Chemistry

STUDY OF THE RATES OF REACTION BETWEEN ß-MONOBROMOPROPIONATE AND THIOSULPHATE IONS IN ISODIELECTRIC MEDIA OF AQUEOUS n-PROPANOL

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SUMMARY: The second order rate constants (k) for the reaction between ß-substituted bromopropionate and thiosulphate ions in isodielectric media of n-propanol-water mixtures have been determined from 283 to 333 K. Efforts have been made to calculate the radii of the activated complex for single sphere (r≠), and double sphere (r_{AB}) models from the linear plots of logarithm of rate constant at zero ionic strength (log k_o) against reverse of the dielectric constant (I/ε). Formation of single sphere activated complex has been discussed. Activation parameters regarding the activated complex like activation energy (E), change in enthalpy (Δ $H^{\neq}$), change in entropy (Δ $S^{\neq}$), and change in free energy of activation (Δ $G^{\neq}$) have also been evaluated

Key Words: ß-monobromopropionate, thiosulphate, n-propanol.

INTRODUCTION

The kinetics of the reaction between β-bromopropionate and thiosulphate ions was studied by LaMer *et. al.* (1). Reaction was found to be 1st order with respect to each reactant. The reaction involves the exchange of bromine by $S_2O_3^{--}$ ions as expressed below :

$$CH_2Br.CH_2COO^{--} + S_2O_3^{--} \rightarrow CH_2(S_2O_3)CH_2COO^{-} + Br^{-} ... (1)$$
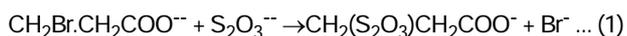
The reaction is free from side reactions, as proposed by Slator (2).

Studies of Amis and Holmes (3) reveal that when ionic reactions with same initial concentration of the reactants are carried out in isodielectric and isocomposition media, different values of the rate constants are obtained due to the different charge separating tendencies of solvents. Higher dielectric constants of media provide greater tendency for reactions to carry out. Solvent effects on the rate constant were mathematically dealt by Amis (4),

Scatchard (5) and Laidler (6). Punniah *et. al.* (7), and Rao *et. al.* (8) studied the solvent effects on the rates of reaction in aqua-organic mixtures and acetic acid mixtures respectively.

Ghaziuddin *et. al.* (9-11) and Uddin *et. al.* (12-14) studied the influence of dielectric constant on rates of ionic reactions in a series of alcohol-water or acetone-water mixtures (mixed solvents) in order to find out the most probable shape of the activated complex.

The present study is concerned with the rates of reaction between sodium ß-bromopropionate and sodium thiosulphate in isocomposition media (16.8% w/w) of n-propanol-water mixtures at different temperatures (10-60°C) in order to evaluate ionic radii of activated complex and effect of dielectric constant on activation parameters.

EXPERIMENTAL

β-bromopropionic acid (Riedel-de-Háen) was used after filtration, Potassium hydrogen phthalate was of W and J George Ltd. Sodium terterate, sodium hydroxide, sodium thiosulphate used were of E. Merck. n-propanol of

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E. Merck was used without further purification. The density of 99.5% n-propanol was 0.8 kg/liter. 16.8% w/w solution of n-propanol-water was used for experimental purposes. Freshly prepared distilled water was redistilled for the preparation of stock solutions. The conductivity of distilled water was checked against the conductometer of model Karl Kolb Cat. No. 243-690 and was found to be 0.08×10^{-6} mhos. Chloroform was used for the preservation of sodium thiosulphate (15).

The kinetic procedure involved the use of a titration method. Reaction of sodium Monobromopropionate and sodium thiosulphate was carried out in isocomposition media of n-propanol-water mixture at different temperatures such as 10°, 20°, 30°, 40°, 50° and 60°C respectively in order to study the medium effects on the rate constant and activation parameters. All experiments were conducted in electricity operated water bath type 52 Haake Kersch which maintained temperature within ±0.1°C. The ionic strength (μ) in this case was varied by changing the reactant concentrations. The values of dielectric constant of 16.8% w/w n-propanol at various temperatures were evaluated from literature (16).

RESULTS AND DISCUSSION

The reaction between β-bromopropionate and thiosulphate is found to follow second order rate law with same initial concentration of reactants:

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \qquad \text{... (2)}$$

where *'a'* is the concentration of ß-bromopropionate and thiosulphate ions, *'x'* being the concentration of product and *'t'* is the time elapsed. The concentration of the reactants were same and kept constant at various dielectric constants (e) at temperature 10°, 20°, 30°, 40°, 50° and 60°C° respectively. The reaction was studied within the range of ionic strength $0.24 \times 10^{-2} - 6 \times 10^{-2}$ mol/dm^3. The values of rate constants calculated by using expression (2) are summarized in Table 1.

The values of rate constants at zero ionic strength (k_O) calculated from the following equations are also tabulated in Table 1.

$$\log k = \log k_0 + \frac{e^3 (8\pi N/1000)^{1/2}}{(\varepsilon KT)^{3/2} \times 2.303} \cdot Z_A Z_B \cdot \sqrt{\mu} \quad \text{.......(3)}$$

where e, N, K, T, Z_A, Z_B represent electronic charge, Avogadro number, Boltzmann constant, temperature and charge of the ions A and B respectively. The results show that the rate constant increases with decreasing the dielectric constant of the media. This is due to the fact that the activity of reactants increases at higher temperature at lower dielectric constant. The effect of ionic strength on the rate constant of the reaction in 16.8% aqueous n-propanol shows an inverse relation. The reaction at low ionic strength show higher values of rate constants because of the effect of structure by ionic orientation (1).

The following equations were used to study the influence of dielectric constant on rate constant:

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

(4) *(for single sphere model)*

$$\ln k_0 = \ln k_\infty - \frac{e^2 \cdot Z_A Z_B}{\varepsilon KT r_{AB}} \qquad \text{..........................(5)}$$
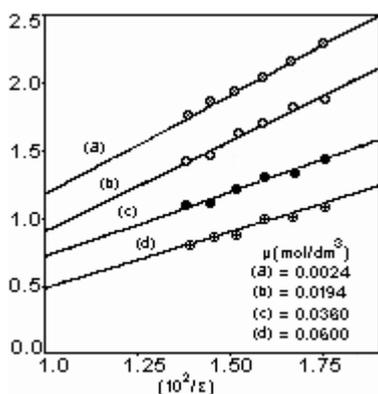
(for double sphere model)

where k_∞ is the rate constant at zero ionic strength and infinite dielectric constant, r_A, r_B represent radius of bromopropionate and thiosulphate ions respectively.

The plots of *log k_O* versus inverse of dielectric constant (1/ε) were drawn. These plots are straight lines with positive slopes. A specimen graph is shown in Figure 1. The slopes indicate that the activated complex is more solvated than the reactants and there is an increase in the electrostatic interaction between the reacting ions at lower dielectric constant. The values of the slopes were used to calculate the radii of single sphere activated complex ($r^{\neq}$) and radii of double sphere activated complex (r_{AB}). The values of $r^{\neq}$ and r_{AB} at different ionic strengths are given in Table 2. Average experimental values of $r^{\neq}$ and r_{AB} are found to be 3.78°A and 4.315°A respectively.

The radii of β-bromopropionate and thiosulphate are calculated as follows:

$$V_{CH_2Br.CH_2COO^-} = 3V_C + 4 + V_{Br} - 1 + 4V_H + 2V_2 - 2$$

(6)

Figure 1: Plots of log k_O against $1/\varepsilon$ at various strengths in n-propanol-water mixture.

since volume $V = \dfrac{4}{3}\pi r^3$

$$\therefore \frac{4}{3}\pi r^3_{CH_2Br.CH_2COO^-} = 3.\frac{4}{3}\pi r^3_C + 4 + \frac{4}{3}\pi r^3_{Br^{-1}} + .$$

$$+ 4.\frac{4}{3}\pi r^3_H + 2.\frac{4}{3}\pi r^3_0 - 2 \qquad\qquad ....(7)$$

substituting the numerical values of radii of ions C^{+4}, Br^{-1}, H^+, O^{-2} taken from Emeleus (17) and Wilson (18) as 0.15A°, 1.95A°, 2.08A°, 1.4A° in equation No. (7), radius of bromopropionate ion was found to be 3.6565°A. Similarly radius of $S_2O_3^{--}$ is calculated and was found to be 2.437A°.

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, i.e.,

$$r_{AB} = r_{CH_2Br.CH_2COO^{--}} + r_{S_2O_3^{-2}} = 6.0935\,A°$$

(8)

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

$$\left(r^{\neq}\right)^3 = r^3_{CH_2Br.CH_2COO^-} + r^3_{S_2O_3^-}$$

$$............(9)$$

$$r^{\neq} = 3.9865\,A°$$

A comparison of the average experimental values of single sphere activated complex ($r^{\neq}$) and double sphere

activated complex (r_{AB}) with the theoretical values it is concluded that Laidler and Eyring's approach (6) of single sphere model holds more closely than the double sphere model proposed by Amis (4) and Scatchard (5).

Rate measurements data tabulated in Table 1 was used to evaluate the activation parameters as a function of ionic strength of the medium. Plots of *log k* against reciprocal of the absolute temperature were drawn and shown in Figure 2. From the Arshenius relation, the values of energy of activation (E_a) were evaluated and tabulated in Table 3. It was observed that energy of activation is related to the ionic strength of the reaction mixture. Results show that

Table 1: Rate measurements data at various temperatures.

Temp.°C	Dielectric Constant	rate constants $k \times 10^2$	(4+ log k_0)
(ε) (dm³.mol⁻¹.s⁻¹) $\mu = 0.24 \times 10^{-2}$ mol dm⁻³			
10	71.6	0.69	1.72
20	68.6	0.90	1.83
30	65.3	1.02	1.88
40	62.2	1.26	1.97
50	59.3	1.56	2.06
60	56.4	2.39	2.14
$\mu = 1.92 \times 10^{-2}$ mol dm⁻³			
10	71.6	0.56	1.40
20	68.6	0.65	1.46
30	65.3	0.95	1.61
40	62.2	1.10	1.67
50	59.3	1.45	1.78
60	56.4	1.79	1.94
$\mu = 3.6 \times 10^{-2}$ mol dm⁻³ $k \times 10^3$ (dm³.mol⁻¹.s⁻¹)			
10	71.6	3.63	1.07
20	68.6	3.89	1.10
30	65.3	4.89	1.18
40	62.2	6.02	1.27
50	59.3	6.79	1.31
60	56.4	11.42	1.40
$\mu = 6.0 \times 10^{-2}$ mol dm⁻³ $k \times 10^3$ (dm³.mol⁻¹.s⁻¹)			
10	71.6	2.39	0.76
20	68.6	2.95	0.84
30	65.3	3.58	0.90
40	62.2	4.38	0.98
50	59.3	5.30	1.05
60	56.4	6.52	1.16

Figure 2: Arrhenius plots (*log k vs 1/T*) at various ionic strengths in
n-propanol-water mixture.
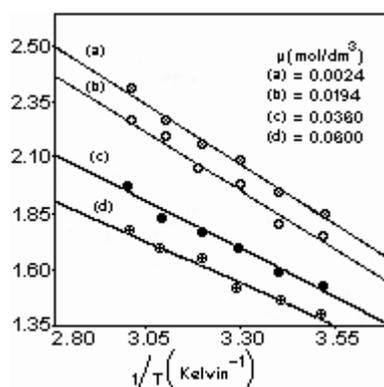
energy of activation decreased with an increase in the ionic strength in isocomposition of solvent. This is due to the fact that at low ionic strength, the reactant is more solvated than the activated complex (19) and there is less electrostatic interaction between ions.

Table 2: Experimental values of r_{AB} (A°) and $r^{\neq}$ (A°)

$\mu \times 10^2$ (mol/dm^3)	r_{AB} (A°)	$r^{\neq}$ (A°)
0.24	3.79	3.60
1.94	3.89	3.64
3.60	4.39	3.82
6.00	5.17	4.05

The values of change in entropy ($\Delta H^{\neq}$), change in free energy ($\Delta G^{\neq}$) and change in entropy of activation ($\Delta S^{\neq}$) were calculated from usual relations as a function of ionic strength and summarized in Table 3. Plots of E_a vs $\sqrt{\mu}$, $\Delta H^{\neq}$ vs $\sqrt{\mu}$ $\Delta G^{\neq}$ vs v $\sqrt{\mu}$ and $\Delta S^{\neq}$ vs $\sqrt{\mu}$ show that linear relationship exists between activation parameters and ionic

Table 3: Activation parameters in n-propanol-water mixture.

$\mu \times 10^2$ (mol/dm^3)	E_a (K Cal/mol)	$\Delta H^{\neq}$ (K Cal/mol)	$\Delta S^{\neq}$ (K Cal/mol)	$\Delta G^{\neq}$ (K Cal/mol)
0.24	4.1194	3.5293	-6.0104	5.3204
1.94	4.0752	3.4852	-6.1877	5.3291
3.60	3.5207	2.9306	-6.5822	4.8922
6.00	3.0702	2.4801	-6.8973	4.5355

strength. The trend of the values of activation parameters as a function of ionic strength in aqueous solutions (20) and mixed solvents are similar. The negative entropy change of activation can be explained due to preferential solvation of the activated complex by the solvent n-propanol as was observed by Grunwald *et. al.* (21). The activated complex more solvated than reactants restricts the motion of activated complex.

REFERENCES

1. LaMer VK, Kamner ME : J Am Chem Soc, 53:2833, 1931.

2. Slator A : J Chem Soc, 87:485, 1905.

3. Amis ES and Holmes FC : J Am Chem Soc, 63:2231, 1941.

4. Amis ES : J Chem Educ, 29:337, 1952.

5. Scatchard G : Chem Rev, 10:229, 1932.

6. Laidler KJ and Eyring H : Ann NY Acad Sci, 39:303, 1940.

7. Punniah G, Sundaram ES : Ind J Chem, 11:395, 1973.

8. Rao PVS, Ramakrishna, Saradamba GV : J Ind Chem Soc, LXV:329, 1988.

9. Ahmed MG, Khan QA, Uddin F : Pak J Sci Ind Res, 21:155, 1978.

10. Ahmed MG, Uddin F : Phillipine J Sci, 109:79, 1980.

11. Ahmed MG, Uddin F : Nig J Sci Tech, 1:81, 1985.

12. Uddin F, Khalid Z : J Phys Chem, 5:101, 1986.

13. Uddin F, Hussain I : Pak J Sci Ind Res, 30:93, 1987.

14. Uddin F, Waqar D, Khalid Z : J Nat Sci Maths, 27:141, 1987.

15. Vogel AI : Text Book of Quantitative Inorganic Analysis, Longman Green, New York, 3rd Ed, 1961.

16. Akerlöf G : J Am Chem Soc, 54:4130, 1932.

17. Emeleus HJ and Anderson JS : Modern Aspects of Inorganic Chemistry, Eng Lang Book Soc, London, 1961.

18. Wilson JG and Newall AB : General and Inorganic Chemistry, Cambridge University Press, UK, 1966.

19. Glasstone S, Laidler KJ, Eyring H : Theory of rate processes, McGraw Hills Book Company, NY, 1941.

20. Khalid Z : M Phil thesis, University of Karachi, 1990.

21. Grunwald E, Bauguman G, Kohnstan G : J Am Chem Soc, 82:5801, 1960.

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