

INFLUENCE OF IONIC STRENGTH ON THE SPECIFIC RATE CONSTANT, ENERGY OF ACTIVATION, AND CHANGE OF ENTHALPY OF ACTIVATION OF PERSULPHATE – IODIDE REACTION

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The influence of ionic strength on the specific rate constant of the reaction between per-sulphate and iodide ions was studied. It was observed that the reaction proceeded more rapidly as the ionic strength was increased, although the concentration of the reacting ions remained the same. The change in ionic strength was brought about by the addition of KCl, an inert electrolyte. This proved the Debye – Huckel – Bronsted equation, and a straight-line relation was recorded to exist if square root of ionic strength, i.e. $\sqrt{\mu}$ is plotted against logarithm of specific rate constant ($\log k$).

The effect of ionic strength on the energy of activation was also studied. It was observed that an increase in ionic strength of the reaction mixture decreased the apparent activation energy (E). A straight-line relation was found to exist if $\sqrt{\mu}$ is plotted against E . The apparent change of enthalpy of activation (ΔH^\ddagger) were calculated from the apparent activation energy values corresponding to the values of ionic strengths. A straight-line was again found to exist if $\sqrt{\mu}$ is plotted against ΔH^\ddagger .

INTRODUCTION

The following equation [1] shows the influence of ionic strength on the specific rate constant of ionic reaction.

$$\log k = \log k_0 + \frac{e^3}{(\epsilon K T)^{3/2}} \frac{(8\pi N/1000)^{1/2}}{2.303} \cdot Z_A \cdot Z_B \cdot \sqrt{\mu},$$

i.e.

$$\log k = \log k_0 + 1.02 Z_A Z_B \cdot \sqrt{\mu} \quad (1)$$

where k is specific rate constant, k_0 is the specific rate constant at zero ionic strength, T is absolute temperature, ϵ is dielectric constant of the medium, e is charge of an electron, K is Boltzmann's constant, N is Avagadro number. Z_A and Z_B are the charges of ions A and B respectively, and μ is the ionic strength.

This equation (1) has been subjected to a considerable number of experimental tests including the reaction between persulphate and iodide by Bronsted, La Mer and others. [2]. Meretoja [3] summarized the work of similar nature by early workers.

The relationship between specific rate constant and energy of activation of the reaction is given by the Arrhenius equation [4], i.e. equation (2),

$$\log k = \log A - \frac{E}{2.303 \cdot RT} \quad (2)$$

where A is reaction factor, E is energy of activation, R is gas constant and T is absolute temperature.

The relationship between energy of activation and ionic strength is given by the following expression:

$$E = \frac{d \log k}{d(1/T)} = \frac{d \log k_0}{d(1/T)} - \frac{3 e^3 (8\pi N/1000)^{1/2}}{2 (\epsilon k)^{3/2}} \times \frac{Z_A Z_B}{2.303} \sqrt{\mu} \quad (3)$$

The plot of energy of activation (E) against square root of the ionic strength ($\sqrt{\mu}$) should be a straight-line, with a negative slope.

In the present work, we have studied the effect of ionic strength on the specific rate constant of persulphate – iodide reaction. An attempt has also been made to study the effect of ionic strength on the activation energy and the change of enthalpy of activation of the reaction.

EXPERIMENTAL

All the chemicals (potassium iodide, potassium persulphate, potassium chloride, sodium thiosulphate and starch) used were of E. Merck (A.R. grade) and without further purification. Freshly prepared distilled water was redistilled before preparing stock solutions [5].

For the determination of rate constant of the reaction, an isolation method [6] was adopted. Calculated volume of the stock solution of KI was added to a reaction mixture so that the concentration of KI in the solution was $2.0 \times 10^{-1} M$. Stock solution of KI were prepared freshly because iodide on standing gets oxidised to iodine. The concentration of potassium persulphate was regulated.

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Calculated volume of KCl stock solution (2.5M) was added to change the ionic strength. The reaction was performed at $20 \pm 0.1^\circ$ in a constant temperature bath (type T52, Haake, Karlsruhe/Germany). The reaction mixture (10 ml) was pipetted out at different time intervals, chilled and titrated against standard sodium thiosulphate solution using 1% starch as an indicator.

The specific rate constant was calculated for the reaction by using the first order rate equation.

For studying the effect of ionic strength on the activation energy, same reaction was performed at $25^\circ, 30^\circ, 35^\circ$, and $40^\circ (\pm 0.1)$ using the same concentration of the reactants but a different ionic strength.

RESULTS AND DISCUSSIONS

The values of the specific rate constant obtained by changing the ionic strength of the reaction mixture, are summarized in Table 1. The values of k_0 obtained by extrapolation of $\log k$ vs $\sqrt{\mu}$ plots at 20° is 3.80×10^{-4}

Table 1. Values of the concentration of the reactants, the ionic strengths, and the specific rate constant at $20 \pm 0.1^\circ$

Concn. of $K_2S_2O_8 \times 10^3 M$	Concn. of $KI \times 10^1 M$	Ionic strength (μ)	Specific rate constant (k) $\times 10^3 \text{ min}^{-1}$
6.5	2.0	0.24	1.04
6.5	2.0	0.35	1.30
6.5	2.0	0.46	1.71
6.5	2.0	0.56	2.03
6.5	2.0	0.66	2.47
6.5	2.0	0.76	2.75
6.5	2.0	0.88	3.33
6.5	2.0	1.02	3.98
5.0	2.0	0.27	1.17
5.0	2.0	0.37	1.44
5.0	2.0	0.47	1.82
5.0	2.0	0.57	2.12
5.0	2.0	0.67	2.52
5.0	2.0	0.77	3.02
5.0	2.0	0.89	3.39
5.0	2.0	1.03	4.17
4.0	2.0	0.27	1.30
4.0	2.0	0.38	1.60
4.0	2.0	0.48	1.99
4.0	2.0	0.57	2.18
4.0	2.0	0.64	2.48
4.0	2.0	0.81	3.16
4.0	2.0	0.91	3.55
4.0	2.0	1.03	4.27
3.0	2.0	0.28	1.38
3.0	2.0	0.38	1.64
3.0	2.0	0.48	2.03
3.0	2.0	0.58	2.28
3.0	2.0	0.68	2.73
3.0	2.0	0.80	3.31
3.0	2.0	0.92	3.80
3.0	2.0	1.05	4.47

Table 2. The values of the specific rate constant for $K_2S_2O_8 = 5.0 \times 10^{-3} M$ and $KI = 2.0 \times 10^{-1} M$ at various temperatures and ionic strengths.

Ionic strength (μ)	Temperature (C)			
	25	30	35	40
Specific rate constant (k) $\times 10^3 \text{ min}^{-1}$				
<i>In the absence of added salt</i>				
0.215	1.08	1.51	1.97	2.71
<i>In the presence of added salt</i>				
0.27	1.30	1.80	2.40	3.31
0.37	1.64	2.19	2.85	3.85
0.47	2.11	2.75	3.47	4.47
0.57	2.51	3.23	3.93	5.01
0.70	2.88	3.55	4.36	5.31
0.85	3.94	4.67	5.49	6.46
1.05	5.43	6.16	6.92	7.94

Table 3. The values of ionic strengths, energy of activation and change of enthalpy of activation.

Ionic strength (μ)	Activation energy (E) (kJ)	Change of enthalpy of activation (ΔH^\ddagger) (kJ)
<i>In the absence of added salt</i>		
0.215	51.39	48.91
<i>In the presence of added salt</i>		
0.27	48.45	45.98
0.37	43.85	41.38
0.47	39.29	36.82
0.57	35.77	33.30
0.70	31.34	28.87
0.85	25.52	23.05
1.05	20.25	17.78

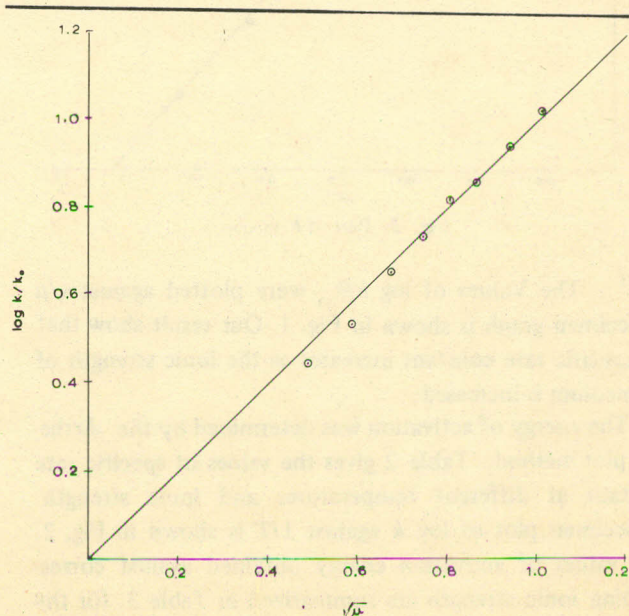
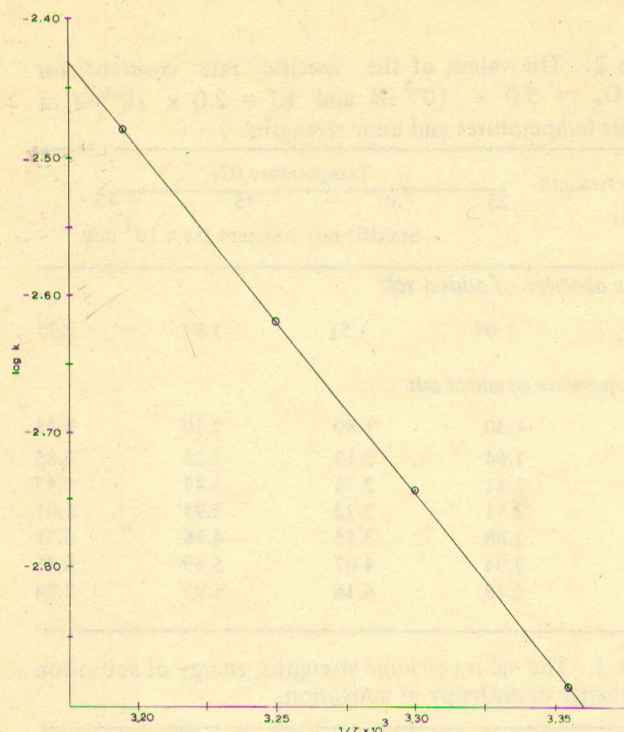
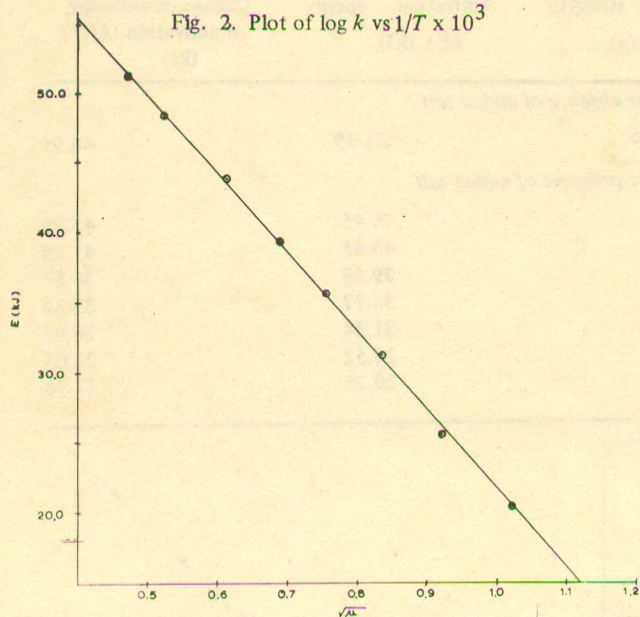
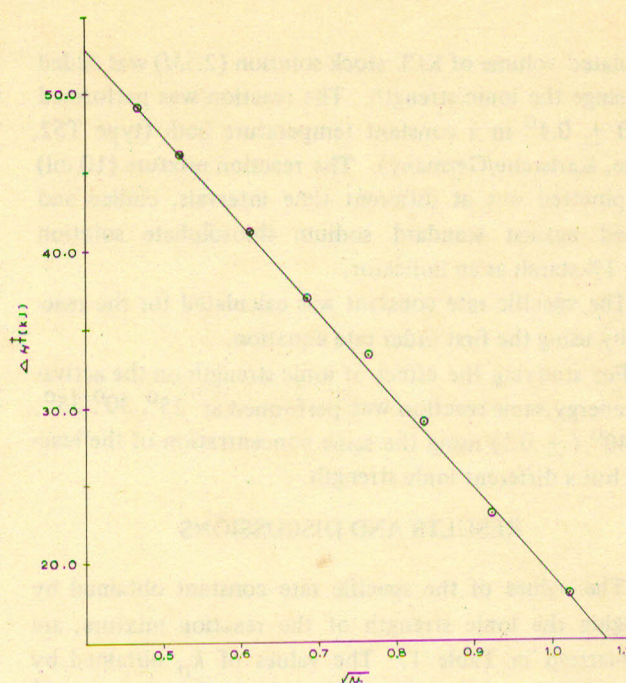


Fig. 1. Plot of $\log k/k_0$ vs $\sqrt{\mu}$

Fig. 2. Plot of $\log k$ vs $1/T \times 10^3$ Fig. 3. Plot of E vs $\sqrt{\mu}$

min^{-1} The Values of $\log k/k_0$ were plotted against $\sqrt{\mu}$. A specimen graph is shown in Fig. 1. Our result show that the specific rate constant increases as the ionic strength of the medium is increased.

The energy of activation was determined by the Arrhenius plot method. Table 2 gives the values of specific rate constant at different temperatures and ionic strength. A specimen plot of $\log k$ against $1/T$ is shown in Fig. 2. The values of activation energy obtained against corresponding ionic strength are summarized in Table 3, for the same concentration of the reactants, i.e. $5.0 \times 10^{-3}M$

Fig. 4. Plot of ΔH^\ddagger vs $\sqrt{\mu}$

potassium persulphate and $2.0 \times 10^{-1}M$ KI. Table 3 shows that energy of activation decreases with a rise in the ionic strength. The energy of activation for a particular reaction remains the same, but due to the difference of ionic strength, the configuration of the transition state changes and results in the decreases of apparent energy of activation in the present work. The plot of apparent energy of activation (E) against $\sqrt{\mu}$ shown in Fig. 3 is linear, and is in accordance with equation (3).

The values of apparent change of enthalpy of activation were obtained using the formula $\Delta H^\ddagger = E_{\text{exp}} - RT$, where T is taken as 298° absolute. The values of apparent energy of activation and apparent change of enthalpy of activation in the absence as well as in the presence of added salt are shown in Table 3. A graph is plotted between the values of apparent change of enthalpy of activation and square root of the ionic strength shown in Fig. 4. The plot is a straight-line, quite in agreement with the theoretical conclusions.

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