



ANDERSON SERANGOON JUNIOR COLLEGE

2024 JC 2 PRELIMINARY EXAMINATION

NAME: _____ () CLASS: 24 / _____

CHEMISTRY

9729/03

Paper 3 Free Response Questions

13 September 2024

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, class and register number 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

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 Examiner's Use				
Paper 3	A1	/ 21	Paper 1 (15%)	/ 30
	A2	/ 16	Paper 2 (30%)	/ 75
	A3	/ 23	Paper 3 (35%)	/ 80
	B4*	/ 20	Paper 4 (20%)	/ 55
	B5*	/ 20	Percentage	
	*Circle the question you have attempted		Grade	

This document consists of **28** printed pages.

Section A

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

- 1 (a) (i) State the full electronic configuration of an Fe^{2+} ion. [1]
- (ii) Explain why $\text{Fe}^{2+}(\text{aq})$ ions are green, whereas aqueous Group 2 metal ions are not coloured. [4]

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- (b) Iron(II) carbonate can be prepared by reacting solutions of the two ions, $\text{Fe}^{2+}(\text{aq})$ and $\text{CO}_3^{2-}(\text{aq})$. Explain why the same method cannot be used to prepare solid iron(III) carbonate. [2]

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Group 2 carbonate	Minimum temperature of decomposition / °C
MgCO ₃	350
CaCO ₃	840
SrCO ₃	1289
BaCO ₃	1360

(i) Write an equation for the thermal decomposition of copper(II) carbonate. [1]

(ii) Use data from the Data Booklet and Table 1.1 to suggest a minimum temperature at which pure copper(II) carbonate decomposes. Explain your reasoning. [3]

[illegible]

- When aqueous sodium hydroxide is added to solution **G**, a blue precipitate **H** is observed. Precipitate **H** dissolves when excess aqueous ammonia is added to form a brown solution **I**. Nitrogen and hydrogen are the only other elements in the octahedral cobalt-containing complex in **I**.

(ii) Addition of concentrated hydrochloric acid to pink solution **G** forms a blue solution **J**. Solution **J** turns pink again when water is added to it.

(iii) Salt **K** has the molecular formula $\text{CoN}_5\text{H}_{17}\text{OCl}_3$ ($M_r = 268.4$). It has one or more ligands which is similar to those found in complex species **G**, **H** and **J**.

When 1.00 g of salt **K** is dissolved in water, the resulting solution required 22.40 cm³ of 0.50 mol dm⁻³ silver nitrate solution for complete reaction.

Calculate the number of moles of free chloride ions per mole of **K** and give the structural formula of the complex ion in **K**. [2]

[illegible]

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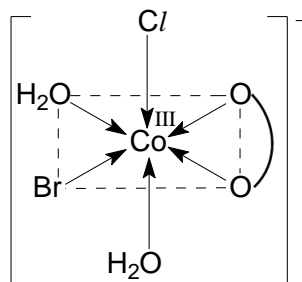
(e) The ethanedioate ion, $\text{C}_2\text{O}_4^{2-}$, can act as a bidentate ligand.

(i) Explain what is meant by a *ligand*. [1]

(ii) The complex $[\text{Co}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)\text{BrCl}]^-$ exists as stereoisomers.

Isomer **L** has the following structure.

The $\text{C}_2\text{O}_4^{2-}$ ligand is represented using $\text{O} \text{---} \text{O}$.



Isomer **L**

Draw an isomer that has an equal and opposite effect on plane polarised light compared to isomer **L**. [1]

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[Total: 21]

- 2 (a) A sample of sulfur contains four stable isotopes as shown in Table 2.1.

Table 2.1

relative isotopic mass of S	percentage abundances / %
31.97	94.99
32.97	0.75
<i>w</i>	4.25
35.97	0.01

The relative atomic mass of sulfur in this sample is 32.06.

Use the data in Table 2.1 to calculate a value for *w* to 2 decimal places.

[1]

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- (b) Table 2.2 lists the boiling points of different sulfur containing compounds.

Table 2.2

compound	formula	M_r	boiling point / °C
thiourea	$\begin{array}{c} \text{S} \\ \\ \text{H}_2\text{N}-\text{C}-\text{NH}_2 \end{array}$	76.1	150
thionyl fluoride	$\begin{array}{c} \text{O} \\ \\ \text{F}-\text{S}-\text{F} \end{array}$	86.1	-44
thionyl chloride	$\begin{array}{c} \text{O} \\ \\ \text{Cl}-\text{S}-\text{Cl} \end{array}$	119.1	79

- (i) Explain the difference in the boiling points between thionyl chloride and thionyl fluoride. [1]
- (ii) Explain why the boiling point of thiourea is much higher than thionyl fluoride with similar molecular mass. [1]

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- (c)** The Contact process used to produce sulfuric acid involves three stages. Using V_2O_5 as a catalyst, stage I achieves 99.5% conversion of sulfur dioxide to sulfur trioxide.

stage I $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

- (i) Write an expression **each** for K_c and K_p of reaction in stage I. [2]
- (ii) Using the ideal gas equation, show that $K_p = K_c(\frac{1}{RT})$. [1]
- (iii) At 723 K, the equilibrium partial pressures of SO_2 , O_2 and SO_3 are 600 Pa, 3300 Pa and 11400 Pa respectively.

Calculate the value of K_p for the reaction in stage I. State the units. [2]

- (iv) When the temperature increases from 723 K to 1000 K, the partial pressure of SO_2 increases. Deduce the sign of ΔH for the forward reaction in stage I. [2]
- (v) State and explain the effect of the presence of a catalyst on the equilibrium position and the value of the equilibrium constant. [2]

[illegible]

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- (d) Sulfur combines with oxygen atom to form four sulfur oxoanions. Table 2.3 shows the average oxidation number of sulfur (S) and number of oxygen atoms in the oxoanions.

Table 2.3

oxoanion	average oxidation number of S	number of oxygen atoms
D	+2	3
E	+3	4
F	x	6
G	+6	y

All four sulfur oxoanions have two sulfur atoms and an overall negative charge of 2.

Only **D** has one central atom.

In **D**, **E** and **F** only,

- the sulfur atoms are bonded directly to each other and
- no oxygen atom is attached to another oxygen atom.

- (i) Suggest a value for x and y in the table. [2]
- (ii) Suggest the structural formulae showing the bonding in **D** and **E**. [2]

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[Total: 16]

3 Many important chemical compounds are derived from benzene.

- (a) X-ray diffraction studies show that all the carbon-carbon bonds in benzene are identical and equal in length.

Explain, in terms of hybridisation and orbital overlap, the identical and equal C–C bond length in benzene. [2]

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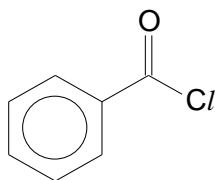
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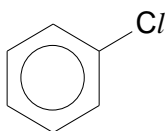
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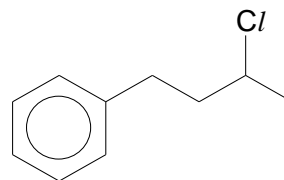
- (b) The three compounds below differ in their rate of hydrolysis when each compound is added separately to water at 25°C.



benzoyl chloride



chlorobenzene



3-chloro-1-phenylbutane

Arrange the three compounds in the order of increasing relative rate of hydrolysis. Explain your answer. [4]

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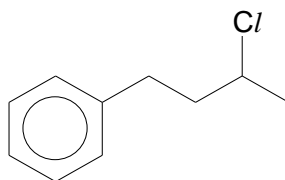
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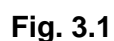
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L, **M** and **N** decolourises aqueous bromine. **L** and **M** are cis-trans isomers of each other.

- (i) State the type of reaction and the reagents and conditions to form **L**, **M** and **N** from 3-chloro-1-phenylbutane. [2]
- (ii) Draw the structures of **L**, **M** and **N**. Label the structures clearly as **L**, **M** and **N**. [2]
- (iii) Explain how molecules **L** and **M** are cis-trans isomers of each other. [1]

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- (i) Using information from the *Data Booklet*, suggest the structure for compound **P**, and reagents and conditions for each of the steps 1 and 2. [3]
- (ii) Suggest the type of reaction that occurred in step 3. [1]

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- (e) Benzoyl chloride readily undergoes a nucleophilic acyl substitution reaction with phenol to form phenyl benzoate.

Fig. 3.2 shows an incomplete mechanism for steps 1 and 2 of the reaction.

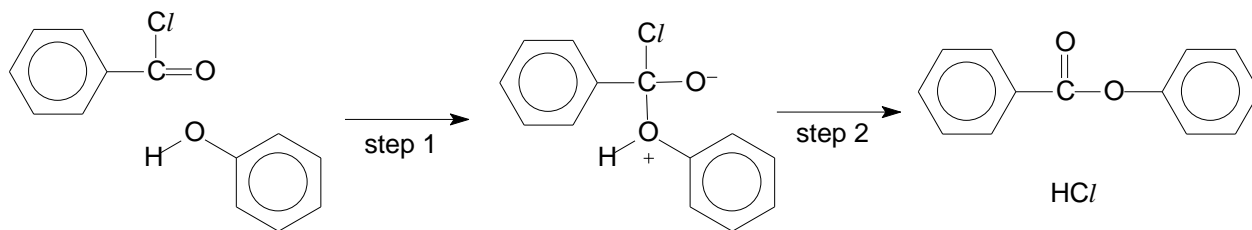
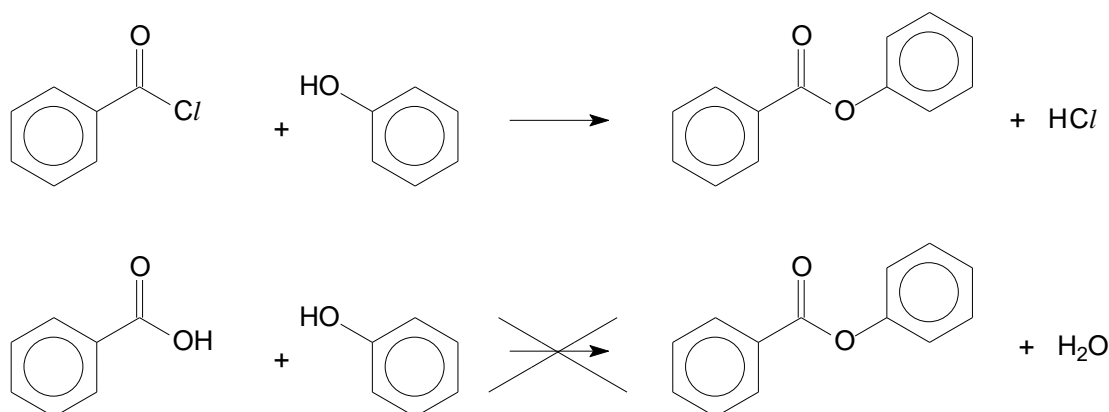


Fig. 3.2

- (i) On Fig. 3.2, draw curly arrows to show the mechanism for these two steps. Show all relevant lone pairs of electrons and dipoles. [3]
- (ii) Unlike benzoyl chloride, benzoic acid cannot undergo nucleophilic acyl substitution with phenol to form phenyl benzoate.



In terms of delocalisation of electrons, suggest why benzoyl chloride is more reactive towards phenol as compared to benzoic acid. [1]

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- (f) In non-polar solvents, benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$, can form a dimer containing two hydrogen bonds.

Draw the structure of the dimer formed. Include lone pairs and dipoles and label the hydrogen bonds. [1]

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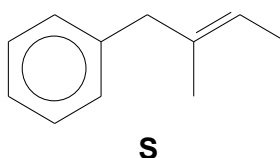
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- (g) Compound **S** undergoes an addition reaction with ICl(g) .



- (i) Draw the structures of the two possible constitutional isomers that could be formed. [1]

- (ii) Draw the structure of the intermediate that forms the major product in the reaction. Give a reason for the structure drawn. [2]

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[Total: 23]

4 (a) With reference to *Data Booklet*, describe and explain the trend in the thermal stability of HCl, HBr and HI. [3]

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- The concentration of $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$ was monitored over a period and the results were recorded in Table 4.1.

time/s	$[\text{CH}_3\text{CH}_2\text{CHBrCH}_3] / \text{mol dm}^{-3}$
0	0.02100
100	0.01800
200	0.01600
300	0.01400
400	0.01200
500	0.01050
600	0.00900
700	0.00800
800	0.00700
900	0.00600
1000	0.00525
1100	0.00450

- (i) Use the data in Table 4.1 to prove that the reaction is first order with respect to $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$. [1]
- (ii) The rate of reaction is also found to be first order with respect to OH^- . Write the rate equation for the nucleophilic substitution of $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$ with aqueous NaOH . Include the units for the rate constant. [1]
- (iii) Describe the nucleophilic substitution mechanism of a **single** enantiomer of $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$ with aqueous NaOH . Show the stereochemistry of the reactant and product clearly in your answer. [3]

[illegible]

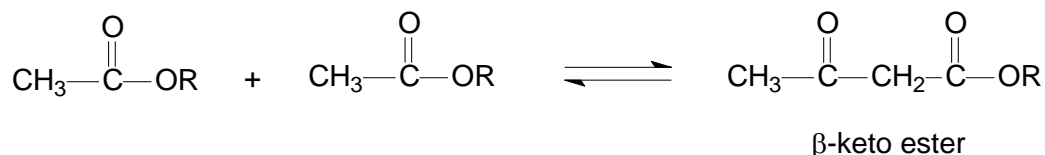
- alkaline aqueous iodine forming a yellow precipitate
- Fehling's reagent and no change is observed
- an excess of LiAlH_4 to form a chiral organic compound **Y**

Suggest possible structures for **V**, **W**, **X** and **Y**.

For each reaction described, state the type of reaction and explain what the information tells you about the functional groups present in each compound. [7]

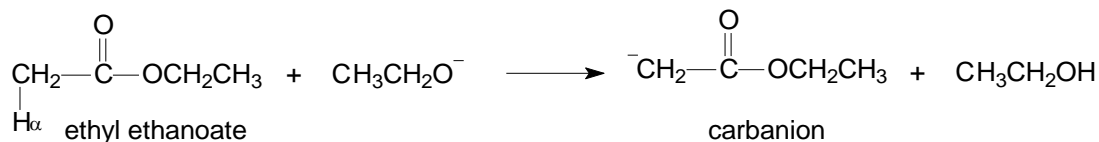
[illegible]

- (d) Claisen condensation reaction is a reversible reaction between two esters to yield a β -keto ester.

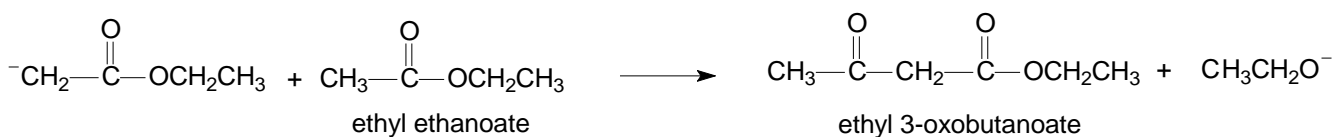


In the synthesis of ethyl 3-oxobutanoate, the α -hydrogen of ethyl ethanoate is removed by the addition of one equivalent of ethoxide ion as shown in equation 4.1. The carbanion formed reacts with another molecule of ethyl ethanoate to form ethyl 3-oxobutanoate in equation 4.2.

equation 4.1



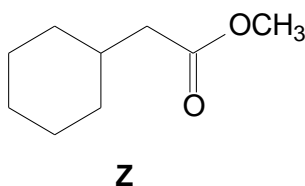
equation 4.2



- (i) Ethyl ethanoate behaves as an acid in equation 4.1 and equation 4.2.

Identify the type of acid behaviour shown by ethyl ethanoate in each of these equations. Explain your answers. [2]

- (ii) Suggest the structure of the final product formed from the Claisen condensation of compound **Z**.



[1]

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$$\text{CH}_3\text{---}\overset{\text{O}}{\parallel}\text{C}\text{---}\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{:}\overset{\cdot\cdot}{\text{CH}}_2\text{---}\overset{\text{O}}{\parallel}\text{C}\text{---}\text{OCH}_2\text{CH}_3 + \text{H}_3\text{O}^+ \quad \text{p}K_{\text{a}} = 25.0$$
$$\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{OCH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\underset{\cdot\cdot}{\overset{-}{\text{C}}\text{H}}-\overset{\text{O}}{\parallel}\text{C}-\text{OCH}_2\text{CH}_3 + \text{H}_3\text{O}^+ \quad \text{p}K_{\text{a}} = 10.7$$

[2]

[illegible]

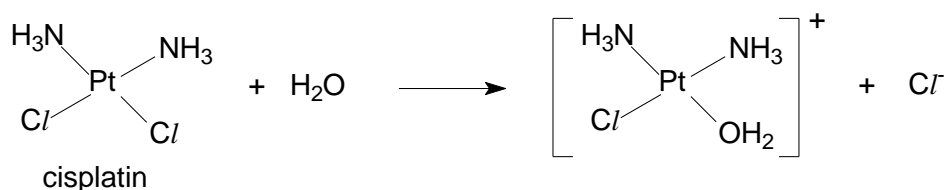
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- 5 (a)** When solid NaCl and AlCl_3 are separately added to water, solutions with different pH values are produced.

Explain why the two chlorides differ in their reaction with water. State the pH of the resulting solutions and write appropriate equations to illustrate your answers. [3]

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- (b) The rate of hydrolysis of the anticancer drug cisplatin can be investigated by monitoring the concentration of the chloride ion formed.



Complete hydrolysis of cisplatin takes more than 24 hours.

A solution of $0.010 \text{ mol dm}^{-3}$ cisplatin was allowed to undergo hydrolysis at pH 7 and 25°C with excess water. At suitable time intervals, an aliquot of the cisplatin mixture was pipetted into a conical flask and quenched.

The amount of chloride ion is titrated against aqueous AgNO_3 using potassium chromate indicator.

Fig. 5.1 shows the concentration of chloride ions formed on hydrolysis of cisplatin against time for this experiment.

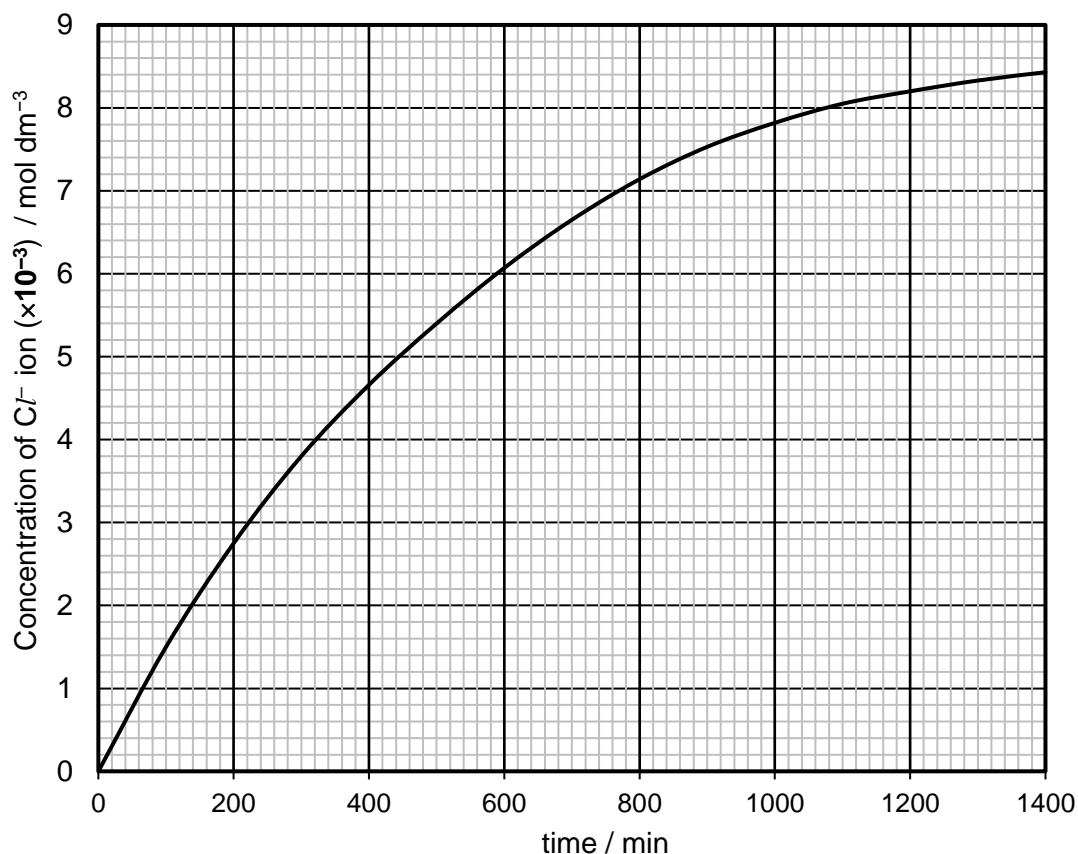


Fig. 5.1

- (i) Considering the total concentration of chloride that will be obtained upon complete hydrolysis of cisplatin, use Fig. 5.1 to show that the reaction is first order with respect to cisplatin. [2]

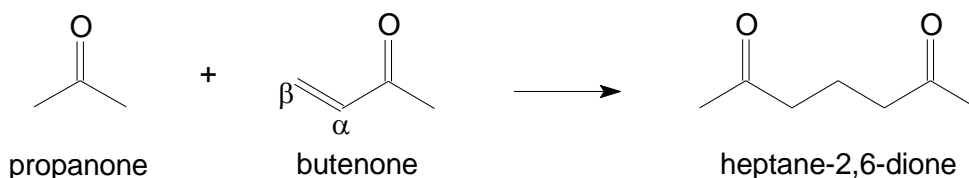
- (ii) The concentration of cisplatin is halved and a new series of experiments was carried out at the same temperature.

Suggest how the gradient at each point will change when a similar graph like the one in Fig. 5.1 was plotted. [1]

- (iii) Suggest why the units for the rate constant for this reaction is s^{-1} despite its rate-determining step being a bimolecular reaction. [1]

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- (c) The formation of heptane-2,6-dione via a *Michael Addition reaction* involves the formation of a carbon-carbon bond between propanone and butenone (an α,β -unsaturated ketone).

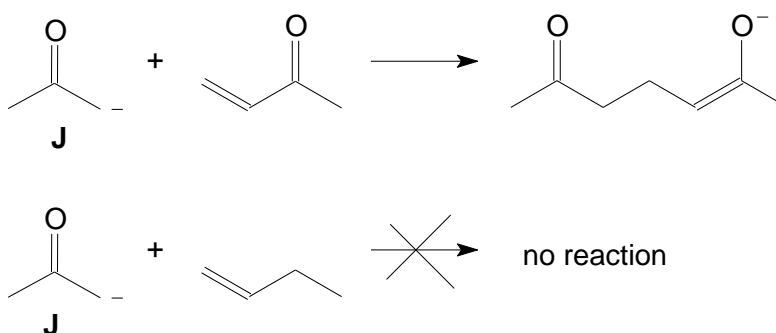


The three steps of the reaction are described in Table 5.1.

Table 5.1

step	equation
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2	
3	

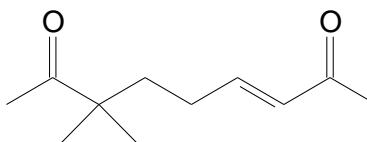
- (i) State the type of reaction in step 1. [1]
- (ii) Complete the nucleophilic addition mechanism for step 2 in Table 5.1 by adding a lone pair and three curly arrows. [1]
- (iii)



No reaction occurs when but-1-ene is used in place of butenone to react with **J** in step 2.

Using the concept of electronegativity and electronic effect, explain why butenone reacts with **J** while but-1-ene does not. [2]

- (iv) Compound **K** undergoes an intramolecular *Michael Addition* reaction to form a product, $C_{11}H_{18}O_2$.

**K**

Suggest a structure for the product formed.

[1]

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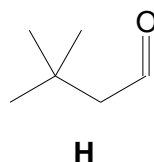
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- (d) A carbon–carbon bond can also be formed between two molecules of compound **H** using suitable reagents and conditions.



Give the systematic name of compound **H**.

[1]

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- (e) **L**, C_6H_9ClO , is a non-aromatic compound.

L reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate but does not react with Tollen's reagent.

1 mole of **L** reacts with 2 moles of hydrogen gas in the presence of solid platinum.

When **L** is heated with potassium manganate(VII) in aqueous sodium hydroxide, then followed by adding sulfuric acid to the resultant mixture, **M** and **N** are formed.

M, $C_2H_4O_2$, liberates carbon dioxide gas upon addition of aqueous sodium carbonate solution.

N, $C_4H_4O_5$, reacts with 2,4-dinitrophenylhydrazine to form an orange precipitate.

1 mole of **N** reacts with 2 moles of aqueous sodium hydroxide.

Suggest possible structures for **L**, **M** and **N**.

For each reaction described, state the type of reaction and explain what the information tells you about the functional groups present in each compound. [7]

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[Turn over

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