

STUDY OF THE RATES OF BIMOLECULAR IONIC REACTION BETWEEN DIBROMOSUCCINATE AND HYDROXIDE IONS

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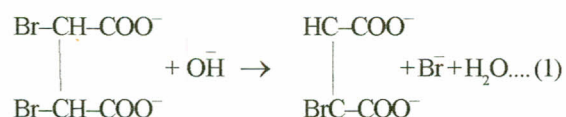
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The effect of dielectric constant (ϵ) and solvent effects on the rates of bimolecular ionic reaction between dibromosuccinate and hydroxide ions have been studied. Two mixed solvents i.e. water-ethanol and water-methanol were used for the measurements of the effect of dielectric constant. The rate constants in different aquo-organic mixtures have been found to lie in the order methanol > ethanol. The radii of the activated complex for water-ethanol and water-methanol media have been evaluated from the slopes of the plots of logarithm of rate constant at zero ionic strength ($\log k_0$) and reciprocal of the dielectric constant ($1/\epsilon$). It is established that the shape of the activated complex in aquo-organic mixtures is similar to Laidler-Eyring's approach of single sphere model in this particular reaction.

Key words: Rate constants, Second order kinetics, Dielectric constant, Solvent effect, Single sphere model.

Introduction

The reaction between dibromosuccinate and hydroxide ions is a second order (Holomberg 1921). The stoichiometric equation is as follows:



(dibromosuccinate ion) (monobromosuccinate ion)

This reaction follows a second order kinetics.

The effect of ionic strength (μ) on rate constant (k) of ionic reactions was studied by Slaton (1905), Erklenes (1986) Uddin *et al* (1981). The dependence of rate constant on dielectric constant of the medium (ϵ) for ionic reactions was mathematically dealt by Christensen (1924), Scatchard (1932, 1939) Laidler-Eyring (1940), Amis (1952), Ray *et al* (1970), Ghaziuddin *et al* (1971, 1978, 1980, 1985), Uddin *et al* (1992, 1995, 1996) also studied the kinetics of ionic reactions in order to find out the most probable shape of the activated complex.

In the previous communications, we reported the kinetics of monobromosuccinate-thiosulphate ions in aqueous media in presence of salts (Uddin and Shahid 1989), and water-ethanol mixtures (Uddin and Yasmeen 1990). It was found worthwhile to extend the work to the studies of reaction between dibromosuccinate and hydroxide ions to elucidate the role of solvent and the effect of dielectric constant on rate constant.

Experimental

Dibromosuccinate, oxalic acid, hydrochloric acid, ethanol and methanol used were of E. merck in the present investigations. Double distilled water was used throughout the course of the experiments.

In order to vary the dielectric constant of the medium, different solvent pairs such as ethanol-water and methanol-water mixtures at 20°C were prepared. The composition of mixtures and respective values of dielectric constant at 20°C taken from Akerlof (1932) are shown in Table 1.

The kinetics study involved the method of titration. Reactants were prepared in a series of water-ethanol and water-methanol mixtures separately. The calculated volumes of stock solutions of disodium dibromosuccinate and sodium

Table 1
Dielectric constant data

Mixture	% w/w	ϵ at 20°C
Ethanol-Water	0.00	80.37
	8.25	75.60
	16.84	70.00
	25.77	65.00
	35.06	59.50
Methanol-Water	44.75	53.75
	0.00	80.37
	8.07	77.00
	16.50	73.00
	25.28	68.60
	34.50	64.00
	44.00	59.60

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hydroxide attained the temperature of the bath. Experimental solutions were then mixed up and 5 ml of reaction mixture titrated against the standard solution of hydrochloric acid at different time intervals.

Results and Discussion

All measurement were made with sets of equal concentration a (1×10^{-3} - 7×10^{-3} mol/dm³) respectively of disodium dibromosuccinate and sodium hydroxide. Integrated second order rate equation of the form $(a-x)^{-1} = kt + a^{-1}$ was used for the calculations of rate constants. The rate constants for the reaction between disodium dibromosuccinate and sodium hydroxide in water-ethanol and water-methanol mixtures at 20°C obtained are in Tables 2 and 3 respectively.

The reaction rates have been found to be faster in methanol-water mixtures than in ethanol-water mixtures. The rate constant at constant ionic strength increases with the decrease in dielectric constant of the medium, because there is an increase in the electrostatic interaction between reacting ions at lower dielectric constant.

The rate constant at zero ionic strength (k_o) for a second order reaction between two ions A and B of charges Z_A , Z_B respectively were calculated using the following Bronsted Debye-Huckel equation:

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

Table 2

Rate constants data in ethanol-water mixtures

[DSDBS]* = [SH]** (mol/dm ³)	Dielectric constants (ϵ)					
	80.37	75.60	70.00	65.00	59.50	53.75
	Rate constant (10 k) (dm ³ /mol. sec.)					
1.0	1.050	5.800	6.360	7.500	10.340	30.00
2.0	0.720	1.180	2.200	2.380	3.030	8.330
4.0	0.075	0.180	0.464	0.537	0.620	0.820
5.0	0.057	0.150	0.318	0.397	0.615	0.789
6.0	0.052	0.089	0.234	0.303	0.296	0.563
7.0	0.013	0.033	0.074	0.096	0.130	0.219
	Rate constant at zero ionic strength ($10^2 k_o$) (dm ³ /mol. sec.)					
1.0	7.320	39.100	40.800	45.700	58.700	159.900
2.0	4.330	6.730	11.700	11.800	13.600	32.800
4.0	0.365	0.851	1.910	1.980	1.990	2.190
5.0	0.255	0.620	1.180	1.310	1.740	1.800
6.0	0.215	0.338	0.788	0.900	0.740	1.120
7.0	0.051	0.117	0.227	0.260	0.291	0.382

*Concentration of disodium dibromosuccinate.

** Concentration of sodium hydroxide.

where e, N, K, T are electronic charge, Avodagro number, Boltzmanns constant and temperature respectively. The values of K_o in water-ethanol and water-methanol mixtures are also tabulated in Table 2 and 3 respectively.

The dependence of K_o on dielectric constant of the medium for single sphere and double sphere models respectively are given by the Laidler-Eyring's equations:

$$\ln k_o = \ln k_o^\infty - \frac{e^2}{4.606 \epsilon KT} \left[\frac{(Z_A + Z_B)^2}{r^\#} - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} \right] \dots \dots (3)$$

$$\ln k_o = \ln k_o^\infty - \frac{e^2}{2.303 \epsilon KT r_{AB}} \cdot Z_A Z_B \dots \dots \dots (4)$$

where K_o^∞ is the value of K_o in a hypothetical medium of infinite dielectric constant. Z_A (= -2), the valence of dibromosuccinate ion, Z_B (= -1) the valence of hydroxide ion, r_A and r_B and the radii of dibromosuccinate and hydroxide ions respectively, $r^\#$ is the radius of activated complex for single sphere model and r_{AB} (radius of the activated complex for double sphere model) is the average distance of approach between the two reacting ions i.e., dibromosuccinate and hydroxide ions.

The values of $\log K_o$ were plotted against $1/\epsilon$ at different ionic strengths and solvents. These plots were straight lines with positive slopes. The specimen graphs are shown in fig 1 and 2 respectively.

The values of radii of activated complex calculated by using the Laidler-Eyring's equations for single and double sphere activated complex are presented in Table 4.

Table 3

Rate constants data in methanol-water mixtures

[DSDBS]* = [SH]** (mol/dm ³)	Dielectric constants (ϵ)					
	80.37	77.00	73.00	68.60	64.00	59.60
	Rate constant (10 k) (dm ³ /mol. sec.)					
1.0	1.050	13.970	21.550	25.000	31.670	39.400
2.0	0.720	1.736	4.080	9.400	10.420	17.500
4.0	0.075	0.625	0.765	1.330	1.550	2.030
5.0	0.057	0.375	0.550	0.906	1.130	1.380
6.0	0.052	0.243	0.313	0.468	0.750	0.920
7.0	0.013	0.195	0.265	0.318	0.467	0.625
	Rate constant at zero ionic strength ($10^2 k_o$) (dm ³ /mol. sec.)					
1.0	7.320	95.100	142.100	158.300	191.000	224.100
2.0	4.330	10.100	22.700	49.300	51.000	79.000
4.0	0.365	2.900	3.330	5.330	5.600	6.600
5.0	0.255	1.600	2.170	3.260	3.600	3.900
6.0	0.215	0.950	1.130	1.530	2.200	2.310
7.0	0.051	0.705	0.880	0.950	1.220	1.400

*Concentration of disodium dibromosuccinate.

** Concentration of sodium hydroxide.

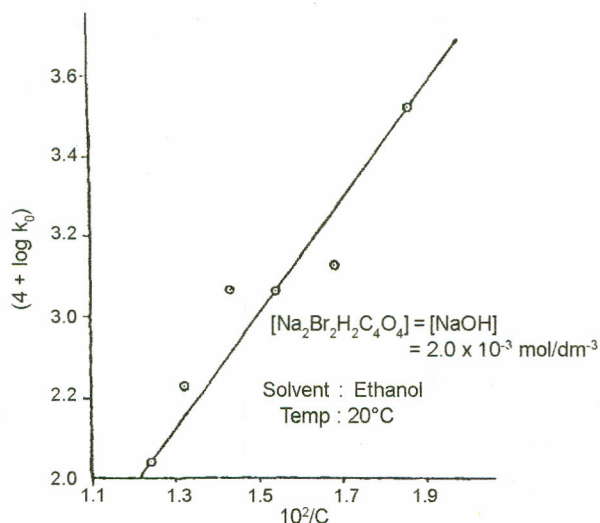


Fig 1. Plot of $\log k_0$ versus $1/s$ for water-ethanol medium.

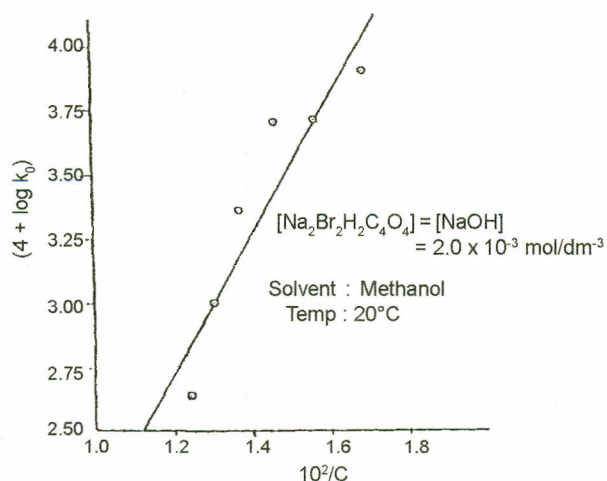


Fig 2. Plot of $\log k_0$ versus $1/s$ for water-methanol medium.

Table 4

Experimental evaluation of ionic radii of activated complex for different models

$[\text{Br}_2\text{Na}_2\text{H}_2\text{C}_4\text{O}_4] \times 10^3$ $= [\text{NaOH}] \times 10^3$ (mol./dm ³)	$r^\#$ (Å)	r_{AB} (Å)
Medium: Water-Ethanol		
1.0	3.097	3.000
2.0	3.500	4.000
4.0	3.689	4.620
5.0	3.511	4.040
6.0	3.752	4.840
7.0	3.506	4.030
Medium: Water-Methanol		
1.0	2.518	1.999
2.0	2.383	1.814
4.0	2.690	2.255
5.0	2.720	2.303
6.0	2.870	2.551
7.0	2.598	2.114

Table 5

Comparison of the values of radii of activated complex

	Theoretical values	Average experimental values (medium: ethanol)	Average experimental values (medium: ethanol)
$r^\#$ (Å)	3.816	3.509	2.630
r_{AB} (Å)	5.798	4.088	2.173

The radius of dibromosuccinate ion is theoretically calculated as follows:

$$V_{\text{Br}_2\text{H}_2\text{C}_4\text{O}_4} = 2V_{\text{Br}^-} + 2V_{\text{H}^+} + 4V_{\text{C}} + 4 + 4V_{\text{O}^{2-}} \dots (5)$$

$$\frac{4}{3}\pi r^3_{\text{Br}_2\text{H}_2\text{C}_4\text{O}_4} = 2\frac{4}{3}\pi r^3_{\text{Br}^-} + 2\frac{4}{3}\pi r^3_{\text{H}^+} + 4\frac{4}{3}\pi r^3_{\text{C}} + 4\frac{4}{3}\pi r^3_{\text{O}^{2-}} \dots (6)$$

$$r_{\text{Br}_2\text{H}_2\text{C}_4\text{O}_4} = 3.525 \text{ \AA} \dots (7)$$

Similarly the value of radius of hydroxide ion (OH^-) is calculated as 2.273 Å.

The theoretical value of the radius of activated complex for single sphere model is calculated assuming that the volume of the single sphere complex is the sum of volumes of the reactants:

$$V^\# = V_A + V_B \dots (8)$$

$$\frac{4}{3}\pi (r^\#)^3 = \frac{4}{3}\pi r_A^3 + \frac{4}{3}\pi r_B^3 \dots (9)$$

$$(r^\#)^3 = (3.525)^3 + (2.273)^3 \dots (10)$$

$$r^\# = 3.816 \text{ \AA} \dots (11)$$

where $V^\#, V_A, V_B$ are volumes of single sphere activated complex, dibromosuccinate ion and hydroxide ion respectively.

The radius of activated complex for double sphere model (r_{AB}) is calculated on the assumption that the radius of activated complex is the sum of radii of reactants:

$$r_{AB} = r_A + r_B \dots (12)$$

$$r_{AB} = 3.525 + 2.273 \dots (13)$$

$$r_{AB} = 5.798 \text{ \AA} \dots (14)$$

In all calculations, the values of the individual ions were taken from literature (Cotton and Wilkinson 1972) and also confirmed from repeated values (Bush *et al* 1978) in this literature.

A comparison of the theoretical and experimental values of $r^{\#}$ and r_{AB} for single sphere and double sphere models respectively as presented in Table 5 has indicated that the shape of the activated complex of the reaction between dibromosuccinate and hydroxide ions could best be described by single sphere model.

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