TAMPINES MERIDIAN JUNIOR COLLEGE

2019 JC2 H2 Chemistry Prelim Exam Paper 2

(Suggested Answers)

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1 **(a)** Carbon forms compounds with Group 16 elements such as oxygen, sulfur and selenium. The properties of some of these compounds are given below.

compound	structure	net dipole moment	boiling point / °C
CO_2	O=C=O	0	sublimes
CS_2	S=C=S	0	46
COS	S=C=O	0.71	–50
COSe	Se=C=O	0.73	–22

(i) Explain, in terms of structure and bonding, the difference in the boiling points of CS_2 and COS.

CS_2 has a **higher boiling point**. Both CS_2 and COS have **simple molecular structures.**
CS_2 has a **larger electron** cloud (or larger number of electrons) than COS. More energy is required to overcome the **stronger instantaneous dipole-induced dipole interactions (or IMF/Dispersion forces) between CS_2 molecules** than the **instantaneous dipole-induced dipole interactions between COS molecules**.

[2]

(ii) Explain why

- CO_2 has no net dipole moment.
- COSe has a greater net dipole moment than COS.

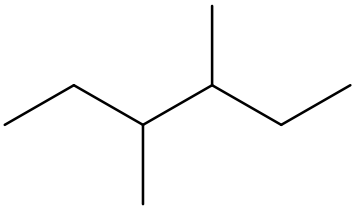
CO_2 has not net dipole moment because it is **linear** and the **dipole moments cancel out**.

COSe has a greater net dipole moment than COS.
There is a **smaller difference between the dipole moment of C=O and C=S in COS than that between C=O and C=Se in COSe**
since **S is more electronegative than Se**.
OR polarity of C=S is greater than that of C=Se.

[2]

Carbon forms the backbone of organic compounds. Hydrocarbons are the simplest organic compounds that contain carbon and hydrogen.

(b) Compound **A** is an isomer of the hydrocarbon octane, C_8H_{18}.

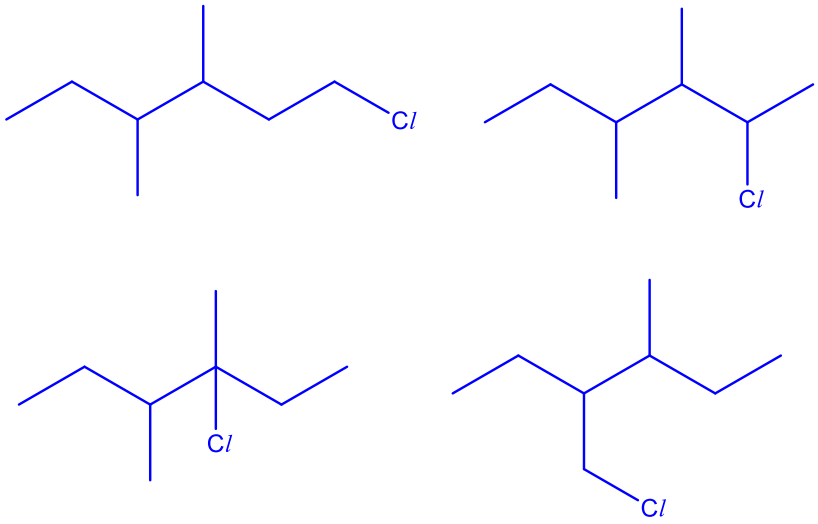


A

Controlled chlorination of compound **A** in the presence of UV light produces different mono-chlorinated products with a molecular formula of $C_8H_{17}Cl$.

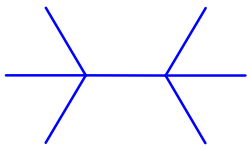
(i) Suggest the total number of constitutional isomers which can be formed from the possible mono-chlorination of compound **A**. Draw the structural formulae of any **two** of these products.

Total number of possible mono-chlorinated products = **4**



[3]

(ii) Draw the **skeletal** formula of the isomer of octane which could produce **only one** possible mono-chlorinated product if it undergoes free radical substitution.



[1]

(c) Besides reaction of alkanes with halogens, the process of thermal cracking, in which large alkane molecules are broken down into smaller alkanes and alkenes, proceeds via free radical mechanism.

The following are reactions involved when propane undergoes thermal cracking.

$CH_3CH_2CH_3 \longrightarrow \bullet CH_3 + \bullet CH_2CH_3$ -- (1)

$CH_3CH_2CH_3 \longrightarrow \bullet H + \bullet CH_2CH_2CH_3$ -- (2)

$\bullet CH_3 + CH_3CH_2CH_3 \longrightarrow CH_4 + \bullet CH_2CH_2CH_3$ -- (3)

$\bullet CH_2CH_3 \longrightarrow \bullet H + CH_2{=}CH_2$ -- (4)

$\bullet CH_3 + CH_2{=}CH_2 \longrightarrow \bullet CH_2CH_2CH_3$ -- (5)

$\bullet CH_3 + \bullet CH_3 \longrightarrow CH_3CH_3$ -- (6)

$2 \bullet CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2$ -- (7)

(i) Reactions (1) and (2) are termed initiation steps. By quoting relevant data from the *Data Booklet*, deduce which one is more likely to occur.

Reaction (1) is more likely to occur as it is easier to break a C-C bond (350 kJ mol^{-1}) compared to a C-H bond (410 kJ mol^{-1}).

[1]

(ii) From reactions (3) to (7), identify those which may be termed propagation steps in the mechanism.

Reactions (3), (4) and (5)

[1]

(iii) Which gas, if detected in the product mixture, would support the occurrence of both reactions (2) and (4)?

Hydrogen

[1]

(iv) Suggest why reaction (7) may be termed a *disproportionation* reaction.

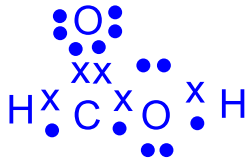
The $\bullet CH_2CH_3$ radical loses a hydrogen (is oxidised) to form ethene and gains a hydrogen (is reduced) to form ethane.

OR
The oxidation number of carbon in $\bullet CH_2CH_3$ increases –3 from to –2 in ethane and decreases from to –3 to form ethane.

[1]

(d) Methanoic acid, H_2CO_2, is the simplest carboxylic acid.

Draw a dot-and-cross diagram of methanoic acid. Suggest the shape around the carbon atom in methanoic acid.



Shape around C atom: **Trigonal planar**

[2]

[Total: 14]

2 Hydrogen peroxide reacts with acidified iodide ions to liberate iodine, according to the following equation:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(aq)$$

In investigations of this reaction, the following results were obtained by varying the volumes of hydrogen peroxide and iodide ions.

experiment	volume of H_2O_2 / cm^3	volume of I^- / cm^3	volume of H_2O / cm^3	initial rate / mol dm^{-3} s^{-1}
1	20.0	20.0	20.0	1.2×10^{-2}
2	20.0	30.0	10.0	1.8×10^{-2}
3	50.0	10.0	0.0	1.5×10^{-2}

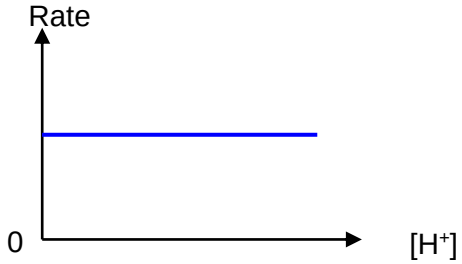
(a) Explain why water was added to experiments 1 and 2.

To ensure the **total volume of the mixture remains constant**, so that **volume of reactant is directly proportional to [reactant]** in the mixture .

[1]

(b) The reaction was determined to be **zero order** with respect to hydrogen ions.

(i) Sketch the rate-concentration graph for H^+ ions.



[1]

(ii) Determine the order of reaction with respect to the other two reactants.

Hence, write down the rate equation.

Let rate= k[H_2O_2(aq)]^m[I^-(aq)]^n
Compare experiments 1 & 2, keeping [H_2O_2(aq)] and total volume constant
$\frac{1.2x10^{-2}}{1.8x10^{-2}} = \frac{k(20.0)^m(20.0)^n}{k(20.0)^m(30.0)^n}$ (or use inspection method)
n = 1

Rate of reaction is **1st order with respect to I^-(aq)** .
Or
Compare experiments 1 & 2, keeping [H_2O_2(aq)] and total volume constant
when [I^-] x 3/2, rate of reaction x 3/2
Order of reaction **w.r.t. I^- = 1**

Compare experiments 1 & 3, keeping total volume constant
$\frac{1.2x10^{-2}}{1.5x10^{-2}} = \frac{k(20.0)^m(20.0)^1}{k(50.0)^m(10.0)^1}$
m = 1
Rate of reaction is **1st order with respect to H_2O_2(aq)** .
Or
Compare experiments 1 & 3, keeping total volume constant
When **[I^-] x 1/2 and [H_2O_2] x 5/2, rate x 5/4 (1/2 x 5/2)**
Since the order wrt. I^- is 1, order wrt to H_2O_2 is 1.

rate= k[H_2O_2(aq)][I^-(aq)]

[3]

(c) In order to further investigate the kinetics of the reaction, experiments 4 and 5 were conducted. The following results were obtained by varying the concentrations of hydrogen peroxide and iodide ions.

experiment	initial [H_2O_2(aq)] / mol dm^{-3}	initial [I^-(aq)] / mol dm^{-3}
4	0.020	0.500
5	0.050	1.000

The half-life of hydrogen peroxide was 9.6 min in experiment 4. Explain and predict the half-life of hydrogen peroxide in experiment 5.

For experiment 4 and 5, since [I^-(aq)] >> [H_2O_2(aq)], [I^-(aq)] is approximately constant.
Thus, rate = k'[H_2O_2(aq)] (a pseudo first order reaction)
where **k' = k[I^-(aq)]**
$t_{1/2} = = \frac{ln\,2}{k'} = \frac{ln\,2}{k[I^-]}$

$t_{1/2}$ of H_2O_2 in experiment 4 = 9.6 min (for [I^-(aq)] = 0.500 mol dm^{-3})

$t_{1/2}$ of H_2O_2 in experiment 5 = **4.8 min** (for [I^-(aq)] = 1.00 mol dm^{-3})

[2]

(d) An alternative method of investigating the rate of the above reaction is by withdrawing aliquots at specified time intervals and titrating the iodine formed in each aliquot with sodium thiosulfate solution.

Suggest how the reaction can be quenched at specified time intervals.

Sudden **cooling** of the reaction mixture or sudden **dilution** through the addition of large volume of water.

[1]

(e) Hydrogen peroxide decomposes easily. Suggest a method whereby the shelf-life of the hydrogen peroxide solution could be increased.

Keep away from light by storing it in a **dark-coloured bottle**.
or
Ensure purity of the solutions, i.e. no contaminants, especially **those that hasten the decomposition of peroxide**.

[1]

[Total: 9]

3 Lithium forms various compounds used for a wide range of purposes. For example, Li_2CO_3 is used as a mood-stabilising drug and LiF is used to record ionising radiation exposure from gamma rays, beta particles and neutrons.

(a) Numerical values of the solubility products of some lithium salts at 298 K are given in the table below.

salt	solubility product
LiF	2.68×10^{-3}
Li_2CO_3	2.14×10^{-2}
Li_3PO_4	3.20×10^{-9}

(i) Write an expression for the solubility product, K_{sp}, of lithium phosphate, including its units.

$K_{sp} = [Li^+]^3 [PO_4^{3-}]$ $mol^4\ dm^{-12}$

[2]

(ii) Using the data above, calculate a value for the solubility of lithium phosphate.

Let solubility of Li_3PO_4 be **s** mol dm^{-3}

$Li_3PO_4(s) \rightleftharpoons 3Li^+(aq) + PO_4^{3-}(aq)$ ----- (1)

s **3s** **s**

$K_{sp} = [Li^+]^3 [PO_4^{3-}]$

$= (3s)^3(s)$

$= 27s^4$

$3.20 \times 10^{-9} = 27s^4$

Solubility of Li_3PO_4 = **s** = **3.30 x 10^{-3}** mol dm^{-3}

[2]

(iii) LiF was precipitated when equal volumes of a solution of 0.050 mol dm^{-3} $LiNO_3$ and a solution of KF were mixed.

Calculate the minimum concentration of the KF solution required for precipitation to occur.

Since equal volumes are mixed, new $[Li^+]$ = 0.050 / 2 = 0.025 mol dm^{-3}

Precipitation occurs when Ionic Product ≥ K_{sp}

$[Li^+][F^-] \geq 2.68 \times 10^{-3}$

$0.025 \times [F^-] \geq 2.68 \times 10^{-3}$

$[F^-] \geq 0.1072$ mol dm^{-3}

$KF \rightarrow K^+ + F^-$

Original concentration of KF= 0.1072 x 2 = **0.214 mol dm^{-3}**

[2]

(iv) Describe and explain how the solubility of Li_2CO_3 is affected by adding solid Na_2CO_3 into the solution.

$Li^+(aq) + CO_3^{2-}(aq) \rightleftharpoons LiCO_3(s)$ ----- (1)

Due to **common ion CO_3^{2-}**, when Na_2CO_3 is added into the solution, **$[CO_3^{2-}]$ increases** . By Le Chatelier's Principle, **equilibrium position** (1) shifts to the **right** to **decrease** $[CO_3^{2-}]$ Hence, **solubility** of **Li_2CO_3 decreases.** .

[2]

(b) When a precipitate is formed, $\Delta G^{\ominus}_{ppt}$, in J mol^{-1}, is given by the following expression.

$$\Delta G^{\ominus}_{ppt} = 2.303\ RT \log K_{sp}$$

For lithium sulfate, Li_2SO_4, K_{sp} = 128 mol^3 dm^{-9} at 298 K.

Using the above expression, determine whether lithium sulfate is soluble in water at 298 K. Explain your answer.

For Li_2SO_4, $\Delta G^{\ominus}_{ppt}$ = $2.303RT \log K_{sp}$
= 2.303 x 8.31 x 298 x log (128)
= **+1.20 x 10^4 J mol^{-1}**

Since **$\Delta G^{\ominus}_{ppt} > 0$** , it implies that the **precipitation** of Li_2SO_4, is **not feasible.** Hence, Li_2SO_4, is **soluble in water at 298K**.

[2]

(c) Another use of Li_2CO_3 is in the processing of metal oxides. When Li_2CO_3 decomposes, it forms Li_2O solid and CO_2 gas according to the following equation.

$$Li_2CO_3(s) \rightarrow Li_2O(s) + CO_2(g)$$

(i) Calculate the standard enthalpy change of reaction for the decomposition of Li_2CO_3 using the following standard enthalpy changes of formation, $\Delta H_f^{\ominus}$.

compound	Li_2CO_3	Li_2O	CO_2
$\Delta H_f^{\ominus}$ / kJ mol^{-1}	−1216	−596	−394

$\Delta H_r^{\ominus}$ = $\Sigma\ \Delta H_f^{\ominus}$(products) − $\Sigma\ \Delta H_f^{\ominus}$(reactants)
= $\Delta H_f^{\ominus}(CO_2) + \Delta H_f^{\ominus}(Li_2O) - \Delta H_f^{\ominus}(Li_2CO_3)$
= −394 −596 – (– 1216)
= **+226 kJ mol^{-1}**

[1]

(ii) The entropy change for the decomposition reaction is positive. Explain the effect on spontaneity of this decomposition reaction as temperature increases.

$\Delta H^{\ominus}$ is positive while **$\Delta S^{\ominus}$ is positive. So $-T\Delta S$ is negative.**

As temperature increases, **$-T\Delta S$** becomes **more negative** so **ΔG** becomes **more negative.** Thus the decomposition becomes **more spontaneous** as temperature increases.

OR

At low *T*,
$|T\Delta S| < |\Delta H|$
$\Rightarrow$ Hence, **$\Delta G > 0$ (+ve)** at **low** temperatures.

At high *T*,
$|T\Delta S| > |\Delta H|$
$\Rightarrow$ Hence, **$\Delta G < 0$ (–ve)** at **high** temperatures.

Thus the decomposition becomes **more spontaneous** as temperature increases.

[2]

[Total: 13]

4 *Use of the Data Booklet is relevant to this question.*

(a) Chemical companies manufacture containers filled with liquid butane for use by campers. The complete combustion of butane produces carbon dioxide and water. The enthalpy change of combustion of butane is –3000 kJ mol^{-1}.

A camper estimates that the liquid butane left in a container would give 1.2 dm^3 of butane gas (measured at room temperature of 20 °C and pressure of 1 atm).

(i) Calculate the mass of water at room temperature that could be brought to boiling point at 100 °C by completely burning this mass of butane, given that the process is only 80% efficient.

No. of moles of butane present = $\frac{1.2}{24}$ = 0.0500 mol

Quantity of heat released by combustion, q' = 3000 × 0.0500 = 150 kJ

Quantity of heat absorbed by water, q = 80% × q' = 80% × 150 = 120 kJ
$q = m\,c\,\Delta T \Rightarrow q = m \times 4.18 \times (100 - 20)$

Mass of water, m = $\frac{120}{334.4}$ = **0.359 kg (or 359 g)** (3 s.f.)

[3]

(ii) Suggest a reason why the combustion process is only 80% efficient.

- **Heat is lost to surroundings** during combustion.
- Some of the **heat is used to vapourise the liquid butane**.

[1]

(b) When burnt in a limited supply of air, butane forms carbon and water. The enthalpy change of this reaction is –1400 kJ mol^{-1}.

(i) Construct a balanced equation for this reaction.

$$C_4H_{10} + \frac{5}{2}O_2 \rightarrow 4C + 5H_2O$$

[1]

(ii) Explain why the enthalpy changes of the two combustion reactions in **(a)** and **(b)** are different.

Due to **complete combustion in (a)**, **more energy is released** due to the **formation of CO_2** (bond formation), compared with **only C formed** in the **incomplete combustion in (b)**. *(or reverse discussion)*

[1]

(iii) State the quantitative information that can be obtained from this difference in enthalpy changes.

(Standard) **Enthalpy change of combustion of carbon** / **ΔH_c (C)**

[1]

(c) The carbon-oxygen *bond energy* in carbon monoxide, CO, is 1077 kJ mol^{-1}.

Carbon monoxide can be formed by the following reaction:

$$C(s) + CO_2(g) \rightarrow 2CO(g) \qquad \Delta H^{\ominus} = +172.5 \text{ kJ mol}^{-1}$$

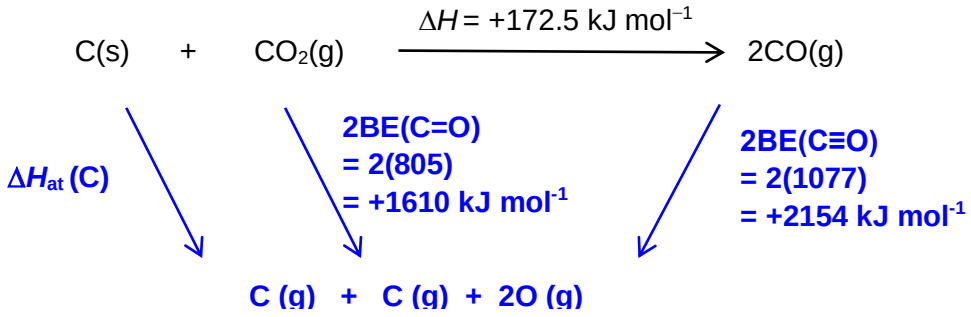
(i) Explain, with the aid of a suitable equation, what is meant by the term *bond energy* of carbon monoxide.

C≡O (g) → C (g) + O (g)

Bond energy of CO is the **energy required** to **break 1 mole of gaseous CO** (triple) **bond** to form **gaseous** (C and O) **atoms**.

[2]

(ii) Determine the enthalpy change of atomisation of carbon by using relevant bond energy data from the *Data Booklet* to complete the energy cycle below. Include relevant information in your cycle.



By Hess' Law,
ΔH_{at} (C) + 2BE(C=O) = ΔH + 2BE(C≡O)
ΔH_{at} (C) + 2(805) = 172.5 + 2(1077)
ΔH_{at} (C) = 172.5 + 2154 – 1610
= +716.5 kJ mol^{-1}

[3]

[Total: 12]

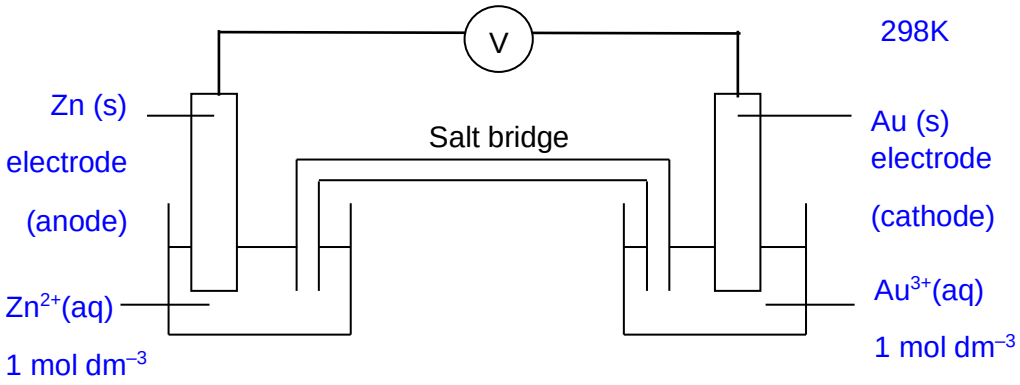
5 *Use of the Data Booklet is relevant to this question.*

A student wanted to study the following reaction.

$$2Au^{3+} + 3Zn \rightleftharpoons 2Au + 3Zn^{2+}$$

He first sets up an electrochemical cell which comprises of Au^{3+}/Au and Zn^{2+}/Zn half-cells prepared under standard conditions.

(a) **(i)** Draw a fully labelled diagram of the electrochemical cell under standard conditions.



[2]

(ii) Given that $E^{\ominus}_{Au^{3+}/Au}$ is +1.50 V, calculate the $E^{\ominus}_{cell}$ of this cell.

$E^{\ominus}_{cell}$ = +1.50 – (–0.76) = **+2.26 V**

[1]

(iii) Suggest a replacement transition element ion-ion half-cell for the Zn^{2+}/Zn half-cell so that the direction of electron flow is reversed.

Co^{3+}/Co^{2+}, Mn^{3+}/Mn^{2+}, MnO_4^-/Mn^{2+}

[1]

(b) When the reaction in **(a)** begins, $[Au^{3+}]$ starts to decrease while $[Zn^{2+}]$ increases. In the study of electrochemical cells, the *Nernst equation*, given below, can be applied to determine the cell potential under non-standard conditions.

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0592}{n} \log_{10} Q$$

where n is the number of moles of electrons transferred and Q is the reaction quotient given by $\frac{[Zn^{2+}]}{[Au^{3+}]}$.

(i) Using your answer in **(a)(ii)**, calculate the new E_{cell} using the Nernst equation, when $[Au^{3+}]$ and $[Zn^{2+}]$ are 0.02 mol dm^{-3} and 2.47 mol dm^{-3} respectively.

$$E_{cell} = +2.26 - \frac{0.0592}{6} \log_{10} \frac{[2.47]}{[0.02]} = \mathbf{+2.24\ V}$$

[1]

(ii) Suggest the value of E_{cell} when the reaction goes to completion.

0 V

[1]

(c) The redox reaction in **(a)** is an example of a spontaneous reaction which proceeds as predicted by the cell potential. However, not every chemical reaction agrees with the theoretical prediction. One example is the reaction between acidified $K_2Cr_2O_7$ and water.

(i) Using information from the *Data Booklet*, calculate $\Delta G^{\ominus}$ for the reaction between acidified $K_2Cr_2O_7$ and water. Based on your value for $\Delta G^{\ominus}$, comment on the spontaneity of the reaction.

$\Delta G^{\ominus} = -nFE^{\ominus}$
$= -12 \times 96500 \times (1.33 - 1.23)$
$= \mathbf{-1.16 \times 10^5\ kJ\ mol^{-1}}$

$\Delta G^{\ominus} < 0$, the **reaction is spontaneous**.

[3]

(ii) The reaction between water and acidified $K_2Cr_2O_7$ has an $E^{\ominus}_{cell}$ greater than 0 V under standard conditions, yet the reaction does not proceed. Suggest a reason for this observation.

The reaction has high activation energy so it cannot take place under standard condition.

[1]

(iii) Another example of a reaction that does not agree with the theoretical prediction is the reaction between Cu^{2+} and I^- according to the equation below.

$$2Cu^{2+}(aq) + 4I^-(aq) \rightleftharpoons 2CuI(s) + I_2(aq) \qquad E^{\ominus}_{cell} = -0.39\ V$$

White precipitate of CuI is formed during the reaction. Suggest a reason why the reaction proceeds despite the $E^{\ominus}_{cell}$ being less than 0 V.

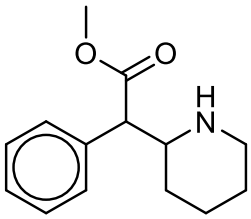
The continuous **precipitation of CuI** from the solution will **shift the equilibrium position to the right** and drive the reaction forward.

[1]

[Total: 11]

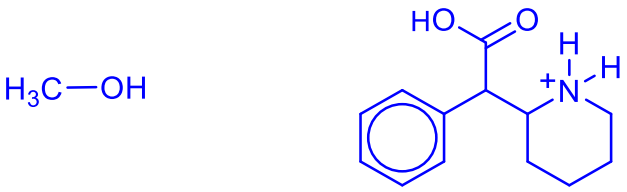
6 Adrenaline is a naturally occurring hormone and stimulant released in the body during times of danger or stress. Stimulant drugs that can mimic the effect of adrenaline have been developed for treatment of various conditions.

(a) Methylphenidate is a stimulant drug commonly used in the treatment of Attention Deficit Hyperactive Disorder (ADHD).



methylphenidate

(i) Draw the structures of the organic products formed when methylphenidate is heated with dilute hydrochloric acid.

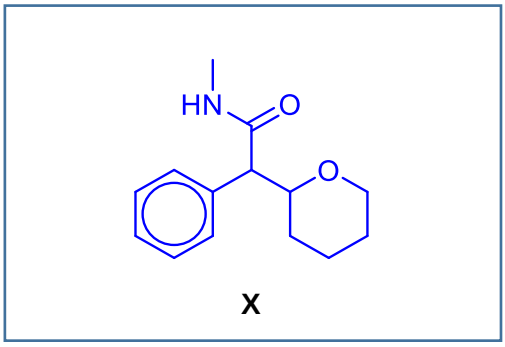


[2]

(ii) An isomer of methylphenidate, compound **X**, is neutral and has the following structural properties:

- contains one aromatic six-membered ring
- contains 

Suggest a structure for compound **X** and state its isomeric relationship to methylphenidate.



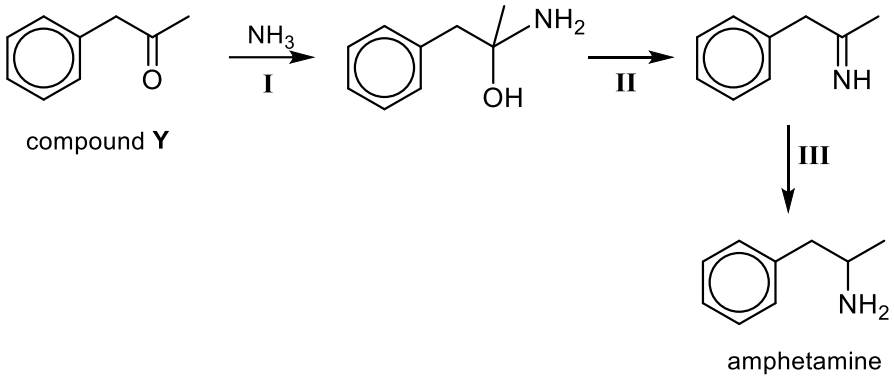
X

isomeric relationship to methylphenidate:

constitutional isomer (OR structural isomer)

[2]

(b) Another stimulant, amphetamine, is prepared commercially from compound **Y** as shown below.



compound **Y**

amphetamine

(i) Suggest the type of reaction occurring in:

[2]

Step **II** **elimination**
Step **III** **addition / reduction**

(ii) Suggest suitable reagents and conditions for the conversion in step **III**. You may assume the R=NH group reacts in a similar manner to the carbonyl group.

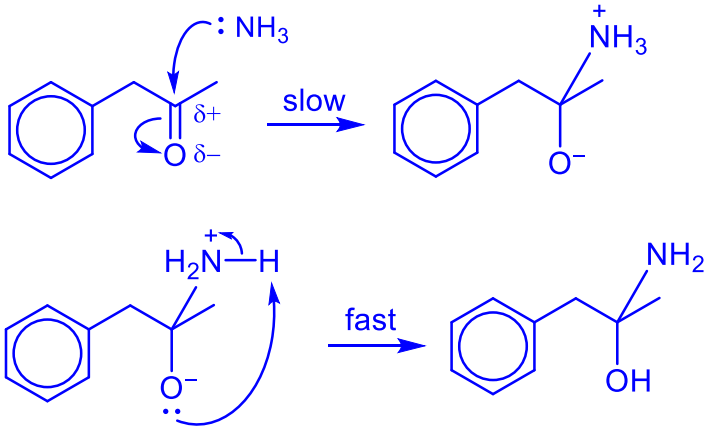
[1]

reagents and conditions: **$NaBH_4$ in ethanol** or **H_2(g) with Ni heat / Pt / Pd**

(iii) Reaction **I** which occurs between compound **Y** and NH_3 is a nucleophilic addition reaction.

Draw the mechanism for this reaction, given that in the rate-determining step, the nucleophilic attack by NH_3, results in an intermediate species containing both a positive and negative charge.

[3]

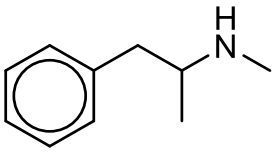


(iv) With reference to the mechanism you have drawn in **(iii)**, explain why the product from step **I** is expected to be optically inactive.

In the slow step, the nucleophile attacks the **trigonal planar carbonyl C** atom with **equal probability from above and below the plane** . This results in the formation of a **racemic mixture** which is optically inactive.

[2]

(c) Methamphetamine is a stimulant which has a structure similar to amphetamine.



methamphetamine

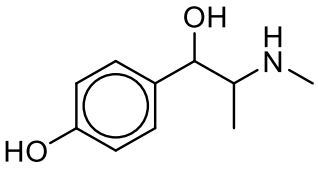
(i) The hydrochloride salt of methamphetamine exists as colourless crystals. Methamphetamine is immiscible with water whereas the salt is soluble in water. With reference to the interactions formed between each of the compounds and water, explain the difference in the solubility of methamphetamine and its salt in water.

Methamphetamine forms instantaneous dipole-induced dipole interactions with water whereas the **salt is able to form ion-dipole interactions with water** .

The **strong interactions formed between the salt and water release sufficient energy to overcome hydrogen bonding between water molecules OR to cause detachment of ions from the crystal lattice** . (OR **weak i.d.-i.d. attraction of methamphetamine are not compatible with strong hydrogen bonding between water**)

[2]

(ii) In the human body, methamphetamine can be converted to compound **Z**.



Z

Describe a simple chemical test which could be used to distinguish between methamphetamine and compound **Z**.

You should state the reagents and conditions required, together with the expected observations for each compound.

Add aqueous Br_2 to each compound

Compound Z will decolourise Br_2 with the formation of a white ppt whereas **methamphetamine will give no visible observation** .

Other possible test reagents: neutral $FeCl_3$ / Na / PCl_5 / hot acidified $K_2Cr_2O_7$ (not $KMnO_4$)

[2]

[Total: 16]

End of Paper 2