SOLVENT EFFECTS IN THE REACTION OF ETHYLOXALATE WITH HYDROXIDE IONS

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The reaction between ethyloxalate and hydroxide ions was studied in a series of ethanol-water mixtures at $25 \pm 0.1°C$ to find out the dependence of reaction rate on dielectric constant of the medium. Attempts were made to calculate the radii of activated complex for single sphere ($r^{\neq}$) and double sphere (r_{AB}) models from the linear plots of logarithm of rate constant at zero ionic strength (k_0) against reciprocal of the dielectric constant ($1/\varepsilon$), in order to find out the most probable shape of the activated complex. A comparison of the experimental values of radii ($r^{\neq}$) and (r_{AB}) respectively with the theoretical values led to the conclusion that activated complex exists as a double sphere model.

Key words: Rate constant, Dielectric constant, Activated complex.

Introduction

The kinetics of reaction between potassium ethyloxalate and sodium hydroxide was studied by Indelli [1]. Reaction was found to be second order. The stoichiometry of the reaction between ethyloxalate ions is as follows:

$$C_2H_5- OOC-COO^- + OH^- \longrightarrow (COO)_2^- + C_2H_5OH \dots (1)$$

The rate equation of this reaction is :

$$-\frac{d[OH^-]}{dt} = k\,[\,C_2H_5 - OOC-COO^-]\,[OH^-] \dots (2)$$

where k is rate constant.

Solvent effects on rate constant of ionic reactions were mathematically treated by Amis [2], Scatchard [3], Laidler Eyring [4] and Ghaziuddin *et al.* [5 - 8]. Solvent effects on the kinetics of reaction between methylorange and persulphate in presence of bromide ion were studied by Rao *et al.* [9]. The effect of dielectric constant on rate of the reaction (anion-anion) in water-alcohol mixtures was studied by Fahim Uddin *et al.* [10 - 16]. They evaluated the radii of activated complex and proposed the shape of the activated complex. No reference could as yet be found in the literature concerning the solvent effect and the shape of the activated complex formed. The present study is designed to investigate the influence of dielectric constant of the medium upon rate in order to confirm the most probable shape of the activated complex.

Experimental

Ethyloxalate, sodium hydroxide and ethyl alcohol used were from E. Merck. A mixed indicator of phenolpthalein and thymol blue was used for the determination of end point at pH 9.0. Potassium hydrogen phthalate (W. J. George Ltd.) was employed for quenching the reaction. Freshly prepared distilled water was redistilled for the preparation of stock solu-

tions [17]. The conductivity of distilled water was checked against the conductometer and was found to be 8.0×10^{-2} Ohm.m^{-1}.

Potassium ehtyl oxalate was prepared by a method described by Neilson [18]. Rate of the reaction was measured in (mol/dm³). Reaction of potassium ethyl oxalate and sodium hydroxide was carried out in a series of water-ethanol mixtures. The ionic strength in this case was varied by changing the reactant concentrations. The values of dielectric constants of water ehtanol mixtures (w/w) were evaluated from the literature [19]. Solutions of potassium ethyl oxalate and sodium hydroxide of the required concentrations were placed in a thermostatic bath (type 52 Haake Karlsch/Germany), to attain the required temperature. Reacting solutions were then mixed up. Times of mixing of the reactants were recorded. The concentration of unreacted sodium hydroxide was determined by titrating 10 ml portion of the reaction mixture at different time intervals using mixed phenolpthalein thymol indicator. The experiments were performed at constant temperature $25 \pm 0.1°C$.

Results and Discussion

Alkaline hydrolysis of ethyloxalate is a bimolecular reaction. Rate constants were calculated using the second order rate expression:

$$k = \frac{1}{t} \cdot \frac{x}{a\,(a-x)} \dots (3)$$

where 'a' is the initial concentration of both hydroxide and ethyl oxalate ions and 'x' is the amount decomposed in time 't'. The values of rate constants for the reaction between potassium ethyl oxalate and sodium hydroxide at various dielectric constants of the medium at different ionic strengths (μ) at 25°C are summarized in Table 1.

Table 1. Rate Constant at Various Dielectric Constants and Ionic Strengths.

$10^3\mu$ (mol.dm^{-3})	ε	% Ethyl alcohol (w/w)	$10^2 k$ (mol. dm^{-3})	$10^2 k_o$ (mol. dm^{-3})
$[C_2H_5C_2O_4^-] = [OH^-] = 2.9 \times 10^{-4}$ mol.dm^{-3}
0.579	78.50	0	5.60	5.30
0.579	73.00	10	5.32	5.00
0.579	67.40	20	5.26	4.90
0.579	61.20	30	5.00	4.60
0.579	56.00	40	4.94	4.50
0.579	49.00	50	4.82	4.30
$[C_2H_5C_2O_4^-] = [OH^-] = 4.7 \times 10^{-4}$ mol.dm^{-3}
0.939	78.50	0	5.48	5.10
0.939	73.00	10	5.09	4.70
0.939	67.40	20	5.03	4.60
0.939	61.20	30	4.98	4.40
0.939	56.00	40	4.84	4.30
0.939	49.00	50	4.74	4.10
$[C_2H_5C_2O_4^-] = [OH^-] = 6.5 \times 10^{-4}$ mol.dm^{-3}
1.299	78.50	0	5.30	4.90
1.299	73.00	10	5.05	4.60
1.299	67.40	20	4.89	4.40
1.299	61.20	30	4.86	4.30
1.299	56.00	40	4.75	4.10
1.299	49.00	50	4.70	4.00
$[C_2H_5C_2O_4^-] = [OH^-] = 8.3 \times 10^{-4}$ mol.dm^{-3}
1.659	78.50	0	4.62	4.20
1.659	73.00	10	4.45	4.00
1.659	67.40	20	4.39	3.90
1.659	61.20	30	4.36	3.60
1.659	56.00	40	4.20	3.60
1.659	49.00	50	4.12	3.40
$[C_2H_5C_2O_4^-] = [OH^-] = 10.1 \times 10^{-4}$ mol.dm^{-3}
1.979	78.50	0	4.10	3.70
1.979	73.00	10	4.04	3.60
1.979	67.40	20	3.99	3.50
1.979	61.20	30	3.95	3.40
1.979	56.00	40	3.92	3.33
1.979	49.00	50	3.70	3.00
$[C_2H_5C_2O_4^-] = [OH^-] = 11.9 \times 10^{-4}$ mol.dm^{-3}
2.379	78.50	0	4.00	3.60
2.379	73.00	10	3.97	3.50
2.379	67.40	20	3.92	3.40
2.379	61.20	30	3.89	3.10
2.379	56.00	40	3.86	3.00
2.379	49.00	50	3.85	2.90

The values of k_o given in the last column of Table 1 were calculated using the following expression:

$$\log k = \log k_o + \frac{e^3 (8\pi N/1000)^{1/2}}{2.303(\varepsilon KT)^{3/2}} Z_A . Z_B \sqrt{\mu} \quad ....(4)$$

where e, N, K, T and ε represent electric charge, Avogadro number, Boltzmann's constant, absolute temperature and dielectric constant respectively. Z_A and Z_B are the charges of ions A and B respectively. The results indicate that the rate constant at constant ionic strength increases as the dielectric constant of the medium is increased. This is due to the fact that there is a decrease in the electrostatic interaction between the reacting ions at higher dielectric constant.

Laidler and Eyring [4] proposed the following relations for the dependence of rate constant on dielectric constant of the medium:

$$\ln k_o = \ln k_\infty - \frac{e^2}{2\varepsilon KT} \left[\frac{(Z_A + Z_B)^2}{r^{\neq}} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right]$$
(for single sphere model)........ (5)

$$\ln k_o = \ln k_\infty - \frac{Z_A . Z_B . e^2}{KT . r_{AB}} . \frac{1}{\varepsilon}$$
(for double sphere model)....... (6)

where k_∞ is the rate constant at zero ionic strength and infinite dielectric constant, r_A and r_B are the radii of the ions A and B respectively. $Z_A = -1$, the valence of ethyloxalate ion and $Z_B = -1$, the valence of hydroxide ion. The values of logarithm of rate constant at zero ionic strength (log k_o) were plotted against the reciprocal of dielectric constant for the reaction between potassium ethyloxalate and sodium hydroxide at different ionic strengths and solvent mixtures at 25°C. Straight line plots with negative slopes are shown Fig. 1.

The values of radii of activated complex, calculated by using Laidler-Eyring's equations (5, 6) for single and double sphere activated complex are presented in Table 2.

The radius of ethyloxalate ion is calculated on the assumption that the volume of this molecule of the compound, which is supposed to be spherical, is the sum of the volumes of individual ions, constituting that ion. The value of radius of ethyloxalate is calculated as follows:

$$V_{C_2H_5C_2O_4} = 4V_{C^{+3}} + 5V_{H^{-1}} + 4V_{O^{-2}} .... (7)$$

$$\frac{4}{3}\pi r^3_{C_2H_5C_2O_4} = \frac{4}{3}.\pi 4r^3_{C^{+3}} + \frac{4}{3}\pi . 5r^3_{H^{-1}} + \frac{4}{3}\pi .4r^3_{O^{-2}} .....(8)$$

$$r^3_{C_2H_5C_2O_4} = 4 (0.772)^3 + 5 (0.30)^3 + 4(0.74)^3$$

$$r_{C_2H_5C_2O_4} = 1.532 \text{ Å} ....(9)$$

Similarly the value of radius of OH$^-$ is calculated as 0.765 Å.

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 the radii of reactants:

$$r_{AB} = r_{OH^-} + r_{C_2H_5C_2O_4^-} \quad \text{.............................. (10)}$$

$$= 0.756 + 1.532 = 2.288\text{Å} \quad \text{.......................... (11)}$$

The radius of activated complex for single sphere model ($r^{\neq}$) is calculated on the basis of assumption that the volume of single sphere activated complex is the sum of volumes of reactants, therefore:

$$V^{\neq} = V_A + V_B \text{..(12)}$$

$$\tfrac{4}{3}\pi\,(r^{\neq})^3 = \tfrac{4}{3}\pi\,(r_A)^3 + \tfrac{4}{3}\pi\,(r_B)^3 \text{...........................(13)}$$

$$r^{\neq} = 1.591\text{Å} \text{... (14)}$$

In all calculations, the values of individual ions were taken from Pauling [20] and confirmed by Coulson [21].

A comparison of the theoretical and experimental values of $r^{\neq}$ and r_{AB} for single and double sphere models shown in Table 3 leads to the conclusion that the shape of the activated complex is more similar to Laidler-Eyring's approach [4] of double sphere activated complex in this particular reaction.
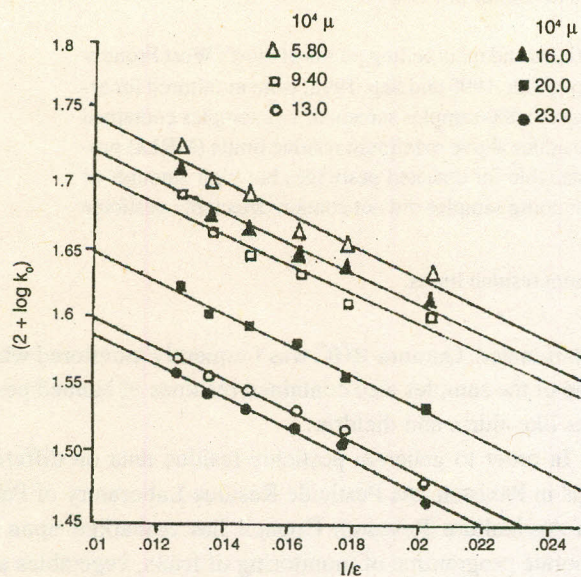

Fig. 1. Plots of log k_o vs $1/\varepsilon$ at various ionic strengths in water-ethanol media.

TABLE 2. RADII OF ACTIVATED COMPLEX.

$10^3\mu$ (mol.dm^{-3})	$r^{\neq}$ (Å)	$r^{\neq}_{AB}$ (Å)
0.579	4.08	2.06
0.939	4.16	2.08
1.299	4.26	2.13
1.659	4.39	2.19
1.979	4.52	2.26
2.379	4.80	2.40
Average	4.36	2.18

TABLE 3. A COMPARISON OF THE AVERAGE EXPERIMENTAL WITH THEORETICAL VALUES OF $r^{\neq}$ AND r_{AB}.

Name of radius	Theoretical value (Å)	Average experimental value (Å)
Radius of single sphere activated complex.	1.591	4.36
Radius of double sphere activated complex.	2.288	2.18

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