Pakistan J. Sci. Ind. Res., Vol. 14, No. 6, December 1971

INFLUENCE OF DIELECTRIC CONSTANT OF THE MEDIUM ON THE SPECIFIC RATE CONSTANT OF IODIDE–PERSULPHATE REACTION

M. Ghaziuddin Ahmed and M. Nayyer Azam

Department of Chemistry, University of Karachi, Karachi 32

(Received November 4, 1971)

Rate of reaction (*k*) between the pursulphate and iodide ions were studied at various concentrations of the reacting ions and at various dielectric constants (ε) of aqueous ethanol mixtures at 25° C. From the plot of log k_0 against ε the values of $r^{\ddagger}$ and r_{AB}, the radius of the transient species for single and double sphere models were calculated. Comparison of the experimental and theoretical values of $r^{\ddagger}$ and r_{AB} showed that the description of the transient species could best be explained by the single sphere model

The variation of the specific rate of reaction between any two ionic species as a function of the dielectric constant of the medium was studied by Amis, Laidler, and Laidler and Eyring.[1-3] Two models were suggested for the shape of 'activated complex' in an ionic reaction, the 'single sphere' and the 'double sphere' models.[4] The two models give the following equations respectively relating the radius of the activated complex with the specific rate constant.

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

$$\ln k = \ln k_0 - \frac{e^2 Z_A Z_B}{\varepsilon K T r_{AB}} \qquad (2)$$

where k = specific rate constant, k_0 = specific rate constant at infinite dielectric constant, e = charge of an electron, Z_A = valence of the ion A, Z_B = valence of the ion B, ε = dielectric constant of the medium, K = Boltzmann constant, T = temperature, r_A = radius of the ion A, r_B = radius of the ion B, $r^{\ddagger}$ =radius of the activated complex for single sphere model, and r_{AB} = radius of the activated complex for the double sphere model.

We have studied the reaction between iodide and persulphate ions in aqueous ethanol mixtures 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.

Experimental

All the chemicals used (potassium iodide, potassium persulphate, sodium thiosulphate, ethanol, methanol and starch) were of E. Merck, G.R. quality. Three drops of chloroform per litre of standard sodium thiosulphate solution were used as preservative.[5]

The dielectric constant was measured with a dipolemeter (type DM 01, manufactured by Wissenschaftlich Techniche Werkstatten GmbH, Weilheim/OBB Germany). The MFL_3 cell was used for the measurements over the dielectric constant range of 21–80. The scale of the instrument was calibrated with methanol of which the reported value[6] of the dielectric constant is 32.63. All measurements were performed at 25°C. The instrument operated on heterodyne beat method by which the oscillations of two high frequency oscillators were brought to superposition in a mixing section. By subsequent amplification, the beats were brought to the screen of a cathode-ray tube which served as an indicator thus making it possible to observe even fraction of a cycle per second beat frequency.

The velocity of the chemical reaction was measured by mixing the stock solution of persulphate and potassium iodide in the aqueous ethanol medium. A measured portion of the reaction mixture was chilled and titrated with standard sodium thiosulphate solution using 1% starch solution as an indicator. Specific rate constant was calculated for the reaction by using the second order rate equation.

Results and Discussion

The values of the specific rate constant for the reaction are summarised in Table 1.

Our results show that the specific rate constant at constant ionic strength decreases as the dielectric constant of the medium is lowered. 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

TABLE 1.—VALUES OF THE CONCENTRATION OF REACTANTS, THE DIELECTRIC CONSTANT OF THE MEDIUM AND THE SPECIFIC RATE CONSTANT.

Concentration of [$K_2S_2O_8$] $\times 10^3$M	Concentration of [KI] $\times 10^2$M	Dielectric constant	Specific rate constant $\times 10^6$M^{-1}l^{+1} min^{-1}	Concentration of [$K_2S_2O_8$] $\times 10^3$M	Concentration of [KI] $\times 10^2$M	Dielectric constant	Specific rate constant $\times 10^6$M^{-1}l^{+1} min^{-1}
1.25	2.50	79.80	6.31	0.63	1.25	48.73	0.42
1.25	2.50	63.05	3.63	0.63	1.25	40.99	0.37
1.25	2.50	52.47	1.95				
1.25	2.50	48.73	1.86	0.63	0.50	79.80	1.17
1.25	2.50	40.99	1.52	0.63	0.50	63.05	0.78
				0.63	0.50	52.47	0.40
1.25	1.25	79.80	4.74	0.63	0.50	48.73	0.36
1.25	1.25	63.05	2.29	0.63	0.50	40.99	0.30
1.25	1.25	52.47	1.58				
1.25	1.25	48.73	1.22	0.25	2.50	79.80	0.80
1.25	1.25	40.99	1.26	0.25	2.50	63.05	0.52
				0.25	2.50	52.47	0.24
1.25	0.50	79.80	3.31	0.25	2.50	48.73	0.24
1.25	0.50	63.05	1.93	0.25	2.50	40.99	0.18
1.25	0.50	52.47	1.01				
1.25	0.50	48.73	0.92	0.25	1.25	79.80	0.56
1.25	0.50	40.99	0.74	0.25	1.25	63.05	0.39
0.63	2.50	79.80	2.17	0.25	1.25	52.47	0.20
0.63	2.50	63.05	1.66	0.25	1.25	48.73	0.20
0.63	2.50	52.47	0.81	0.25	1.25	40.99	0.16
0.63	2.50	48.73	0.72				
0.63	2.50	40.99	0.64	0.25	0.50	79.80	0.52
				0.25	0.50	63.05	0.33
0.63	1.25	79.80	2.14	0.25	0.50	52.47	0.16
0.63	1.25	63.05	1.07	0.25	0.50	48.73	0.16
0.63	1.25	52.47	0.51	0.25	0.50	40.99	0.13

TABLE 2.—VALUES OF $k_0 \times 10^6$M^{-1}l^{+1} min^{-1} AND THE CORRESPONDING CONCENTRATION OF REACTANTS, IONIC STRENGTHS AND DIELECTRIC CONSTANTS.

			Dielectric constant ε	$k_0 \times 10^6$M^{-1}l^{+1}min^{-1}			
[$K_2S_2O_8$] $\times 10^3$M	[Ki] $\times 10^2$M	$\mu \times 10^2$	79.80	63.05	52.47	48.73	40.99
1.25	2.50	2.88	2.90	1.20	0.45	0.37	0.18
1.25	1.25	1.63	2.64	0.99	0.53	0.39	0.26
1.25	0.50	0.88	2.16	1.05	0.45	0.38	0.23
0.63	2.50	2.69	1.03	0.57	0.20	0.15	0.08
0.63	1.25	1.44	1.23	0.49	0.18	0.13	0.08
0.63	0.50	0.69	0.80	0.45	0.20	0.16	0.11
0.50	2.50	2.58	0.38	0.18	0.06	0.05	0.02
0.50	1.25	1.33	0.33	0.18	0.08	0.06	0.04
0.50	0.50	0.58	0.37	0.20	0.09	0.08	0.05

Table 3.—Experimental Values of $r^{\ddagger}$ and r_{AB}.

$\mu \times 10^2$	$r^{\ddagger}$ A°	r_{AB} A°
2.88	3·13	4·06
2.69	3·25	4·57
2.58	3·20	4·35
1.63	3·27	4·64
1·44	3·04	3·72
1·33	3·36	5·07
0.88	3·25	4·57
0.69	3·45	5·59
0.58	3·36	5·07

effect of ionic strength on the specific rate constant as is obvious from the following equation.

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

where $k_0 =$ specific rate constant at zero ionic strength, $N =$ Avogadro number, $\mu =$ ionic strength.

Other terms have the same meaning as in equations 1 and 2.

The values of k_0 extrapolated from equation 3 for each ionic strength are summarized in Table 2.

The plot of logarithm of specific rate constant at zero ionic strength against the reciprocal of the dielectric constant (50–80) was a straight line. A representative graph is shown in Fig. 1. However, deviation from linearity was observed for values of the dielectric constant below 50. This may be due to the preferential association of water molecules with the reacting ions. Similar behaviour was observed by Scatchard,[7] and Amis and Potts.[5]

The experimental values of $r^{\ddagger}$ and r_{AB}, calculated from the slopes of straight lines using equations 1 and 2 respectively, are summarized in Table 3.

The average experimental values of $r^{\ddagger}$ and r_{AB} are 3.26A° and 4.62A° 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 of persulphate ion, $r^{\ddagger}$ and r_{AB} can be calculated using radii of iodide, sulphur and oxygen.[8] On this basis the values of

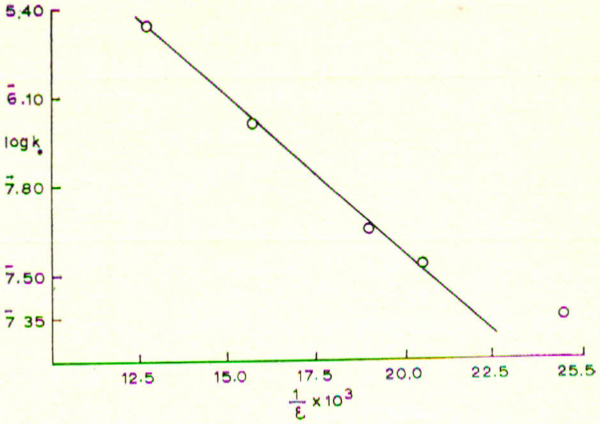

Fig. 1.—Plot of log K_0 against $1/\varepsilon$

r_{I^-}, $r_{S_2O_8^{2-}}$, $r^{\ddagger}$ and r_{AB} were found to be 2.16A°, 2.80A°, 3.18A° and 4.96A° respectively.

Comparison of average experimental value of $r^{\ddagger}$ and r_{AB}, 3·26A° and 4.62A° respectively, with their theoretical values suggest that the description of the activated complex could best be given by 'single sphere' model for the reaction under consideration.

References

1. E.S. Amis, J. Chem. Ed., **29**, 337, (1952).
2. K. J. Laidler, *Chemical Kinetics* (McGraw Hill, New York, 1965), p. 212.
3. K. J. Laidler and H. Eyring, Ann. N.Y. Acad. Sci., **39**, 303 (1940).
4. K. J. Laidler, *Reaction Kinetics* (Pergamon, Oxford, 1963), p. 10, 17 and 19.
5. E.S. Amis and J.E. Potts, J. Am. Chem. Soc., **63**, 2883 (1941).
6. *Hand Book of Chemistry and Physics* (Chemical Rubber Company, Cleveland, Ohio, 1965), 46th edition, p. E 50.
7. G.S. Scatchard, J. Chem. Phys., **7**, 657 (1939).
8. T. Moeller, *Inorganic Chemistry* (John Wiley, New York, 1965), p. 140.