SALT EFFECTS IN THE KINETICS OF REACTION BETWEEN IODIDE AND BROMATE IONS

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A bimolecular reaction between potassium iodide and potassium bromate in presence of sodium nitrate was studied at various ionic strengths (μ) and temperatures. The results showed that the rate constants (k) increased with the increase in ionic strength of the medium. The values of energy of activation (E) and activation parameters such as change in enthalpy of activation ($\Delta H^\#$), change in entropy of activation ($\Delta S^\#$) and change in free energy of activation ($\Delta G^\#$) were evaluated as a function of ionic strength of the medium.

Key words: Salt effects, Kinetic reaction, Iodide, Bromate Ions.

Introduction

The electrolytic effect on the rates of ionic reaction was observed by (Indelli 1971). It was concluded that the rate is much influenced by size and charge of cations or anions of the added electrolyte with the concentration of the reactants and temperature.

Holmberg in 1921 studied the effect of added electrolyte such as sodium nitrate on the rates of reaction in solution, and designated this phenomenon as cation catalysis. The reduction of a bromate ion by an iodide ion is a fourth order reaction, but in the presence of excess sulphuric acid, it behaves as a pseudo second order reaction (King and Lister 1968; Taube and Dodeg 1949). Added electrolytic effects in different anion-anion reaction were studied by several workers (Uddin and Ahmed 1980; Uddin *et al.* 1996). Previously (Uddin and Ahmed 1979) studied the kinetics of reaction between potassium iodide and potassium bromate in presence of sulphuric acid to find out the effect of ionic strength of the medium on rate constant.

In the present paper, details on the kinetics of the reaction between iodide and bromate ions in presence of sodium nitrate are presented. Furthermore, it has been our object to investigate the influence of ionic strength on temperature coefficient of rate constants.

Experimental

The chemicals used for the preparation of the reaction mixtures were all analytical grade. Doubly distilled water was used.

Rates of the reactions were determined spectrophotometrically. Change in ionic strength was brought about by

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the addition of calculated volume of stock solutions of sodium nitrate. Calculated volumes of stock solutions of (i) potassium bromate (ii) potassium iodide (iii) sulphuric acid were pipetted out separately. Time was recorded when the solutions of potassium iodide and potassium bromate were mixed. After different time intervals, absorbance of the reaction mixture were recorded on UV-160 A (UV visible recording spectrophotometer Shimadzu) with cps controller at 425 nm. The molar absorption coefficient of iodine was taken as 492 cm²/mole (Uddin and Ahmed 1979). The reaction was performed at 20, 25, 30, 40 and 45°C using the same concentration of the reactants but different ionic strengths, to determine energy of activation of the reaction.

Results and Discussion

The rate constants of the reaction were determined using second order rate expression for same concentration of the reactants. The results of the experiments for the measurements of rate constants between iodide and bromate ions at different ionic strengths and temperatures in presence of sodium nitrate are summarized in Table 1. The results show that the rate constant increases with the increase in ionic strength. This is in accordance with the theory of Bronsted-Deby-Huckel equation (Debye and Huckel 1923).

The values of $\log_k$ were plotted against ($\sqrt{\mu}/1+\sqrt{\mu}$) as suggested by (Kilpatrick 1934) and shown in Fig 1. The average value of $Z_A.Z_B$ comes out to be 1.09 which is almost equal to the theoretical value as 1.00. The Livingston's plots i.e. log k/k_o versus ($\sqrt{\mu}/1+\sqrt{\mu}$) at each temperature are also shown in Fig 2. The average value of $Z_A.Z_B$ comes out to be 1.073.

The values of the rate constants at zero ionic strength (k_o) were also obtained by extrapolation of logk against

Table 1
Rate measurements for the reaction between iodide and bromate ions

$10\sqrt{\mu}$	Temperature* °C				
	20	25	30	40	45
(mol./dm³)^½	Rate constants (10^2 k.dm²/mol.s.)				
In the absence of NaNO₃					
0.277	1.1	1.6	2.7	3.0	5.0
In the presence of NaNO₃					
0.294	1.3	2.4	3.3	3.6	6.3
0.420	1.7	3.0	3.8	4.0	7.2
0.526	3.1	3.4	4.4	4.7	8.1
0.614	3.5	3.7	5.0	9.8	3.7
0.690	3.7	4.4	5.2	9.2	11.0
0.822	5.5	5.9	6.3	10.0	16.0

* [KI] = [KBrO₃] = 1.25 x 10⁻³ mol.dm⁻³, [H₂SO₄] = 2.5 x 10⁻² mol.dm⁻³

Table 2
Activation parameters of the reaction in presence of NaNO₃

Ionic strength $\sqrt{\mu}$ x 10¹ (mol.dm⁻³)	E (K.J/mol.)	$\Delta H^{\#}$ (K.J/mol.)	$\Delta S^{\#}$ (J/mol.deg.)	$\Delta G^{\#}$ (K.J/mol.)
0.277	42.00	39.52	-463.51	177.60
0.294	41.12	38.64	-464.66	177.10
0.420	36.48	34.00	-478.02	176.49
0.526	35.16	32.68	-478.17	175.54
0.614	32.04	29.56	-486.04	175.40
0.690	28.45	25.97	-501.46	175.12
0.822	26.35	23.86	-508.98	174.40
Zero	49.60	47.60	- 82.27	179.50

($\sqrt{\mu}/1+ \sqrt{\mu}$) plots at each temperature. Bronsted Kilpartrick's equation now may be represented as:

$$\log k = -2.58 + 1.01 Z_A Z_B (\sqrt{\mu}/1+ \sqrt{\mu}) \ Z_A Z_B \text{ at } 20°C \quad (1)$$
$$\log k = -2.14 + 1.02 Z_A Z_B (\sqrt{\mu}/1+ \sqrt{\mu}) \ Z_A Z_B \text{ at } 25°C \quad (2)$$
$$\log k = -1.98 + 1.03 Z_A Z_B (\sqrt{\mu}/1+ \sqrt{\mu}) \ Z_A Z_B \text{ at } 30°C \quad (3)$$
$$\log k = -1.85 + 1.05 Z_A Z_B (\sqrt{\mu}/1+ \sqrt{\mu}) \ Z_A Z_B \text{ at } 40°C \quad (4)$$
$$\log k = -1.67 + 1.055 Z_A Z_B (\sqrt{\mu}/1+ \sqrt{\mu}) \ Z_A Z_B \text{ at } 45°C \quad (5)$$

The values of apparent energy of activation were calculated using Arrhenius equation (Atkins 1998):

$$K = A. \exp (-E/RT) \quad (6)$$

Where A is Arrhenius factor, constant for a particular reaction. The Arrhenius plots i.e. $\log_k$ versus 1/T were drawn. A specimen graph at $\mu = 0.477$ mol. dm⁻³ is shown in Fig 3. The

Table 3
Temperature coefficients of rate constants

Ionic strength μ x 10¹ (mol.dm⁻³)	$\dfrac{K_{25}}{K_{20}}$	$\dfrac{K_{30}}{K_{25}}$	$\dfrac{K_{40}}{K_{30}}$	$\dfrac{K_{45}}{K_{40}}$	Average values
0.77	1.45	1.67	1.11	1.66	2.94
0.87	1.84	1.37	1.09	1.75	1.51
1.77	1.76	1.26	1.05	1.80	1.47
2.77	1.09	1.29	1.06	1.72	1.29
3.77	1.05	1.35	1.10	1.78	1.32
4.77	1.18	1.18	1.76	1.19	1.32
6.77	1.07	1.06	1.58	1.60	1.32

values of E as a function of ionic strength were tabulated in Table 2. Results show that energy of activation is dependent upon the ionic strength of reaction mixture. It was observed that energy of activation decreased with the increase in ionic strength, due to decrease of effective distance between the ions for the reaction.

The values of energy of activation were plotted against square root of the ionic strength. Plot shown in Fig 4 is linear with negative slope. From this plot the exptrapolated value of energy of activation (E) corresponding to zero ionic strength is 49.61 KJ/mol.

The values of change in enthalpy of activation ($\Delta H^{\#}$) were calculated by using the formula.

$$\Delta H^{\#s} = E - RT \quad (7)$$

and summarized in Table 2. A straight line was obtained when $\Delta H^{\#}$ is plotted against $(\mu)^{½}$ as shown in Fig 5. The values of change in enthalpy of activation at zero ionic strength is 47.60 KJ/mol.

The values of change of entropy of activation were calculated by using the following expression.

$$A= \frac{KT}{h} \exp (\Delta S^{\#}/R)$$

and where K is Boltzmann's constant, h is Planck's constant, where A is frequency factor which is obtained from the intercept of Arrhenius plots. $\Delta S^{\#}$ is the change in entropy of activation while other symbols have their usual meanings.$\Delta S^{\#}$ values are also tabulated in Table 2. The values of change in entropy of activation are negative which indicate a loss of entropy as a charge increased on activation complex. It was observed that as the ionic strength increased, the $\Delta S^{\#}$ decreased. This is due to the fact that the magnitude of frequency factor decreased with rise in ionic strength. The plot between $\Delta S^{\#}$ vs. $\sqrt{\mu}$ is shown is Fig 6. strength the value of change of entropy of activation is-82.27 J/mol. deg.
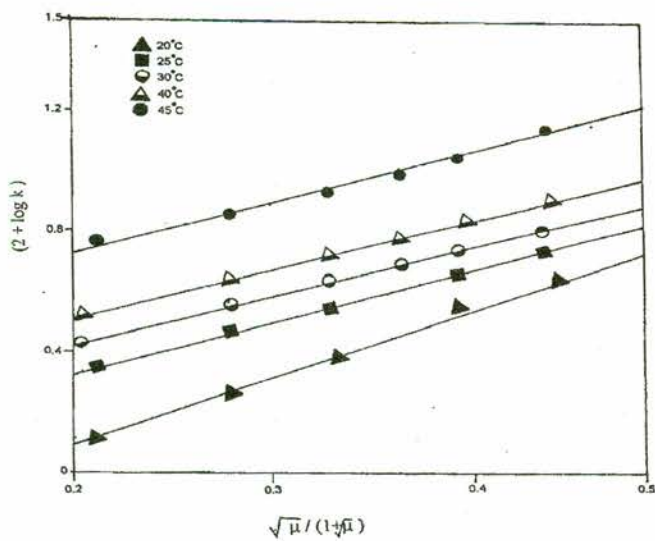
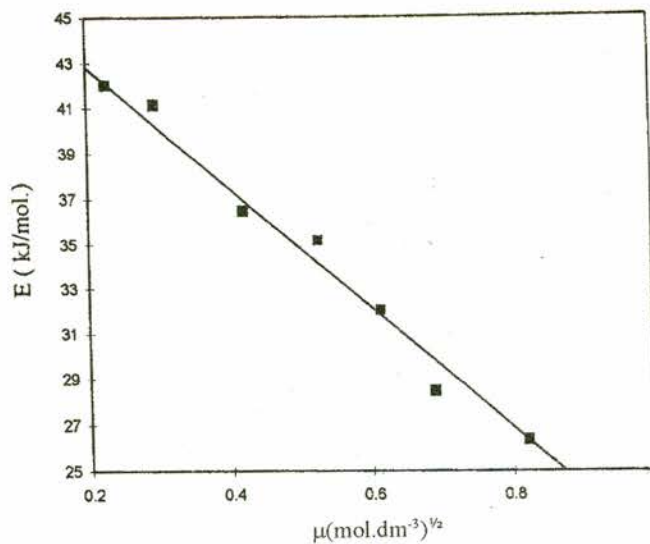**Fig 1.** Plots of log k versus $(\sqrt{\mu}/1+\sqrt{\mu})$
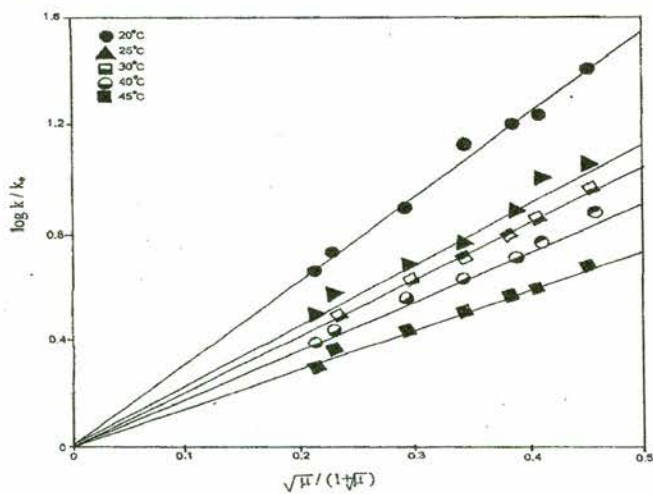

Fig 2. Plots of log k/k$_o$ versus $(\sqrt{\mu}/1+\sqrt{\mu})$

Fig 3. Plot of log k versus 1/T.

Fig 4. Plots of E versus $\sqrt{\mu}$
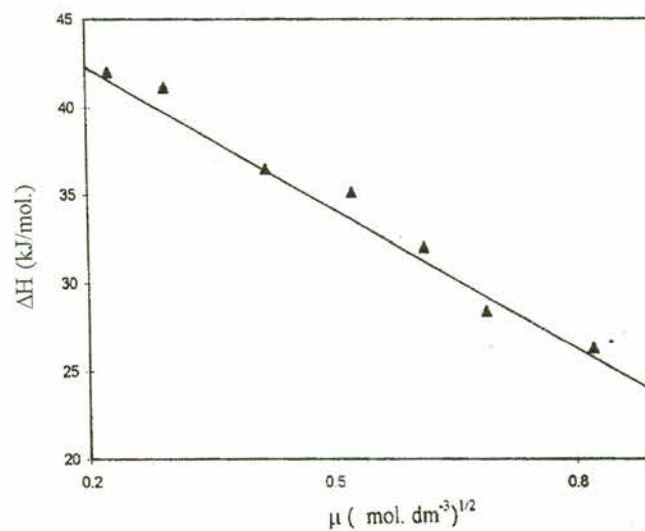
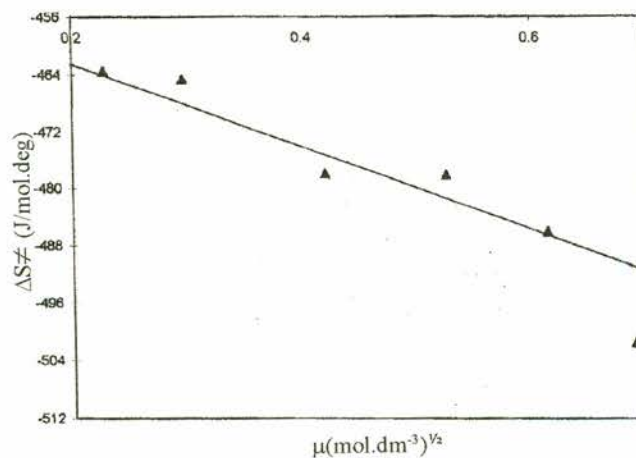**Fig 5.** Plots of $\Delta H^{\#}$ versus $\sqrt{\mu}$
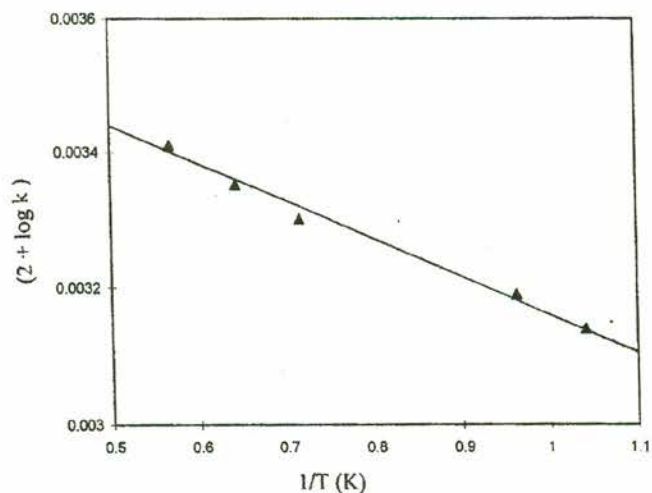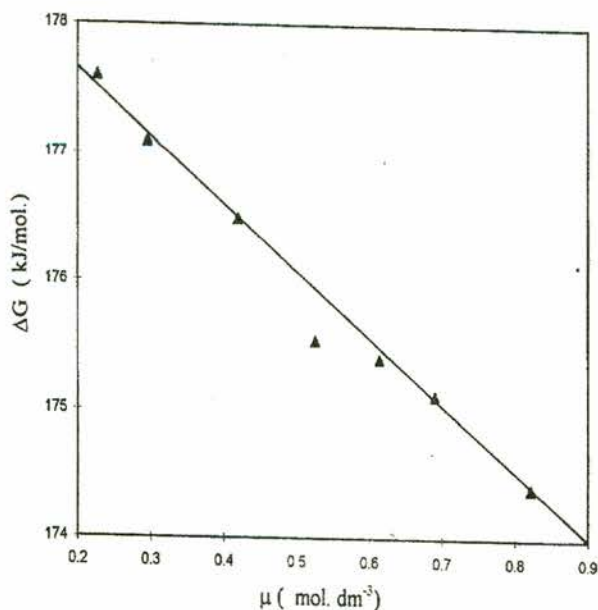

Fig 6. Plots of $\Delta S^{\#}$ versus $\sqrt{\mu}$

Fig 7. Plots of $\Delta G^{\#}$ versus $\sqrt{\mu}$

The values of change in free energy of activation ($\Delta G^{\#}$)were also calculated by using the formula.

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S \qquad (9)$$

and summarized in Table 2. The plot between $\Delta G^{\#}$ vs. $\sqrt{\mu}$ is shown in Fig 7. It was found that as the ionic strength increases, the values of $\Delta G^{\#}$ decreases. The change in free energy of activation for a particular reaction remains the same, but due to the variation in ionic stength, the configuration of the activated state changes and results in the decrease of free energy change of activation in the present work. At zero ionic strength, the value of change of free energy of activation is 179.50 KJ/mol.

The values of temperature coefficient of rate constants per five degree and ten degree rise in temperature are tabulated in Table 3. The average value of temperature coefficient in presence of Na NO$_3$ are found to be 1.59 per five degree rise in temperature. Our results are in agreement with the results of (Uddin *et al* 1986) for the reaction between monochloroacetate and thiosulphate ions.

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