

Topic: Reaction Kinetics (Olympiad)**[AJC Prelim 2012/ P3/ Q5(a)]**

- 1 (a) The oxidation of acidified iodide ions by hydrogen peroxide is represented by



To determine the order of reaction, ***n***, with respect to iodide ions, the rate can be followed by adding a small but fixed volume of sodium thiosulfate solution to the constant volume system of reaction mixture together with 1 cm³ of starch solution and measuring the time taken for the blue black colour to appear. The results are given below.

Experiment	[I ⁻ (aq)] / mol dm ⁻³	Time (t) / s
1	0.0040	74.0
2	0.0060	49.4
3	0.0080	37.0
4	0.010	30.0
5	0.012	25.0

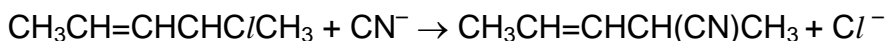
- (i) Explain the relationship between the time taken for the formation of the blue black colour and the initial rate of reaction.
- (ii) In the experiments, the concentrations of hydrogen peroxide and hydrogen ions used are very much higher than that of the iodide solution.
Explain why this is necessary.
- (iii) Evaluate 1/*t* for each experiment and hence plot a suitable graph to determine the order of reaction, ***n***, with respect to iodide ions.
State clearly your reasoning.
- (iv) Further studies show that the rate equation for the reaction is

$$\text{Rate} = k [\text{I}^-]^n [\text{H}_2\text{O}_2]$$

Based on this information and your answer to **(a)(iii)**, state **two** conclusions you can make about the mechanism of this reaction.

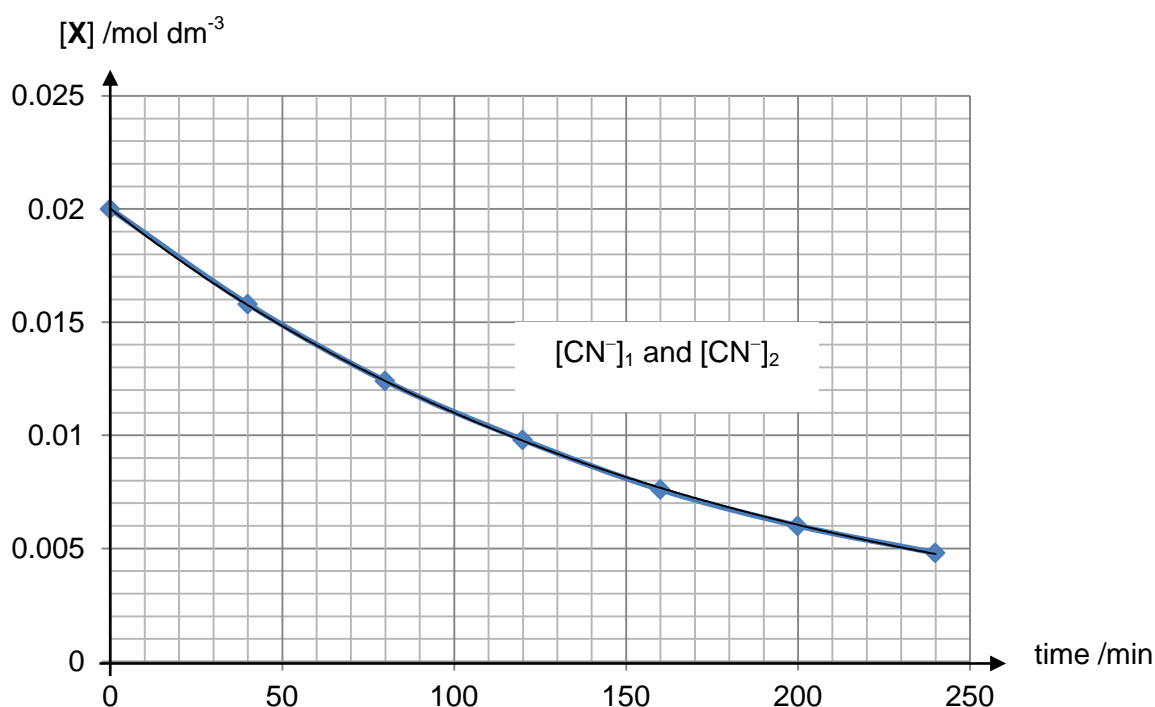
[VJC Prelim 2013/ P3/ Q2(a)]

2 (a) Compound **X**, $\text{CH}_3\text{CH}=\text{CHCHCl}/\text{CH}_3$, reacts with alcoholic KCN according to the following equation:



To investigate the above reaction, two separate experiments were performed using **different initial** concentrations of CN^- . In each experiment, the concentration of **X** in the reaction mixture was determined at different times as the reaction progresses. The same graph was obtained in both experiments, as shown below:

The following results were obtained:



- (i) Explain why the reaction requires an alcoholic instead of an aqueous medium to take place.
- (ii) Referring to the graphs above, deduce the order of reaction with respect to each of the reactants, CN^- and **X**.
- (iii) State, with a reason, whether the reaction proceeds by the $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanism.
- (iv) Hence, sketch a well labelled reaction pathway diagram for the reaction, given that the reaction is exothermic.
- (v) Suggest why the reaction of **X** is more likely than that of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCl}/\text{CH}_3$ to exhibit the mechanism stated in (ii).

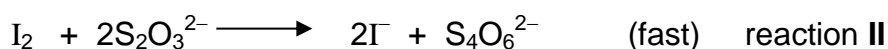
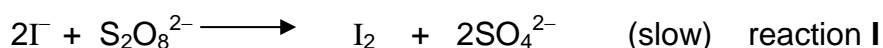
[NYJC Prelim 2013/ P2 / Q2(a)]

- 3** One of the most important features of the transition elements is that they exhibit variable oxidation states. This question illustrates the various oxidation states shown by iron in its compounds.

The reaction between iodide ions, I^- , and peroxidisulfate ions, $\text{S}_2\text{O}_8^{2-}$, is slow.

The reaction can be catalysed by adding a small amount of Fe^{2+} ions.

The initial rate of the slow reaction between iodide ions and peroxidisulfate ions can be studied by using thiosulfate ions. The equations for the reactions are as follows.



In the presence of a constant amount of thiosulfate ions, the iodine being slowly produced by reaction I will immediately react in reaction II until all the thiosulfate ions has been used up. At that point, free iodine will be present in the solution, which will cause a sudden appearance of a deep blue colour if starch is present.

A series of experiments was carried out using different volumes of the five reagents. The following results were obtained.

Expt	Volume of $\text{S}_2\text{O}_8^{2-}/\text{cm}^3$	Volume of I^-/cm^3	Volume of $\text{S}_2\text{O}_3^{2-}/\text{cm}^3$	Volume of distilled water $/\text{cm}^3$	Volume of starch $/\text{cm}^3$	Time for the appearance of deep blue colour/s
1	20	20	10	5	5	30
2	20	15	10	10	5	40
3	5	25	10	15	5	t_3
4	10	15	10	20	5	80

- (i)** If the orders of reaction with respect to peroxidisulfate ions and iodide ions are both one respectively, deduce an expression relating the volume of these two reactants and time taken for the appearance of deep blue colour.

Explain your reasoning.

- (ii)** Hence, predict the time, t_3 , required for the appearance of deep blue colour in experiment 3.

[3]

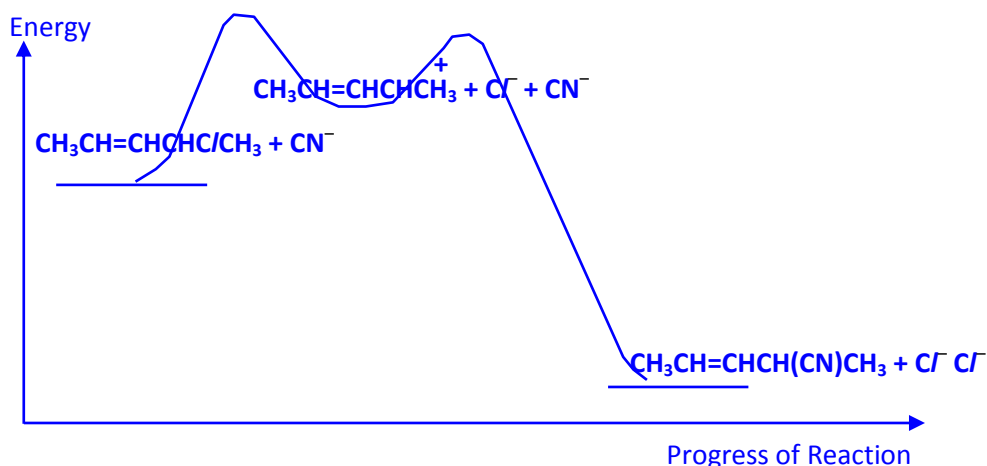
Topic: Reaction Kinetics (Suggested Answers)

[AJC Prelim 2012/ P3/ Q5(a)]

- 1 (i) Since a fixed volume of thiosulfate is used in each experiment, rate can be measured by the time taken for fixed amount of iodine liberated, i.e. $\text{rate} \propto 1/t$.
- (ii) So that $[\text{H}_2\text{O}_2]$ and $[\text{H}^+]$ are kept effectively constant and will not affect the rate of reaction / rate is only affected by the concentration of $[\text{I}^-]$.
- (iii) evaluate $(1/t)$
labelled axes: y-axis – $(1/t)$; x-axis – $[\text{I}^-]$
best-fit straight line drawn through the origin
correctly plotted points
- $\text{Rate} \propto [\text{I}^-]^n [\text{H}_2\text{O}_2]^y [\text{H}^+]^z$
- Since $\text{rate} \propto 1/t$ and $[\text{H}_2\text{O}_2]$ and $[\text{H}^+]$ are effectively constant, $1/t \propto [\text{I}^-]^n$.
- Since a straight line which passes through the origin is obtained when $(1/t)$ is plotted against $[\text{I}^-]$, $n = 1$.
- (iv) 1. It is a multi-step mechanism.
2. H^+ is not involved in the rate-determining step.
3. 1 (mol) of I^- and 1 (mol) of H_2O_2 are involved in the rate-determining step.

[VJC Prelim 2013/ P3/ Q2(a)]

- 2 (a) (i) Halogenoalkane X is not soluble in water as it cannot form hydrogen bond with water.
- (ii) For $[\text{X}]$ -time graph, it shows two constant half-lives of 115 min. (Must draw construction lines clearly).
Hence, reaction is first order w.r.t. X.
Gradient of the tangent at time=0 remains the same for two different initial $[\text{CN}^-]$, the reaction rate is independent of $[\text{CN}^-]$. Hence, reaction is zero order w.r.t. CN^- .
- (iii) Since the reaction is 1st order w.r.t. X and zero order w.r.t. CN^- , the rate-determining / slow step involves 1 molecule of X and no CN^- .
Mechanism is therefore $\text{S}_{\text{N}}1$.
- (iv) Reaction pathway diagram:



- (v) The carbocation formed with X is $\text{CH}_3\text{C}^+\text{H}-\text{CHCHCH}_3$. As the p-orbital of the positively charged carbon overlaps with the p-orbitals of the alkene carbons, the positive charge is further dispersed. Hence, the carbocation is stabilized and hence its formation is more favoured.

[NYJC Prelim 2013/ P2/ Q2(a)]

3 (i) $\text{Rate} = k [\text{S}_2\text{O}_8^{2-}][\text{I}^-]$

* Since total volume of solution is constant,
concentration of a reactant \propto volume of reactant

* $\text{rate} \propto 1/\text{time}$

$$1/\text{time} = k (\text{volume of } \text{S}_2\text{O}_8^{2-}) (\text{volume of } \text{I}^-)$$

$$(\text{volume of } \text{S}_2\text{O}_8^{2-}) (\text{volume of } \text{I}^-) \times \text{time} = \text{constant}$$

- (ii) time for expt 3, $t_3 = 96 \text{ s}$