

**CATHOLIC JUNIOR COLLEGE**  
**JC2 PRELIMINARY EXAMINATIONS**  
**Higher 2**

CANDIDATE  
NAME

CLASS

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**CHEMISTRY**

Paper 2 Structured Questions

**9647/02**

**Monday 22 August 2016**

**2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

Write your name and class 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, or correction fluid.

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

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.

**ANSWER SCHEME**

	For Examiner's Use		
<b>Paper 1</b>			<b>40</b>
<b>Paper 2</b>	<b>Q 1</b>	<b>12</b>	<b>72</b>
	<b>Q 2</b>	<b>15</b>	
	<b>Q 3</b>	<b>15</b>	
	<b>Q 4</b>	<b>15</b>	
	<b>Q 5</b>	<b>15</b>	
<b>Paper 3</b>	<b>Q 1</b>	<b>20</b>	<b>80</b>
	<b>Q 2</b>	<b>20</b>	
	<b>Q 3</b>	<b>20</b>	
	<b>Q 4</b>	<b>20</b>	
	<b>Q 5</b>	<b>20</b>	
<b>Total</b>			<b>192</b>

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This document consists of **18** printed pages.

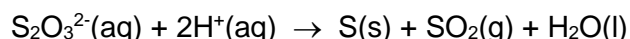
## 1 Planning (P)

One method of studying the kinetics of a chemical reaction, to find the order of reaction with respect to a particular reactant, is to measure the initial rates, by using the 'clock experiment'.

To determine the initial rate, we can measure the time taken for a prominent visual change to occur in the course of a reaction.

When aqueous sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ , is added to a solution containing dilute hydrochloric acid,  $\text{HCl}$ , a fine, pale yellow precipitate of solid sulfur will be formed after a while. This is the prominent visual change that can be clearly identified.

The overall equation for the reaction is represented as follows:



The initial rate of this reaction is determined by measuring the time taken for sufficient precipitate of sulfur to be formed to just obscure a 'cross' marked on a piece of white paper below a reaction container.

A student carried out a series of preliminary experiments, using approximate volumes of the two reactants and each reaction mixture was made up to the same total volume with deionised water. The student found that the time taken for the pale yellow precipitate to appear doubled when the volume of hydrochloric acid added was halved.

- (a) (i) State the relationship between the initial rate of reaction and the time taken for the pale yellow precipitate to appear.

$$\text{rate} \propto \frac{1}{\text{time}} \quad \text{OR}$$

Rate of reaction is inversely proportional to time, the time taken for the pale yellow precipitate to appear is low/short if the rate is high.....[1]

- (ii) Explain why it is necessary to top up the reaction mixture with deionised water to the same total volume.

$$\text{volume} \propto \text{concentration} \quad \text{or}$$

To ensure that the total volume of the resultant reaction mixture remains the same in all experiments so that the volume of each reactant is proportional to its concentration in the resultant solution.

When the volume of that reactant added doubles, its concentration in the resultant solution doubles.....[1]

- (b) Hence, based on the results of the student's preliminary experiments, predict the order of the reaction with respect to  $\text{H}^+$  ions.

The time taken for the pale yellow precipitate to appear doubled when the volume of hydrochloric acid added was halved.

Since  $\text{volume} \propto \text{concentration}$  and  $\text{rate} \propto \frac{1}{\text{time}}$ , when the concentration of hydrochloric acid added was halved, the rate was halved.

$\therefore$  rate of reaction  $\propto [\text{H}^+]$  or the reaction is first order with respect to  $\text{H}^+$ .

[1]

- (c) You are to design an experiment to study the kinetics of the reaction between  $\text{S}_2\text{O}_3^{2-}$  ions and  $\text{H}^+$  ions.

The following data in tabulated form is shown below.

experiment	volume of $1.00 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3 / \text{cm}^3$	volume of $1.00 \text{ mol dm}^{-3} \text{ HCl} / \text{cm}^3$	volume of deionised water / $\text{cm}^3$	time taken for the 'marked cross' to be obscured / s
1	10	20	20	$t_1$
2	20	20	10	$t_2$
3	10	10	30	$t_3$

- (i) Fill in the blanks in the table above, appropriate volumes of the reactants and deionised water to be used in experiments 2 and 3 such that the order of reaction with respect to  $\text{S}_2\text{O}_3^{2-}$  and  $\text{H}^+$  ions can be determined and verified. [1]

Appropriate volumes of reactants and deionised water stated correctly in experiments 2 and 3.

- (ii) Outline in a series of numbered steps, how **experiment 1** could be carried out. Your **plan** should include:
- the **apparatus** used to measure the various volumes,
  - the **order** that the various solutions are mixed,
  - how the **time** to determine the rate of reaction is measured, and
  - other **experimental details** to ensure the **consistency** of the experiment.

Based on the table in (c)(i), explain how the results of any two of the three experiments can be used to determine the order of reaction with respect to  $\text{S}_2\text{O}_3^{2-}$  ions.

.....

.....

.....

- [7]

### ***Inspection Method***

Order	Explanation
0	If $t_2 = t_1$ , then the rates for both reactions remain unchanged, though the concentration of $S_2O_3^{2-}$ is doubled. So the reaction rate is independent of the change in concentration of $S_2O_3^{2-}$ . <b>Zero</b> order.
1	If $t_2$ is halved that of $t_1$ , the rate for experiment 2 is twice that of experiment 1. Since the rate is doubled when the concentration of $S_2O_3^{2-}$ is doubled, the reaction is <b>first</b> order with respect to $S_2O_3^{2-}$ .
2	If $t_2$ is four times less than that of $t_1$ , the rate for experiment 2 is four

	times greater than that of experiment 1. Since the rate is four times greater when the concentration of $\text{S}_2\text{O}_3^{2-}$ is doubled, the reaction is <b>second</b> order with respect to $\text{S}_2\text{O}_3^{2-}$ .
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OR

V x t method

Order	Explanation
<b>0</b>	$t$ is constant, $t_1 = t_2$
<b>1</b>	$(V_{\text{S}_2\text{O}_3^{2-}}) \times t = \text{constant}$ or $10 \times t_1 = 20 \times t_2$
<b>2</b>	$(V_{\text{S}_2\text{O}_3^{2-}})^2 \times t = \text{constant}$ or $10^2 \times t_1 = 20^2 \times t_2$

[3]

- (d) Identify one potential safety hazard in this experiment and state how you would minimise this risk.

$\text{HCl(aq)}$  is corrosive, wear hand gloves to prevent direct contact with it.

$\text{SO}_2$  gas liberated is toxic, wear protective mask or perform the experiment in a well ventilated place or using a fume cupboard. [1]

Either one

[Total: 12]

- 2 Silver halides (silver chloride, silver bromide and silver iodide) are useful in qualitative analysis as they are insoluble in water. In qualitative analysis, silver nitrate is added to a test solution to identify the presence of halide ions by forming a precipitate.

- (a) (i) When aqueous silver nitrate was added to a test solution which was known to contain a halide ion, a cream precipitate was formed.

Identify the precipitate and deduce the identity of the halide ion present in the solution.

The cream precipitate formed is AgBr, hence the solution contains Br<sup>-</sup> ions. [1]

.....[1]

- (ii) To confirm the identity of the halide, aqueous ammonia was added dropwise, and the precipitate remained unchanged at first, but as more ammonia was added, the precipitate dissolved.

With the aid of an equation, briefly explain why the precipitate dissolved.

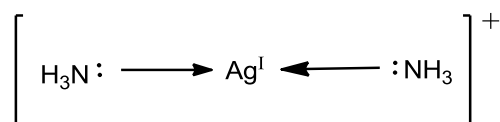


.....

When excess/concentrated ammonia is added, a soluble complex ion is formed.

.....[2]

- (iii) Draw the structure of the silver-containing product in solution after the precipitate dissolved, displaying any lone pair of electrons where appropriate.



[1]

In photography, after an image is developed, sodium thiosulfate, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, is used to dissolve any remaining silver halide away, to “fix” the image and ensure that it does not change upon further exposure to light.

- (iv) An equal volume of sodium thiosulfate was added to the solution from (ii). State the type of reaction that occurred when sodium thiosulfate was added.

Ligand exchange/displacement reaction.

.....[1]

- (v) Suggest the identity of the silver-containing product which has a coordination number of 2.



.....[1]

- (b) The table below shows data about silver and two other metals, iron and copper.

	silver	iron	copper
electronic configuration	[Kr] 4d <sup>10</sup> 5s <sup>1</sup>	[Ar] 3d <sup>6</sup> 4s <sup>2</sup>	[Ar] 3d <sup>10</sup> 4s <sup>1</sup>
conductivity at room temperature/ S m <sup>-1</sup>	6.3 x 10 <sup>7</sup>	1.0 x 10 <sup>7</sup>	?

- (i) Explain, in terms of structure and bonding, why the three metals have **high** electrical conductivity.

The three transition metals have giant metallic structures with strong metallic bonds between metal cations and a sea of delocalized electrons.

They have many d and s valence electrons which can be delocalized and hence can conduct electricity through the movement of the electrons. [2]

- (ii) Silver and copper are known to be excellent metallic conductors at room temperature. Noting the electronic configuration, suggest the value of the conductivity of copper at room temperature.

Any value between 1.1 x 10<sup>7</sup> – 6.2 x 10<sup>7</sup>

..... S m<sup>-1</sup> [1]

Actual value: 5.9 x 10<sup>7</sup> S m<sup>-1</sup> (units are Siemens per metre, reciprocal of resistivity)

- (iii) Iron is used as a catalyst in the synthesis of ammonia in the Haber process. State the type of catalysis and explain clearly how it carries out its function.

Iron can act as a heterogeneous catalyst in the Haber process.

It has partially-filled 3d orbitals which allows the ready exchange of electrons to and from reactant molecules (N<sub>2</sub> and H<sub>2</sub>). Reactants are adsorbed onto the surface, weakening the bonds and thereby lowering the activation energy, as well as increasing the surface concentration of reactants, thus increasing the rate of reaction.

..... [3]

- (c) When a jar is filled with gaseous hydrogen iodide, HI, and a red-hot glass rod inserted into the jar, violet fumes are observed.

- (i) State the identity of the violet fumes.

I<sub>2</sub>.....[1]

- (ii) When the same procedure is carried out with HBr instead of HI, no fumes are observed, but on strong heating, reddish-brown vapour is obtained.

With reference to values in the *Data Booklet*, explain the difference in the behaviour of HBr and HI.

From Data Booklet,.....

BE of H–I = 299 kJ mol<sup>-1</sup>.....

BE of H–Br = 366 kJ mol<sup>-1</sup>.....

As the bond energy of is H–Br greater/stronger than H–I, (due to smaller atomic size/radius, and shorter bond length), H–Br does not decompose when heated by contact with a red-hot glass rod, but requires stronger heating/more energy to decompose......

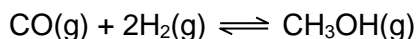
.....[2]

[Total: 15]



- 3 Methanol is one of the alternative fuels proposed to replace fossil fuels. It has the advantage of more efficient production and ease of storage as compared to other alternatives.

Methanol can be formed from carbon monoxide and hydrogen as shown below.



The reaction was investigated by mixing 3.2 mol of CO and 3.2 mol of H<sub>2</sub> in a 10.0 dm<sup>3</sup> sealed vessel, and equilibrium was established at 120 °C under a pressure of 1.60 x 10<sup>6</sup> Pa.

- (a) (i) Assuming ideal gas behaviour, determine the total amount of gas in moles, at equilibrium.

$$pV = nRT$$

$$n = \frac{pV}{RT} = \frac{(1.60 \times 10^6)(10.0 \times 10^{-3})}{(8.31)(273+120)}$$

$$n = 4.899 \text{ or } 4.90 \text{ mol}$$

[2]

- (ii) Hence, calculate the amounts of CO, H<sub>2</sub> and CH<sub>3</sub>OH in moles, present at equilibrium.

	CO	+	2H <sub>2</sub>	$\rightleftharpoons$	CH <sub>3</sub> OH
Initial /mol	3.2		3.2		0
Change / mol	- x		- 2x		+x
Equilibrium/ mol	3.2 - x		3.2 - 2x		x

$$n = 4.90 = 3.2 - x + 3.2 - 2x + x$$

$$4.9 = 6.4 - 2x$$

$$n(\text{CH}_3\text{OH}) = x = 0.750 \text{ mol}$$

$$n(\text{CO}) = 3.2 - 0.75 = 2.45 \text{ mol}$$

$$n(\text{H}_2) = 3.2 - 2(0.75) = 1.70 \text{ mol}$$

[3]

- (iii) Write an expression for the equilibrium constant,  $K_c$  for the above reaction, and use your answers in (a)(ii) to calculate its value under the stated conditions.

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$

$$K_c = \frac{\frac{0.75}{V}}{\frac{2.45}{V} \left( \frac{1.7}{V} \right)^2} = \frac{0.75}{2.45 \left( \frac{1.7}{10} \right)^2}$$

$$K_c = 10.6 \text{ mol}^{-2} \text{ dm}^6$$

[2]

- (b) Standard Gibbs free energy change,  $\Delta G^\circ$  is related to  $K_c$  by the following equation.

$$\Delta G^\circ = -RT \ln K_c$$

where  $\Delta G^\circ$  is in **joules per mole**,  $T$  is the temperature at which equilibrium is established and  $R$  is the molar gas constant.

- (i) Use this equation and your answer in (a) to calculate  $\Delta G^\circ$  for the formation of methanol from carbon monoxide and hydrogen at 120 °C.

$$\Delta G^\circ = - (8.31)(273+120) \ln 10.6$$

$$\Delta G^\circ = -7710 \text{ J mol}^{-1}$$

[1]

- (ii) With reference to the *Data Booklet*, calculate the enthalpy change of formation of methanol from carbon monoxide and hydrogen. Use 1072 kJ mol<sup>-1</sup> for the bond energy of C≡O bond.

<u>Δ Bonds broken (ΔH)</u>		<u>Bonds formed (ΔH)</u>	
2 H-H	2(+436)	3 C-H	3(410)
C≡O	1072	C-O	360
		O-H	460
 $\Delta H^\circ = 2(+436) + 1072 - 3(410) - 360 - 460$			
$= -106 \text{ kJ mol}^{-1}$			

[2]

- (iii) Hence, state briefly why higher temperature is not used industrially for the formation of methanol from carbon monoxide and hydrogen.

The forward reaction is exothermic. Higher temperature will result in position of equilibrium to shift to the left, resulting in lower yield of product, hence it is not preferred.

[2]

- (iv) Use your answers in (b)(i) and (ii) to calculate the standard entropy change for the reaction at 298 K.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta G^\circ - \Delta H^\circ}{-T}$$

$$= \frac{-7710 - (-106 \times 10^3)}{-298} = -330 \text{ J K}^{-1} \text{ mol}^{-1}$$

[1]

- (v) Explain the significance of the sign of the calculated entropy change and comment if this is expected.

Calculated entropy change is negative as expected which means the entropy has decreased, therefore the system becomes less disordered as there is a decrease in number of moles of gas after the reaction.

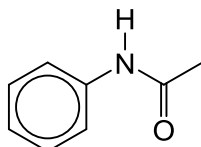
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.....[2]

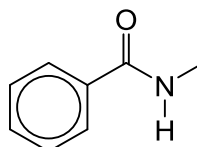
[Total:15]

- 4 (a) Acetanilide was the first aniline derivative found to possess analgesic and antipyretic properties. It was introduced into medical practice under the name of the drug, Antifebrin.

Suggest the reagents and conditions that can be used to distinguish acetanilide from compound X. State clearly the expected observations for each compound.



Acetanilide



Compound X

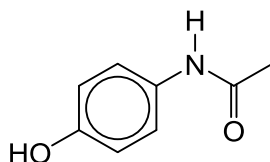
Reagents and conditions Step 1: NaOH(aq), heat

Step 2: Br<sub>2</sub>(aq), rtp

Observations . Orange aqueous bromine discharged and white ppt was formed for acetanilide. However, no such decolourisation and precipitation observed for compound X.

OR Ethylamine gas released by compound X after base hydrolysis which turns moist red litmus paper blue. However, gas released will not turn moist red litmus paper blue for acetanilide. [2]

- (b) It was later discovered that acetanilide was toxic and thus paracetamol, a derivative of acetanilide, was produced.



Paracetamol

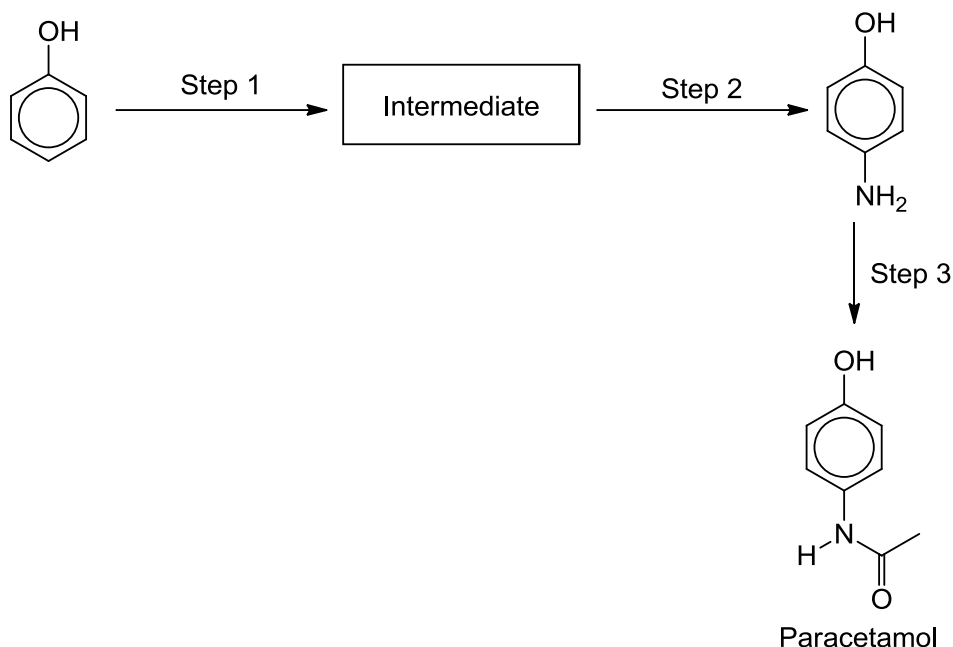
- (i) State the shape about N atom in paracetamol and hence identify the type of hybridisation involved.

Shape about N atom Trigonal planar

Hybridisation of N .sp<sup>2</sup>

[2]

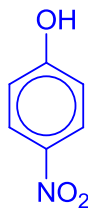
- (ii) A reaction scheme was proposed for the synthesis of paracetamol from phenol. Fill in the boxes provided with the reagents, conditions and intermediates for the synthesis.



Reagents and conditions:

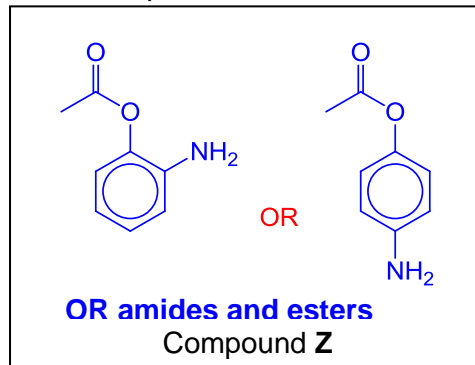
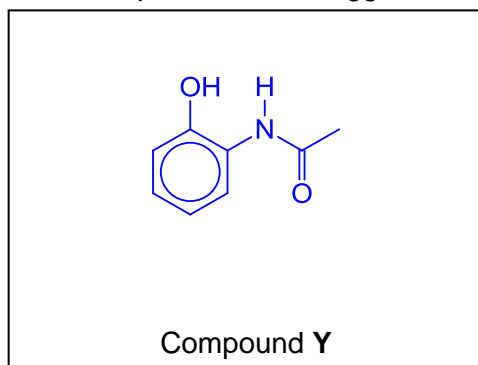
- Step 1 Dilute  $\text{HNO}_3$ , rt
- Step 2 1) Sn, conc  $\text{HCl}$ , heat 2)  $\text{NaOH(aq)}$ , rt
- Step 3  $\text{CH}_3\text{COC/}$

Structure of intermediate:



[4]

- (iii) In the synthesis of paracetamol from phenol, two possible side-products, compound **Y** and **Z**, are formed. Given that only compound **Y** is a position isomer of paracetamol, suggest the identities of compound **Y** and **Z**.



[2]

- (iv) Predict, with explanation, how the boiling point of paracetamol might compare to that of compound Y.

**Paracetamol has a higher boiling point than compound Y.**

**Paracetamol can form more extensive intermolecular hydrogen bonding as unlike compound Y, paracetamol does not have intramolecular hydrogen bonding.**

[2]

- (c) In a typical pain relief tablet, there are 500 mg of paracetamol.

- (i) An adult can consume up to a maximum dosage of 4000 mg of paracetamol within 24 hours. The average adult weight is 62 kg. Calculate the number of tablets a child who weighs 45 kg, can consume within 24 hours. (Maximum dosage is dependent on weight of an individual.)

**Max paracetamol a child can consume**

$$= \frac{4000}{62} \times 45 = 2903 \text{ mg}$$

**Max no. of tablets that can be consumed**

$$= \frac{2903}{500} = 5.81 \text{ tablets}$$

**≈ 5 tablets**

[2]

- (ii) It was recommended to consume the tablets at 6 hours intervals. Using your answer in (c)(i), calculate the recommended number of tablets the child should take at each interval without exceeding dosage.

**No. of times to consume tablets in 24 h**

$$= \frac{24}{6} = 4 \text{ times}$$

**Max no. of tablets that can be consumed each time**

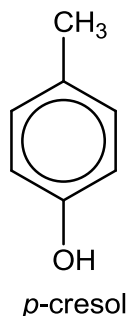
$$= \frac{5}{4} = 1.25 \text{ tablets}$$

**≈ 1 tablet**

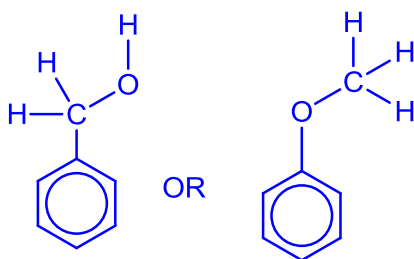
[1]

[Total: 15]

- 5 The compound *p*-cresol is used in the production of antioxidants. It is also used in the fragrance and dye industries.



- (a) Draw the displayed formula of a functional group isomer of *p*-cresol, and describe a laboratory test that will distinguish these two compounds. You should state the reagents used and the observations expected.

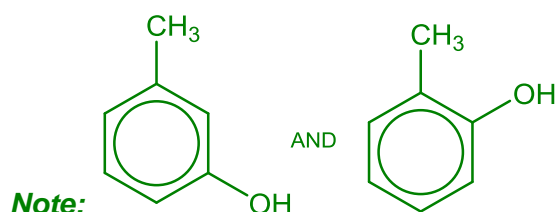


To separate test tube containing each sample, add neutral FeCl<sub>3</sub>. Violet colouration will be formed with *p*-cresol whereas no violet colouration for its isomer. OR

To separate test tube containing each sample, add aqueous Br<sub>2</sub>. Orange bromine solution decolourise and a white precipitate is formed with *p*-cresol. whereas no decolourisation of orange bromine solution with its isomer. [3]

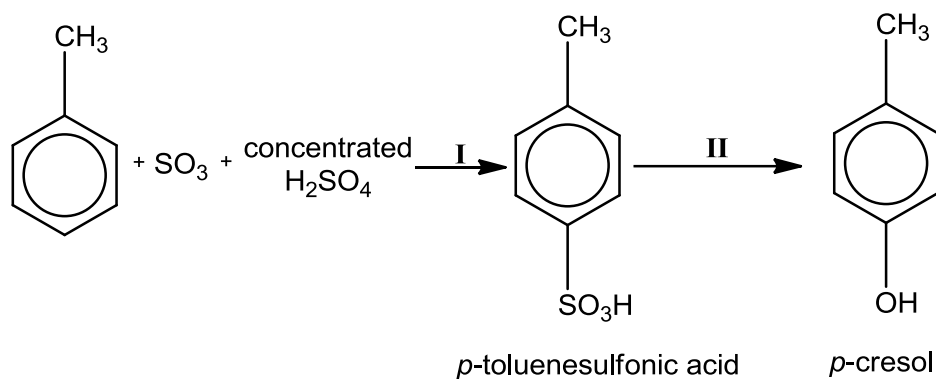
**NOT ACCEPTED: PCl<sub>5</sub>**

**Note: Oxidation using KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> is not accepted for *p*-cresol and phenylmethanol since both can undergo side-chain oxidation.**



**are not accepted because these are positional isomers of *p*-cresol. Positional isomers have the same carbon chain, but different positions of functional groups. Functional group isomers have different functional groups.**

- (b) *p*-Cresol can be prepared industrially by a 2-step process as shown below.

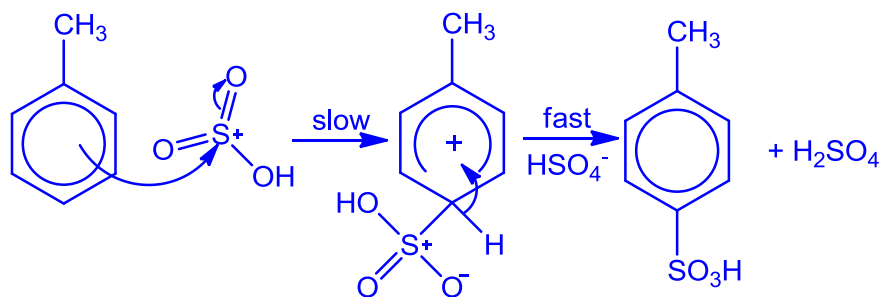


Reaction I involves sulfonation of methyl benzene to give *p*-toluenesulfonic acid. The proposed mechanism of reaction I involves electrophilic substitution.

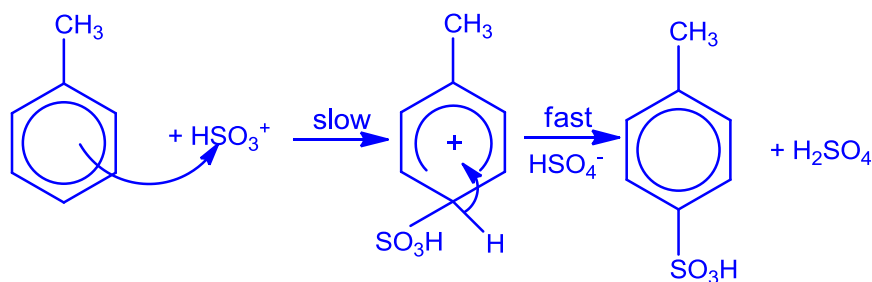
- (i) The first step of the proposed mechanism of reaction I involves acid-base reaction in the generation of an electrophile,  $\text{HSO}_3^+$ . Write an equation to show how the electrophile  $\text{HSO}_3^+$  is formed.



- (ii) Complete the proposed mechanism to produce *p*-toluenesulfonic acid as shown above. In the mechanism, show clearly the curly arrows to indicate the movement of electrons and all charges.



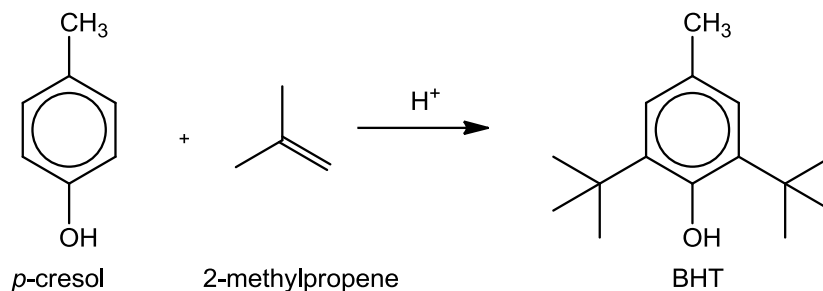
OR



[3]



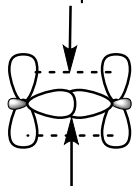
- (c) *p*-Cresol is used in the production of antioxidants such as butylated hydroxytoluene, BHT, which is mainly used as an antioxidant in the food industry. The reaction involves a dialkylation of *p*-cresol with 2-methylpropene in the presence of an acid catalyst given below.



- (i) Draw a labelled diagram to show how the orbitals overlap to form the C=C bond in 2-methylpropene and state the type of hybridisation involved.

sp<sup>2</sup> hybridisation

side-on overlap between unhybridised p orbital (to form pi bond)



head-on overlap between sp<sup>2</sup> hybrid orbitals (to form sigma bond)

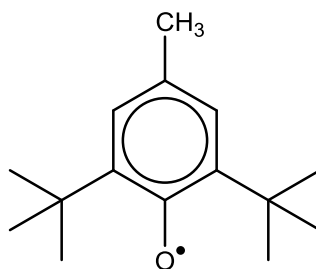
[2]

- (ii) Explain why 2-methylpropene cannot exhibit geometric isomerism.

One carbon atom of the C=C double bond has the same methyl group ...  
attached to it.

[1]

- (iii) In order for BHT to act as an antioxidant, it forms a very stable radical on the oxygen atom as shown below. Suggest an explanation why this stable BHT radical is unable to react further with other molecules.



BHT radical

The 2 large/bulky alkyl groups pose steric hindrance (repel incoming molecules) that prevent the radical to react with other molecules. OR The radical is stable due to the delocalisation of unpaired electron from oxygen atom into the benzene ring. OR Presence of electron-donating alkyl groups will stabilize the radical. [1]

- (iv) Compound **R**,  $C_{14}H_{20}O_2$ , is a metabolite derived from the biotransformation of BHT. It is structurally related to BHT,  $C_{15}H_{24}O$ , and is also a cyclic compound.

State the type of reaction and deduction for the following observations.

- I 1 mole of compound **R** will react with 2 moles of 2, 4-DNPH.

Type of reaction: Condensation

Deduction: Compound R is a (aldehyde/ketone) carbonyl compound [1]

- II Compound **R** will not react with Tollens' reagent.

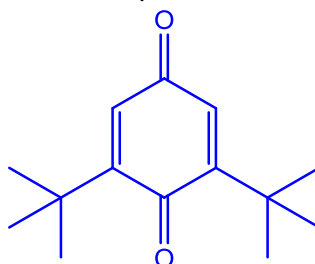
Deduction: Compound R has no aldehyde present. (Compound R is a ketone and not an aldehyde) [1]

- III 1 mole of compound **R** will decolourise 2 moles of aqueous  $Br_2$  but no  $HBr$  is formed.

Type of reaction: Electrophilic addition

Deduction: Compound R has 2 alkene functional groups. [1]

- IV Deduce the structure of compound **R**.



[1]

[Total: 15]