INFLUENCE OF DIELECTRIC CONSTANT AND IONIC STRENGTH ON THE SPECIFIC RATE CONSTANT OF BROMIDE-PERSULPHATE REACTION

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Abstract. Rates of reaction between persulphate and iodide ions were studied at various concentrations of the reacting ions and at various dielectric constant (D) of aqueous ethanol mixtures at 50°C. This reaction is found to be second order and a mechanism is suggested for the reaction.

From the plot of log k''_o against $1/D$, the value of $\gamma\neq$ and γ_{AB}, the radii of the transient species for single and double sphere models are calculated. Comparison of the experimental and theoretical values of $\gamma\neq$ and γ_{AB} shows that the description of the transient species can best be explained by the single sphere model.

A variety of studies have been carried out for the determination of rate of reaction between various inorganic ions in solution[1-3] and different mechanisms were suggested. The variation of the specific rate constant of reaction between any two ionic species as a function of the dielectric constant of the medium and the ionic strength of the solution were studied by Amis,[4] Laidlar,[5] Laidler and Eyring[6] and Subhani and Lacewala.[7] Two models were suggested for the shape of the activated complex, in an ionic reaction, the single sphere, and the 'double sphere' models.[1] The two models give the following relationships respectively relating the radius of the activated complex with the specific rate constant at zero ionic strength (k_o).

$$\ln k''_o = \ln k'_o - \frac{e^2}{2DkT}\left[\frac{(Z_A+Z_B)^2}{\gamma\neq} - \frac{(Z_A)^2}{\gamma_A} - \frac{(Z_B)^2}{\gamma_B}\right] \quad (1)$$

$$\ln k''_o = \ln k'_o - \frac{Z_A . Z_B\, e^2}{DkT\, \gamma_{AB}} \quad (2)$$

where k''_o, specific rate constant at zero ionic strength; k'_o, specific rate constant at infinite dielectric constant; e, charge of an electron; Z_A Valance of the ion A; Z_B, Valance of the ion B; D, dielectric constant of the medium; k, Boltzman constant; T temperature; γ_A radius of the ion A; γ_B radius of the ion B; $\gamma\neq$ radius of the activated complex for the single sphere model; and γ_{AB} radius of the activated complex for double sphere model. Laidler[5] has given relationship between the logarithmic function of specific rate constant and square root of ionic strength to describe the effect of ionic strength on the reaction rate bewteen ions

$$\ln k'' = \ln k_o'' + \frac{e^3}{(DkT)^{3/2}}\frac{(8\pi N)^{1/2}}{1000}\, Z_A Z_B\sqrt{\mu} \quad (3)$$

where k''_o, specific rate constant at zer oionic strength; N, Advogadro number ; k'', observed rate constant; ($\sqrt{\mu}$), ionic strength of the solution; and D, k, T, Z_A, Z_B and e have the same meaning as in equations (1) and (2).

The kinetics of the reaction between iodide and persulphate was studied by King and Jacobs.[8] It was thought that it would be interesting to look for the kinetic studies of the reaction between bromide and persulphate ions. The reaction between bromide and persulphate ions was also studied in aqueous ethanol mixture of different dielectric constant in order to find out the dependence of the rate constant on the dielectric constant of the medium. The radius of the activated complex for this reaction was also calculated by using equations (1) and (2) to find out which model was more probable for the shape of the activated complex.

For the study of the effect of dielectric constant on the reaction rate it was necessary to undertake the studies of the influence of the ionic strength on this reaction rate between bromide and persulphate ions. These studies enable us to evaluate k''_o with the help of equation (3) as that was required in equations (1) and (2).

Experimental

All the chemicals used (potassium bromide, potassium persulphate, sodium thiosulphate, ethanol, methanol etc.) were of A.R. grade.

All solutions were prepared in triply distilled water.[9]

The dielectric constant was measured with a dipolemeter (type DM ol, Wissenschaftlich. The MFL₃ cell was used for the measurement over the dielectric constant range 41.5–79. The scale of the instrument was calibrated with methanol of which the reported values[10] of the dielectric constant is 32.63. '

All measurements were performed at 50°C. The instrument was operated as described by Subhani and Lacewala.[7]
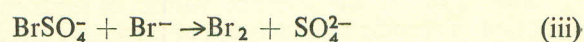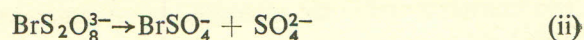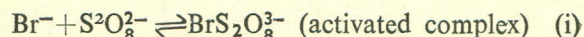
The velocity of the chemical reaction was measured by mixing 10 ml each of the stock solution of persulphate and bromide ions in the aqueous ethanol medium at 50°C and the stop watch was started to record the time. A portion of the reaction mixture was then immediately transferred to the 1-cm spectrophotometric cell and covered with top and was kept

in thermostat bath attachment in the Unicam SP 500 spectrophotometer at 50°C. The measurements of the absorption due to bromine produced were recorded at wavelength (λ) = 390 nm. The concentration of bromide was calculated using 930 cm²/mole experimentally determined value of extinction coefficient of bromine at 50°C at that wavelength. Specific rate constants were obtained from the second order plots as they were the only linear plots.

Results and Discussions

Linear plots were obtained when the reciprocal of concentration at any time (t) was plotted against time t. These plots showed that the reaction between persulphate and bromide ions obeys second order kinetics.

The most probable mechanism for this reaction is analogous to that of for the second order reaction between persulphate and iodide ions and can be written as

$$Br^- + S_2O_8^{2-} \rightleftharpoons BrS_2O_8^{3-} \text{ (activated complex)} \quad \text{(i)}$$

$$BrS_2O_8^{3-} \rightarrow BrSO_4^- + SO_4^{2-} \quad \text{(ii)}$$

$$BrSO_4^- + Br^- \rightarrow Br_2 + SO_4^{2-} \quad \text{(iii)}$$

The step (i) is the rate determining step and thus the reaction follows a second order kinetics.

The values of the specific rate constant for the reaction at 50°C show that the specific rate constant at constant ionic strength decreases as the dielectric constant of the medium is lowered (Table 1). This is presumably due to the decrease in the activity of the reactants at lower dielectric constant. It was also noted that for the same value of the dielectric constant of the medium and for the same concentration of $S_2O_8^{2-}$ ion a decrease in the ionic strength lower the specific rate constant. This is due to the effect of ionic strength on the specific rate constant as is obvious from equation (3) mentioned above.

TABLE 1. VALUES OF THE SPECIFIC RATE CONSTANTS CONCENTRATION OF REACTANTS AND THE DIELECTRIC CONSTANT OF THE MEDIUM AT 50°C.

Dielectric constant (D)	Concn of $KBr \times 10^2$ ml^{-1}	Concn of $K_2S_2O_8 \times 10^3$ ml^{-1}	Specific rate constant $k'' \times 10^6$ 1 M^{-1} min^{-1}	Dielectric constant (D)	Concn of $KBr \times 10^2$ ml^{-1}	Concn of $K_2S_2O_8 \times 10^3$ ml^{-1}	Specific rate constant $k'' \times 10^6$ 1 M^{-1} min^{-1}
79·0	2·5	2·5	5·902	49·1	0·75	0·75	1·08
70·3	2·5	2·5	4·02	45·03	0·75	0·75	0·63
65·5	2·5	2·5	3·77	41·5	0·75	0·75	0·54
56·3	2·5	2·5	2·75	79·0	0·5	0·75	3·98
49·1	2·5	2·5	2·00	70·3	0·5	0·75	2·56
45·03	2·5	2·5	1·71	65·5	0·5	0·75	2·29
41·5	2·5	2·5	1·34	56·3	0·5	0·75	1·43
79·0	2·5	1·5	5·55	49·1	0·5	0·75	0·82
70·3	2·5	1·5	3·83	45·03	0·5	0·75	0·58
65·5	2·5	1·5	3·62	41·5	0·5	0·75	0·46
56·3	2·5	1·5	2·66	79·0	2·5	0·75	5·64
49·1	2·5	1·5	1·90	70·3	2·5	0·75	3·66
45·03	2·5	1·5	1·58	65·5	2·5	0·75	3·41
41·5	2·5	1·5	1·49	56·3	2·5	0·75	2·44
79·0	2·5	1·0	4·75	49·1	2·5	0·75	1·50
70·3	2·5	1·0	3·73	45·03	2·5	0·75	1·47
65·5	2·5	1·0	3·48	41·5	2·5	0·75	1·26
56·3	2·5	1·0	3·07	79·0	0·75	2·5	4·87
49·1	2·5	1·0	3·07	70·3	0·75	2·5	3·02
45·03	2·5	1·0	1·62	65·5	0·75	2·5	2·71
41·5	2·5	1·0	1·03	56·3	0·75	2·5	2·02
79·0	1·5	1·5	4·88	49·1	0·75	2·5	1·18
70·3	1·5	1·5	3·27	45·03	0·75	2·5	0·84
65·5	1·5	1·5	2·82	41·5	0·75	2·5	0·74
56·3	1·5	1·5	2·21	79·0	2·5	0·5	5·28
49·1	1·5	1·5	1·51	70·3	2·5	0·5	4·35
45·03	1·5	1·5	1·11	65·5	2·5	0·5	3·69
41·5	1·5	1·5	0·80	56·3	2·5	0·5	2·66
79·0	0·5	0·5	3·98	49·1	2·5	0·5	1·55
70·3	0·5	0·5	2·51	45·03	2·5	0·5	1·14
65·5	0·5	0·5	1·97	41·5	2·5	0·5	1·16
56·3	0·5	0·5	1·19	79·0	0·5	2·5	4·42
49·1	0·5	0·5	0·70	70·3	0·5	2·5	3·10
45·03	0·5	0·5	0·57	65·5	0·5	2·5	2·38
41·5	0·5	0·5	0·46	56·3	0·5	2·5	1·53
79·0	0·75	0·75	4·03	49·1	0·5	2·5	0·97
70·3	0·75	0·75	2·57	45·03	0·5	2·5	0·81
65·5	0·75	0·75	2·54	41·5	0·5	2·5	0·69
56·3	0·75	0·75	1·29				

The values of k''_0 extrapolated from the plots of $\ln k''$ against $\sqrt{\mu}$ from equation (3), for each dielectric constant and ionic strength, are summarized in Table 2.

The plot of the average values of logarithmic function of specific rate constant at zero ionic strength ($\log_{10} k'_0$) against the reciprocal of the dielectric constant (41.5–79) (as given in Table 3) was a straight line (Fig. 1).

However, deviation from linearity was observed for values of the dielectric constant below 45. This may be due to the preferential association of water molecules with the reacting ions. Similar behaviour was observed by Scatchard,[11] Amis and Potts,[13] and Subhani and Lacewala.[7]

The experimental value of $\gamma_{\pm}$ and γ_{AB}, calculated from the slope of the straight line in Fig. 1 and using equations (1) and (2) respectively, are summarized in Table 4.
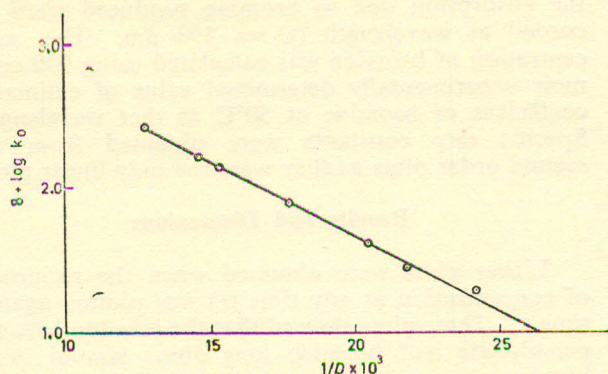

Fig. 1

TABLE 2. Values of k''_0 (Specific Rate Constant at Zero Ionic Concentration) and the Corresponding Concentration of Reactants, Ionic Strength and Dielectric Constants of the Medium at 50°C.

Dielectric constant (D)	Concn of KBr×10² ml⁻¹	Concn of K₂S₂O₈ ×10³ ml⁻¹	Specific rate constant at zero ionic strength $(k_0'')\times10^6$ 1 M⁻¹ min⁻¹	Ionic strength (μ) ×10²	Dielectric constant (D)	Concn of KBr×10² m l⁻¹	Concn of K₂S₂O₈ ×10³ ml⁻¹	Specific rate constant at zero ionic strength $(k_0'')\times10^6$ 1M⁻¹ min⁻¹	Ionic strength (μ) ×10²
79.0	2.5	2.5	2.75	3.25	49.1	0.75	0.75	0.65	0.975
70.3	2.5	2.5	1.65	3.25	45.03	0.75	0.75	0.24	0.975
65.5	2.5	2.5	1.37	3.25	41.5	0.75	0.75	0.18	0.975
56.3	2.5	2.5	0.78	3.25	79.0	0.5	0.75	2.77	0.725
49.1	2.5	2.5	0.42	3.25	70.3	0.5	0.75	1.68	0.725
45.03	2.5	2.5	0.29	3.25	65.5	0.5	0.75	1.42	0.725
41.5	2.5	2.5	0.18	3.25	46.3	0.5	0.75	0.79	0.725
79.0	2.5	1.5	2.68	2.95	49.1	0.5	0.75	0.39	0.725
70.3	2.5	1.5	1.64	2.95	45.03	0.5	0.75	0.25	0.725
65.5	2.5	1.5	1.38	2.95	71.5	0.5	0.75	0.17	0.725
56.3	2.5	1.5	0.80	2.95	79.0	2.5	0.75	2.8	2.725
49.1	2.5	1.5	0.43	2.95	60.3	2.5	0.75	1.62	2.725
45.03	2.5	1.5	0.28	2.95	55.5	2.5	0.75	1.35	2.725
41.5	2.5	1.5	0.20	2.95	46.3	2.5	0.75	0.77	2.725
79.0	2.5	1.0	2.79	2.80	49.1	2.5	0.75	0.36	2.725
70.3	2.5	1.0	1.60	2.80	45.03	2.5	0.75	0.29	2.725
65.5	2.5	1.0	1.36	2.80	71.5	2.5	0.75	0.2	2.725
49.1	2.5	1.0	0.85	2.80	79.0	0.75	2.5	2.9	1.5
45.03	2.5	1.0	0.38	2.80	60.3	0.75	2.5	1.65	1.5
41.5	2.5	1.0	0.24	2.80	55.5	0.75	2.5	1.36	1.5
79.0	2.5	1.0	0.16	2.80	46.3	0.75	2.5	0.74	1.5
70.3	1.5	1.5	2.70	1.95	49.1	0.75	2.5	0.41	1.5
65.5	1.5	1.5	1.64	1.95	5.03	0.75	2.5	0.25	1.5
56.3	1.5	1.5	1.29	1.95	41.5	0.75	2.5	0.19	1.5
94.1	1.5	1.5	0.83	1.95	79.0	2.5	0.5	2.65	2.65
45.03	1.5	1.5	0.45	1.95	70.3	2.5	0.5	1.57	2.65
41.5	1.5	1.5	0.28	1.95	65.5	2.5	0.5	1.48	2.65
79.0	1.5	1.5	0.17	1.95	56.3	2.5	0.5	0.69	2.65
70.3	0.5	0.5	2.38	0.65	49.1	2.5	0.5	0.38	2.65
65.5	0.5	0.5	1.69	0.65	45.03	2.5	0.5	0.23	2.65
56.3	0.5	0.5	1.25	0.65	41.5	2.5	0.5	0.19	2.65
49.1	0.5	0.5	0.68	0.65	79.0	0.5	2.5	2.75	1.25
45.03	0.5	0.5	0.35	0.65	70.3	0.5	2.5	1.78	1.25
41.5	0.5	0.5	0.26	0.65	65.5	0.5	2.5	1.41	1.25
79.0	0.75	0.75	0.19	0.65	56.3	0.5	2.5	0.70	1.25
70.3	0.75	0.75	2.65	0.975	49.1	0.5	2.5	0.37	1.25
65.5	0.75	0.75	1.58	0.975	45.03	0.5	2.5	0.27	1.25
56.3	0.75	0.75	1.46	0.975	41.5	0.5	2.5	0.20	1.25

Table 3. Average Values for the Specific Rate Constants (k_o'') at Zero Ionic Strength and the Values of Dielectric Constant of the Medium at 50°C.

Dielectric constant (D)	Average specific rate constant at zero ionic strength $(k_o'') \times 10^6$ m^{-1} min^{-1}
79·0	2·75
70·3	1·660
65·5	1·380
56·3	0·758
49·1	0·398
45·03	0·263
41·5	0·185

Table 4. Experimental and Theoretical Values of γ_{AB} and $\gamma\neq$.

	Experimental values (Å)	Theoretical value (Å)
γ	3·02	3·084
γ_{AB}	5·15	4·75

The experimental value of $\gamma\neq$ and γ_{AB} are 3.02 Å and 5.15 Å respectively. Assuming the volume of single sphere equal to the sum of volumes of spheres from which the single sphere has been built up, the radius $\gamma\neq$ and γ_{AB} can be calculated using radii of bromide, sulphur and oxygen.[12] On this basis the value of γ_{Br^-}, $\gamma_{S_2O_8^{2-}}$, $\gamma\neq$ and

γ_{AB} were found to be 1.95, 2.80, 3.084 and 4.75 Å respectively.

A comparison of the experimental values of $\gamma\neq$ and γ_{AB} 3.02 and 5.15 Å respectively, with their theoretical values (Table 4) suggests that the description of the activated complex could best be given by 'single sphere' model for the reaction under consideration.

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