RAFFLES INSTITUTION
2020 YEAR 6 PRELIMINARY EXAMINATION

Higher 2

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9729/02

Paper 2 Structured Questions **15 September 2020**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index number in the spaces provided at the top of this page.
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.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided. Do not write anything in it.
You are reminded of the need for good English and clear presentation in your answers.

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 Examiner's Use	
1	**/ 9**
2	**/ 16**
3	**/ 16**
4	**/ 15**
5	**/ 19**
Total	**/ 75**

This document consists of **23** printed pages.

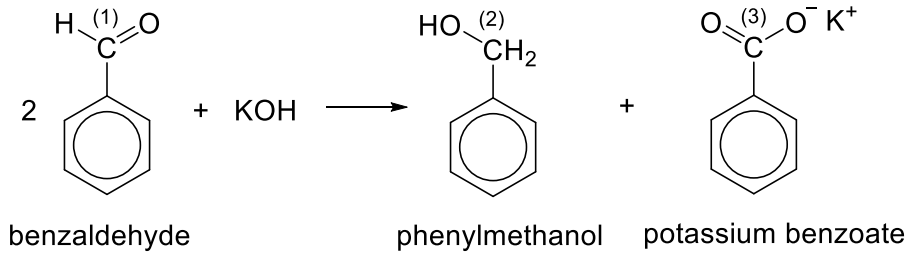
Answer **all** the questions in the spaces provided.

For examiner's use

1 (a) The Cannizzaro reaction involves the conversion of aldehyde into a primary alcohol and a carboxylate ion under alkaline conditions.

Benzaldehyde is heated with potassium hydroxide to give phenylmethanol and potassium benzoate, as shown in equation 1.

equation 1



benzaldehyde phenylmethanol potassium benzoate

(i) State the oxidation numbers of C(1), C(2) and C(3).

oxidation number of C(1) = …….

oxidation number of C(2) = …….

oxidation number of C(3) = ……. [2]

(ii) Hence, state the type of reaction for equation 1.

……. [1]

(b) A student suggested performing the Cannizzaro reaction in a non-alkaline medium as shown in equation 2.

equation 2 $2C_6H_5CHO(l) + H_2O(l) \longrightarrow C_6H_5CH_2OH(l) + C_6H_5COOH(s)$

Table 1.1 shows some data on the standard enthalpy changes of formation, $\Delta H_f^{\ominus}$, and standard enthalpy change of vapourisation, $\Delta H_{vap}^{\ominus}$.

Table 1.1

$\Delta H_f^{\ominus}$ of benzaldehyde, $C_6H_5CHO(l)$	–87.0 kJ mol^{-1}
$\Delta H_f^{\ominus}$ of phenylmethanol, $C_6H_5CH_2OH(l)$	–160.7 kJ mol^{-1}
$\Delta H_f^{\ominus}$ of benzoic acid, $C_6H_5COOH(s)$	–385.2 kJ mol^{-1}
$\Delta H_{vap}^{\ominus}$ of water, $H_2O(l)$	+44.0 kJ mol^{-1}

For examiner's use

(i) Using relevant data from the *Data Booklet*, calculate $\Delta H_f^{\ominus}(H_2O(g))$.

[1]

(ii) Using the standard enthalpy changes given in Table 1.1 and your answer in **(b)(i)**, draw an appropriate energy cycle and calculate the standard enthalpy change, $\Delta H_r^{\ominus}$, for the reaction shown in equation 2.

[3]

For examiner's use

(iii) Table 1.2 shows the standard entropy, $S^{\ominus}$, of the species involved in equation 2.

Table 1.2

compound	standard entropy, $S^{\ominus}$ / J K^{-1} mol^{-1}
benzaldehyde, $C_6H_5CHO(l)$	221.2
phenylmethanol, $C_6H_5CH_2OH(l)$	216.7
benzoic acid, $C_6H_5COOH(s)$	167.6
water, $H_2O(l)$	70.0

Using the data in Table 1.2 and your answer to **(b)(ii)**, calculate $\Delta G^{\ominus}$ at 298 K for the reaction shown in equation 2.

Hence, comment on the feasibility of the reaction at 298 K.

[2]

[Total: 9]

For examiner's use

2 (a) The concentration of halide ions in a sample can be determined by back titration via the Volhard method. An excess amount of $AgNO_3$ is first added to a sample containing halide ions to form silver halide precipitates. The silver halide precipitates are then filtered off. The amount of remaining Ag^+ ions in the filtrate is determined by titration with aqueous KSCN.

$$Ag^+(aq) + SCN^-(aq) \longrightarrow AgSCN(s)$$

$Fe(NO_3)_3$ solution is added as an indicator. The end-point is reached when a blood red complex of $[FeSCN]^{2+}$ is observed.

Sample **X** contains equimolar amounts of Cl^- and Br^- ions. 15.0 cm^3 of 0.700 mol dm^{-3} aqueous $AgNO_3$ was first added to a 25.0 cm^3 of sample **X** and the resulting mixture was filtered. 10.0 cm^3 of the filtrate was then titrated against 0.100 mol dm^{-3} aqueous KSCN, using $Fe(NO_3)_3$ as an indicator. A blood red colouration was observed when 14.25 cm^3 of aqueous KSCN was added.

(i) Explain the effect on the titre value if the silver halide precipitates were not filtered away before titration.

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...……..[2]

(ii) Calculate the amount of remaining Ag^+ ions in 10.0 cm^3 of the filtrate.

[1]

(iii) Show, by calculation, that the concentration of Cl^- ions in sample **X** is 0.0960 mol dm^{-3}.

For examiner's use

[3]

(b) The values of the solubility product, K_{sp}, of AgCl and AgBr at 25 ^{o}C are given in Table 2.1.

Table 2.1

compound	K_{sp} (at 25 °C)
AgCl	1.77×10^{-10}
AgBr	5.35×10^{-13}

To separate the two halide ions in 25.0 cm^3 of sample **X** via selective precipitation, just enough solid $AgNO_3$ was added to precipitate the maximum amount of AgBr from the mixture, without precipitating AgCl.

(i) Given that the concentration of Cl^- ions in sample **X** is 0.0960 mol dm^{-3}, calculate the concentration of Ag^+ ions in the solution at the end of the separation.

[1]

For examiner's use

(ii) Calculate the concentration of Br^- ions remaining in the solution at the end of the separation.

[1]

(iii) Using your answers in **(b)(i)** and **(b)(ii)**, calculate the mass of solid $AgNO_3$ that was added to separate the halide ions.
[M_r of $AgNO_3$ = 169.9]

[3]

For examiner's use

(c) The solubility product, K_{sp}, of Ag_2CrO_4 at 25 °C is 1.12×10^{-12} mol^3 dm^{-9}.

0.100 mol of potassium chromate(VI), $K_2CrO_4(s)$, was dissolved in 500 cm^3 of a saturated solution of Ag_2CrO_4 at 25 °C.

(i) Calculate the solubility of Ag_2CrO_4 in water **before** the addition of $K_2CrO_4(s)$.

[1]

(ii) Calculate the solubility of Ag_2CrO_4 **after** the dissolution of $K_2CrO_4(s)$.

[2]

(iii) Hence, calculate the mass of Ag_2CrO_4 precipitated after the dissolution of K_2CrO_4.
[M_r of Ag_2CrO_4 = 331.8]

[2]

[Total: 16]

For examiner's use

Question 3 starts on the next page.

For examiner's use

3 Urea is well known for its agricultural and biological importance.

Hydrolysis of urea can take place in both alkaline and acidic conditions, as well as in the presence of the enzyme urease.

(a) The kinetics of the hydrolysis of urea, $CO(NH_2)_2$, in alkaline medium is studied using different concentrations of $CO(NH_2)_2$ and OH^- ions as shown in Table 3.1.

$$CO(NH_2)_2 + 2OH^- \longrightarrow 2NH_3 + CO_3^{2-}$$

Table 3.1

experiment	initial $[CO(NH_2)_2]$ / mol dm^{-3}	initial $[OH^-]$ / mol dm^{-3}
A	0.015	2.00
B	0.015	1.00
C	0.030	4.00

Fig. 3.1 shows how $[NH_3]$ in the reaction mixture varies with time for experiments A and B.

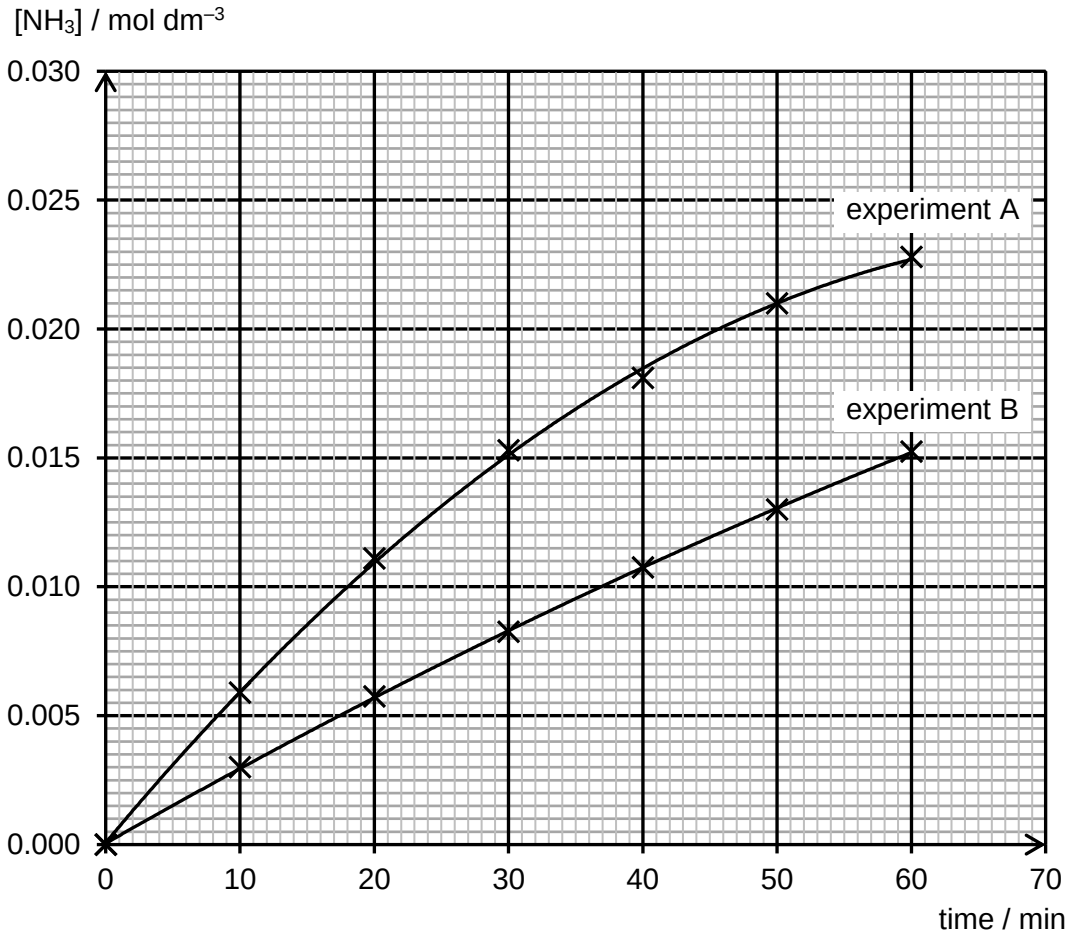

Fig. 3.1

For examiner's use

(i) For experiment A, determine the concentration of NH_3 when the reaction goes to completion.

[1]

(ii) Using the graphs in Fig. 3.1, show that the reaction is first order with respect to both $CO(NH_2)_2$ and OH^- ions.

You are required to show clearly all working, including any construction lines on Fig. 3.1.

[3]

(iii) Calculate a value for the rate constant, *k*, of experiment A, and state its units.

[2]

For examiner's use

(iv) Deduce the half-life of $CO(NH_2)_2$ in experiment C, giving your reasoning.

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...……..[2]

(v) With the aid of a Boltzmann distribution curve, explain how an increase in temperature causes an increase in the rate of the reaction.

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...…….. [3]

For examiner's use

Question 3 continues on the next page.

For examiner's use

(b) The determination of the concentration of urea in blood and urine is frequently carried out by measuring the rate of hydrolysis of urea in the presence of the enzyme urease.

$$CO(NH_2)_2 + 2H_2O \xrightarrow{\text{urease}} 2NH_4^+ + CO_3^{2-}$$

The mechanism for the catalytic action of urease is shown below.

step 1: urease + reactants ⇌ **Y** (fast)

step 2: **Y** ⟶ urease + products (slow)

Y represents the urease-reactants complex.

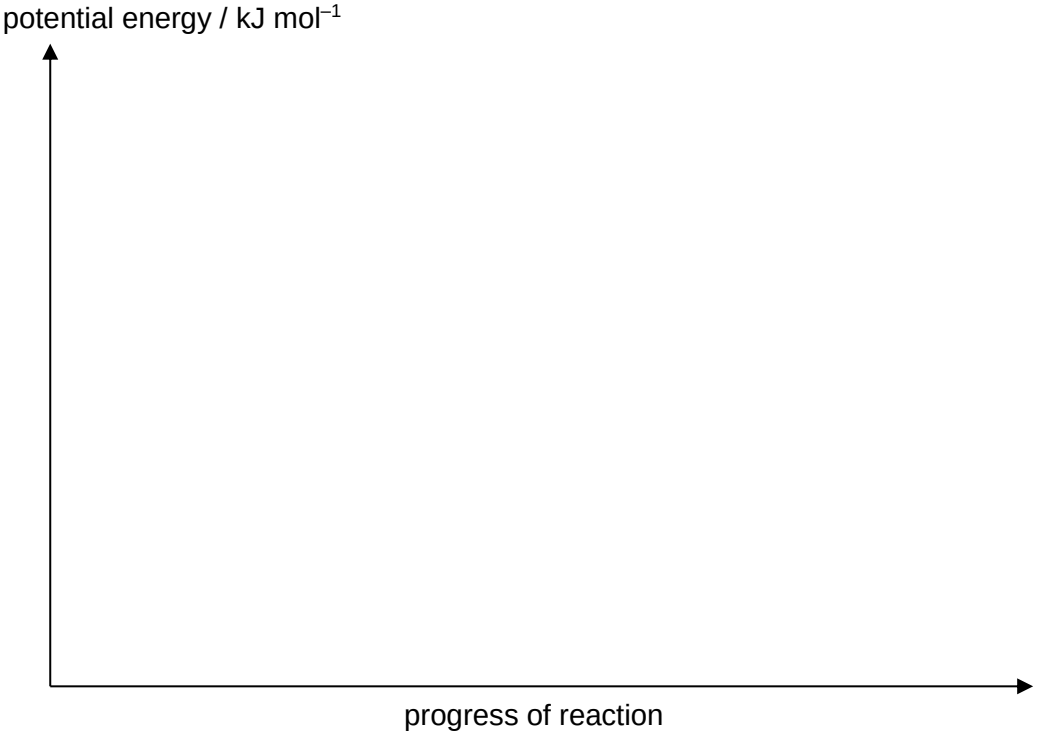
Table 3.2 shows the enthalpy changes, ΔH, and activation energies, E_a, of each step of the mechanism.

Table 3.2

step	ΔH / kJ mol^{-1}	E_a / kJ mol^{-1}
1	+13.6	*z*
2	–26.2	+38.7

The difference between the energies of the transition states in steps 1 and 2 is found to be 30.3 kJ mol^{-1}.

(i) Using the information above, sketch a labelled energy profile diagram for the hydrolysis of urea by urease on the axes given below.



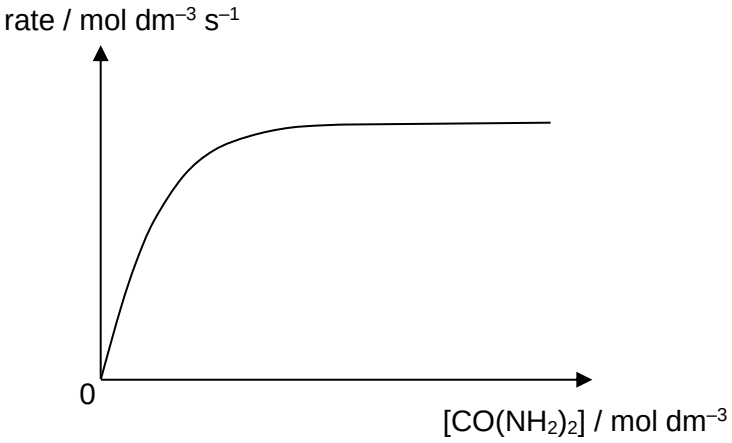
[2]

For examiner's use

(ii) Hence, determine the value of *z*.

[1]

(iii) The graph below shows the rate of hydrolysis at varying concentrations of $CO(NH_2)_2$ in the presence of a fixed amount of urease.



Account for the shape of the graph.

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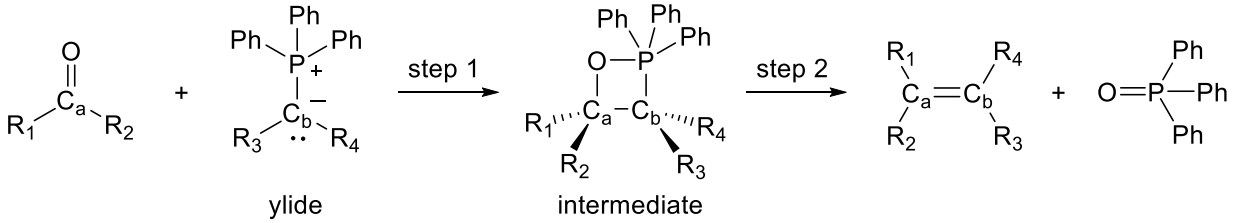
...……..[2]

[Total: 16]

4 The Wittig reaction shown in Fig. 4.1 is a useful synthetic method to convert carbonyl compounds to alkenes. It involves the use of an ylide.

For examiner's use



R_1, R_2, R_3, R_4 = H, alkyl or aryl
Ph = phenyl (C_6H_5)

Fig. 4.1

(a) Suggest the type of reaction for step 1.

……[1]

(b) **(i)** State the hybridisation of the C_a atom in the intermediate in Fig. 4.1.

……[1]

(ii) The bond angle of O−C_a−C_b in the intermediate in Fig. 4.1 is 90°.

Using your answer in **(b)(i)**, suggest why step 2 of the Wittig reaction in Fig. 4.1 happens very readily.

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……[1]

(c) Unlike the carbonyl reactant, the alkene product does not react with the negatively charged C_b on the ylide.

Explain why this is so.

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……[1]

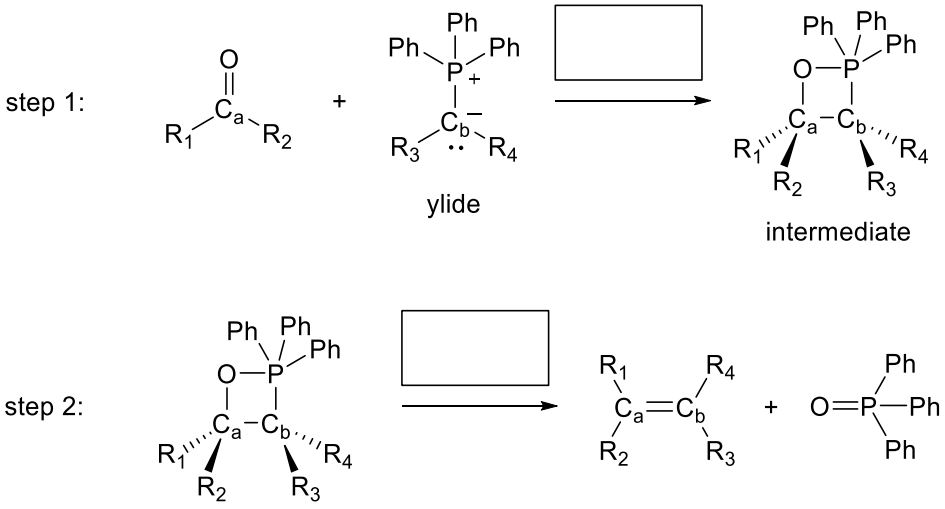
For examiner's use

(d) The mechanism for steps 1 and 2 of the Wittig reaction in Fig. 4.1 is described below.

Step 1: The C_a–O π bond is broken, and the C_a–C_b and O–P bonds are formed, simultaneously, to give the intermediate. This is the rate determining step.

Step 2: The C_a–O and C_b–P bonds are broken, and the C_a–C_b and O–P π bonds are formed, simultaneously, to give the products.

Complete the diagram below to suggest the mechanism of the Wittig reaction in Fig. 4.1. Show relevant dipoles and use curly arrows to indicate the movement of electron pairs. Indicate the slow and fast steps in the mechanism.



[2]

(e) **(i)** Suggest the structure of the alkene formed in the Wittig reaction shown in Fig. 4.2.

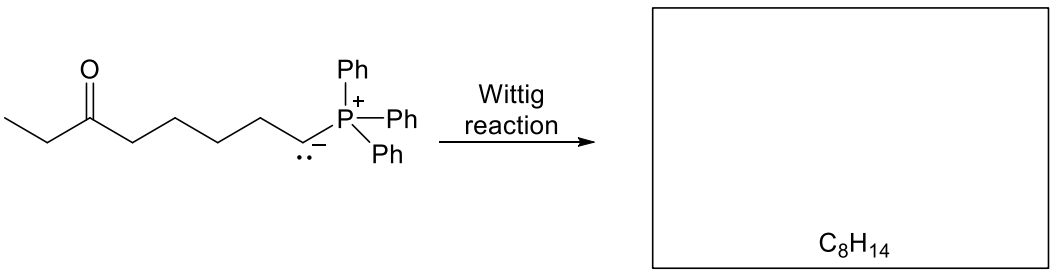


Fig. 4.2

[1]

For examiner's use

(ii) Suggest the structures of the carbonyl compound and the ylide that would produce the alkene in Fig. 4.3.

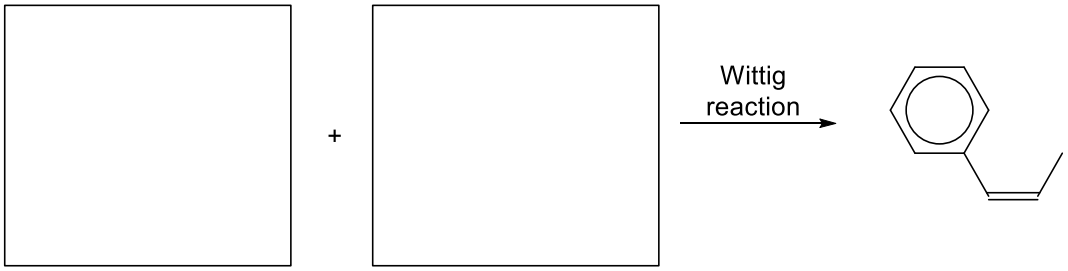


Fig. 4.3

[2]

Acetoin is one of the compounds that gives butter its characteristic flavour.

Fig. 4.4 shows acetoin undergoing Wittig reaction followed by oxidation to form compound **W**.

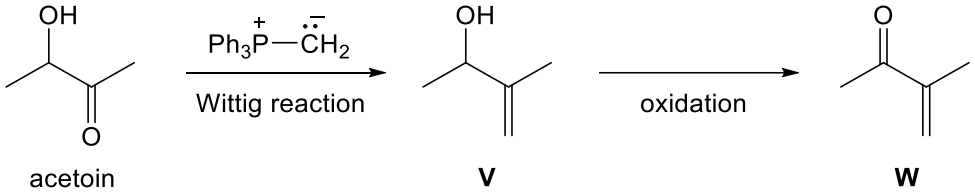


Fig. 4.4

(f) **(i)** State the reagents and conditions for the oxidation step in Fig. 4.4.

……..……...[1]

(ii) Explain why compound **W** cannot be obtained if acetoin were oxidised before undergoing the Wittig reaction.

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……..……...[1]

For examiner's use

(g) Fig. 4.5 shows the conversion of acetoin into oxalyl chloride, $C_2O_2Cl_2$, via a series of reactions.

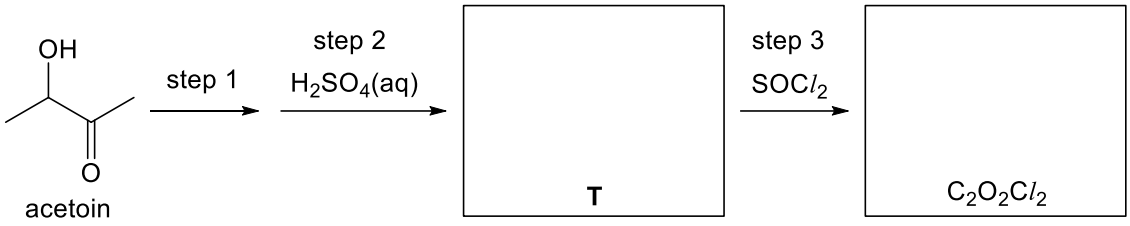

Fig. 4.5

(i) Draw the structures of **T** and oxalyl chloride in the respective boxes in Fig. 4.5. [2]

(ii) Suggest the reagents and conditions for step 1.

……[1]

(h) Oxalyl chloride reacts with reagent **U** in a 1:1 mole ratio as shown below.

$$C_2O_2Cl_2 + \mathbf{U} \xrightarrow[\text{room temperature}]{} CO + CO_2 + 2HCl$$

Suggest the identity of **U**.

……[1]

[Total: 15]

For examiner's use

5 (a) Group 2 nitrates decompose on heating to form the metal oxide, nitrogen dioxide and oxygen, as shown by the following equation.

$$2M(NO_3)_2(s) \longrightarrow 2MO(s) + 4NO_2(g) + O_2(g) \quad \text{where M = Mg, Ca, Sr or Ba}$$

Explain why the temperature required for the decomposition of Group 2 nitrates increases down the group.

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……[2]

(b) Metal aqua complexes have the general formula of $[M(H_2O)_n]^{a+}$, where n is the number of water molecules coordinated to the metal ion M^{a+} by dative covalent bonds.

(i) Be^{2+} forms an aqua complex with n = 4 while the other Group 2 metal ions form aqua complexes with n = 6. Suggest why only a maximum of four water molecules can be coordinated to Be^{2+} in the aqua complex of Be^{2+}.

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……[2]

Some metal aqua complexes hydrolyse in water to form H^+ ions as shown by the equation below.

$$[M(H_2O)_6]^{a+}(aq) \rightleftharpoons [M(H_2O)_5(OH)]^{(a-1)+}(aq) + H^+(aq)$$

The acidity of metal aqua complexes can be compared using their pK_a values. The pK_a values of the aqua complexes of Mg^{2+} and Al^{3+} are shown in Table 5.1.

Table 5.1

metal aqua complex	$[Mg(H_2O)_6]^{2+}$	$[Al(H_2O)_6]^{3+}$
pK_a	11.4	5.0

For examiner's use

(ii) Explain why the pK_a of $[Mg(H_2O)_6]^{2+}$ is higher than that of $[Al(H_2O)_6]^{3+}$.

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……[2]

$Mg^{2+}(aq)$ and $Al^{3+}(aq)$ exist as $[Mg(H_2O)_6]^{2+}$ and $[Al(H_2O)_6]^{3+}$ respectively.

When reacted separately with aqueous Na_2CO_3, $Mg^{2+}(aq)$ and $Al^{3+}(aq)$ each forms a white precipitate. However, effervescence is observed only for $Al^{3+}(aq)$.

(iii) By using the data given in Table 5.1 and the information shown below, explain why effervescence is observed for $Al^{3+}(aq)$ and identify the gas produced.

$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$ $\quad pK_{a1} = 6.4$

$HCO_3^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H^+(aq)$ $\quad pK_{a2} = 10.3$

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……[2]

(iv) Complete the table below.

	identity of precipitate
precipitate formed between $Na_2CO_3(aq)$ and $Mg^{2+}(aq)$	
precipitate formed between $Na_2CO_3(aq)$ and $Al^{3+}(aq)$	

[2]

For examiner's use

(c) Aluminium oxide and phosphorus pentachloride are compounds of Period 3 elements.

(i) Aluminium oxide dissolves in excess NaOH(aq) to form a colourless solution.

Write an equation to show the dissolution of aluminium oxide in excess NaOH(aq).

……..……..[1]

(ii) On adding phosphorus pentachloride to water, dense white fumes are observed.

Write an equation for the reaction and state the pH of the resultant solution formed.

……..……..…

……..……..[2]

(d) Calcium and copper are both Period 4 elements.

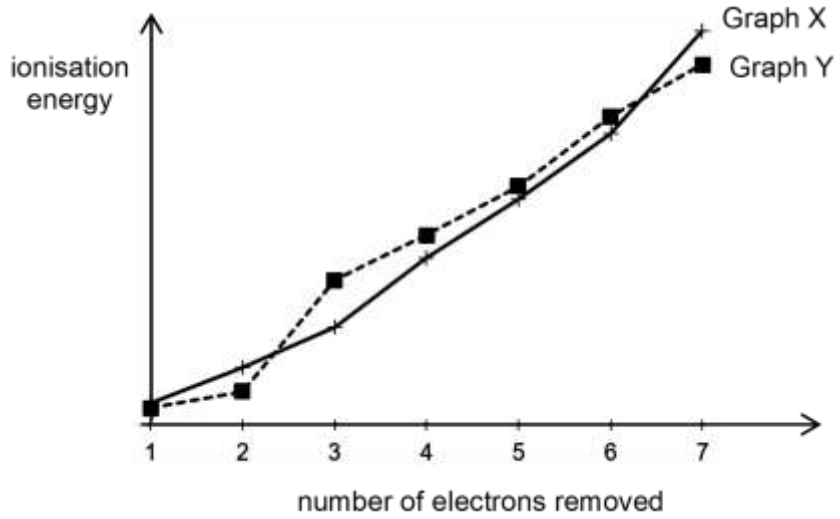
(i) State the electronic configurations of calcium and copper(I) ion, Cu^+.

electronic configuration of calcium …….…….

electronic configuration of copper(I) ion, Cu^+ …….……..
[2]

For examiner's use

The graphs below show the first seven ionisation energies of calcium and copper.



(ii) Which graph shows the successive ionisation energies for calcium? Explain your answer.

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……[2]

(iii) A student accidentally mixed a solution containing aqueous copper(II) chloride with aqueous calcium chloride. The student suggested electrolysing the solution using graphite electrodes to separate copper from the calcium ions. Using relevant data from the *Data Booklet*, explain whether the method works.

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……[2]

[Total: 19]