Mechanisms

Question Paper 2

Level	Pre U
Subject	Chemistry
Exam Board	Cambridge International Examinations
Topic	Mechanisms- Organic Chemistry
Booklet	Question Paper 2

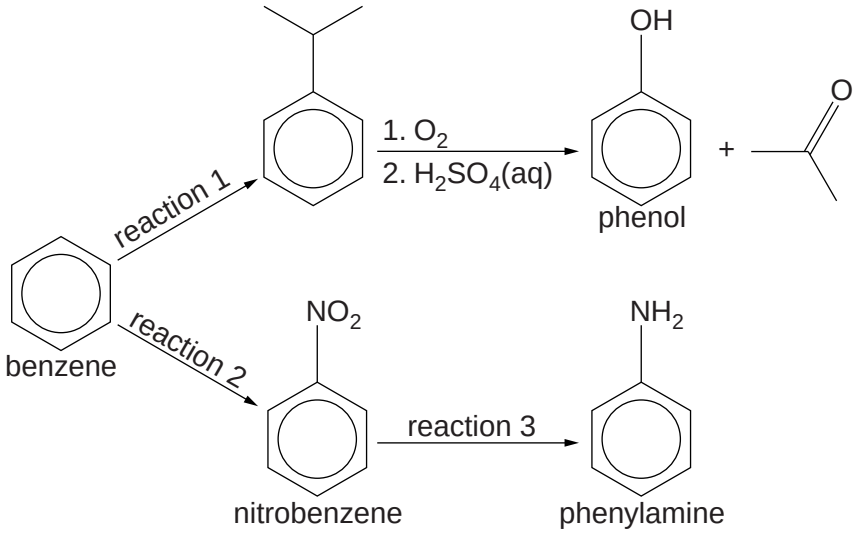
Time Allowed: **73 minutes**

Score: **/61**

Percentage: **/100**

Grade Boundaries:

1. Some reactions starting from benzene, C_6H_6, are shown.



(a) (i) Reactions 1 and 2 both proceed by electrophilic substitution.

Give the names of the reagent(s) needed, catalyst used and the identity of the electrophile in each case.

Reaction 1

reagent(s) .....

catalyst .....

electrophile .....

Reaction 2

reagent(s) .....

catalyst .....

electrophile .....[6]

(ii) For reaction 3, state the type of reaction undergone by nitrobenzene and the reagents needed.

reaction type .....

reagents .....[2]

(b) Phenol reacts readily with bromine water at room temperature, whereas nitrobenzene does not react with bromine water under these conditions.

(i) State what would be observed on addition of bromine water to phenol until in excess.

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.....[2]

(ii) Give the equation for the reaction between excess bromine and phenol.

.....[2]

(iii) Explain why phenol is brominated under these conditions whereas nitrobenzene is not.

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.....[4]

(c) The pK_a for phenol is about 10 while the value for ethanol is about 16.

Explain the relative magnitudes of these values.

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.....[2]

(d) **(i)** Write an equation for the reaction of phenylamine with hydrochloric acid.

.....[1]

(ii) State and explain the relative basicities of ammonia, ethylamine and phenylamine.

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.....[3]

[Total: 22]

2. Halogenoalkanes react with sodium hydroxide in two different ways depending on the solvent, the temperature and the structure of the halogenoalkane.

(a) Under appropriate conditions (S)-(+)-2-bromobutane was reacted with sodium hydroxide to produce a mixture of three isomeric alkenes.

(i) State the type of reaction taking place.

.....[1]

(ii) State the conditions necessary to bring about this type of reaction.

.....

.....[2]

(iii) Give the displayed formulae and names of the three alkenes formed.

[3]

(b) If (S)-(+)-2-bromobutane is hydrolysed with sodium hydroxide to form an alcohol then the reaction will proceed by a mixture of the S_N1 and S_N2 mechanisms.

(i) State the conditions necessary for the hydrolysis of (S)-(+)-2-bromobutane by sodium hydroxide.

.....

.....[1]

(ii) Complete Fig. 3.1 to show the S_N1 mechanism of hydrolysis of (S)-(+)-2-bromobutane with sodium hydroxide. Include all necessary curly arrows, lone pairs and full or partial charges.

[4]

Fig. 3.1

(iii) Explain fully why one of the two mechanisms, S_N1 or S_N2, gives rise to an optically active product while the other mechanism gives an optically inactive product.

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.....[5]

(iv) Give the full name of the product formed by the S_N2 mechanism.

.....[1]

(c) A structural isomer of (S)-(+)-2-bromobutane undergoes hydrolysis almost exclusively by the S_N1 mechanism.

Identify this isomer and explain why the S_N1 mechanism is preferred over the S_N2 mechanism.

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.....[3]

[Total: 20]

3. **(a)** The reaction shown represents the hydrogenation of a vegetable oil.

$$RCH{=}CHR'(l) + H_2(g) \rightarrow RCH_2CH_2R'(l)$$

This reaction can be catalysed by several different transition metals and gives an example of heterogeneous catalysis.

State the three stages involved in a typical reaction involving a heterogeneous catalyst.

1. .....

2. .....

3. ..... [1]

(b) An example of homogeneous catalysis is the use of iron(II) ions or iron(III) ions to catalyse the reaction between iodide ions and peroxodisulfate ions, $S_2O_8^{2-}$. This reaction is given in equation 3.1.

equation 3.1 $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$

The relevant half-equations are given in Table 3.1.

Table 3.1

half-equation	$E^{\ominus}$ /V
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	+2.01
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54

(i) What is meant by the term *homogeneous catalysis*?

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..... [1]

(ii) Use the data in Table 3.1 to calculate the standard cell potential, $E^{\ominus}_{cell}$, of the reaction shown in equation 3.1.

..... V [1]

(iii) Use your answer from **(b)(ii)** to calculate the standard Gibbs energy change, $\Delta_r G^{\ominus}$, of the reaction shown in equation 3.1. Give the sign and units in your answer.

..... [2]

(iv) Explain how your answer to **(b)(iii)** confirms that the reaction shown in equation 3.1 represents the feasible direction of reaction.

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..... [1]

(v) State and explain why, despite being feasible, the reaction shown in equation 3.1 is not seen to occur in the absence of a catalyst.

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..... [2]

(vi) By constructing suitable equations from the data in Table 3.1, explain why the reaction between iodide and peroxodisulfate can be catalysed by either iron(II) or iron(III) ions.

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..... [3]

(c) Fig. 3.1 represents part of the structure of chymotrypsin, an enzyme produced by the pancreas that is responsible for catalysing the hydrolysis of certain proteins in the small intestine during the digestive process.

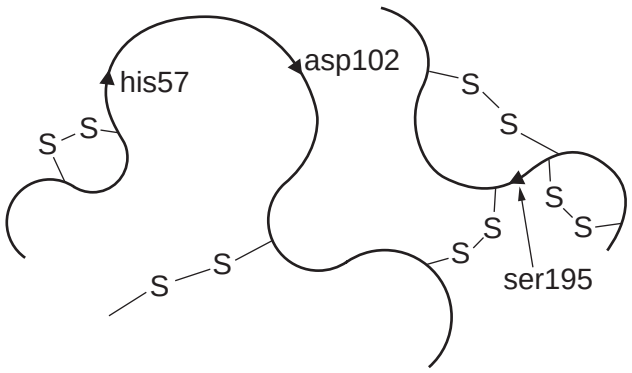

Fig. 3.1

The three main amino acids involved in the catalytic activity of the enzyme are labelled in Fig. 3.1 as his57, asp102 and ser195.

(i) What is the name of the region of the enzyme molecule that contains the three labelled amino acids and interacts with the protein being hydrolysed?

.....[1]

The first stage of the mechanism of action of chymotrypsin is illustrated in Fig. 3.2.

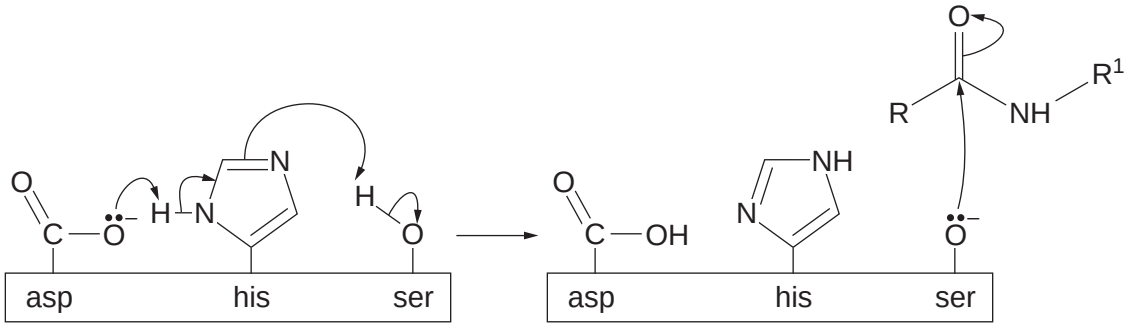

Fig. 3.2

(ii) Explain what is represented by a curly arrow as used in the mechanism shown in Fig. 3.2.

.....[1]

(iii) With reference to Fig. 3.2, explain why the action of this enzyme would be inhibited if the pH was too low.

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.....[2]

(iv) Chymotrypsin is denatured by sodium hydroxide, with the mechanism dependent on the pH.

- At pH12 the reaction is first order with respect to both the chymotrypsin and the hydroxide.
- In the presence of excess alkali the denaturation of the enzyme was monitored.
- The plot of the time course of the reaction is shown in Fig. 3.3.

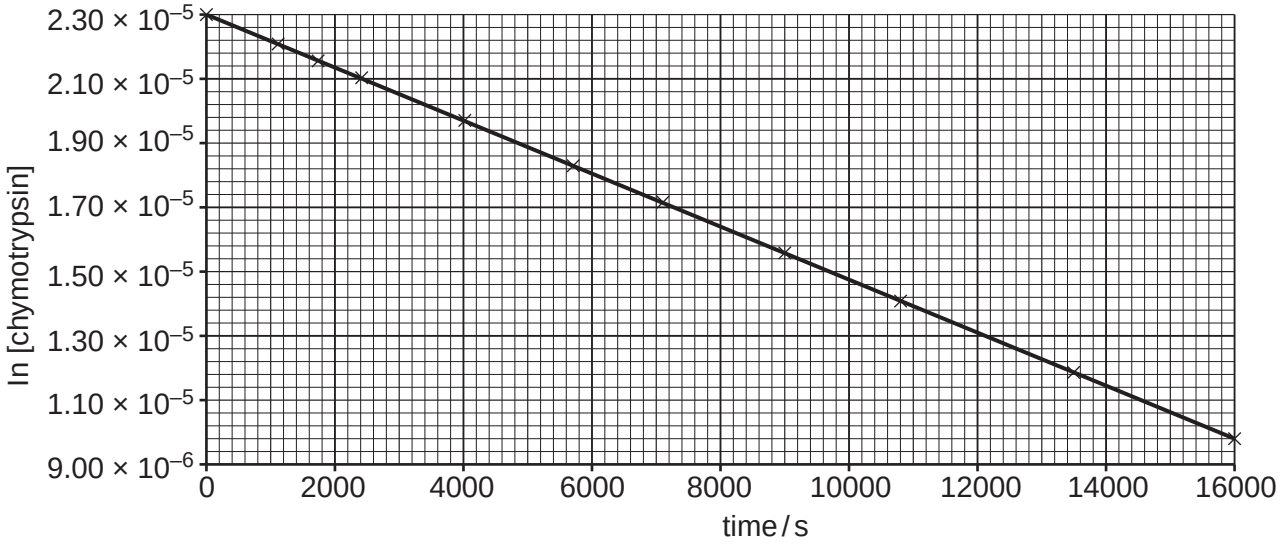

Fig. 3.3

The first order rate equation, equation 8 in the Data Booklet, can be rewritten as in equation 3.2.

equation 3.2 $\ln C_t = -kt + \ln C_0$

Given that equation 3.2 is in the form $y = mx + c$, explain how the graph in Fig. 3.3 confirms that the denaturation is first order with respect to chymotrypsin and how the conditions chosen give rise to first order kinetics overall.

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..... [2]

(v) Use the graph in Fig. 3.3 to calculate the value of the first order rate constant for this denaturation.

k = ... [2]

[Total: 19]