STUDY OF THE EFFECT OF IONIC STRENGTH ON THE SPECIFIC RATE CONSTANT, ACTIVATION ENERGY AND CHANGE OF ENTHALPY OF ACTIVATION OF BROMIDE– BROMATE REACTION

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The reaction between potassium bromide and potassium bromate is of fourth order. In the presence of large excese of sulphuric acid it, however, behaves as *pseudo* second order. This reaction was studied in order to find out the dependence of the specific rate constant on the ionic strength of the medium. The change in ionic strength was brought about by the addition of potassium chloride, an inert electrolyte. 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. A straight-line relation was found to exist if logarithm of specific rate constant (log k) is plotted against the square root of ionic strength, i.e. $\sqrt{\mu}$.

The influence of ionic strength on the activation energy was also studied. It was observed that the apparent energy of activation (E) decreased as the ionic strength of the reaction mixture was increased. A straight-line was found to exist if E is plotted against $\sqrt{\mu}$. The values of apparent change of enthalpy of activation ($\Delta H^{\neq}$) were calculated, from the apparent activation energy values corresponding to the values of ionic strength. A straight-line relation was again found to exist if $\Delta H^{\neq}$ is plotted against $\sqrt{\mu}$.

INTRODUCTION

While reactions of high order are not common, the reactions in acid solution of bromate ion by a bromide ion is of fourth order, as reported by Hinshelwood [1], Bray and Davis [2], and Young and Bray [3]. This is clearly expressed by the following ionic equation:

$$2H^+ + Br^- + BrO_3^- = HBrO + HBrO_2 \qquad (1)$$
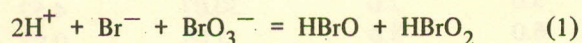
However, in the presence of large excess of sulphuric acid the number of hydrogen ions is so large, that they relatively undergo no change of concentration. Equation (1) could, therefore, be expressed as:

$$Br^- + BrO_3^- = HBrO + HBrO_2 \qquad (2)$$
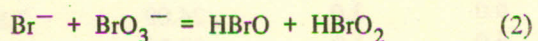
Thus in the presence of large excess of sulphuric acid, the reaction of bromate by a bromide ion is of *pseudo* second order.

The effect of ionic strength on the specific rate constant of ionic reaction is given by the following expression [4]:

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

$$\text{i.e. } \log k = \log k_0 + 1.02\, Z_A \cdot Z_B \cdot \sqrt{\mu} \qquad (3)$$

where k is specific rate constant, k_0 is the specific rate constant at zero ionic strength, e is the charge of an electron, ϵ is dielectric constant of the medium, K is Boltzmann's constant, T is absolute temperature and 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 (3) has been listed a number of times, particularly by Bronsted [5] and La Mer [6], and more recently by Davis [7]. This equation has usually been used to measure the rate of ionic reactions in media of varying ionic strength.

The relationship between specific rate constant and energy of activation of the reaction is given by the Arrhenius equation [8]:

$$\log k = \log A - \frac{E}{2.303\, RT} \qquad (4)$$

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

The relationship between activation energy and ionic strength given earlier by Ghaziuddin *et al.* [9] is expressed by the following expression:

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

$$\frac{Z_A Z_B \sqrt{\mu}}{2.303} \qquad (5)$$

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.

Ghaziuddin *et al.* [9] studied the effect of ionic strength on the specific rate constant, energy of activation and change of enthalpy of activation of iodide — persulphate reaction.

In the present work, the influence of ionic strength on the specific rate constant of bromide — bromate reaction was studied. An attempt has also been made to study the effect of ionic strength on the energy of activation, and change of enthalpy of activation of this reaction.

EXPERIMENTAL

All the chemicals (potassium bromide, potassium bromate, potassium chloride and sulphuric acid) used in this investigation were of E. Merck, A.R. grade and without further purification. Freshly prepared distilled water was redistilled before preparing stock solutions [10].

Spectrophotometric method was adopted for the estimation of concentration of bromine evolved at different intervals of time. The wavelength of 390 nm at which the maximum absorbance for bromine lies was selected from the plots of absorbance versus corresponding wavelength (λ) as already determined by Ghaziuddin *et al.* [11] in order to record observations in this experimental work.

Determination of the specific rate constant of the reaction between Br^- and BrO_3^- ions was followed spectrophotometrically using a Pye Unicam SP 500 model spectrophotometer with cell holder attached to a constant temperature water-bath. The temperature stability of the cell holder was within $\pm 0.5^o$, for the measurement of optical density of the reaction mixture. Calculated volume of the stock solution of potassium bromate and sulphuric acid were pipetted out in an iodine flask. The concentration of sulphuric acid in each case was maintained to be 1.0×10^{-1} M. Calculated volume of the stock solution of potassium chloride was then added to change the ionic strength. Calculated volume of the stock solution of potassium bromide was then added to the above mentioned reaction mixture and time was recorded with a stop watch. This reaction was performed at 25°. Spectrophotometer cell was then filled with this reaction mixture immediately after thorough shaking. Then the absorbance of the reaction mixture was recorded. The specific rate constant of the reaction was calculated using integrated form of the equation for the second order reaction.

For studying the effect of ionic strength on the energy of activation, the reaction was performed at various temperatures, i.e. 30, 35, 40 and 45°, using the same concentration of the reactants but different ionic strengths.

RESULTS AND DISCUSSIONS

The values of the specific rate constants botained by varying the ionic strength of the reaction mixture, are tabulated in Table 1. The values of the logarithm of the specific rate constant (log k) were plotted against square root of the

Table 1. Values of the concentration of the reactants, the ionic strengths, and the specific rate constant at 25°.

Concn of [KBr] $\times$ 10^3 M	Concn of [KBrO$_3$] $\times$ 10^3 M	Ionic strength $\times$ 10^1 (μ)	Specific rate constant (k) M^{-1} 1^{+1} . min^{-1}.
4.0	2.0	3.06	0.89
4.0	2.0	6.06	1.20
4.0	2.0	9.06	1.48
4.0	2.0	12.06	1.74
4.0	2.0	15.06	2.09
4.0	2.0	18.06	2.51
4.0	2.0	21.06	2.75
4.0	2.0	24.06	3.16
4.0	2.0	27.06	3.63
4.0	2.0	30.06	4.07
5.0	2.0	3.07	0.91
5.0	2.0	6.07	1.26
5.0	2.0	9.07	1.58
5.0	2.0	12.07	1.90
5.0	2.0	15.07	2.29
5.0	2.0	18.07	2.63
5.0	2.0	21.07	3.16
5.0	2.0	24.07	3.47
5.0	2.0	27.07	3.98
5.0	2.0	30.07	4.57
6.0	3.0	3.09	0.97
6.0	3.0	6.09	1.30
6.0	3.0	9.09	1.70
6.0	3.0	12.09	2.09
6.0	3.0	15.09	2.51
6.0	3.0	18.09	2.88
6.0	3.0	21.09	3.47
6.0	3.0	24.09	3.89
6.0	3.0	27.09	4.57
6.0	3.0	30.09	5.25
7.0	3.0	3.10	1.02
7.0	3.0	6.10	1.45
7.0	3.0	9.10	1.90
7.0	3.0	12.10	2.29
7.0	3.0	15.10	2.88
7.0	3.0	18.10	3.31
7.0	3.0	21.10	3.98
7.0	3.0	24.10	4.47
7.0	3.0	27.10	5.25
7.0	3.0	30.10	6.16

Table 2. The values of the specific rate constant for [KBr] = $5.0 \times 10^{-3} M$ and [KBrO$_3$] = $2.0 \times 10^{-3} M$ at various temperatures and ionic strengths.

Ionic strength	Temp (°C)			
$\mu \times 10^1$	30	35	40	45
	Specific rate constant ($k M^{-1}.1^{+1}.min^{-1}$.)			
In the absence af added salt				
3.07	1.15	1.37	1.61	1.93
In the presence of added salt				
6.07	1.47	1.73	.197	2.26
9.07	1.77	2.05	2.34	2.61
12.07	2.24	2.51	2.75	3.09
15.07	2.54	2.75	3.02	3.39
18.07	2.92	3.16	3.39	3.71
21.07	3.39	3.55	3.76	4.12
24.07	3.76	3.98	4.22	4.52
27.07	4.42	4.62	4.79	5.01
30.07	4.95	5.13	5.31	5.56

Table 3. The values of ionic strengths (μ), apparent energy of activation, and apparent change of enthalpy of activation.

Ionic strength (μ) $\times 10^1$	Apparent energy of activation (kJ)	Apparent change of enthalpy of activation (kJ)
In the absence of added salt		
3.07	23.72	21.24
In the presence of added salt		
6.07	20.50	18.02
9.07	17.86	15.38
12.07	16.11	13.63
15.07	14.14	11.66
18.07	11.63	9.15
21.07	9.96	7.48
24.07	8.45	5.97
27.07	6.78	4.30
30.07	5.48	3.00

Fig. 1. Plot of log $k \times 10^1$ vs $\sqrt{\mu} \times 10^1$.

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

ionic strength ($\sqrt{\mu}$) as shown in Fig. 1. The value of specific rate constant at zero ionic strength, i.e. k_o obtained from the extrapolation of log k versus $\sqrt{\mu}$ plots at 25° is $0.437 M^{-1}.1^{+1}: min^{-1}$. The values of log k/k_o vs $\sqrt{\mu}$ were plotted. A specimen graph is shown in Fig. 2 The value of Z_A or Z_B is 0.75. Our results show that the specific rate constant increases as the ionic strength of the medium is increased. The kinetic salt effect in the reaction $BrO_3^- + Br^- + 2 H^+ \longrightarrow$ (fourth order) studied by Sclar and

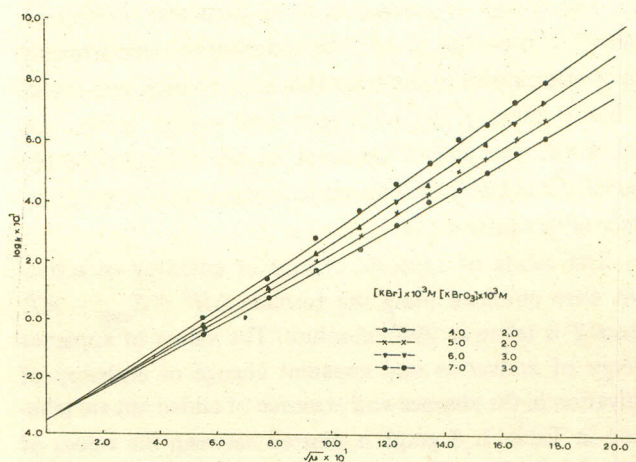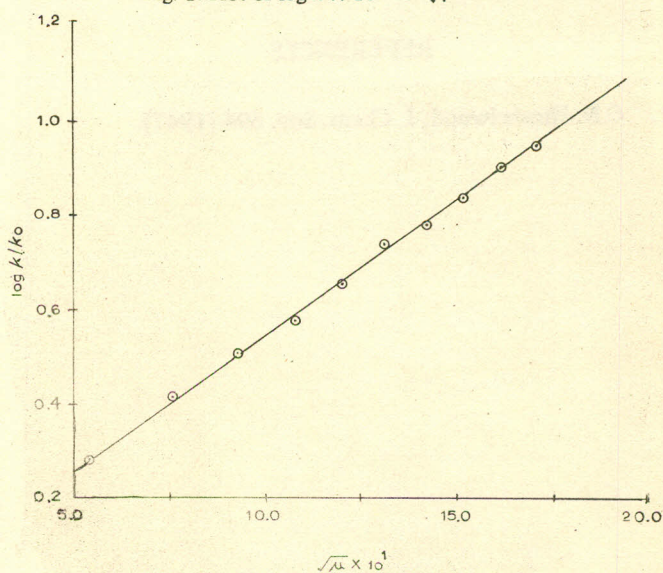Riesch [12] gives the decrease in rate with increasing ionic strength. In our work, since there is a large excess of H^+ ions, the configuration of the transition state is effected by the Br^-, BrO_3^-. The addition of KCl effects the transition state and the configurations followed by the addition of KCl requires less energy to form the products and this increases the rate of reaction.

The energy of activation was determined by Arrhenius plot method. Table 2 gives the values of specific rate constant at different temperatures and ionic strengths. A plot of log k against reciprocal of the temperature i.e., $1/T$ is a linear plot with a negative slope. The values of activation energy against corresponding ionic strengths are summarized in Table 3. For the same concentration of the reactants, i.e. $5.0 \times 10^{-3} M$ potassium bromide and $2.0 \times 10^{-3} M$ potassium bromate. These results show that the activation energy decreases with the increase in the ionic stren-

gth. The energy of activation for a particular reaction remains the same, but due to the variation in ionic strength, the configurations of the transition state change, and results in the decrease of apparent activation energy, in this present work. The plot of apparent energy of activation (E) against $\sqrt{\mu}$ is linear, having negative slope and is in accordance with equation (5).

The values of apparent change of enthalpy of activation were obtained using the formula $\Delta H^{\ddagger} = E_{exp} - RT$, where T is taken as 298° absolute. The values of apparent energy of activation and apparent change of enthalpy of activation in the absence and presence of added salt are tabulated in Table 3. A graph is plotted between the values of apparent change of enthalpy of activation ($\Delta H^{\ddagger}$) and $\sqrt{\mu}$. The plot is a straight line with a negative slope, quite in agreement with the theory.

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