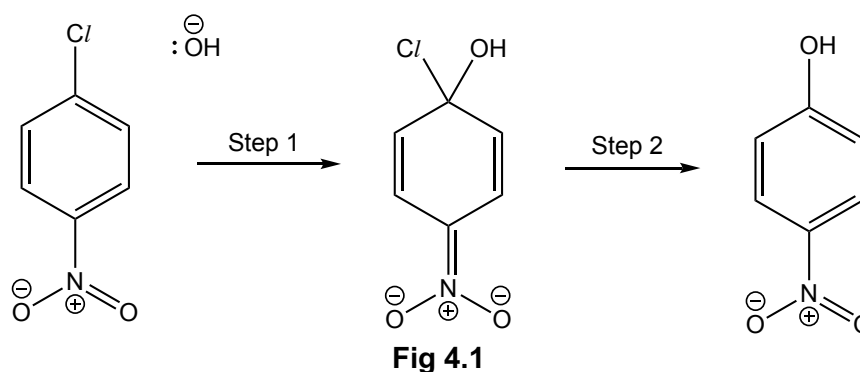
[2]

(ii) However, 4-nitrophenol can be synthesised from 1-chloro-4-nitrobenzene with sodium hydroxide.

Explain if you would nitrate chlorobenzene or chlorinate nitrobenzene to ensure a high yield of 1-chloro-4-nitrobenzene.

[1]

(iii) The proposed mechanism for the conversion of 4-nitrochlorobenzene to 4-nitrophenol with sodium hydroxide is shown in Fig 4.1.



Draw curly arrows for Step 1.

[1]

(iv) By considering the mechanism in (iii), or otherwise, will 3-nitrochlorobenzene react with sodium hydroxide to form 3-nitrophenol? Explain your answer.

[2]

(v) Draw a labelled energy profile diagram for the conversion of 4-nitrochlorobenzene to 4-nitrophenol with the hydroxide ion.

[3]

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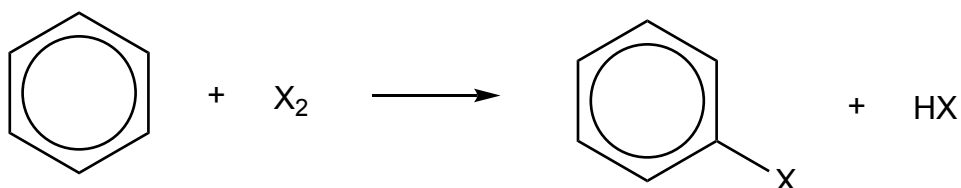
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(c) (i) Use the *Data Booklet* to complete Table 4.1.

[2]



X	$\Delta H / \text{kJ mol}^{-1}$
F	
Cl	
I	

Table 4.1

ΔH is the enthalpy change of reaction.

- (ii) Using your answer to (i), explain why the iodination of benzene is harder as compared to its chlorination. [2]
- (iii) Under the presence of concentrated nitric acid, iodine is converted to the stronger electrophile I^+ . Given that 2 moles of nitric acid react with 1 mole of I_2 , deduce the oxidation state of the nitrogen-containing byproduct. [1]
- (iv) Hence, write a balanced equation for the generation of the electrophile I^+ . [1]
- (v) The fluorination of benzene does **not** proceed with F_2 in the presence of AlF_3 . AlF_3 is an ionic compound.

Explain why AlF_3 is ionic, whereas AlCl_3 is simple covalent. [2]

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(b) The Bischler-Napieralski reaction uses a strong phosphorus containing Lewis acid POCl_3 .

(i) Draw a dot-and-cross diagram of POCl_3 . [1]

(ii) The Bischler-Napieralski reaction has the following simplified mechanism in Fig 5.1.

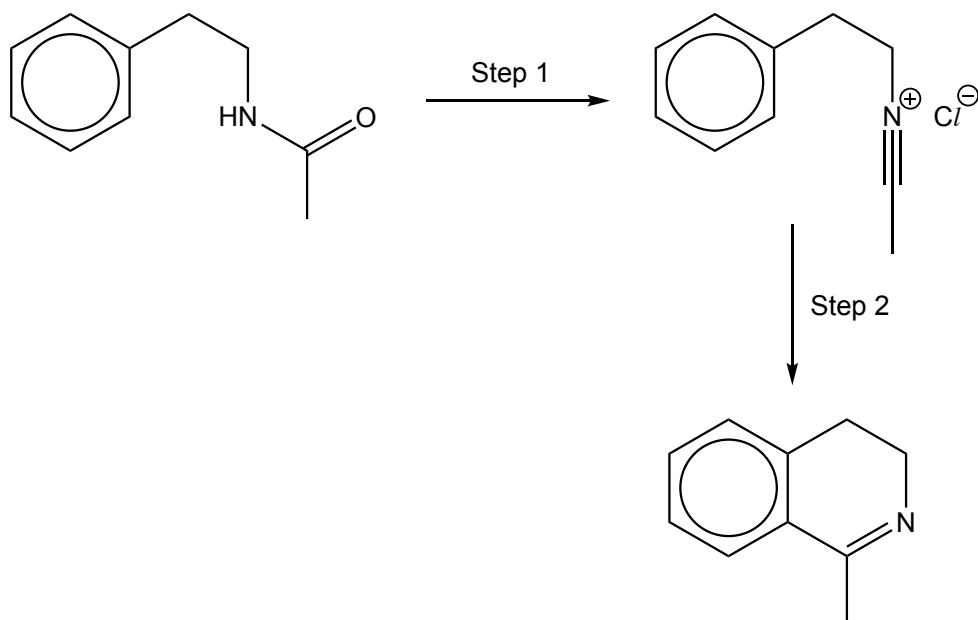


Fig 5.1

Draw curly arrows to describe the mechanism for Step 2. [2]

(iii) Apart from a substitution reaction, classify the Bischler-Napieralski reaction under **one** other *type of reaction*. [1]

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- (c) The Wittig reaction is a useful reaction to create C=C double bonds from carbonyl compounds. The Wittig reagent has a generic structure $R^1R^2C=PPh_3$ where R is an alkyl group or H atom. Fig 5.2 shows an example.

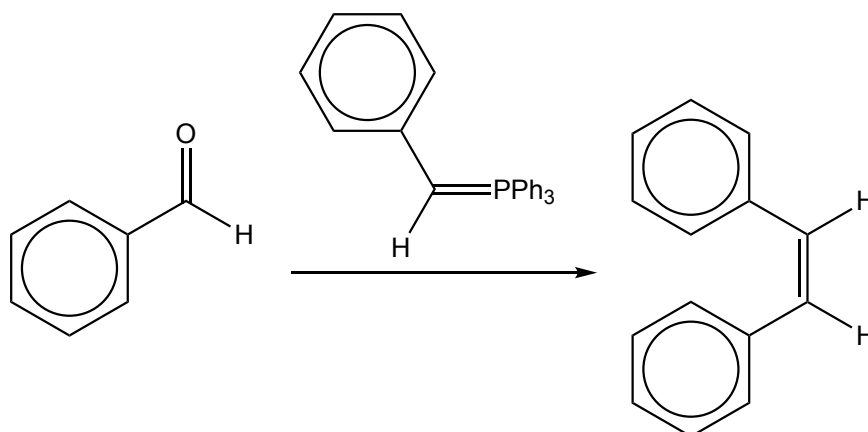
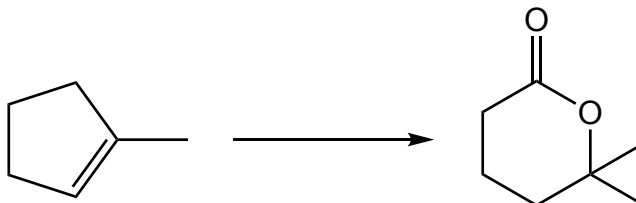


Fig 5.2

The by-product of Fig 5.2 is $Ph_3P=O$. (Ph = $-C_6H_5$)

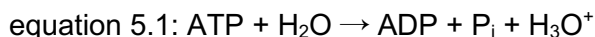
- (i) Using an appropriate Wittig reagent in one of your steps, describe the reactants and conditions to achieve the following conversion below. [7]



- (ii) State the type of reaction occurring in Fig 5.2. [1]

(d) Phosphorous is a building block in many living things. Apart from DNA, phosphorous can be found in ATP. ATP stores energy in living things which can be used later. When ATP releases energy, ADP is formed, together with a free phosphate group, P_i .

(i) The balanced equation for the conversion of ATP to ADP is shown in equation 5.1.



In the conditions of a human body for equation 5.1,
 $\Delta G = -31 \text{ kJ mol}^{-1}$ and $\Delta H = -20 \text{ kJ mol}^{-1}$.

Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, is a good source of energy for the body. The standard Gibbs' Free energy of combustion of glucose is $-2880 \text{ kJ mol}^{-1}$. For every molecule of glucose, as many as 38 ATP molecules can store the energy released by its oxidation in the presence of O_2 .

However, when the body is deprived of oxygen, glycolysis occurs instead. For every mole of glucose oxidised, only 2 ATP molecules are synthesised.

Calculate the percentage efficiency of the storage of energy when the body is deprived of oxygen and when the body is not deprived of oxygen. [1]

(ii) Protein synthesis is a highly non-spontaneous process.

Free amino acids are linked together to form a polypeptide, which eventually becomes a protein through folding into specific, restricted conformations.

Suggest a thermodynamic factor to account for its non-spontaneity. [1]

(iii) Myoglobin is a protein in the body that stores 1 molecule of oxygen and has around 150 peptide links. The formation of a mole of peptide links has $\Delta G = +17 \text{ kJ mol}^{-1}$.

10^{20} molecules of myoglobin were synthesised in a body during a short nap. Estimate the amount of glucose needed to provide energy for this synthesis. [2]

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