

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

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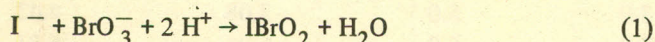
(Received April 21, 1979)

The reduction of a bromate ion by an iodide ion is a fourth order reaction. However, in the presence of large excess of sulphuric acid it behaves as *pseudo* second order. The effect of the ionic strength on the specific rate constant was studied. It was observed that as the ionic strength was increased, the reaction proceeded more rapidly, although the concentration of the reacting ion was the same. Potassium chloride, an inert electrolyte, was added for the variation of ionic strength. A straight-line relation was seen to exist if logarithm of the specific rate constant ($\log k$) is plotted against the square root of ionic strength ($\sqrt{\mu}$).

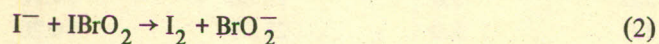
The effect of ionic strength of the reaction mixture on the energy of activation (E) of the reaction was also studied. It was seen that as the ionic strength was increased, the apparent energy of activation decreased. A plot of square root of the ionic strength against the apparent energy of activation resulted in a fairly good straight line. Using the data for apparent energy of activation corresponding to the values of ionic strength, the apparent change of enthalpy of activation (ΔH^\ddagger) was calculated. A straight-line relation was again found to exist when ΔH^\ddagger is plotted against $\sqrt{\mu}$.

INTRODUCTION

King and Lister [1] have postulated the slowest step of the reaction between bromate and iodide ions to be;



with a reactive intermediate $IBrO_2$ as proposed by Taube and Dodgen [2]. This reaction is followed by :



However, in the presence of large excess of sulphuric acid, it behaves as a *pseudo* second order reaction.

Theoretical treatment of the influence of ionic strength on the rates of reactions between ions were given by Bronsted [3], Christiansen [4] and Scatchard [5]. The relationship between logarithm of the specific rate constant ($\log k$) and square root of the ionic strength ($\sqrt{\mu}$) is given by the Laidler equation [6]:

$$\ln k = \ln k_0 + e^3 (8\pi N/1000)^{1/2} / (\epsilon KT)^{3/2} \cdot Z_A Z_B \cdot \sqrt{\mu} \quad (3)$$

$$\text{i.e. } \log k = \log k_0 + 1.02 Z_A Z_B \cdot \sqrt{\mu}$$

where k is the specific rate constant, k_0 is the specific rate constant at zero ionic strength, e is the electronic charge, N is Avagadro Number, ϵ is dielectric constant of the medium, K is Boltzmann's constant, T is absolute temperature. Z_A and Z_B are the charges of ions A and B respectively, and μ is the ionic strength. This equation has usually been used to measure the rates of ionic reactions in media of different ionic strength. According to this equation, a plot of $\log k$ against $\sqrt{\mu}$ will give a straight-line of slope $1.02 Z_A Z_B$. Davis's study [7] of the applicability of this equation to reactions between ions leads to the conclusion that the equation holds with high accuracy for a number of such reactions.

Arrhenius equation [8] gives the relationship between specific rate constant and energy of activation;

$$\log k = \log A - E/2.303 RT \quad (4)$$

where A is a reaction factor, E is energy of activation, R is gas constant.

Previously we have reported following expression which gives the relationship between energy of activation and ionic strength [9]:

$$E = \frac{d \log k}{d(1/T)} = \frac{d \log k_0}{d(1/T)} - \frac{3 e^3 (8\pi N/1000)^{1/2}}{2 (\epsilon K)^{3/2} T^{1/2} \times Z_A Z_B \cdot \sqrt{\mu}} \quad (5)$$

The plot of energy of activation against square root of the ionic strength should be a straight-line, with a negative slope.

Change of enthalpy of activation (ΔH^\ddagger) is obtained using the following expression:

$$\Delta H^\ddagger = E_{\text{exp}} - RT \quad (6)$$

where E_{exp} is energy of activation determined experimentally.

We have studied the effect of ionic strength on the specific rate constant, energy of activation and change of enthalpy of activation of iodide – persulphate and bromide – bromate reactions respectively [9, 10].

In this paper the reaction between iodide and bromate ions was studied in order to find out the dependence of specific rate constant, energy of activation and change of enthalpy of activation on the ionic strength of the medium.

EXPERIMENTAL

All the chemicals (KI, KBrO_3 , KCl and sulphuric acid) used were of Merck (A.R. grade) and without further purification. All solutions were prepared in triply distilled water [11].

Spectrophotometric method was employed for the (i) estimation of concentration of iodine evolved at different interval of time, (ii) determination of specific rate constant and energy of activation of the reaction between iodide and bromate ions. All the observations were recorded at 425 nm obtained from the plots of absorbance versus wavelength (λ). The molar absorption coefficient of iodine was taken as $492 \text{ cm}^2/\text{mole}$ in order to relate absorbance to concentration. The rate of the reaction was followed spectrophotometrically using a Pye Unicam SP 500 spectrophotometer with cell holder attached to a constant temperature bath. The temperature stability of the cell holder was within $\pm 0.5^\circ$.

Calculated volumes of the stock solutions of KI were freshly prepared because iodide on standing gets oxidised to iodine. The change in ionic strength was brought about by the addition of stock solution of calculated volumes of KCl. Calculated volumes of stock solution of (i) potassium bromate and sulphuric acid and (ii) potassium iodide were pipetted out separately in iodine flasks and kept in a water-bath for about $\frac{1}{2}$ hr. The concentration of sulphuric acid in each case was maintained to be $1.0 \times 10^{-1} M$. The solutions (i) and (ii) were mixed and time was recorded with a stop watch. The reaction was performed at 20° . 1-cm cuvette was then filled with this reaction mixture immediately after

thorough shaking. Then the absorbance of the reaction mixture was recorded. The specific rate constants of the reaction were calculated using second order rate equation.

In the case of measurements for the determination of activation energies, the same procedure was followed at $25, 30, 35$ and 40° , using the same concentration of the reactants but different ionic strengths.

RESULTS AND DISCUSSIONS

The measurements of the rates of reaction between iodide and bromate ions are summarized in Table 1. The initial concentrations of the reactants are given in columns

Table 1. Values of specific rate constants corresponding to the concentration of [KI], $[\text{KBrO}_3]$ and ionic strength at $20 \pm 0.5^\circ$.

Concn of $[\text{KBrO}_3] \times 10^3 M$	Concn of $[\text{KI}] \times 10^3 M$	Ionic strength $\mu \times 10^1$	Sp rate constant $(k) M^{-1} \text{ l}^+ \text{ Min}^{-1}$
2.0	4.0	3.06	4.36
2.0	4.0	6.06	6.02
2.0	4.0	9.06	7.95
2.0	4.0	12.06	9.95
2.0	4.0	15.06	11.80
2.0	4.0	18.06	13.87
2.0	4.0	21.06	15.76
3.0	5.0	3.08	4.43
3.0	5.0	6.08	6.31
3.0	5.0	9.08	8.06
3.0	5.0	12.08	10.07
3.0	5.0	15.08	11.95
3.0	5.0	18.08	14.10
3.0	5.0	21.08	16.20
5.0	7.0	3.12	4.50
5.0	7.0	6.12	6.45
5.0	7.0	9.12	8.30
5.0	7.0	12.12	10.24
5.0	7.0	15.12	12.13
5.0	7.0	18.12	14.33
5.0	7.0	21.12	16.39
6.0	8.0	3.14	4.58
6.0	8.0	6.14	6.65
6.0	8.0	9.14	8.47
6.0	8.0	12.14	10.56
6.0	8.0	15.14	12.39
6.0	8.0	18.14	14.47
6.0	8.0	21.14	16.61

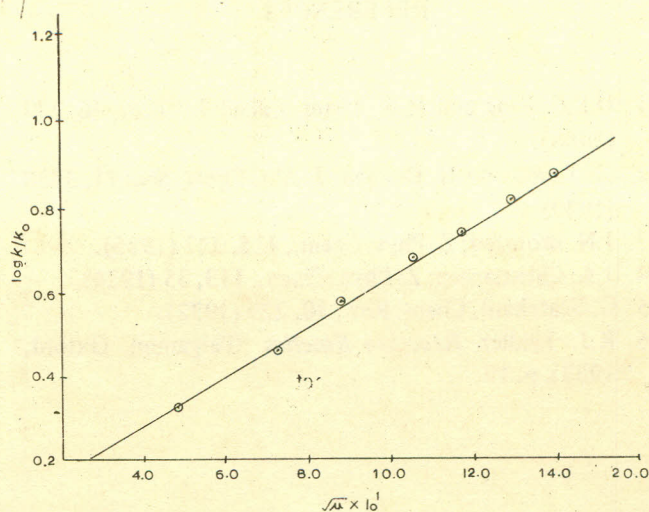
Table 2. Specific rate constants at various temperatures and ionic strengths.

[KBrO ₃] = 2.0 × 10 ⁻³ M, and KI = 4.0 × 10 ⁻³ M				
Ionic strength (μ) × 10 ¹	Temperature (°C)			
	25	30	35	40
specific rate constant (k) M ⁻¹ · l ⁺¹ · min ⁻¹				
In the absence of KCl				
3.06	4.68	5.26	5.93	6.47
In the presence of KCl				
6.06	6.58	7.35	7.81	8.51
9.06	8.38	9.34	9.74	10.49
12.06	10.41	11.37	11.83	12.61
15.06	12.54	13.30	14.00	14.75
18.06	14.39	15.47	16.17	16.98
21.06	16.34	17.58	18.28	19.05

Table 3. The evaluation of the values of apparent energy of activation and apparent change of enthalpy of activation.

Ionic strength (μ) × 10 ¹	Apparent energy of activation (E) (kJ)		Apparent change of enthalpy of activation (ΔH [‡]) (kJ)
	In the absence of KCl		
3.06	16.21		13.74
In the presence of KCl			
6.06	11.92		9.45
9.06	10.50		8.03
12.06	10.12		7.65
15.06	8.58		6.11
18.06	6.69		4.22
21.06	5.23		2.76

1 and 2. The ionic strength (μ) and the second order rate constant (k) are listed in the last two columns. At 20°, the value of the specific rate constant at zero ionic strength, i.e. k₀ obtained by extrapolation of log k against √μ plots is 2.09 M⁻¹ · l⁺¹ · min⁻¹. The values of log k/k₀ vs √μ were plotted. The average value of Z_A Z_B is 0.61. As suggested by La Mer and Greenspan [12], the low value of Z_A Z_B may be due to the fact that the limiting slope for the Debye - Huckel activity coefficient is not necessarily applicable in rate equation. A specimen graph shown in Figure 1 is a straight-line passing through the origin. The results of the rate measurements show that an increase in

Fig. 1. Plot of log k/k₀ vs √μ × 10¹.

ionic strength of the medium increased the specific rate constant which is in conformity with the - Bronsted equation.

The reaction between iodide and bromate ions was studied at [KI] = 4.0 × 10⁻³M and [KBrO₃] = 2.0 × 10⁻³M and at temperatures ranging from 25 to 40° for the evaluation of activation energies. The values of the specific rate constants corresponding to the ionic strength values are tabulated in Table 2. Arrhenius plots, i.e. log k vs 1/T plots obtained were linear having negative slopes. The values of energy of activation calculated from the slopes of those plots were summarized in Table 3. Our results show that the activation energy decreased with a rise in the ionic strength. The energy of activation for a particular reaction remains the same, but due to the variation in ionic strength, the configurations of the activated state change and results in the decrease of apparent activation energy, in this present study. The plot of apparent energy of activation versus square root of the ionic strength is linear with a negative slope and is in agreement with the theoretical equation. From this plot, the value of slope is 9.44 kJ, and the extrapolated value of E corresponding to zero ionic strength is 21 kJ.

Table 3 gives the values of apparent energy of activation and apparent change of enthalpy of activation in the absence as well as in the presence of inert electrolyte. The ΔH[‡] values were calculated using equation (6). Linear plot was obtained when the values of apparent change of enthalpy of activation (ΔH[‡]) were plotted against √μ. The plot is a fairly good straight line having negative slope, and is in accordance with the theory.

From our experimental data, the calculated value of change of entropy of activation (ΔS[‡]) was found to be independent of ionic strength and its value is nearly 107.0 joules per degree.

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