Anglo-Chinese Junior College

JC2 Preliminary Examination
Higher 2

A Methodist Institution
(Founded 1886)

CANDIDATE NAME		FORM CLASS	
TUTORIAL CLASS		INDEX NUMBER	

CHEMISTRY **9729/03**

Paper 3 Free Response

1 September 2025

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	/ 15
2	/ 24
3	/ 21
Section B	
4 / 5	/ 20
Presentation	
Total	/ 80

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

Section A

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

1 The Mars Curiosity rover's landing in August 2012 was achieved using hydrazine fuelled rocket thrusters. The rapid decomposition of hydrazine, N_2H_4, over a suitable catalyst to produce hot gaseous elements as products provides the thrust. Ammonia can be formed as an intermediate during the decomposition.

(a) Write a balanced equation for hydrazine decomposing to ammonia and nitrogen gas. [1]

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(b) Hydrazine may be obtained from the reaction between ammonia and hydrogen peroxide as shown in equation 1.

equation 1 $2NH_3(g) + H_2O_2(l) \rightarrow N_2H_4(l) + 2H_2O(l)$ $\Delta H_r^\ominus = -241.0$ kJ mol^{-1}

Table 1.1 shows the standard enthalpy change of formation, $\Delta H_f^\ominus$, for some compounds in equation 1.

Table 1.1

compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
NH_3	−46.1
H_2O_2	−187.8
H_2O	−285.8

Calculate the standard enthalpy change for the decomposition of hydrazine to its elements. [2]

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(c) The first ever rocket-powered fighter plane, the Messerschmitt Me 163, was powered by the reaction between a hydrazine-methanol fuel mixture, known as 'C-Stoff', and hydrogen peroxide, known as 'T-Stoff'.

(i) Hydrazine reacts with hydrogen peroxide as shown in equation 2.

equation 2 $N_2H_4(l) + 2H_2O_2(l) \rightarrow N_2(g) + 4H_2O(l)$

State the oxidation number of nitrogen and oxygen in the reactants and products. [1]

(ii) Methanol reacts with hydrogen peroxide to form carbon dioxide and water.

Write a balanced equation for this reaction. [1]

(iii) The fighter plane would hold 225 dm^3 of hydrazine and 862 dm^3 of methanol.

Table 1.2 shows the standard enthalpy change of combustion, $\Delta H_c^{\ominus}$, and densities of hydrazine and methanol.

Table 1.2

compound	$\Delta H_c^{\ominus}$ / kJ mol^{-1}	density / g cm^{-3}
N_2H_4	−622.2	1.021
CH_3OH	−726.0	0.7918

Use data in Table 1.2 to calculate the heat energy evolved during the combustion of this quantity of rocket fuel at standard conditions. Assume that hydrazine and methanol are fully combusted. [2]

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(d) Hydrazine is also commonly combined with dinitrogen tetroxide, N_2O_4, in rocket fuels.

(i) Reactions used in rocketry produce chemically stable gaseous products.

Suggest the products that are formed in the reaction between N_2H_4 and N_2O_4. [1]

(ii) Pure N_2O_4, when warmed, does not immediately decompose into its elements, but instead forms a brown gas.

Suggest the identity of this brown gas. [1]

(iii) N_2H_4 does not exhibit ideal gas behaviour.

State and explain two reasons for its deviation from ideal gas behaviour. [2]

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e) A derivative of hydrazine with formula $C_2H_8N_2$ was used as rocket fuel in the Apollo missions. Draw two isomers of $C_2H_8N_2$ containing an N–N bond. [1]

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(f) Phosphorus is one element below nitrogen in the Periodic Table.

Describe the reactions of the oxide and chloride of phosphorus with water. Write equations where appropriate and suggest the pH of the solutions formed. [3]

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[Total: 15]

2 Cocoa trees have been used as a source of food for more than 5,000 years. In modern times, they are used to make chocolates.

(a) Palmitic acid and stearic acid are saturated fatty acids, while oleic acid and linoleic acid are unsaturated fatty acids commonly found in chocolates.

An example of an unsaturated fatty acid is shown below in Fig. 2.1.

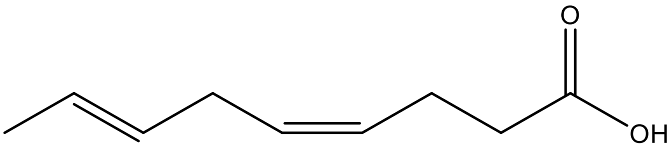


Fig. 2.1

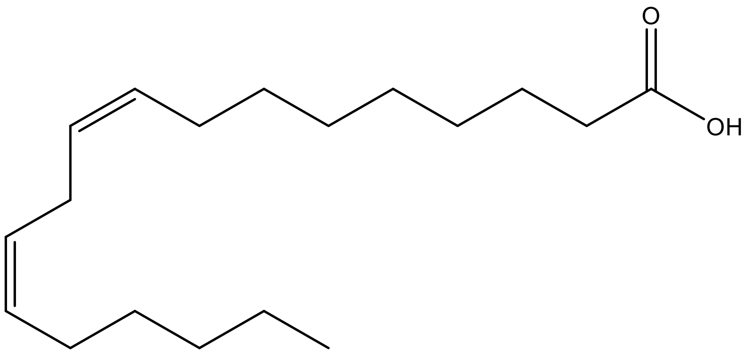
The systematic name of the unsaturated fatty acid in Fig. 2.1 is *cis*,*trans*-4,7-nonadienoic acid. The numbers indicate the positions of the alkene functional groups, and "dien" indicates that there are two alkenes in the chain.

Table 2.2 shows the percentage composition of fatty acids found in three different cocoa butter samples.

Table 2.2

fatty acid	% of fatty acids in cocoa butter samples		
	A	B	C
palmitic acid	28	25	35
stearic acid	35	40	40
oleic acid	31	28	21
linoleic acid	6	7	4

(i) The structure of linoleic acid is shown below.



Given that 'octadeca' refers to an 18-carbon chain, write the systematic name for linoleic acid. [1]

(ii) Using given information about the arrangement of atoms about the C=C bond of unsaturated fatty acids and data in Table 2.2, state and explain which cocoa butter sample is expected to have the highest melting point. [2]

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(b) A chocolatier investigated the quality of two varieties of cocoa beans from the same producer. Table 2.3 shows the results of the chemical analysis.

Table 2.3

chemicals	variety of cocoa beans	
	D	E
theobromine (mg / g)	12.5	15.2
epicatechin (mg / g)	4.8	6.1
ash content (% mass)	3.0	3.5
reducing sugars (% mass)	2.5	3.0

(i) The ash content of cocoa beans is determined by burning the sample until all organic matters are combusted, leaving behind the inorganic residue, which is reported as the percentage mass of the original sample.

Suggest one use for determining the ash content. [1]

(ii) Chocolate is poisonous to dogs as they metabolise theobromine much more slowly compared to humans. The median lethal dose of theobromine for dogs is 120 mg per kg of body weight.

A 60 g of a dark chocolate bar contains 85% cocoa content of variety E.

Calculate the percentage of a chocolate bar, to 1 decimal place, that would be the median lethal dose for a small dog weighing 5.4 kg. [2]

(iii) Theobromine is metabolised more slowly than caffeine in the human body. Following a first-order kinetics, the half-life of theobromine is 8 hours.

The integrated rate law for a first-order reaction is given.

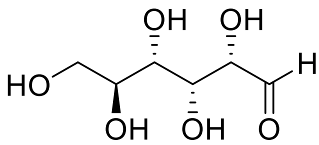
$$\ln [A]_t = -kt + \ln[A]_0$$

where k = rate constant
t = time
$[A]_t$ = concentration of A at time t
$[A]_0$ = initial concentration of A

A social media influencer consumed a large quantity of giant chocolate bars during a broadcast. An immediate blood test revealed a theobromine level of 15.5 mg dm^{-3}.

Calculate the time taken for his theobromine level to fall below 1.5 mg dm^{-3}. [2]

(iv) D-glucose is one of the main reducing sugar molecules found in chocolates. The structure of D-glucose is shown below.



With reference to the changes in the reaction of D-glucose with Fehling's solution, explain why D-glucose is called a reducing sugar. [1]

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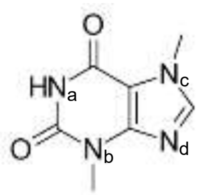
(c) Theobromine is the principal alkaloid in cocoa beans. In the structure below, four nitrogen atoms are labelled N_a, N_b, N_c and N_d.



Theobromine has a pK_b value of 4.1.

(i) Theobromine is an aromatic compound. It is known that N_a, N_b and N_c are not basic, while N_d is basic in nature. All the nitrogen atoms are sp^2 hybridised and lie on the same plane.

With reference to the orbitals, explain why N_c is not basic while N_d is basic. [2]

(ii) To study the effects of theobromine on certain biological systems, a buffer solution at a pH of 10.1 is prepared by adding 300 cm^3 of 0.500 mol dm^{-3} of hydrochloric acid to 700 cm^3 of theobromine solution, which is in excess.

Calculate the original concentration of the theobromine solution used to make the buffer solution. [3]

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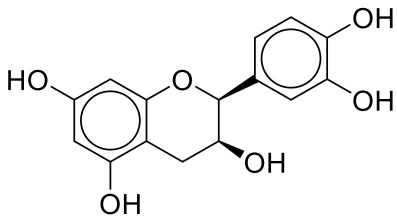
(d) Compared to other types of chocolate, dark chocolate is richer in epicatechin, which is an antioxidant.



epicatechin

Fig 2.4 shows a possible synthetic pathway of epicatechin in the laboratory.

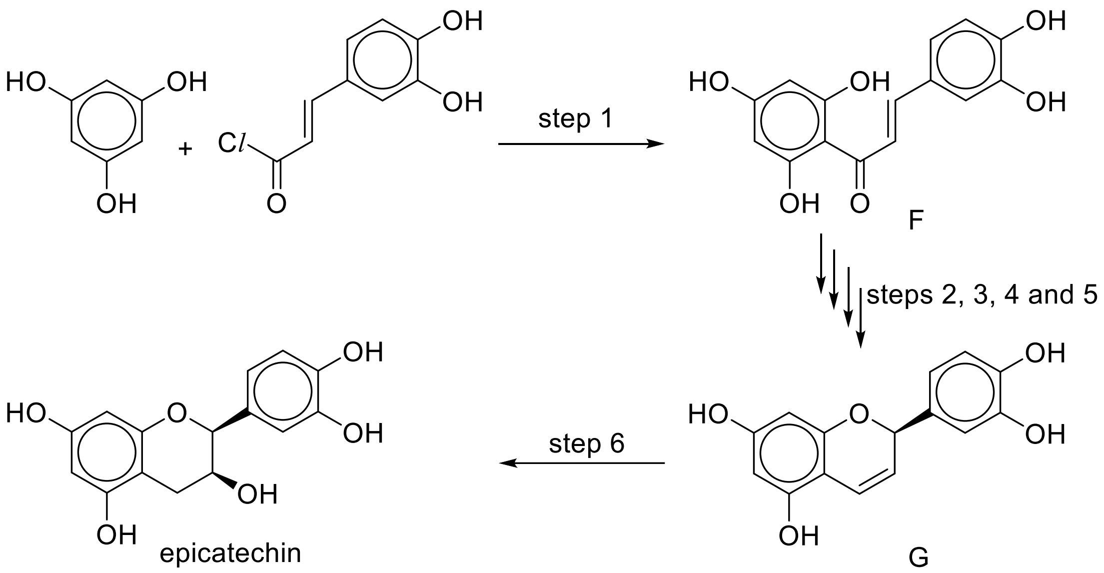
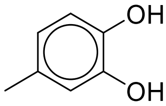


Fig. 2.4

(i) In step 1, electrophilic substitution occurs to form F in the presence of $AlCl_3$.

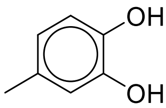
Draw the mechanism for step 1. Show the relevant curly arrows and charges, and all the products formed.

You may represent the non-reacting group  with R. [3]

(ii) Intermediate G can be formed from F in four steps. The reactions involved are:

- electrophilic addition,
- acid-base reaction and intramolecular nucleophilic substitution,
- reduction, and
- elimination.

Suggest reagents and conditions for each step. Draw the structure of the intermediate compound formed after each step.

You may represent the non-reacting group  with R. [7]

[Total: 24]

3 Iron is the fourth most abundant element in the crust of the Earth, deposited mainly by meteorites in its metallic state.

(a) Depending on the arrangement of the particles in the solid state, iron exists as a few allotropes, one of which is α-iron.

Paramagnetism and ferromagnetism are two types of magnetic behaviour found in materials. In ferromagnetic materials, the magnetic moments due to unpaired electrons in each particle align strongly in the same direction, resulting in them behaving as magnets. In paramagnetic materials, however, the magnetic moments are randomly oriented such that they can only behave as magnets when an external magnetic field is applied.

At room temperature, α-iron is ferromagnetic, but it becomes paramagnetic above 770 ^{o}C.

With reference to the electronic configuration of $_{26}$Fe, explain why this is so. [2]

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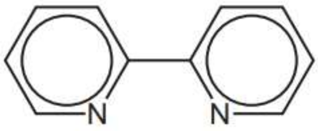
(b) Bipyridine, bipy, is a bidentate ligand.



bipy

(i) A molecule with a conjugated system has multiple p orbitals overlapping with each other, resulting in delocalised electrons.

A compound is said to be aromatic when it has a conjugated, planar and cyclic structure with [4n + 2] π electrons (where n = 0 or a positive integer 1, 2, 3, etc.).

Given that bipyridine is an aromatic compound, with each ring maintaining its own aromaticity, deduce the total number of π electrons present in the molecule.

Explain your answer. [2]

(ii) Explain what is meant by the term *bidentate ligand*. [1]

(iii) The 3d orbitals in an isolated Fe^{2+} ion are degenerate.

Draw a diagram to show the relative energies of the 3d orbitals' energy levels in an isolated Fe^{2+} ion **and** when Fe^{2+} ion forms an octahedral complex. [2]

(iv) The octahedral complex ion $[Fe(bipy)_3]^{2+}$ exists as two stereoisomers.

Using  to represent the structure of bipy, draw three-dimensional diagrams to show the two stereoisomers of $[Fe(bipy)_3]^{2+}$. State the type of stereoisomerism shown. [3]

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(c) The relationship between the energy of a photon of light and its wavelength is shown.

$$E = \frac{hc}{\lambda}$$

E = energy of a photon, in J
h = Planck constant = 6.63×10^{-34} J s
c = speed of light in a vacuum = 3.00×10^{8} m s^{-1}
λ = wavelength, in m

Fig. 3.1 shows the visible spectrum with the approximate range of wavelengths for each colour of light.

	violet	blue	green	yellow	orange	red
λ / nm	380–450	450–495	495–570	570–590	590–620	620–700

Fig. 3.1

(i) Calculate the amount of energy, in J, in 1 photon of light that contains the maximum amount of energy in the visible spectrum. [2]
[1 nm = 1×10^{-9} m]

(ii) Transition metal complexes are often coloured due to the absorption of photons of light at specific wavelengths. The colour observed is complementary to the colour absorbed.

$[Fe(H_2O)_6]^{2+}$ is green in colour, while $[Fe(H_2O)_6]^{3+}$ appears yellow.

With reference to Fig. 3.1 and the electronic configuration of the two complex ions, suggest why they exhibit different colours. [2]

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(d) Prussian Blue is a deep blue solid. The word 'blueprint' was coined from the use of Prussian Blue on sensitised paper to lay out detailed plans for architectural and engineering projects in the 19th century.

(i) Prussian Blue can be precipitated out by adding a solution of Fe^{3+}(aq) to a solution of $[Fe(CN)_6]^{4-}$(aq).

Write a balanced chemical equation, with state symbols, for the formation of Prussian Blue. [1]

Standard electrode potentials can be used to compare the stability of different complex ions of a given transition element.

Table 3.2 lists electrode potentials for some electrode reactions of Fe^{3+} / Fe^{2+} systems.

Table 3.2

electrode reaction	$E^\ominus$ / V
$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$[Fe(bipy)_3]^{3+} + e^- \rightleftharpoons [Fe(bipy)_3]^{2+}$	+0.96

(ii) State and explain which iron(II) complex is the most stable. [2]

(iii) Given,

$Fe^{3+}(aq) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{3-}(aq)$ $\Delta G^\ominus = -250$ kJ mol^{-1}

$Fe^{2+}(aq) + 6CN^-(aq) \rightleftharpoons [Fe(CN)_6]^{4-}(aq)$ $\Delta G^\ominus = -210$ kJ mol^{-1}

Calculate $\Delta G^\ominus$ for $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$, and hence construct an energy cycle to calculate the $E^\ominus$ for $[Fe(CN)_6]^{3-}(aq) + e^- \rightleftharpoons [Fe(CN)_6]^{4-}(aq)$. [4]

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[Total: 21]

Section B

Answer **one** question from this section.

4 (a) Trichloroethanoic acid decarboxylates steadily in aqueous solution at room temperature and pressure.

$$CCl_3CO_2H(aq) \rightarrow CHCl_3(aq) + CO_2(g)$$

In an experiment, 100.0 cm^3 of an aqueous trichloroethanoic acid was allowed to decarboxylate at room temperature and pressure, and the volume of CO_2 collected was tabulated against time. The results are as shown in Table 4.1.

Table 4.1

vol. of CO_2 (V_t) / cm^3	9.5	17.0	22.5	32.5	35.5	37.5	40.0
time / s	500	1000	1500	3000	4000	5000	∞
$V_\infty - V_t$ / cm^3							

(i) Calculate $V_\infty - V_t$ and fill in the table accordingly. [1]

(ii) Explain the significance of $V_\infty - V_t$. Make reference to V_∞ and V_t. [2]

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(iii) Plot a suitable graph on Fig. 4.2 on page 21 that will allow you to determine the rate equation for the decarboxylation reaction, ensuring it can be extrapolated to t = 0 s. [3]

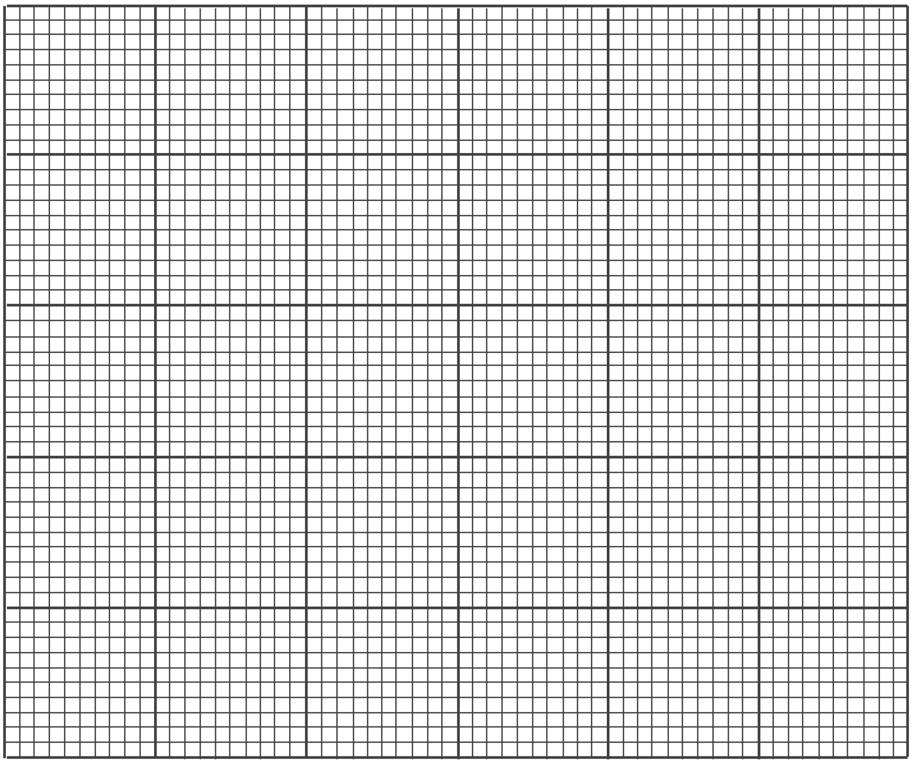

Fig. 4.2

(iv) Calculate the initial concentration of the trichloroethanoic acid used in the experiment. [2]

(v) Use your graph in Fig. 4.2 to deduce the order of reaction with respect to trichloroethanoic acid, calculate the value of the rate constant, and write an expression for the rate equation. Show how you obtained your answer. [3]

(vi) Use the graph to estimate the time taken for the initial concentration of trichloroethanoic acid to fall by 10 %. [1]

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(b) **(i)** The pK_a of trichloroethanoic acid is 0.52 while that of ethanoic acid is 4.76. Explain why the pK_a of trichloroethanoic acid is smaller. [2]

(ii) With reference to the pK_a value of trichloroethanoic acid, state an assumption about its dissociation and use it to estimate the pH of 0.05 mol dm^{-3} trichloroethanoic acid. [2]

(iii) Suggest if partial neutralisation of trichloroethanoic acid can result in a buffer solution. [1]

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(c) Draw the mechanism for the decarboxylation of trichloroethanoic acid, showing all curly arrows, lone pairs and charges. The steps are as follows:

Step 1: Water reacts with trichloroethanoic acid as a Brønsted-Lowry base.

Step 2: Loss of CO_2 from the conjugate base from step 1.

Step 3: Formation of $CHCl_3$ from the intermediates formed in steps 1 and 2. [3]

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[Total: 20]

5 Iodoform reaction is a chemical reaction in which a methyl ketone or a secondary alcohol with a methyl group in the alpha position is oxidised to a carboxylate by reaction with aqueous OH^- and I_2. Ethanoic acid, esters of ethanoic acid and ethanoyl chloride do not undergo the iodoform reaction even though they possess the methyl keto, CH_3CO–, moiety in their structures.

(a) Fig. 5.1 shows the mechanism of the different stages in the iodoform reaction.

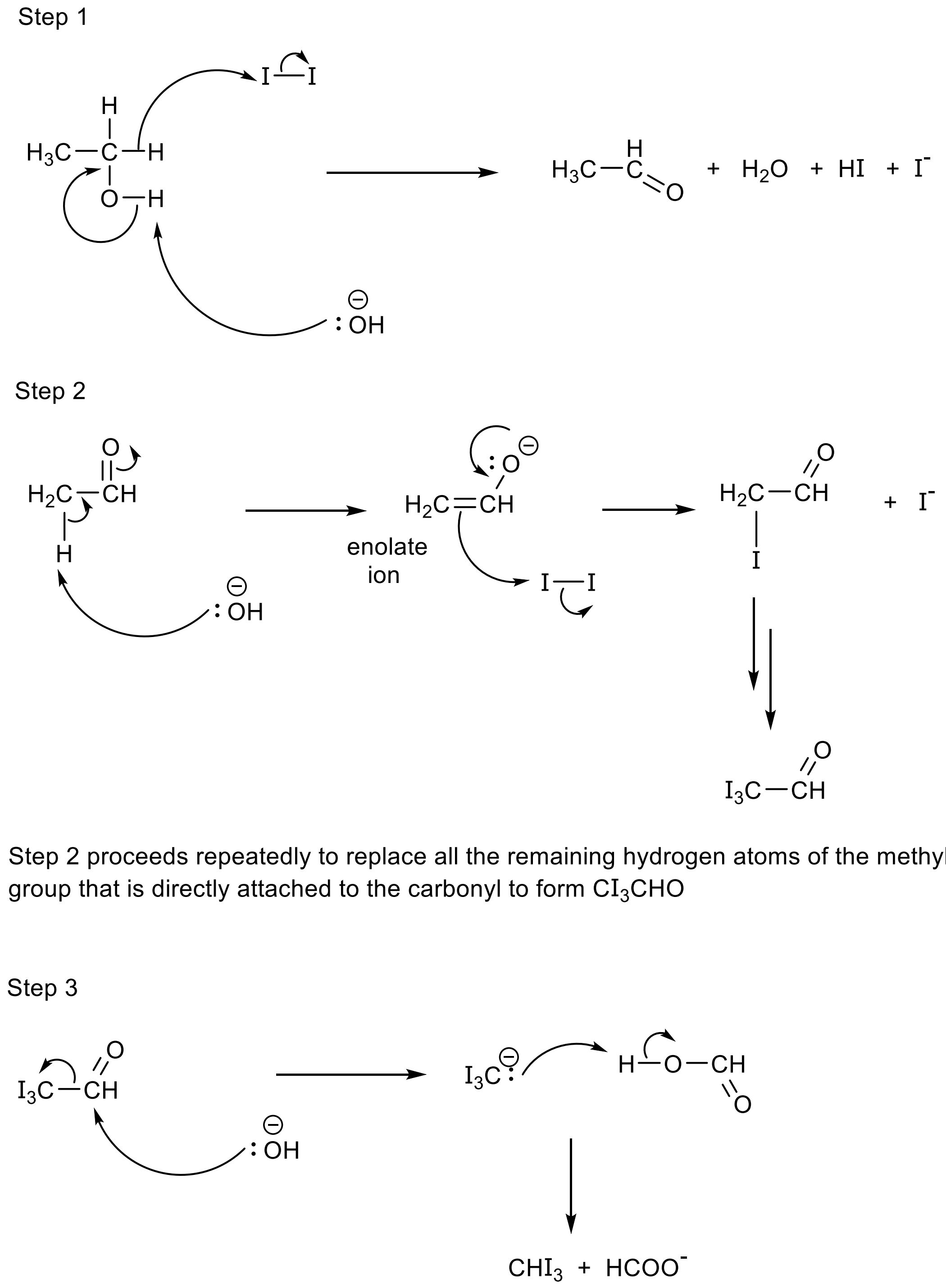

Fig. 5.1

(i) Outline the portion of step 2 in the mechanism for the repeated replacement of the remaining H atoms in CH_2ICHO to form CI_3CHO. Show all lone pairs, dipoles, charges and curly arrows. [4]

(ii) The repeated replacement of the hydrogen atom is made possible by the repeated abstraction of the H^+ by OH^- from the α-methyl group.

State the behaviour of the methyl ketone in this step and explain how it can give up the H^+. [2]

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(iii) Based on the mechanism, explain why only ketones with the α-methyl group can undergo the iodoform reaction while acids such as ethanoic acid or esters, such as, CH_3COOCH_3, which have the α-methyl group do not undergo a similar reaction. [2]

(iv) In step 3, the triiodoethanal undergoes a substitution reaction instead of the expected addition reaction with the nucleophile, OH^-.

Suggest why this reaction occurs. [2]

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(b) Study the reaction scheme in Fig. 5.2. State the reagents and conditions for each step from steps 1 to 7, as well as the identities of U, V and W. [10]

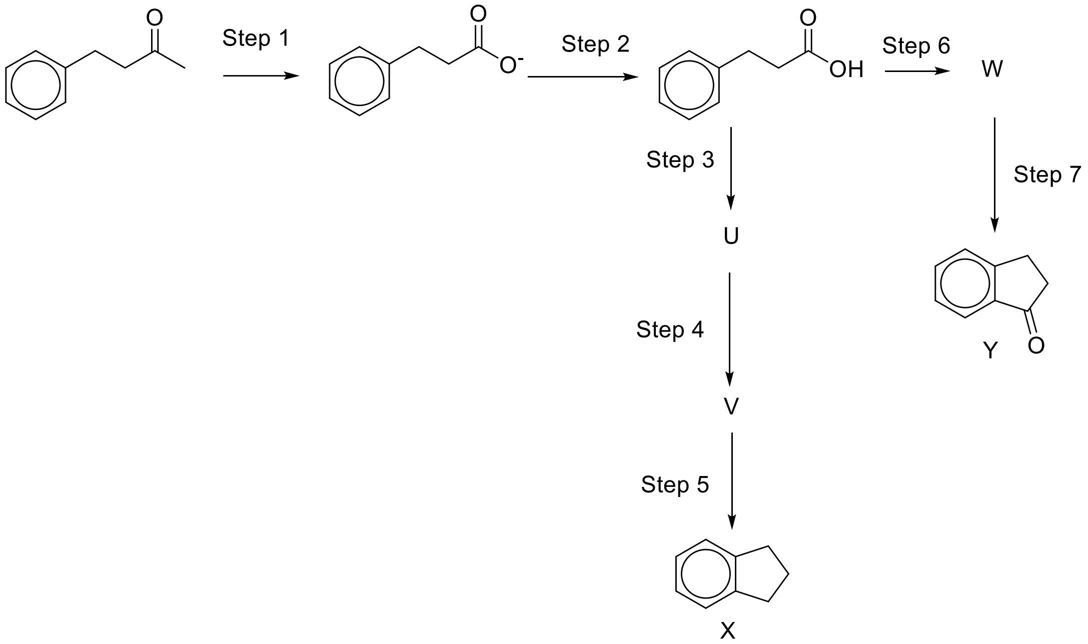

Fig. 5.2

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[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.