Anglo-Chinese Junior College

JC2 Preliminary Examination
Higher 2

A Methodist Institution
(Founded 1886)

CANDIDATE NAME		FORM CLASS	2			
TUTORIAL CLASS	2CH				INDEX NUMBER				

CHEMISTRY

9729/03

Paper 3 Free Response

27 August 2024
2 hours

Candidates answer on the Question Paper.
Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your index number and name on all the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
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.
Circle the number of the question you have attempted.

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

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiners' use only	
Section A	
1	**/ 20**
2	**/ 20**
3	**/ 20**
Section B	
4 / 5	**/ 20**
Presentation	
Total	**/ 80**

Section A

Answer **all** the questions in this section.

1 (a) Describe the variation in the behaviour of Period 3 chlorides NaC*l*, A*l*C*l*$_3$ and PC*l*$_5$ separately with water.

Write equations for any reactions described and state the pH of the resultant solutions. [3]

……

……..

……..

……..

……..

……..

……..

……..

……..

……..

(b) When soil becomes acidic, aluminium leeches out of minerals into the soil. High aluminium content in soil affects root growth and causes the roots to be brittle. These problems are minimised if the topsoil pH is maintained above 5.5.

In a study of a soil condition, a sample of soil water was titrated with $EDTA^{4-}$, a hexadentate ligand, to determine its aluminium ion concentration.

equation 1 $[Al(H_2O)_6]^{3+}(aq) + EDTA^{4-}(aq) \rightleftharpoons [Al(EDTA)]^{-}(aq) + 6H_2O(l)$

(i) State the type of reaction in equation 1. [1]

(ii) The concentration of aluminium ions in the soil water sample was found to be 2.90×10^{-5} mol dm^{-3}. Calculate the pH of the water sample, given that the aqueous complex of Al^{3+} has a K_a value of 7.9×10^{-6}.

You may assume that the complex of Al^{3+} behaves as a weak monobasic acid, HA. [1]

(iii) Another 25 cm^3 sample of soil water was found to contain 0.250 mol dm^{-3} of NaH_2PO_4. 20 cm^3 of solution **A** which contains aqueous Na_2HPO_4 was added to the water sample to obtain a solution buffered at pH 6.8.

Calculate the concentration of HPO_4^{2-} in solution **A**, given that the pK_a value of $H_2PO_4^-$ is 7.2. [3]

(c) The reactions of ethylbenzene to form **H**, **J** and **K** are shown in Fig.1.1.

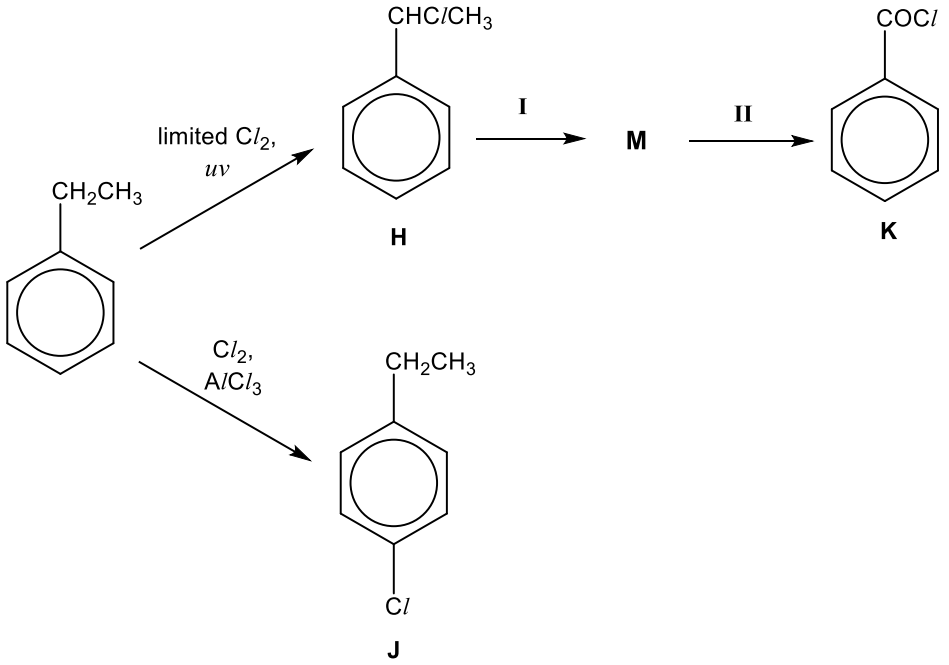


Fig. 1.1

(i) Suggest the reagents and conditions needed for reactions **I** and **II** and suggest the structure of **M** in Fig. 1.1. [3]

(ii) Describe and explain the relative ease of hydrolysis of **H**, **J** and **K**. [3]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(d) Graphene is a nanomaterial comprising of a single layer of graphite. Compared with copper, it has higher tensile strength and similar electrical conductivity while having lower mass. An experiment was conducted to electroplate copper onto graphene.

In the experiment, a copper anode and graphene cathode was immersed in aqueous copper(II) sulfate as the electrolyte.

(i) Describe the observations at the cathode and the electrolyte after some time. [1]

(ii) The graphene at the cathode is a square with a length of 0.1 m.

Assume that each copper occupies a cube length of 3.0×10^{-12} m, the graphene has no thickness and there is uniform plating of copper.

Calculate

1. the amount of Cu atoms to cover **both** sides of the graphene with a depth of 500 atoms
2. the time required to achieve this using a current of 5.0 A. [3]

(iii) The student replicated this experiment to electroplate graphene with A*l*. He replaced aqueous $CuSO_4$ with aqueous $Al(NO_3)_3$ and the copper plate with an aluminium plate.

Using $E^{\ominus}$ values from the *Data Booklet*, suggest if this experiment will be successful. [2]

…….

…….

…….

…….

…….

…….

…….

…….

…….

…….

…….

…….

…….

…….

…….

…….

…….

[Total: 20]

2 The oxime functional group R–C=N–OH undergoes a rearrangement reaction to form amide in the presence of aluminium oxide. During the reaction, the alkyl group that is trans to the OH group migrates to the N atom. Fig. 2.1 shows an example of this rearrangement.

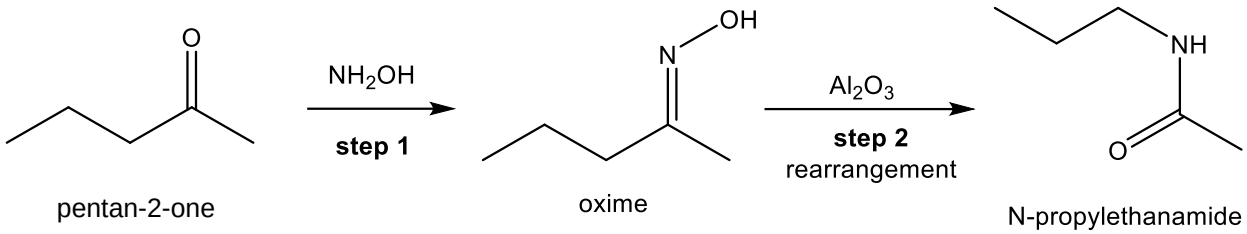


Fig. 2.1

(a) **(i)** Write a balanced equation for step 1 and suggest the type of reaction that occurred. [2]

(ii) A molecule of oxime contains both σ and π bonds.

Draw labelled diagrams to show how orbitals of the C atom and N atom overlap to form

- a σ bond
- a π bond [2]

(iii) Oximes may exist as cis-trans isomers. State and explain the feature of the oxime molecule which allows them to show cis-trans isomerism. [1]

(iv) Suggest a simple chemical test to distinguish pentan-2-one and N-propylethanamide shown in Fig. 2.1. [2]

…….

…….

…….

…….

…….

…….

…….

…….

…….

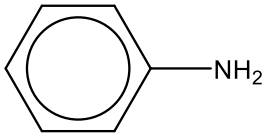
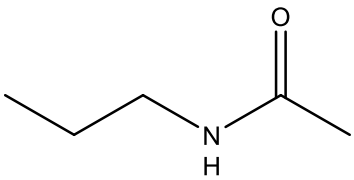
…….

…….

…….

(b) The pK_b values of three nitrogen containing compounds are given in Table 2.1.

Table 2.1

name	structure	pK_b
phenylamine		9.4
ethylamine	$CH_3CH_2NH_2$	3.4
N-propylethanamide		14.4

Rank the compounds in order of increasing basicity and explain your reasoning. [3]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(c) Zwitterion **A** $C_5H_9NO_2$ reacts with hot acidified potassium manganate(VII) to form compound **B** $C_3H_7NO_2$ and compound **C**, $C_2H_2O_4$. Compound **C** further oxidises to form a gas that forms white precipitate in limewater. **B** does not rotate plane polarised light.

Compound **A** also reacts with $SOCl_2$ to form **D** C_5H_8NOCl which further reacts to form a neutral compound **E** C_5H_7NO.

E is also formed when the oxime **F** C_5H_7NO reacts in the presence of aluminium oxide.

(i) Describe the formation of a *zwitterion*. [1]

(ii) Suggest possible structures for **A**, **B**, **C**, **D, E** and **F**. For each reaction, state the type of reaction described and explain what the information tells you about the functional groups present in each compound. [9]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 20]

BLANK PAGE

3 (a) (i) Using relevant $E^{\ominus}$ values from the *Data Booklet*, describe the trend in reactivity of Group 2 metals as reducing agents. [2]

(ii) Using the *Data Booklet* or otherwise, explain another property of Group 2 metals that supports this trend. [2]

……

……

……

……

……

……

……

……

……

……

……

……

(b) Thermogravimetric analysis, TGA, is an analytical technique primarily used to characterise materials by measuring the change in mass that occurs as a sample is heated at a constant rate.

A thermogram from the TGA of calcium carbonate and magnesium carbonate is shown in Fig. 3.1.

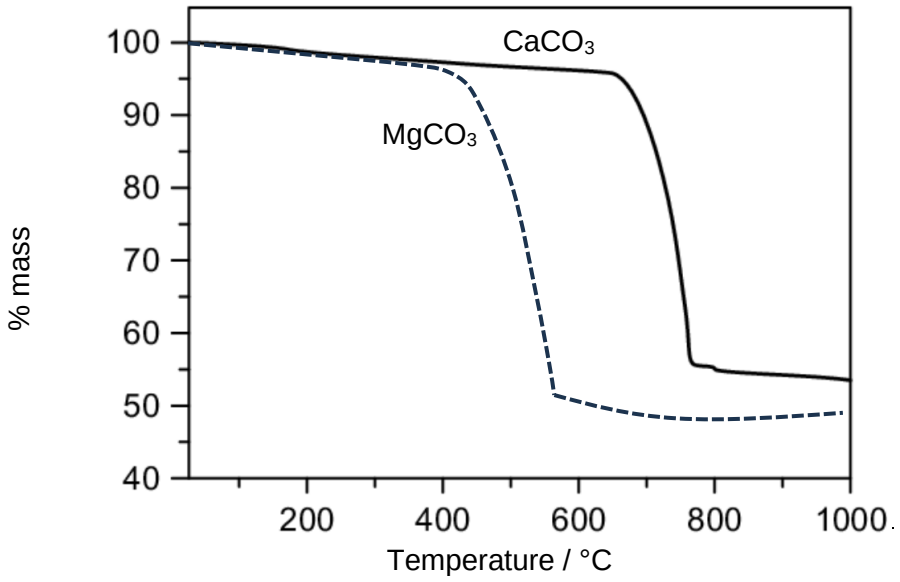


Fig. 3.1

(i) For both samples, the thermogram shows significant loss in mass when the temperature is high enough.

Write an equation for the heating of calcium carbonate at about 800 °C. [1]

(ii) With reference to your equation in **(b)(i)**, explain the differences between the thermogram of calcium carbonate and magnesium carbonate in terms of

- the temperature when the carbonate starts to have significant decrease in mass,
- the final mass of product obtained, given that the same initial mass is used for both carbonates. [4]

(iii) Explain the difference in melting points of calcium carbonate and magnesium carbonate in terms of structure and bonding. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(c) **(i)** Explain what is meant by the term *standard enthalpy change of combustion*. [1]

……

……

……

……

A bomb calorimeter consists of a thermally-insulated sealed metal container immersed in water. A sample of calcium is placed into the metal container, after which the container is filled with high pressure of excess oxygen. The sample is then ignited and the temperature change in the surrounding water is recorded.

Some data is recorded in Table 3.1.

Table 3.1

mass of calcium / g	1.41
mass of water / g	150
temperature of water before ignition / °C	28.6
temperature of water after ignition / °C	56.0
heat capacity of calorimeter, C_p / J K^{-1}	191
specific heat capacity of water, c / J g^{-1} K^{-1}	4.18

(ii) The heat released, q, can be found using the following relationship.

$$q = (C_p + mc)\,\Delta T$$

Together with the information in Table 3.1, calculate the enthalpy change of combustion of calcium. [2]

(iii) The experiment was repeated with 1 bar of oxygen gas. The value of the enthalpy change of combustion obtained was smaller than that in **(c)(ii)**.

Suggest a reason for the discrepancy. [1]

……

……

……

……

……

……

……

……

……

(d) The decarboxylation of carboxylic acids to obtain alkenes can be achieved in a series of steps.

The overall balanced equation of the reaction process is shown.

$$R\text{–}COOH + Pb(CH_3CO_2)_4 \xrightarrow{Cu(CH_3CO_2)_2} \text{alkene} + CO_2 + 2CH_3COOH + Pb(CH_3CO_2)_2$$

The process of decarboxylation of butanoic acid, $CH_3CH_2CH_2COOH$, with lead tetraethanoate, $Pb(CH_3CO_2)_4$ in the presence of catalytic amounts of $Cu(CH_3CO_2)_2$ is shown in Fig. 3.2.

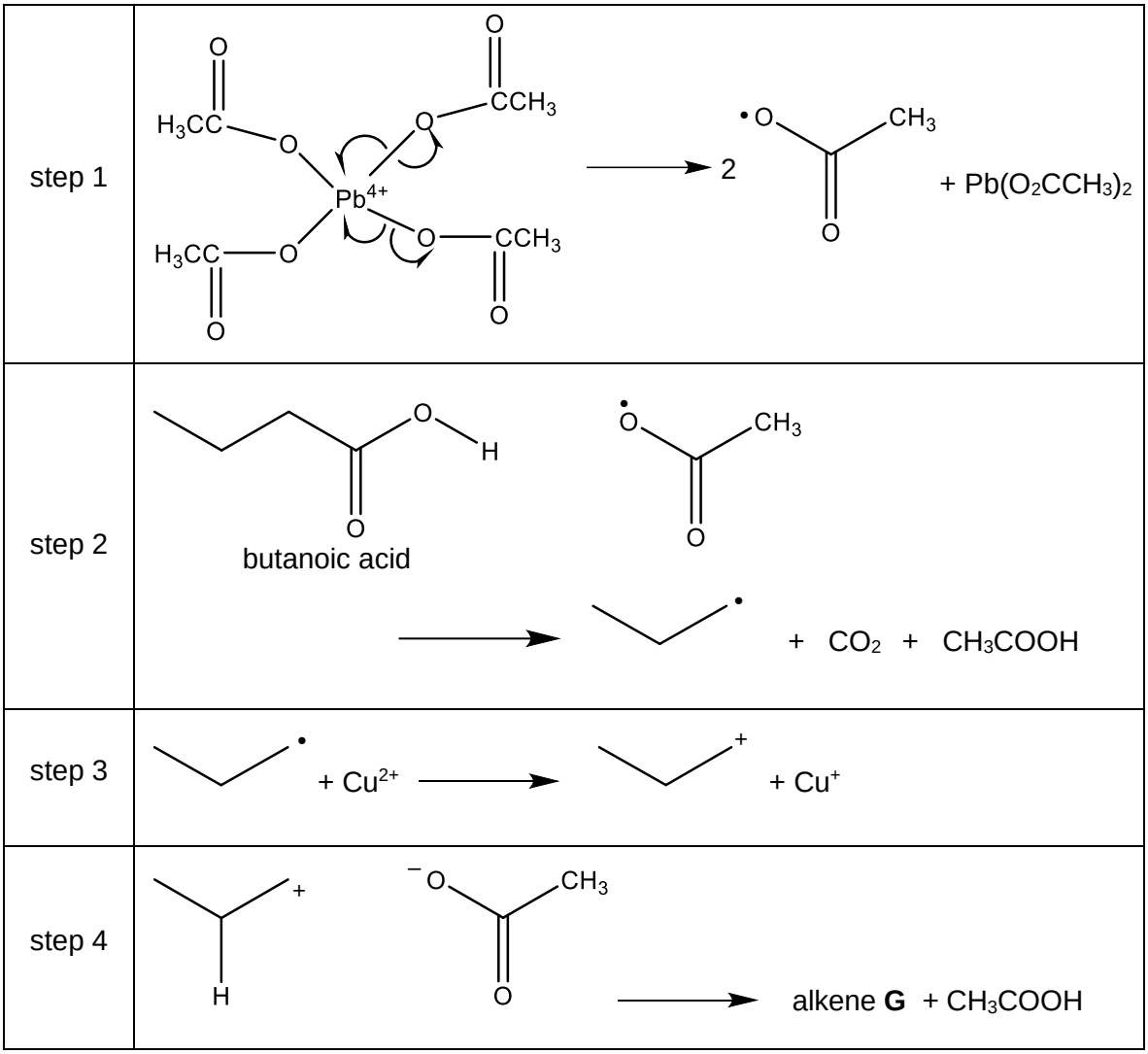


Fig. 3.2

(i) Steps 1 and 2 of the decarboxylation process involve the generation of free radicals. The mechanism of step 1 has been drawn in Fig. 3.2. Complete the mechanism on step 2 on Fig. 3.2 by adding **five** half arrows. [1]

(ii) Complete the mechanism of step 4 on Fig. 3.2 by adding **two** full arrows, hence deduce the structure of **G**. [2]

(iii) Name the types of reaction for steps 3 and 4. [2]

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[Total: 20]

Section B

Answer **one** question from this section.

4 (a) The zinc-air battery involves a porous zinc electrode that reacts to form zincate, $Zn(OH)_4^{2-}$.

$$Zn(OH)_4^{2-}(aq) + 2e^- \rightleftharpoons Zn(s) + 4OH^-(aq) \qquad E^\ominus = -1.25\ V$$

The other electrode in the battery is the oxygen electrode in an alkaline medium.

(i) Draw a fully labelled diagram of the experimental set-up used to measure this $E^\ominus_{cell}$ and indicate the direction of electron flow. [3]

(ii) Calculate the standard Gibbs free energy change, $\Delta G^\ominus$, for the oxidation of one mole of zinc in the zinc-air battery. [2]

(iii) Predict how the E_{cell} will change when water is added into the $Zn(OH)_4^{2-}/Zn$ half-cell. [2]

(iv) The zinc-air battery can be recharged and is relatively cheaper to produce.

Suggest one **other** advantage of using the zinc-air battery. [1]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

(b) (i) In the Contact Process, vanadium oxide catalyses the formation of sulfur trioxide, which is eventually converted to sulfuric acid through further reactions.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

State the type of catalyst in this reaction and describe how vanadium oxide speeds up this gaseous reaction. [3]

(ii) In aqueous solution, vanadium ions form complexes of which the colours are lilac $[V(H_2O)_6]^{2+}$, green $[V(H_2O)_6]^{3+}$ and blue $[VO(H_2O)_5]^{2+}$.

Explain why vanadium ions are often coloured in aqueous solutions. [3]

(c) In the nitration of benzene, sulfuric acid and nitric acid are used to generate the highly reactive nitronium ion.

Fig. 4.1 shows the incomplete mechanism for the formation of the nitronium ion.

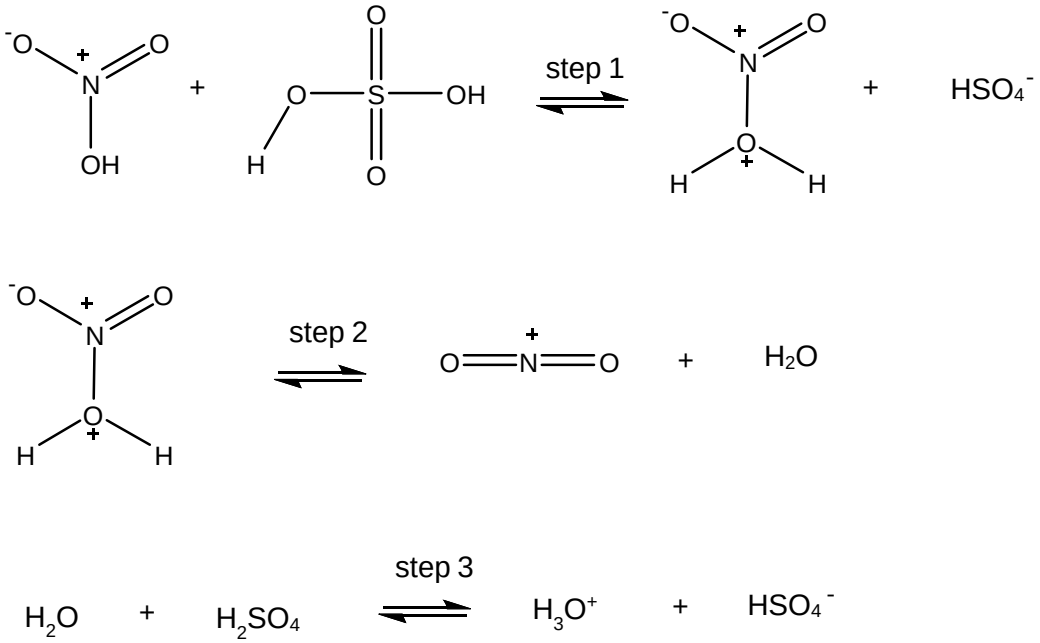


Fig. 4.1

(i) On Fig. 4.1, draw curly arrows, partial charges and insert relevant lone pairs in steps 1 and 2 to complete the mechanism for the formation of the nitronium ion. [2]

(ii) State the role of sulfuric acid in step 1. [1]

……

……

……

……

……

……

……

……

……

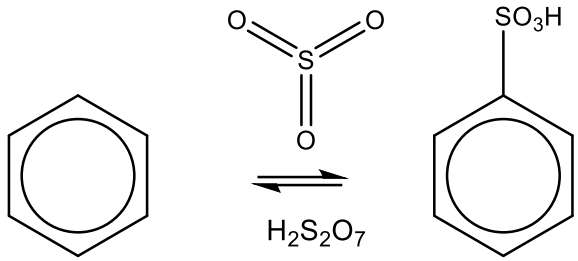
……

……

……

……

(d) **(i)** Benzene can also undergo electrophilic substitution with sulfur trioxide in the presence of fuming sulfuric acid.



Explain why sulfur trioxide can act as an electrophile. [1]

(ii) Suggest a mechanism for the reaction between benzene and sulfur trioxide. Show the displayed structure of the electrophile, the structure of the intermediate and the movement of electron pairs by using curly arrows. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

[Total: 20]

BLANK PAGE

5 The "OXO" reaction is industrially important in making aldehydes and ketones from alkenes. For example, propanal can be synthesised from ethene, C_2H_4, as shown in the following equation.

$$CH_2{=}CH_2(g) + CO(g) + H_2(g) \rightleftharpoons CH_3CH_2CHO(g) \qquad \Delta H < 0$$

(a) In an experiment, an equimolar mixture of C_2H_4, CO and H_2 is added to a sealed vessel and heated to 500 K in the presence of rhodium catalyst. At equilibrium, 99% of C_2H_4 has reacted. The total pressure in the vessel is 40.8 atm at equilibrium.

(i) Write the expression for the equilibrium constant, K_p, for this reaction. Use your expression to calculate the value of K_p for this reaction. Include its units. [4]

(ii) The actual conditions used for the manufacturing of propanal in the OXO process is 480 K and 100 atm in the presence of a rhodium based catalyst.

Explain the conditions used for the manufacture of propanal. [2]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

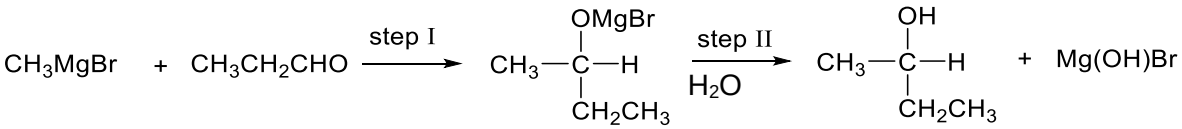
.....

.....

.....

(b) The Grignard reagent is a class of covalent compounds involving magnesium. One example of a Grignard reagent is CH_3MgBr which is prepared by treating magnesium metal with bromomethane in an ether solvent.

A typical example of the use of a Grignard reagent is the two-step reaction of CH_3MgBr with propanal, CH_3CH_2CHO, to form butan-2-ol.



(i) State the types of reaction for steps I and II. [2]

(ii) State the reagents and conditions to convert butan-2-ol to 2-bromobutane. [1]

.....

.....

.....

.....

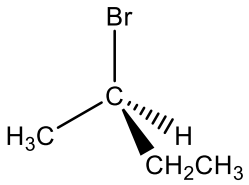
.....

.....

.....

"R" and "S" are used to denote enantiomers. R and S isomers rotate plane polarised light in opposite directions.

The R isomer of $CH_3CH_2CHBrCH_3$ is shown below.

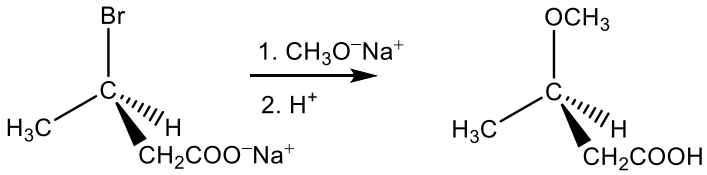


When a sample of the R isomer of $CH_3CH_2CHBrCH_3$ is heated with $CH_3O^-Na^+$ in methanol, the S isomer of $CH_3CH_2CH(OCH_3)CH_3$ is obtained.

(iii) Name and draw the reaction mechanism for this reaction using the given structure of the R isomer of $CH_3CH_2CHBrCH_3$. Show relevant lone pairs of electrons, dipoles and curly arrows. [3]

(iv) In the presence of $CH_3O^-Na^+$, the R isomer of 3-bromobutanoic acid, $CH_3CH(Br)CH_2COOH$ is converted to $CH_3CH(Br)CH_2COO^-Na^+$.

When the R isomer of $CH_3CH(Br)CH_2COO^-Na^+$ is reacted with $CH_3O^-Na^+$ followed by acidification, the R isomer of $CH_3CH(OCH_3)CH_2COOH$ was obtained.



Explain why this is so. [1]

(v) Explain why 3-bromobutanoic acid is a stronger acid than butanoic acid. [2]

……

……

……

……

……

……

……

……

……

……

……

……

(c) Butanoic acid can be converted to calcium butanoate, $(CH_3CH_2CH_2COO)_2Ca$ when reacted with calcium hydroxide. Calcium butanoate supplements are sometimes used to support digestive health as it is known to have anti-inflammatory properties and supports the health of the colon.

(i) Write an equation for the reaction between butanoic acid and calcium hydroxide. [1]

(ii) Given that the solubility of calcium butanoate is 0.0161 mol dm^{-3}, calculate the K_{sp} of calcium butanoate stating its units. [2]

(iii) Calculate the solubility of calcium butanoate in a solution containing 0.1 mol dm^{-3} of calcium chloride. [1]

(iv) The $\Delta G^{\ominus}_{sol}$ of an ionic compound in J mol^{-1}, is given by the following expression.

$$\Delta G^{\ominus}_{sol} = -RT \ln K_{sp}$$

Calculate the $\Delta G^{\ominus}_{sol}$ in kJ mol^{-1}, for calcium butanoate. [1]

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

[Total: 20]

Additional answer space

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

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……

……