Mechanisms

Question Paper 1

Level	Pre U
Subject	Chemistry
Exam Board	Cambridge International Examinations
Topic	Mechanisms- Organic Chemistry
Booklet	Question Paper 1

Time Allowed: **52 minutes**

Score: **/43**

Percentage: **/100**

Grade Boundaries:

1. 2-bromobutane reacts with potassium hydroxide by either elimination or nucleophilic substitution depending on a combination of factors.

(a) State the conditions needed to bring about each of these reactions.

(i) elimination

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(ii) nucleophilic substitution

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.....[3]

(b) 2-bromobutane is a *chiral* molecule and, when it is prepared by the reaction between but-1-ene and hydrogen bromide, a *racemate* is formed. The enantiomers in the *racemate* can be converted to *diastereoisomers* by covalent derivatisation with suitable *chiral* reagents. Pure samples of each of the enantiomers can then be obtained by simple separation techniques as the *diastereoisomers* have different physical and chemical properties.

Give definitions of each of the words in italics.

(i) *chiral* .....

.....

.....[1]

(ii) *racemate* .....

.....

.....[1]

(iii) *diastereoisomers* .....

.....

.....[1]

(iv) Draw suitable diagrams of the two different enantiomers of 2-bromobutane.

[2]

(c) When R-(–)-2-bromobutane undergoes nucleophilic substitution with potassium hydroxide under appropriate conditions the reaction proceeds predominantly by the S_N2 mechanism. When the progress of the reaction is followed in a polarimeter the optical activity is seen to change gradually from –23.1° via zero to +13.5°.

(i) Draw a curly-arrow mechanism for the reaction that is taking place. Show the 3-D structures of the reactant and product clearly.

[4]

(ii) Give the systematic name of the organic product.

.....[2]

(d) The kinetics of the reaction of a different bromoalkane (RBr) with aqueous alkali were investigated at 323 K. The results are shown in Table 2.1.

Table 2.1

experiment	[RBr] / mol dm^{-3}	[OH$^-$] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.05	0.10	4.0×10^{-4}
2	0.15	0.10	1.2×10^{-3}
3	0.10	0.20	1.6×10^{-3}

(i) Deduce the order of reaction with respect to RBr and with respect to the hydroxide ion, OH$^-$.

Give reasons for each of your answers.

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.....[4]

(ii) Write the rate equation for the reaction.

.....[1]

(iii) Calculate the value of the rate constant, *k*, at 323 K and give its units.

.....[3]

(iv) Draw the skeletal formula of RBr, which is an isomer of 2-bromobutane.

[1]

[Total: 23]

2. **(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, $S_2O_8^{2-}$, as shown.

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

The relevant half-equations and standard electrode potentials are given in the table.

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 standard electrode potentials given to calculate the standard cell potential, $E^{\ominus}_{cell}$, for the reaction between iodide ions and peroxodisulfate ions.

..... V [1]

(iii) Use your answer from **(b)(ii)** to calculate the standard Gibbs energy change, $\Delta_f G^{\ominus}$, of the reaction between iodide ions and peroxodisulfate ions. Give the sign and units in your answer.

.....[2]

(iv) Explain how your answer to **(b)(iii)** confirms that the reaction between iodide ions and peroxodisulfate ions shown in **(b)** represents the feasible direction of reaction.

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..... [1]

(v) State and explain why, despite being feasible, the reaction between iodide ions and peroxodisulfate ions is not seen to occur in the absence of a catalyst.

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..... [2]

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

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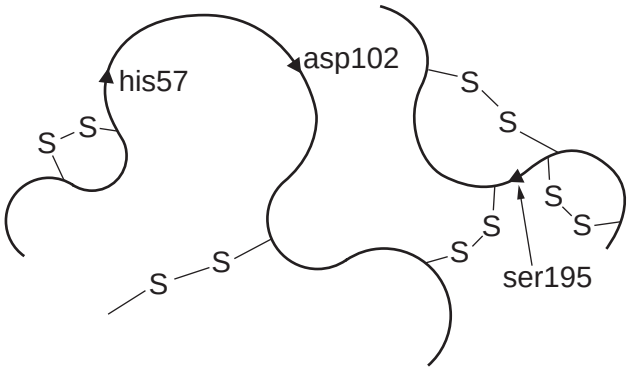
..... [3]

(c) 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, is shown.

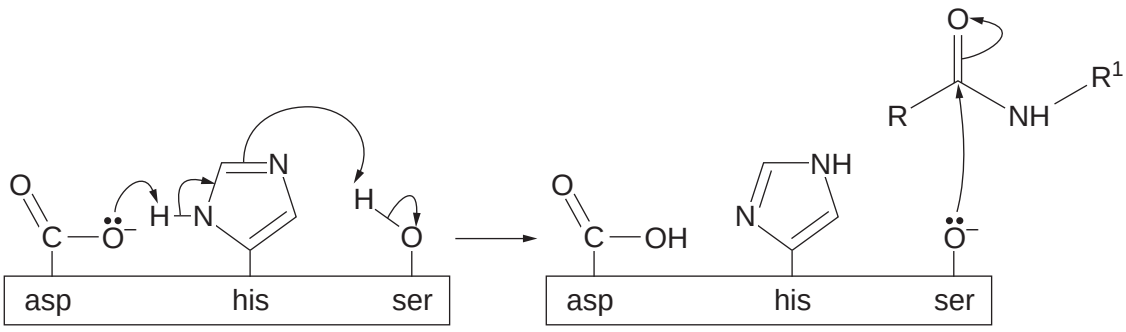


The three main amino acids involved in the catalytic activity of the enzyme are labelled as his57, asp102 and ser195.

(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.



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

.....[1]

(iii) Name the type of acid-base behaviour shown by the O^- in serine in its interaction with the protein chain.

..... [1]

(iv) With reference to the illustration of the mechanism, explain why the action of chymotrypsin would be inhibited if the pH was too low.

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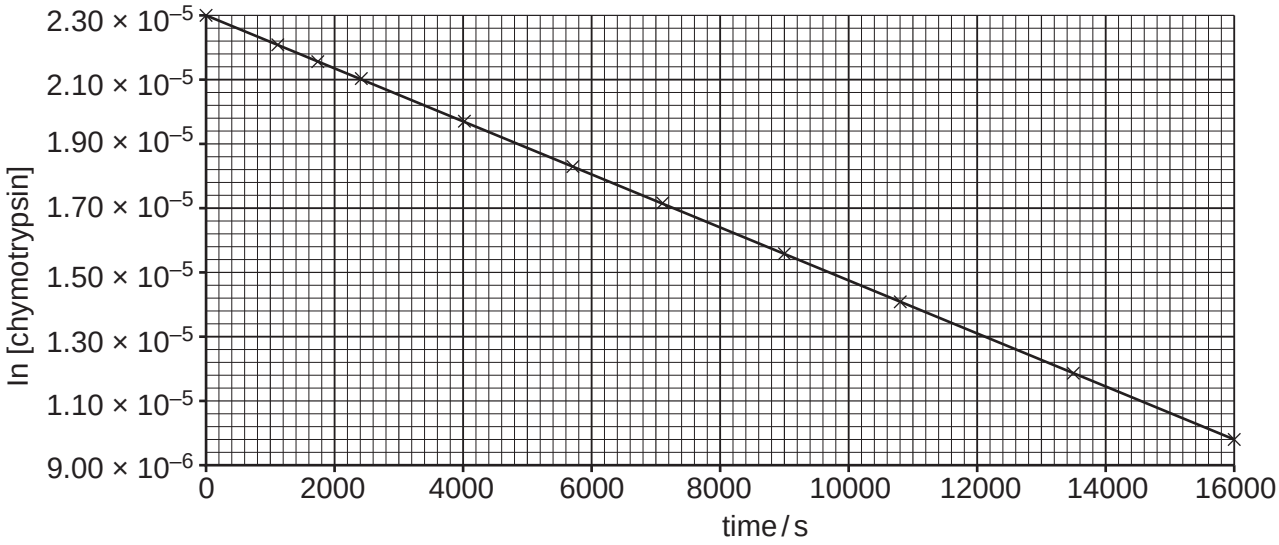
.....[2]

(v) 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.



The first order rate equation given in the *Data Booklet* can be rewritten.

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

Given that this equation is in the form $y = mx + c$, explain how the plot of the time course of the reaction 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]

(vi) Use the plot of the time course of the reaction to calculate the value of the first order rate constant for this denaturation.

k = ...[2]

[Total: 20]