

KINETIC STUDY OF THE SALT EFFECTS ON THE RATE OF REACTION BETWEEN MONOCHLORO ACETATE AND THIOSULPHATE IONS

Fahim Uddin*, Hajira Tahir and Abida Khatoon

Department of Chemistry, University of Karachi, Karachi-75270, Pakistan

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A bimolecular reaction was studied between monochloroacetate and sodium thiosulphate ions in the presence of magnesium chloride. The temperature dependence of rate constant was evaluated at 40-70 °C. The values of activation energy (E) and activation parameters such as change in enthalpy of activation (ΔH^\ddagger), change in entropy of activation (ΔS^\ddagger), and change in free energy of activation (ΔG^\ddagger) were estimated as a function of ionic strength (μ) of the medium.

Keyword: Bimolecular reaction, Activation parameters, Salt effect, Ionic strength.

Introduction

The reaction of sodium thiosulphate with sodium chloroacetate shows a second order reaction kinetics, with the same initial concentration of reactants as reported by (Slator 1905). This is expressed by following ionic reaction:



The rate equation can be written as:

$$-d[\text{S}_2\text{O}_3^{2-}]/dt = k [\text{S}_2\text{O}_3^{2-}] [\text{CH}_2\text{ClCOO}^-] \dots \dots \dots (2)$$

where k is rate constant of the reaction. From the evaluation of rate constants it was concluded that the rate of reaction is influenced by a number of factors including ionic strength of the medium, charge and size of the cations and anions of the added electrolytes, concentration and temperature of the reacting species (Giacomelli and Indeli 1968; Ferrant and Indeli 1977; Uddin and Ahmad 1980; Uddin and Hussain 1985; Uddin *et al* 1986 and 1989) An equation for the reaction rate in terms of the ionic charges and the ionic strength of the medium at 25°C was given by (Laidler 1987).

$$\log k = \log k_0 + 1.02 \cdot Z_A Z_B \mu^{1/2} \dots \dots \dots (3)$$

where k_0 is the rate constant at zero ionic strength, Z_A and Z_B are the charges of the ions A and B.

(Scatchard 1939) assumed a definite model of a activated complex in an ionic reaction using the following equation for the rate constant of the reaction:

$$\ln k = \ln k_0 \cdot \left\{ e^3 (8\pi N_A / 1000)^{1/2} / (\epsilon K_B T)^{3/2} \right\} \cdot Z_A Z_B \mu^{1/2} \dots \dots \dots (4)$$

where e , N_A , ϵ , K_B , and T are electronic charge, Avogadro number, dielectric constant of the medium, Boltzmann's constant and temperature respectively.

The Activation energy of the reaction was estimated using the Arrhenius equation (Uddin *et al*, 2001).

$$\log k = \log A - E / 2.303 RT \dots \dots \dots (5)$$

where A is frequency factor, R is gas constant.

The relationship between energy of activation and ionic

strength is given by (Ahmed *et al* 1979):

$$E = -2.303 R d \log k / d (1/T) - \{ 3e^2 R (8\pi N_A / 1000)^{1/2} / 2 (\epsilon K_B T)^{3/2} T \} Z_A Z_B \mu^{1/2} \dots \dots \dots (6)$$

The salt effect on the rate of reaction between monochloroacetate and thiosulphate reaction was studied in presence of uni-univalent salt earlier (Ahmed *et al* 1979, Uddinand Shahid 1996; Uddin *et al* 2001), but no reference could be found out in presence of bivalent-univalent ions. Therefore, in the present work, the influence of ionic strength of the medium on the rate constant and activation energy of bimolecular reaction in the presence of magnesium chloride was studied. Activation parameters such as change in enthalpy of activation (ΔH^\ddagger), change in entropy of activation (ΔS^\ddagger), and change in free energy of activation (ΔG^\ddagger), were also estimated as a function of ionic strength of the medium.

Experimental

All chemicals are reagents used were of analytical grades. Stock solutions were prepared in double distilled water. Calculated volumes of stock solution of sodium chloroacetate and sodium thiosulphate were pipetted out separately in a flask and kept in thermostatic water bath (type 52 Haak

Table -1

Rate constant measurements for the reaction between monochloroacetate and sodium thiosulphate ions

Ionic strength $10^3 \mu$ (mol. dm ⁻³)	Rate constants $10^2 k$ (mol ⁻¹ dm ³ s ⁻¹)				
	Temperature °C				
	40°C	50°C	60°C	70°C	
1.92	In absence of Mg Cl ₂				
	0.85	1.10	1.42	1.85	
3.25	In presence of Mg Cl ₂				
	0.87	1.16	1.57	2.00	
	4.58	0.88	1.22	1.66	2.14
	7.23	0.90	1.25	1.80	2.16
	9.90	1.00	1.33	1.83	2.40
Zero	0.75	0.98	1.20	1.40	

*Author for correspondence

Table 2
Activation parameters of the reaction between monochloroacetate and sodium thiosulphate ions

Ionic Strength $10^3 \mu$ (mol. dm ⁻³)	E kJ mol ⁻¹	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger Jk mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹
In absence of Mg Cl ₂				
1.92	24.02	21.54	-91.74	53.23
In presence of Mg Cl ₂				
3.25	23.75	21.27	-91.80	51.30
4.58	23.27	20.80	-104.29	48.92
7.23	22.17	19.69	-106.08	48.60
9.90	20.32	17.84	-106.35	48.10
Zero	26.40	24.50	-70.50	57.80

Karlstuhe) for half an hour.

The change in ionic strength was brought about by the addition of calculated volume of magnesium chloride. Time was recorded when the solutions of sodium chloroacetate and sodium thiosulphate were mixed. At various time intervals reaction mixture was titrated against iodine solution using starch indicator.

For the determination of activation parameters the same procedure was performed at 40-70 °C with the step of 10±0.1°C using the same initial concentrations of reactants i.e. monochloroacetate and thiosulphate ions but different ionic strength.

Results and Discussion

The rate constants of the reaction between monochloroacetate and thiosulphate in the presence of magnesium chloride were measured at various ionic strengths and temperatures. Integrated second order rate equation of the formula: $(a-x)^{-1} = kt + a^{-1}$ was used for the calculation of rate constants, where a is the initial concentration of reactants. x is the rate amount decomposed in time t . The values of rate constant increase with the increase in ionic strength and temperature as shown in Table 1. This is in accordance with the Bronsted theory, (Bronsted and Lamer 1924).

Bronsted-Huckel equation was used to determine the values of $Z_A Z_B$. The average values of $Z_A Z_B$ were obtained from the Livingston's plots i.e. $\log k$ against $(\mu)^{1/2}$. A specimen graph is shown in Fig 1. The average value was found to be 1.857 which is closer to the theoretical value i.e. 2.00.

The values of rate constants at zero ionic strength (k_0) were obtained by extrapolation of plots of $\log k$ against $(\mu)^{1/2}$ at each temperature as summarized in Table 1.

The specimen Arrhenius plot: $\log k$ Vs. $1/T$ at ionic strength

Table 3
Temperature coefficients

Ionic strength $10^3 \mu$ (mol. dm ⁻³)	K_{50}/k_{40}	K_{60}/k_{50}	K_{70}/k_{60}	Average
In absence of Mg Cl ₂				
1.92	1.29	1.29	1.31	1.29
In presence of Mg Cl ₂				
3.25	1.33	1.35	1.27	1.32
4.58	1.38	1.36	1.29	1.34
7.23	1.37	1.44	1.20	1.33
9.90	1.33	1.37	1.31	1.33

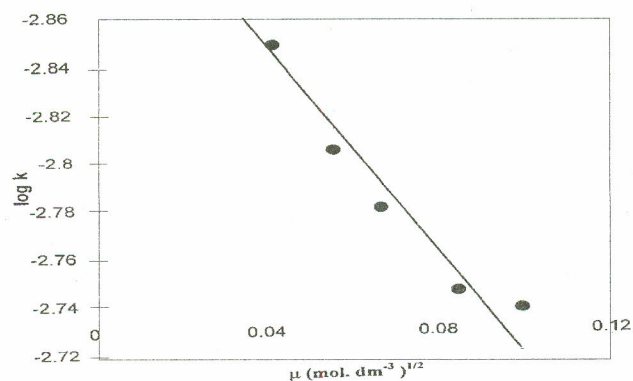


Fig 1 Plot of $\log k$ vs. $\mu^{1/2}$ at 60 °C.

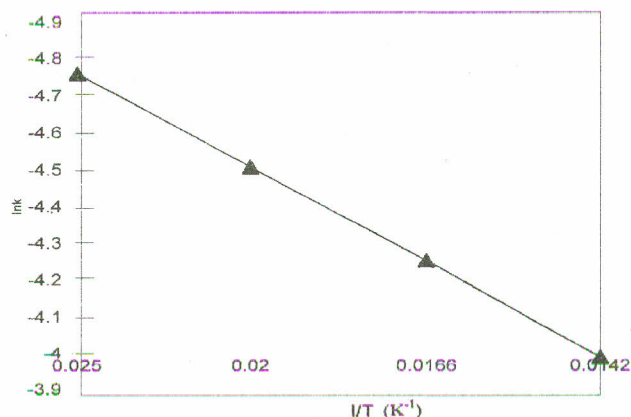


Fig 2 Plot of $\log k$ vs. $1/T$ at $\mu = 0.00192$ mol. dm⁻³.

($\mu = 0.00192$ mol. dm⁻³ is shown in Fig 2. The results from the graph show that the values of activation energy decrease with the increase in ionic strength of the medium. This may be due to decrease in effective distance between the ions and also configuration of the activated complex. This is in agreement with the result reported earlier (Uddin and Ahmed 1981).

The values of activation energy were calculated as a function of ionic strength using Arrhenius equation and summarized in Table 2 :

$$k = A \exp(-E/RT) \dots \dots \dots (7)$$

where k is the rate constant and A is frequency factor obtained from the intercept of Arrhenius plots.

The values of change in enthalpy of activation (ΔH^\ddagger) were calculated using the Eyring's transition state equation (Laidler 1987) and summarized in Table 2:

$$\Delta H^\ddagger = E - RT \dots \dots \dots (8)$$

where ΔH^\ddagger was plotted against square root of the ionic strength. A straight line was obtained.

The values of change in entropy of activation ΔS^\ddagger were calculated using the following expression:

$$A = (k_b T/h) \exp(\Delta S^\ddagger/R) \dots \dots \dots (9)$$

where h is Planck's constant and k_b is the Boltzman constant. The negative values of entropy of activation indicate the loss of entropy as a consequence of the increased charge on the activated complex with respect to the charge of the separated ions.

The decreasing trend of ΔS^\ddagger , with the increase in ionic strength is due to the fact that there exist inter conversion of some translational and rotational degree of freedom of the reactants to vibrational degree of freedom of the activated complex. At zero ionic strength, the value of ΔS^\ddagger was found to be $-70.5 \text{ J.mol}^{-1} \text{ deg}^{-1}$.

The values of change in free energy of activation ΔG^\ddagger , were calculated using the equation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \dots \dots \dots (10)$$

Table 2 shows the values of ΔG^\ddagger as a function of ionic strength in the presence of magnesium chloride. The values of ΔG^\ddagger decrease with the increase in ionic strength, indicating the formation of activated complex. At zero ionic strength the value of free energy of activation is $57.8 \text{ k J.mol}^{-1}$.

The values of temperature coefficient of rate constants per ten degree rise in temperature are summerized in Table 3. The temperature coefficients are found to independent of ionic strength. This is also in agreement with the results available in literature (Uddin and Ahmed 1981; Uddin and Shahid 1996).

Conclusion

It was found that the rate constants for a bimolecular reaction in the presence of bivalent-univalent ions also increase with the increase of ionic strength. This is in accordance with the Bronsted- Debye-Huckel theory. It was also found that the energy of activation decreased with the increase in ionic strength of the medium. This may be due to change in configuration of the activated complex and decrease in effective distance between the ions.

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