

# The Influence of Dielectric Constant Variations on the Kinetics of Reaction Between Bromate and Tellurite Ions in Aqueous Ethanol Mixed Solvents

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(Received 31st September, 1989, revised 30th January, 1990)

**Summary:** The rate of the reaction between potassium bromate and potassium tellurite decreases with an increase in the mole fraction of ethanol in aqueous ethanol mixtures at 308 K. A comparison of the experimental and theoretical values of the radius of the activated complex indicates that a double sphere model is the most suitable shape for the activated state formed in the reaction. Electrostatic and non-electrostatic contributions to the changes in free energy of activation and entropy values are 14.06 kJ/mole, 95.57 kJ/mole and -54.19 J/K/mole in 0.153 mole fraction of ethanol in water. The activation parameters correlates well with the dielectric constants of the media.

## Introduction

According to electron transfer theory, changes in dielectric properties are expected to affect the reorganisation of a solvent molecule around the reactant and the activated complex. The water alcohol mixtures exhibit pronounced structural and dielectric changes at different composition ratios. In the previous paper [1] the effect of dielectric changes on the kinetics of the reaction between iodate and bromide ions was evaluated. In the present study the effect of the addition of ethanol to aqueous solution on the kinetics of the reaction between bromate and tellurite ions is presented.

The reaction is found to be a second order reaction, according to the equation,



Hence, the rate equation can be written as,

$$k = 1/t \times a/(a-x)$$

where,  $\text{BrO}_3^- = \text{TeO}_3^{2-}$  and

$a$  = initial concentration of reactants

$x$  = concentration of tellurite ion after time

't'.

## Experimental

The reactions were carried out in a thermostatic bath at 308K and  $313 \pm 0.1\text{K}$ . The kinetics were followed by quenching the reaction mixture with known quantities of iodine (10 ml) followed by the addition of an excess of potassium iodide solution and estimating the excess iodine spectrophotometrically at 350 n.m. The molar absorptivity and

maximum absorption wavelength of iodine in water and water-ethanol mixtures were predetermined with reference to standard solutions. Methods used in the literature were used to standardize the iodine solutions [2]. Independent experiments showed that the "Beer's Law" is obeyed in water-alcohol mixed solvents. The reaction was also followed by measuring the concentration of total iodine in the aqueous solution by iodometry. Both methods gave the same rate constant. When the mixtures of iodine and potassium iodide in mixed solvents were left standing for 24 hours, the absorbance of the solutions changed slightly (below 5%). The change was neglected, as the absorption measurements were taken within half and hour of each experimental run. Irradiation of light of 350 n.m. had no effect on the reaction rate. A Pye-Unicam spectrophotometer SP 8000 with matched quartz cells was used for absorption measurements.

Sodium sulphate was used to maintain a constant ionic strength. The reaction was carried out at different ionic strengths and the rate constant values were extrapolated to zero ionic strength.

The ethanol concentrations used in the reaction media were 1.2, 4.4, 7.2, 9.6, 11.2 and 15.3 mole percent.

The reagents used were potassium bromate, potassium tellurite, iodine, potassium iodide, sodium sulphate of analaR grade, and absolute ethyl alcohol from Merck.

### Theory

The effect of dielectric constant ( $\epsilon$ ) on the specific rate constant ( $k\epsilon$ ) for ion-ion and dipole-dipole interactions [3-6] is given by the following expressions:

$$\ln.k\epsilon = \ln.k_0 - Z_a Z_b e^2 / 2.303KT.R_{ab}.1/\epsilon \quad (1)$$

$$\ln.k\epsilon = \ln.k_0 - 1/KT.(\epsilon - 1)/(2\epsilon + 1) \quad (2)$$

where,  $k_0$  is the specific rate constant at zero ionic strength and at infinite dielectric constant,  $Z$  is the valence of ions and  $a$  and  $b$ ,  $K$ ,  $T$ , and  $e$  are Boltzmann's constants, temperature and the charge on electron respectively.  $R_{ab}$  is the radius of the activated complex.

Equation (1) predicts that at a constant temperature the logarithm of the rate constant is inversely proportional to the dielectric constant of the medium and that the slope of the line is proportional to the size of the activated complex.

For dipole-dipole interactions, equation 2, predicts a linear relationship between the logarithm of the rate constant and  $\epsilon - 1/2\epsilon + 1$ .

Free energy of activation was calculated by using the expression,

$$KG_{tot} = RT (\ln KT/h - \ln K\epsilon)$$

Where:  $K$ , is the Boltzmann's constant;  $h$ , is Plank constant  $T$ , is the absolute temperature;  $R$ , is the Gas constant and  $k\epsilon$  is the rate constant at a given dielectric constant of the medium.

The free energy contribution due to electrostatic interactions ( $\Delta G_{e.s}$ ) was calculated by using the quation

$$\Delta G_{e.s} = N.Z_a Z_b e^2 / \epsilon R_{ab}$$

Where:  $N$ , is the Avagadro's number,  $Z_a$  and  $Z_b$  are the charges on ions,  $a$  &  $b$ ;  $e$  is the electrostatic charge;  $\epsilon$ , is the dielectric constant; and  $R_{ab}$  is the radius of the activated complex.

The free energy contribution, due to non-electrostatic attractions  $\Delta G_0$  was evaluated from the relationship;

$$\Delta G_{tot} = \Delta G_0 + \Delta G_{e.s}$$

The free entropy of activation was calculated by using the expression:

$$\Delta S_{e.s} = \Delta G_{e.s} \cdot d \ln \epsilon / dT.$$

A constant value -0.0043 was taken [7] for  $d \ln \epsilon / dT$ . The values for standard enthalpy  $\Delta H^\circ$  and entropy  $\Delta S^\circ$  were deduced by using the expressions [8].

$$\Delta S^\# = \Delta S^\circ + \int 1/\epsilon$$

$$\Delta H^\# = \Delta H^\circ - \int 1/\epsilon$$

### Results and Discussion

Table-1 provides the data for the rate constants at two different temperatures at various dielectric constant values of aqueous- ethanol mixtures. Table 2 presents the data for the activation parameters of the reaction at various concentrations of ethanol in the reaction mixtures. Fig. 1 and 2 depict the variations of the logarithm of the rate constant with  $1/\epsilon$  and  $\epsilon - 1/2\epsilon + 1$  respectively. The entropy changes with solvent polarity in relation to  $\epsilon - 1/2\epsilon + 1$  is shown in Fig. 3. Fig. 4, represent the compensation relationship between  $\Delta H^\# + \Delta H^\circ$  and  $\Delta S^\# + \Delta S^\circ$ .

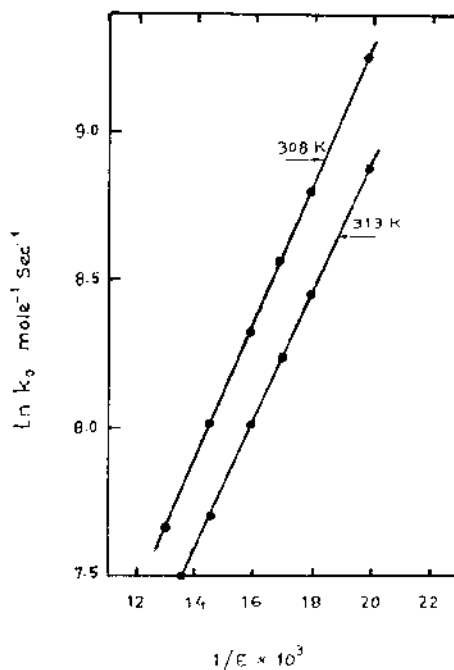


Fig.1: Linear relationship between the logarithm of rate constant and the reciprocal of dielectric constant.

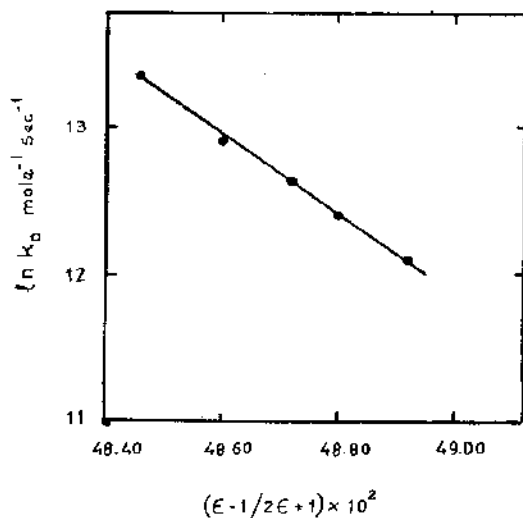


Fig.2: Linear relationship between the logarithm of rate constant and  $E-1/2E+1$ .

Table 1: Rate constant values at various dielectric constants

dielectric constant	Rate Constant <sup>(a)</sup> $k \times 10^{-6}$ $\text{mole}^{-1}\text{Sec}^{-1}$	$k \times 10^{-6}$ $\text{mole}^{-1}\text{Sec}^{-1}$
15)	306 K	313 K
13.0	7.8	9.2
14.5	5.4	7.5
16.0	4.05	4.5
17.1	3.19	4.3
18.0	2.5	3.5
20.0	1.6	2.5

(a); Average of three readings  
m; Ionic strength.

It is evident from Table 1 that the rate of reaction between bromate tellurite ions decreases with the progressive addition of ethanol to the aqueous solutions. The decrease in the rate constant in mixed solvents can be ascribed to the formation of an activated complex more polar ( $\text{BrO}_3^- \cdots \text{TeO}_3^{2-}$ ) than the reactants and is in agreement with Debye-Huckel-Bronsted theory of ionic reactions. Similar results were observed in case of other ionic reactions carried out in aqueous ethanol mixed solvents [1,10].

The variations in the values of  $\Delta G_{c.s.}$  (9,14 to 14.06 kJ/mole) with a decrease in the dielectric constant of the medium (Table 2) indicate the formation of a negatively charged activated complex. Furthermore, a comparison of  $\Delta G_{Z_0}$  values (95.5 kJ/mol for  $X_m = 0.15$ , mole fraction of ethanol)

with those of  $\Delta G_{e.s.}$  (14 kJ/mole; for  $X_m = 0.15$ ) suggests that possibly the formation of activated complex may involve the orientation of ions in mixed solvents.  $K_{S_{e.s.}}$  have negative values and their magnitude increase as the proportion of ethanol increases in the mixed solvents. This increase (-35.18 J/mole/K for  $X_m = 0.01$  to -54.19 J/mole/K for  $X_m = 0.15$ ) indicates the formation of a highly ordered activated complex at higher concentrations of ethanol in such mixtures. It was observed in Fig. 3, that the entropy of activation depends on the polarity of medium to the same extent as the energy of activation. Moreover, a compensation effect in the reaction was observed (Fig. 4) as the sum of

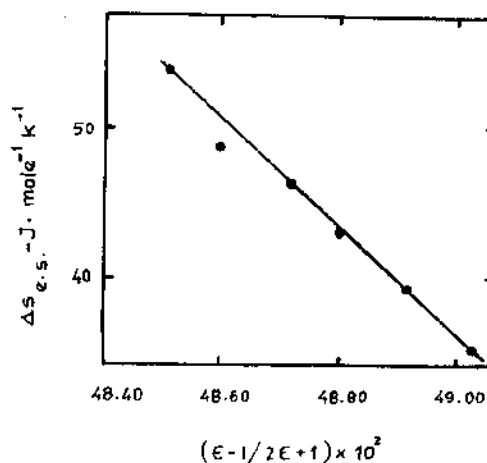


Fig.3: Variations of entropy changes with  $E-1/2E+1$

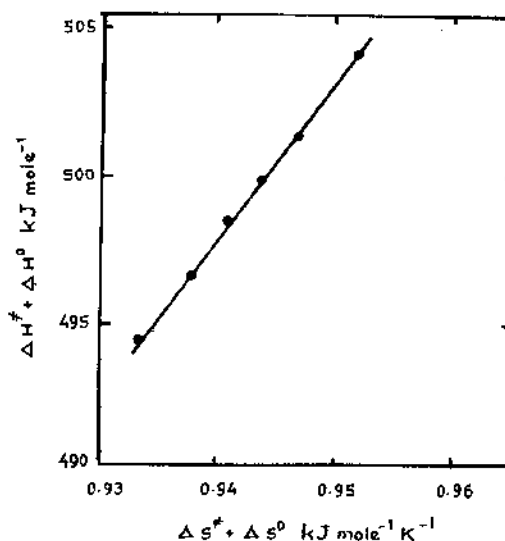


Fig.4: Plot of the compensation relationship between  $\Delta H^* + \Delta H^\circ$  and  $\Delta S^* + \Delta S^\circ$ .

Table 2: Activation Parameters at different Ethanol concentrations.

Ethanol mole fraction, $\times 10^{-3}$	$\Delta S_{\text{e.s.}}(\pm 1)$ J mole <sup>-1</sup> K <sup>-1</sup>	$\Delta G_{\text{e.s.}}(\pm 0.5)$ kJ mole <sup>-1</sup>	$\Delta G_0(\pm 0.5)$ kJ mole <sup>-1</sup>	$\Delta H^\ddagger + \Delta H_0$ kJ mole <sup>-1</sup>	$\Delta S^\ddagger + \Delta S^\circ$ kJ mole <sup>-1</sup> K <sup>-1</sup>
0.012	35.18	9.14	96.41	949.28	0.933
0.044	35.29	10.19	96.29	496.52	0.938
0.072	43.05	11.25	96.0	498.38	0.941
0.096	46.33	12.02	95.84	499.87	0.944
0.112	48.82	12.66	95.81	501.36	0.947
0.153	54.19	14.06	95.57	504.16	0.9952

standard and activated enthalpies ( $\text{KH}^\ddagger + \text{KH}^\circ$ ) correlated with the values of standard and activated entropies ( $\text{KS}^\ddagger + \text{KS}^\circ$ ).

The theoretical values of the radius of the activated complex for a single and a double sphere model are  $3.11 \text{ \AA}^\circ$  and  $4.95 \text{ \AA}^\circ$  respectively. The radii of individual ions i.e.,  $r(\text{BrO}_3^-) = 2.45 \text{ \AA}^\circ$  and  $r(\text{TeO}_3^{2-}) = 2.5 \text{ \AA}^\circ$  were taken from literature [9]. A comparison of the size of the activated complex obtained from the slope of the line according to the Laidler equation (6) shown in Fig. 1, i.e.  $474 \text{ \AA}^\circ$  with those of the theoretical values leads to the conclusion that the shape of the activated complex appears to be more similar to a double sphere model.

The size of the activated complex changed from  $4.74 \text{ \AA}^\circ$  to  $4.85 \text{ \AA}^\circ$ , when the temperature of the reaction was raised from 308K to 313 K. This increase in the size of the activated complex is likely due to the lack of solvation of the transient species at higher temperatures.

The plots of the logarithm of the specific rate constant at zero ionic strength were straight lines (Fig. 1 and 2). The expressions relating the rate constant to  $1/\epsilon$  and  $\epsilon - 1/2\epsilon + 1$  as a function of the dielectric constant of a medium are based on different models of ion-ion and dipole-dipole interactions. The linear plots obtained in each case thus suggest that the first order Coulombic forces predominate in stabilizing the activated complex, and the ion-ion interaction model is sufficiently accurate to describe the formation of activated complex in aqueous-ethanol mixtures of high dielectric constants (40). Similar dependence of the rate con-

stant on  $1/\epsilon$  has been observed by several workers [10-14] in case of ionic reactions carried out in mixed solvents.

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