DEPENDENCE OF SPECIFIC RATE CONSTANT, ENERGY OF ACTIVATION, AND THERMODYNAMIC PARAMETERS OF THE MONOCHLOROACETATE–THIOSULFATE REACTION, ON IONIC STRENGTH OF THE MEDIUM

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الخلاصة :

أظهرت الدراسات التي أجريت على التفاعل بين آحادي كـلور خلاست الصوديوم وتيوسولفات الصوديوم بـ ٥٠° م وبتراكيز مختلفة للشوادر المتفاعلة وبفروم شاردية مختلفة (μ) بوجود كلور الصوديوم ككرليت ، إن ثابت السرعة النوعي (k) يتزايد بزيادة الفرم الشاردي رغم المحافظة على تركيز ثابت . وتتطابق العلاقة بين لوغاريتم $(\sqrt{\mu})$ مع معادلة ديباي — هيوكل — وبرونستد . وتظهر هذه النتائج ونتائج أخرى بدرجات مختلفة من الحراراة تتأرجح بين ٢٥ و٤٥° م إن الزيادة في الفرم الشاردى تؤدي إلى تقصان في طاقة النشط الظاهرية (E). ووجد أيضاً أن التغير في أنثالبية التنشيط $(\Delta H\ddagger)$ والتغير في طاقة التنشيط الحرة $(\Delta E\ddagger)$ تتناقص بزيادة الفرم الشاردي بينما يزداد تغير أنتروبية التنشيط $(\Delta S\ddagger)$.

ABSTRACT

Studies on the reaction between sodium monochloracetate and sodium thiosulfate at 50°C and at various concentrations of the reacting ions and various ionic strengths (μ), with sodium chloride as the electrolyte, showed that the specific rate constant (k) increased with the ionic strength, although the concentrations of the reacting ions were kept constant. The relation between log k and $\sqrt{\mu}$ is in conformity with the Debye–Hückel–Brønsted equation. These results and others at various temperatures between 25 and 45°C showed that an increase in the ionic strength decreased the apparent energy of activation (E). It has also been found that the change of enthalpy of activation $(\Delta H\ddagger)$ and the change of free energy of activation $(\Delta G\ddagger)$ decrease with increasing ionic strength whereas the change of entropy of activation $(\Delta S\ddagger)$ increases.

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INTRODUCTION

It has been shown by Slator [1] that sodium thiosulfate reacts with certain organic halogen compounds such as halogen-substituted acetates and that the reactions proceed with a measurable velocity. The reaction between sodium chloroacetate and sodium thiosulfate was studied by Slator [2] and found to be a bimolecular, second order displacement reaction:

$$ClCH_2COO^- + S_2O_3^{--} \longrightarrow CH_2S_2O_3COO^{--} + Cl^-$$

The variation of the specific rate constant of the reaction between any two ionic species as a function of ionic strength of the medium was studied by Brønsted [3], Christiansen [4], and Scatchard [5]. Laidler [6] has given a relationship between log k and $\sqrt{\mu}$ to describe the effect of ionic strength on the reaction rate between ions at 50°C:

$$\log k = \log k_0 + 1.075\, Z_A Z_B \cdot \sqrt{\mu} \qquad (1)$$

where k is the specific rate constant observed; k_0 that at zero ionic strength; Z_A and Z_B are the charges of ions A and B respectively; and μ is the ionic strength.

The Arrhenius equation [7] is used in order to find out the relationship between the specific rate constant and the energy of activation. The slope and intercept of the Arrhenius plot give the values of energy of activation (E) and logarithm of the frequency factor (log A).

Ghaziuddin *et al.* [8] reported the following expression for the relationship between energy of activation (E) and ionic strength:

$$E = -2.303\, R\left[\frac{\mathrm{d}\log k_0}{\mathrm{d}(1/T)}\right] - \frac{3e^3 R(8\pi N/1000)^{1/2}\cdot Z_A Z_B}{2(\varepsilon K)^{3/2}\cdot T^{1/2}}\sqrt{\mu} \qquad (2)$$

where e, N, K, and T are the electronic charge, Avagadro number, Boltzmann's constant, and absolute temperature respectively, and ε is the dielectric constant of the medium.

The change of enthalpy of activation ($\Delta H\ddagger$) and the change of free energy of activation ($\Delta G\ddagger$) are obtained using the following expressions [11, 12]:

$$\Delta H\ddagger = E_{\exp} - RT \qquad (3)$$

$$\Delta G\ddagger = \Delta H\ddagger - T\Delta S\ddagger \qquad (4)$$

where $E_{\exp}$ and R are the energy of activation (determined experimentally) and the gas constant, respectively.

Previously we have studied the effect of ionic strength on the specific rate constant, energy of activation, and change of enthalpy of activation of iodide–persulfate [8], bromide–bromate [9], and iodide–bromate [10] reactions respectively.

In the present work, the reaction between monochloroacetate and thiosulfate ions was studied in order to find out the dependence of the specific rate constant, energy of activation, and change of enthalpy of activation on the ionic strength of the medium. An attempt has also been made to determine the effect of ionic strength on the change of entropy of activation and change of free energy of activation of this reaction.

EXPERIMENTAL

Monochloroacetic acid, iodine, sodium thiosulfate, sodium hydroxide, starch, were of E. Merck, A. R. quality and were used without further purification. All solutions were prepared in triply distilled water [13]. Three drops of chloroform per liter of standard sodium thiosulfate solution were used as preservative [14].

The titrometric method was adopted for the determination of the specific rate constant of the reaction between monochloroacetate and thiosulfate ions. The measured volume of the stock solution of sodium chloride (2.0 M) was added to change the ionic strength. Calculated volumes of stock solutions of (i) sodium monochloroacetate and (ii) sodium thiosulfate were pipetted out in separate flasks and kept in a constant temperature bath (type T 52, manufactured by Haake, Karlsrühe/Germany) for about half an hour. The reactants were then mixed and the time recorded with a stop watch after half of the reactants had been transferred to the reaction mixture vessel kept in a constant temperature bath at 50 ± 0.1°C. 10 ml of the reaction mixture was pipetted out at intervals of one hour, and titrated against standard (M/200) iodine solution using 1% starch as indicator. The specific rate constants of the reaction were calculated using the integrated form of the equation for second order reactions.

For the evaluation of activation energies and some other related parameters, the same procedure was followed at different temperatures i.e. 45, 40, 35, 30, and 25°C, and at different ionic strengths provided that the concentration of the reactants were the same in each run.

Table 1. The Effect of the Total Ionic Strength on the Monochloroacetate–Thiosulfate Ions Reaction at 50 ± 0.1°C

$\sqrt{\mu} \times 10^1$ $(\text{mol dm}^{-3})^{1/2}$	$[(\log k)+6]$	$[\text{ClCH}_2\text{COO}^-] \times 10^2$ (mol dm^{-3})	$[\text{S}_2\text{O}_3^{--}] \times 10^2$ (mol dm^{-3})
1. 1.80	1.53	1.00	0.75
2.35	1.60	1.00	0.75
2.92	1.73	1.00	0.75
3.74	1.90	1.00	0.75
4.90	2.15	1.00	0.75
6.16	2.40	1.00	0.75
7.07	2.53	1.00	0.75
7.87	2.75	1.00	0.75
8.37	2.85	1.00	0.75
2. 2.40	1.62	2.00	1.25
2.74	1.70	2.00	1.25
3.16	1.80	2.00	1.25
4.00	1.95	2.00	1.25
5.10	2.20	2.00	1.25
6.32	2.44	2.00	1.25
7.21	2.58	2.00	1.25
8.12	2.80	2.00	1.25
8.94	2.93	2.00	1.25
3. 2.65	1.73	2.50	1.50
3.46	1.82	2.50	1.50
4.58	2.05	2.50	1.50
5.66	2.25	2.50	1.50
6.71	2.50	2.50	1.50
7.75	2.80	2.50	1.50
8.37	2.88	2.50	1.50
8.94	2.95	2.50	1.50
9.49	3.05	2.50	1.50
4. 2.83	1.80	2.00	2.00
4.00	1.99	2.00	2.00
4.90	2.20	2.00	2.00
6.25	2.48	2.00	2.00
7.42	2.70	2.00	2.00
8.06	2.85	2.00	2.00
8.66	2.95	2.00	2.00
9.22	3.05	2.00	2.00
9.75	3.15	2.00	2.00

RESULTS AND DISCUSSIONS

In the first series of experiments the ionic strength was varied from 0.325×10^{-1} to 9.5×10^{-1} mol dm^{-3}. The values of the square root of the ionic strength ($\sqrt{\mu}$) and the logarithm of the specific rate constant (log K) are given in Table 1 when log k was plotted against $\sqrt{\mu}$, a straight line was obtained. Extrapolation to zero ionic strength gave a value of log k_0 of -4.90, at 50°C. Livingston plots [15] (log k − log k_0) *vs* $\sqrt{\mu}$ plots were drawn at four different sets of concentration of the reactants. Out of these four sets of experiments performed at 50 ± 0.1°C, a specimen graph of one set consisting of 9 points corresponding to 9 different values of μ, is shown in Figure 1. The average value of $Z_A \cdot Z_B$ obtained from the slope is 1.97, which shows that the step involves the reaction between two ions of similar charges i.e. monochloroacetate and thiosulfate ions, as expected from Equation (1).

It is a well-known fact that alkali metal salts are highly ionized, so the concentrations of sodium chloride used in this system do not greatly effect the equilibrium $\text{Na}_2\text{S}_2\text{O}_3 \leftrightarrows \text{Na}^+ + \text{NaS}_2\text{O}_3^- \leftrightarrows 2\text{Na}^+ + \text{S}_2\text{O}_3^{2-}$. Kappana [16] found that an increase in total ionic concentration increased the specific rate constant, and this was in accordance with the Brønsted theory of reaction rate in ionic reactions. Our results also lead to the

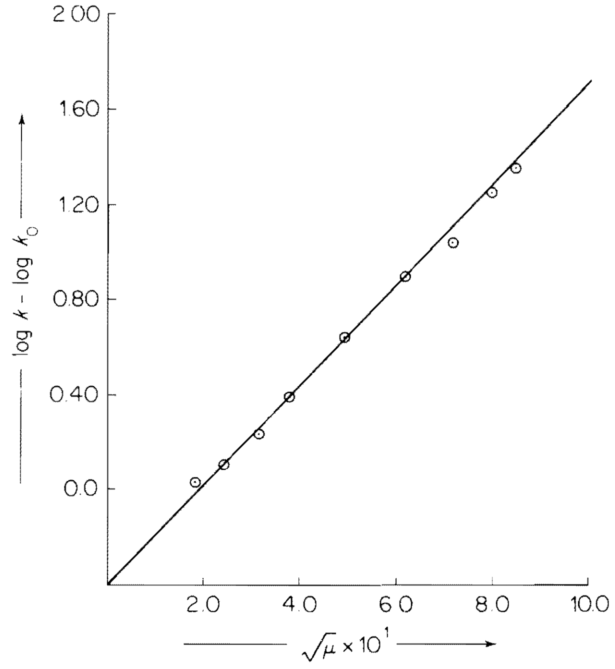

Figure 1. Dependence of Reaction Rates on Ionic Strength at 50 ± 0.1°C

conclusion that, as the ionic strength of the medium is increased, the specific rate constant increases; the experimental average value of the slope (2.12) agrees well with the theoretical value (2.15).

In the second series of experiments, the same reaction was carried out at various temperatures, in order to determine the energy of activation (E). Log k values at different temperatures and values of $\sqrt{\mu}$ are tabulated in Table 2. Values of log k_0 at different temperatures ranging from 45–25°C were also determined from the plots of log k *vs* $\sqrt{\mu}$, and also tabulated in Table 2. At 25°C, Equation (1) becomes: $\log k = -5.95 + 2.04\sqrt{\mu}$. Activation energies ($E$) were calculated from the negative slopes of the Arrhenius plots. These E values and the corresponding values of the square root of the ionic strength are summarized in Table 3.

Our results lead to the conclusion that the activation energy decreases with increasing ionic strength. The energy of activation for a particular reaction remains the same, but as in our previous reports [8, 9 and 10], energy of activation decreases with increasing ionic strength. This is due to the fact that as the ionic strength varies, the configuration of the activated complex changes, which results in a decrease of the apparent energy of activation (E). The E *vs* $\sqrt{\mu}$ plot obtained is linear with a negative slope and is in agreement with the theoretical equation. From this plot, the extrapolated value of E corresponding to zero ionic strength is 80.0 kJ mole^{-1}. The value of E reported in the literature [17] is 77.40 kJ mol^{-1}, which is in good agreement with our experimental value.

The apparent changes of enthalpy of activation ($\Delta H\ddagger$) were calculated using Equation (3). Table 3 also gives the values of apparent energy of activation (E) and apparent change of enthalpy of activation ($\Delta H\ddagger$) in the absence as well as in the presence of inert electrolyte. The $\Delta H\ddagger$ *vs* $\sqrt{\mu}$ plot obtained is a straight line having negative slope, in agreement with the theory.

Table 2. Rate Measurements at Various Temperatures

$[\mathrm{ClCH_2COO^-}] = 1.0 \times 10^{-2}$ mol dm^{-3}, $[\mathrm{S_2O_3^{--}}] = 0.75 \times 10^{-2}$ mol dm^{-3}

$\sqrt{\mu} \times 10^1$ (mol dm^{-3})$^{1/2}$	Temperature °C 45	 40	 35	 30	 25
	[(log k)+6]				
1.80	1.33	1.20	1.00	0.80	0.63
2.35	1.42	1.30	1.10	0.90	0.75
2.92	1.58	1.43	1.30	1.08	0.95
3.74	1.77	1.57	1.45	1.33	1.20
4.90	2.10	2.00	1.80	1.70	1.55
6.16	2.32	2.20	2.12	2.00	1.90
7.07	2.48	2.40	2.28	2.20	2.10
7.87	2.70	2.65	2.58	2.45	2.38
8.37	2.80	2.75	2.70	2.60	2.53
	[(log k_0)+6]				
Zero	0.90	0.73	0.53	0.30	0.05

From the intercepts of the Arrhenius plots, at different ionic strengths, log A values were determined, and thence the change of entropy of activation ($\Delta S\ddagger$) were calculated using the following expression [18]:

$$A = (KT/h) \cdot \exp(\Delta S\ddagger/R) \tag{5}$$

where h is Planck's constant. For reactions between ions of like charges, negative values of $\Delta S\ddagger$ indicate greater electrostriction when the activated complex is formed. It was observed that as the ionic strength

Table 3. Apparent Energy of Activation and Some Thermodynamic Parameters of the Reaction

$\sqrt{\mu} \times 10^1$ (mol dm^{-3})$^{1/2}$	Apparent Energy of Activation E(kJ mole^{-1})	Apparent Change of Enthalpy of Activation $\Delta H\ddagger$(kJ mole^{-1})	Apparent Change of Entropy of Activation $\Delta S\ddagger$(J mole^{-1} deg^{-1})	Apparent Change of Free Energy of Activation $\Delta G\ddagger$(kJ mole^{-1})
		In the Absence of Sodium Chloride		
1.80	68.19	65.71	−351.81	170.55
		In the Presence of Sodium Chloride		
2.35	63.19	60.71	−348.94	164.69
2.92	58.41	55.93	−344.53	158.60
3.74	53.80	51.32	−340.70	152.85
4.90	47.69	45.21	−332.47	144.29
6.16	40.53	38.05	−325.39	135.02
7.07	31.00	28.52	−320.60	124.06
7.87	27.42	24.94	−314.85	118.77
8.37	22.65	20.17	−311.99	113.14

increases, the change in entropy of activation increases. This is due to the fact that the magnitude of the frequency factor increases with a rise in ionic strength. The plot of apparent change of entropy of activation against the square root of the ionic strength obtained is linear with a positive slope and is in accordance with the theory. From $\Delta H\ddagger$ and $\Delta S\ddagger$ values, the apparent change of free energy of activation ($\Delta G\ddagger$) was calculated using expression (4). The $\Delta S\ddagger$ and $\Delta G\ddagger$ values corresponding to various values of $\sqrt{\mu}$ in the absence as well as in the presence of an inert electrolyte are also tabulated in Table 3. Studies of the dependence of $\Delta H\ddagger$, $\Delta G\ddagger$, and $\Delta S\ddagger$ on ionic strength lead to the conclusion that $\Delta H\ddagger$ and $\Delta G\ddagger$ decrease with the increase in ionic strength, whereas $\Delta S\ddagger$ increases with a rise in ionic strength of the medium. This is in accordance with the theory.

REFERENCES

[1] A. Slator, *J. Chem. Soc*, **85** (1904), p. 1286.
[2] A. Slator, *J. Chem. Soc*, **87** (1905), p. 481.
[3] J. N. Brønsted, *Z. Physik Chem.* **115** (1925), p. 337.
[4] J. A. Christiansen, *Z. Physik Chem.*, **113** (1924), p. 35.
[5] G. Scatchard, *Chem. Rev.*, **10** (1932), p. 229.
[6] K. J. Laidler, *Reaction Kinetics*, Oxford, Pergamon Press, 1963, p. 19.
[7] B. Stevens, *Chemical Kinetics*, London, Chapman and Hall, 1961, p. 41.
[8] M. Ghaziuddin Ahmed, Fahim Uddin and Jawed Akhter Jafri, *Pakistan. J. Sc. Ind. Res.*, **22** (1979), p. 128.
[9] Fahim Uddin and M. Ghaziuddin Ahmed, *Pakistan. J. Sc. Ind. Res.*, **22** (1979), p. 177.
[10] Fahim Uddin and M. Ghaziuddin Ahmed, *Pakistan. J. Sc. Ind. Res.*, **22** (1979), p. 181.
[11] K. J. Laidler, *Chemical Kinetics*, New York, McGraw-Hill, 1965, p. 90.
[12] J. L. Latham, *Elementary Reaction Kinetics*, London, Butterworths, 1962, p. 51.
[13] A. I. Vogel, *A Textbook Of Quantitative Analysis*, New York, Longmans, Green, 3rd Edition, 1961, p. 172.
[14] E. S. Amis and J. E. Potts, *J. Am. Chem. Soc.*, **63** (1941), p. 2883.
[15] R. Livingston, *J. Chem. Educ.*, **7** (1930), p. 2887.
[16] A. N. Kappana, *J. Ind. Chem. Soc.*, **5** (1928), p. 293.
[17] E. Bekier, *Roczniki*, **16** (1936), p. 64.
[18] P. W. Atkins, *Physical Chemistry*, New York, Oxford University Press, 1978, p. 913.

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