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STUDY OF THE EFFECTS OF DIELECTRIC CONSTANTS ON THE SPECIFIC RATE CONSTANT OF BROMIDE-BROMATE REACTION

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The reaction between potassium bromide and potassium bromate is a fourth order reaction. However, in presence of large excess of sulphuric acid it behaves as a pseudo-second order reaction. The reaction was studied in a series of water - ethanol mixtures at various dielectric constants (ϵ) at 25°. From the linear plots of $\log k_0$ i.e., logarithm of specific rate constant at zero ionic strength against the reciprocal of the dielectric constant ($1/\epsilon$), the values of r^\ddagger and r_{AB} , the radii of the activated complex for single and double sphere models respectively were calculated. A comparison of the theoretical and experimental values of the radii, i.e. r^\ddagger and r_{AB} for single and double sphere models has indicated that the shape of the activated complex is more similar to Laidler-Eyring's approach of single sphere activated complex in this particular reaction.

INTRODUCTION

The effect of dielectric constant of the medium on the specific rate constant was mathematically dealt by Amis [1], Scatchard [2], Laidler [3], and Laidler-Eyring [4]. The two models suggested for the shape of the activated complex for the ionic reaction are the single sphere and the double sphere models, are represented mathematically by expressions 1 and 2 respectively:

$$\ln k_0 = \ln k - \frac{(e^2)}{2\epsilon KT} \left[\frac{(Z_A + Z_B)^2}{r^\ddagger} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (1)$$

$$\ln k_0 = \ln k - \frac{e^2 Z_A Z_B}{KT r_{AB}} \times \frac{1}{\epsilon} \quad (2)$$

where K is Boltzmann's constant, T is absolute temperature, ϵ is dielectric constant of the medium, e is the charge of an electron, k_0 and k are the specific rate constant at zero ionic strength and at infinite dielectric constant respectively. Z_A , Z_B and r_A , r_B are the charges and the radii of ions A and B respectively, r^\ddagger and r_{AB} are the radii of the activated complex for single sphere and double sphere models respectively.

Ghaziuddin and Nayyar [5] studied the reaction between iodide and persulphate ions in aqueous ethanol mixtures of different dielectric constants in order to find out

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the dependence of the rate constant on the dielectric constant of the medium. The reactions between halide ions and bromate ions in acidic medium were studied and mechanisms were proposed by Hinshelwood [6], King and Lister [7] and Taube and Dodgen [8].

In the present work, the reaction between bromide and bromate ions has been studied to confirm whether the activated complex consists of single sphere or double sphere model. The radius of the activated complex for the two models was determined experimentally and was compared with the theoretical values.

EXPERIMENTAL

All the chemicals used (potassium bromate, potassium bromide, sulphuric acid, acetone, ethanol, methanol, etc.) were of E. Merck (A.R. grade) and without further purification. The method prescribed by Vogel [9] was used for the preparation of absolute methanol. Freshly prepared distilled water was redistilled three times before preparing necessary solutions [10].

The dielectric constant was measured as described earlier [5] with a dipolemeter (type DM 01). All measurements were performed at 25°. 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 optical density versus corresponding wavelength (λ) in order to record

observations in this experimental work.

The rate of the reaction between bromide and bromate ions was followed spectrophotometrically using a Unicam SP 600 spectrophotometer for the measurement of optical density of the reaction mixture. In order to carry out the reaction 10 ml of each potassium bromate and sulphuric acid was pipetted out in an iodine flask at 25°. The concentration of sulphuric acid in each case was maintained at $1.0 \times 10^{-1} M$. Potassium bromide (10 ml) was then added to the above-mentioned solution and the stop watch was started to record the time. 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 by using the second order rate equation.

RESULTS AND DISCUSSIONS

The effect of ionic strength on the specific rate constant is given by the following equation and the results are summarized in Table 1.

$$\ln k = \ln k_0 + \frac{e^3}{(\epsilon K T)^{3/2}} \left(\frac{8 \pi N}{1000} \right)^{1/2} Z_A Z_B \sqrt{\mu} \quad (3)$$

where k is the specific rate constant, N is Avagadro number and μ is the ionic strength of the medium. Other terms have the same meanings as in equations 1 and 2. The concentrations used in the present work are considerably low and as such the applicability of Debye-Hückel equation is reasonable.

Our results show that the specific rate constant at constant concentration of the reactants increases as the dielectric constant of the medium is lowered. This is due to the increase in the activity of the reactants at lower dielectric constant. The values of k_0 calculated from equation 3 are presented in Table 2. The plot of logarithm of the specific rate constant at zero ionic strength versus the reciprocal of the dielectric constant for the reaction between bromide and bromate ions at 25° is a straight line of positive slope. A representative graph is shown in Fig. 1. The positive slope can be accounted, with the help of the mechanism given by King and Lister [7]. According to this mechanism the activated complex comprises of a positively charged brominium ion Br^+ , and a negatively charged bromite ion BrO_2^- .

Assuming the volume of the molecule of a compound which is supposed to be an spherical is a sum of volume of

Table 1 Values of the concentration of reactants, the dielectric constant of the medium and the specific rate constants.

Concn of [KBr] $\times 10^3 M$	Concn of [KBrO ₃] $\times 10^3 M$	Dielectric constant (ϵ)	Specific rate constant $M^{-1} \cdot l^{+1} \text{min}^{-1}$
10.0	1.0	67.66	3.12
10.0	1.0	59.70	3.58
10.0	1.0	55.71	4.02
10.0	1.0	51.12	4.52
10.0	1.0	46.33	5.30
8.0	2.0	67.66	1.37
8.0	2.0	59.70	1.92
8.0	2.0	55.71	2.32
8.0	2.0	51.12	3.34
8.0	2.0	46.33	4.68
5.0	0.8	67.66	1.29
5.0	0.8	59.70	1.76
5.0	0.8	55.71	2.18
5.0	0.8	51.12	2.87
5.0	0.8	46.33	3.88
6.6	3.3	67.66	1.38
6.6	3.3	59.70	2.00
6.6	3.3	55.71	2.39
6.6	3.3	51.12	3.54
6.6	3.3	46.33	5.03

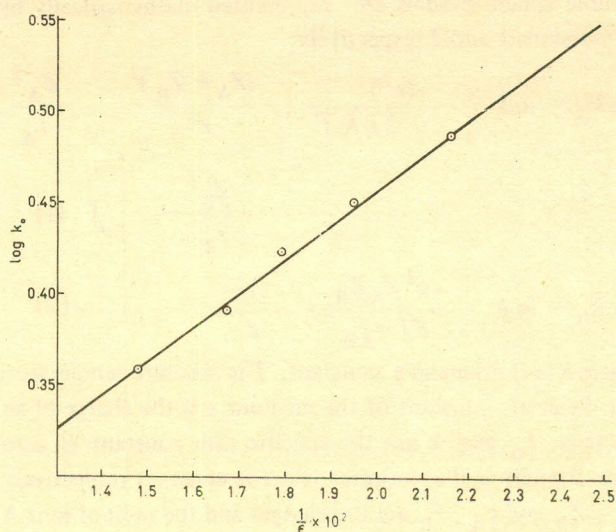


Fig. 1. Plot of $\log k_0$ vs. $1/\epsilon \times 10^2$

individual ions consisting the compound. The radius of BrO_2^- ion, r_{AB} , and r^\ddagger , can be calculated taking the numerical values of the radius of bromide and oxygen ions

Table 2. Values of k_0 and the corresponding concentration of reactants, and dielectric constants.

[KBr] $\times 10^3$ M	[KBrO ₃] $\times 10^3$ M	67.77	Dielectric constants (ϵ) k_0 M ⁻¹ min ⁻¹			
			59.70	55.71	51.12	46.33
10.0	1.0	2.29	2.47	2.66	2.82	3.08
8.0	2.0	1.02	1.35	1.56	2.13	2.79
5.0	0.8	1.03	1.34	1.61	2.04	2.61
6.6	3.3	1.04	1.40	1.61	2.27	3.00

Table 3. Experimental values of r^\ddagger and r_{AB} .

[KBr] $\times 10^3$ M	[KBrO ₃] $\times 10^3$ M	r_{AB} Å	r^\ddagger Å
10.0	1.0	12.18	2.57
8.0	2.0	3.80	2.08
5.0	0.8	4.06	2.12
6.6	3.3	3.58	2.05

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from Moeller [11] and confirmed by Pauling [12]. The value of the radius of the brominium ion has been taken approximately as 1.04 Å. On this basis the values of $r_{\text{BrO}_2^-}$, r_{AB} , and r^\ddagger were found to be 2.34, 3.38 and 2.41 Å respectively.

The experimental values of r_{AB} and r^\ddagger calculated from the slope of straight line, by applying equations 1 and 2 respectively, are tabulated in Table 3. The average experimental values of r_{AB} and r^\ddagger are 5.93 and 2.21 Å respectively.

A comparison of theoretical and experimental values of r_{AB} and r^\ddagger indicates that the shape of the activated complex for the reaction between bromide and bromate ions could best be explained on the basis of a single sphere model.