Application of Model Rate Equations on Chlorate Tellurite Reaction

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Summary:The kinetics of the reaction between chlorate and tellurite ions has been studied in aqueous-ethanol mixtures (upto 0.16 ethanol mole fraction) at 308 K. The reaction rate is retarded by an increase in the ethanol content of the solvent medium. The distances of closest approach of solvent molecules to the transition state have been calculated and were found to be related to the degree of solvation. The logarithm of the rate constant which correlated with $1/D$ and $D-1/2D+1$ is found to be a linear function of $1/D^{1/2}$.

Introduction

A number of solvent dependent parameters like $\log k$, E_T, Y etc. have been used to define the polarity of a solvent. These individual parameters have been obtained with different standard processes and with solvents of specific properties. Despite the multiplicity of possible solute-solvent interactions, in addition to specific hydrogen bonding, electron pair donor/electron pair acceptor and overall solvophobic interactions, these parameters are used empirically to predict the solvation ability of a solvent. Combination of these parameters, in the form of different equations are also used to predict the different solvent effects.

In the previous paper [1], the use of dielectric constant as a measure of solvent polarity in the iodate-bromide reaction in organo-aqueous mixtures was evaluated. In the present study the effect of the variations of dielectric constant of the medium on the nature and the dimension of the activated complex for the reaction between chlorate and tellurite ions in water and water- ethanol mixtures is presented. This reaction is found to be of second order according to the following reaction,

$$ClO_3^- + TeO_3^{-2} \longrightarrow ClO_2^- + TeO_4^{-2}$$
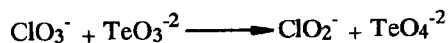
The rate equation can thus be written as,

$$k = 1/t \ x/a(a-x); \ (ClO_3^-) = (TeO_4^{-2})$$

where,

a = initial concentration of reactants
b = concentration of tellurate ion after time "t".

Experimental

The reactions were carried out in a thermostatic bath at 308K and 313 $\pm$ 0.1K. The kinetics was 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 nm. 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 standardise the iodine solutions [3]. 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 an hour of each experimental run. Irradiation of light of 350 n.m. has 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 concentration used in the reaction media were 2.0, 4.8, 7.2, 10.4, 13.2, and 16.0 mole percent.

Table-1: Activation parameters at different ethanol concentrations

Ethanol mole fraction Xm	$\Delta S_{e.s}$ -J/K mole^{-1} ($\pm$ 1.0)	$\Delta G_{e.s}$ kJ mole^{-1} (± 0.5)	ΔG_0 kJ mole^{-1} (± 0.5)	$\Delta H^* + \Delta H^\circ$ kJ mole^{-1}	$\Delta S^* + \Delta S^\circ$ kJ kJ/K mole^{-1}
0.020	38.05	8.22	96.19	484.30	0.925
0.048	42.04	9.08	96.07	486.09	0.931
0.072	45.4	9.81	96.16	487.83	0.935
0.104	50.0	10.80	96.14	490.40	0.940
0.132	53.9	11.65	96.15	492.09	0.943
0.160	57.6	12.45	96.04	494.10	0.947

The reagents used were potassium chlorate, potassium tellurite, iodine, potassium iodide, sodium sulphate, of analaR grade and absolute ethanol obtained from Merck.

Results

Table-1, provides the data for the activation parameters for the reaction at various concentrations of ethyl alcohol in the reaction mixtures. Table-2, presents the data for the rate constants at two different temperatures at various dielectric constant values of ethanol water mixtures. Fig.1 and 2 depict the variations of the logarithm of the rate constant with 1/D and D- 1/2D + 1 respectively, while Fig. 3 demonstrates the change in the logarithm of the rate constant in relation to $1/D^{1/2}$. The entropy changes with solvent polarity in relation to D-1/2D + 1 is shown in Fig. 4. Fig. 5, represents the compensation relationship between $\Delta H^* + \Delta H^\circ$ and $\Delta S^* + \Delta S^\circ$.

Theory

The free energy required [4] to transfer an ion of radius, r, charge, Ze, and dipole moment, μ, from a medium of unit relative permittivity to one of relative permittivity,D_r, where, $D_r = D/D_0$, D_0, being the permittivity of the free space is given as,

(1) $\Delta G_{e.s} = -Z^2.e^2 /2r(1 - 1/D_r) - 3/8. 2/r^3 (1- 2/Dr)$

The electrostatic contribution to the free energy due to ion-ion reactions, ion-dipole and

Table-2: Rate constant values at various dielectric constants; $\mu = O$

Dielectric Constant 1/Dx 10^3	Rate K_A 10^{-6} mole^{-1} sec^{-1} 308 K	Constant K_B 10^{-6} mole^{-1} sec^{-1} 313 K
13.4	12.3	-
14.8	9.2	12.4
16.0	6.83	9.4
17.6	4.57	6.56
19.0	3.38	4.76
20.3	2.5	3.60

K = Average of three readings.

$(ClO_3^- = TeO_3^{-2} = 5 \times 10^{-2} M$

dipole-dipole interactions are included in the above equation. The rate coefficient for the formation of an activated complex of radius, R_{ab}, in a medium of high permittivity being

(2) $\ln k_D = \ln k_0 - e^2/2KT (1-1/D_r) [Z^2_a/r_a + Z^2_b/r_b - Z_a + Z_b/R_{ab} -3/8KT(1-2D_r [\mu^2_a/r^3_a + \mu^2 b/r^3 b- \mu^2_{ab}/R^2_{ab}]$

For ion-ion reactions, when $\mu_a = \mu_b = O$ and $r_a = r_b = R_{ab}$

the above equation reduces to;

(3) $\ln k_D = \ln k_0 - Z_a.Z_b/2D_r KT. 1/R_{ab}$

Equation (3) predicts that at constant temperature, the logarithm of the rate coefficient is inversely proportional to the permittivity of the medium and that the slope of the line is proportional to the size of the activated complex, R_{ab}. For uncharged dipolar molecules, and for ion-dipole interactions the contribution due to the second term is small and the main effect of the solvent is then predicted by the expression,

(4) $\ln.k_D = \ln k_o + 3/8KT\ (1 - 2/D_r)\ \Sigma\mu^2/R^3_{ab}$

where

$\Sigma\ \mu^2/R^3_{ab} = \mu^2_a/r^3_a + \mu^2_b/r^3_b - \mu^2_{ab}/R^3_{ab}$
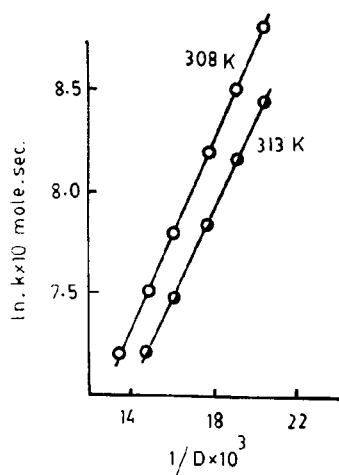

Fig.1: Linear relationship between the logarithm of the rate constant and the reciprocal of the dielectric constant.
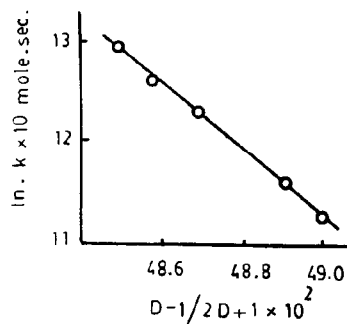

Fig.2: Linear relationship between the logarithm of the constant and D-1/2D+1.

The above expression predicts a linear relationship between the logarithm of the rate coefficient and the reciprocal of the dielectric constant. A similar expression but predicting a linear relationship between the logarithm of the rate coefficient and D- 1/2D+1 for dipole-dipole interactions is,

Taking into consideration, the charge distribution on the activated complex, and the susceptibility of the free energy of the solute particles to the variations in the polarity of a medium, an expression similar to the equation (2) derived by Hiromi [6] is,

(5) $\ln.k_D = \ln.k_o - 1/KT.(D-1)/(2D+1)\ \Sigma\mu^2/R^3_{ab}.$

(6) $\ln k_D = \ln k_o + e^2/2DKT\ \Sigma L_i/r_i$

where,

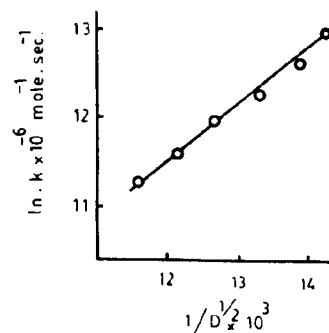$\Sigma L_i/r_i = L_a/r_a + L_b/r_b - L_{ab}/r_{ab}$

Fig. 3: Linear relationship between the logarithm of the rate constant and the reciprocal of the square root of the dielectric constant.
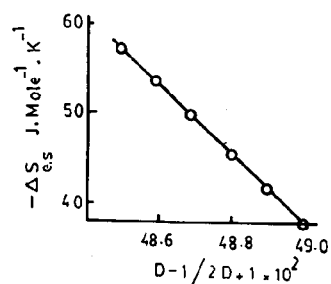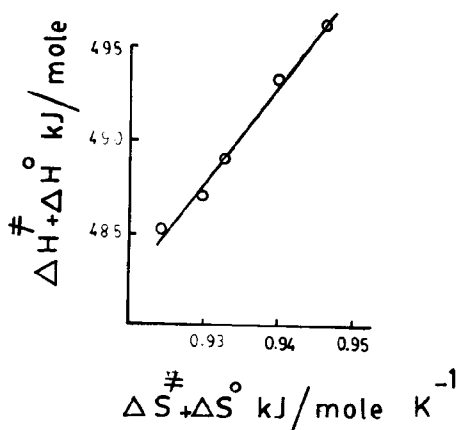

Fig.4: Variations of entropy changes with D-1/2D+1.

Fig. 5: Plot of compensation relationship between DH^+ + ΔH° and Δs^+ ΔS°.

This expression also predicts a linear relationship between the logarithm of the rate coefficient and the reciprocal of the dielectric constant.

For ion-dipole interactions, Amis [7] proposed anexpression in terms of ionic charge and dipole moment,

(7) $\ln k_D = \ln k_o + Z_a.e/Dr.KT\mu/R^2_{ab}$

Considering the inductive interactions [8] between the highly polar activated complex and the surrounding dielectric, the internal reaction field effect is given by the expression,

$4\pi N \mu^2/9\ KT = 2D_r/(n^2 + 2)^2$

The expression (7) can be written as,

(8) $\ln k_D = \ln k_o + Z_a.e/KTR_{ab}..\text{"B"}/D^{1/2}$

where

$\text{"B"} = 9KT/(n^2 + 2)^2 . 2\pi N$ and $n\sim 1$

The refractive index of the medium, could be taken to be near about unity for water-ethanol mixture. k_D, is the rate coefficient at a given dielectric constant, k_o, is the rate coefficient at infinite dielectric constant, K, is the Boltzmann's constant, and T, is the absolute temperature.

This expression predicts a linear relationship between the logarithm of the rate coefficient and $1/D^{1/2}$.

Discussion

The radius of the activated complex, calculated from Fig.1, corresponding to equation 3 is 4.52 A°. The theoretical value calculated for a single sphere model, according to the equation, $r^\#$ $(r^3_a + r^3_b)^{1/3}$ (taking the values of r (ClO_3^{-2}) = 2.35 A° and r (TeO_3^{-2}) = 2.5 A°) is 3.05 A°, therefore the shape of the activated complex appears to be more similar to a double sphere model. As the formation of the activated complex would involve an approach of like charges $(ClO_3^{-}----TeO_3^{-2})$ and is expected to be more polar the reactants, a decrease in the rate constants with decreasing dielectric constant, is consistent with the electrostatic expectations. The linear plot obtained according to equation (3), indicates that the free energy of activation, ΔGH consists of the contributions due to electrostatic interactions $\Delta Ge.s.$ and the non-electrostatic attractions, ΔGo.

Since $\Delta Ge.s. = NZ_a Z_b. e^2/Dr.R_{ab}$ and ΔGH = RT (p $\ln.KT/a$ h-$\ln$ k_D), ΔGo is easily calculated from the relationship $\Delta GH = \Delta Ge.s + \Delta Go$. Because of the low temperatures employed to study the reaction, the value of transmission coefficient was taken as unity. ΔGo arises mainly from the making and breaking of the bonds in forming the activated complex and is considered independent of the electrical properties of the solvent. In fact the value of ΔGo is fairly constant with a mean value of 96.12 k.J./mole. $\Delta Ge.s.$ is the free energy change associated with the electrostatic forces between the two reactants, as they are brought together. The free entropy of activation was calculated by the expression $\Delta Se.s = \Delta Ge.s..$ (dln. D/dT) and by taking a constant value of (d.ln D/dT) as-0.00463 [9]. The result of the calculations are shown in Table-1. The negative values for the entropy is a result of electro-restrictive freezing of solvent molecules around the charged activated complex in solution. The large negative value of entropy observed for the ethanol mole fraction of 0.16 indicates the formation of a highly ordered activated complex. As seen in Fig. 4, it was observed that the entropy of activation

depends to the same extent as the free energy of activation, on the polarity of the medium. Since the temperature dependence of the rate constant was not measured separately, the values of (ΔH^* + ΔH^o) and (ΔS^* + ΔS^o), i.e., the sum of activated and standard enthalpies and entropies were deduced from the relationships: viz, $\Delta S^* = \Delta S^o$ + . 1/Dr and DH* = ΔH^o + 1/Dr respectively [10].

Equation (8) includes the effect of the reactive field which takes account of the electronic component of inductive interactions of the activated complex and the surrounding dielectric. A linear plot is obtained between the logarithm of the rate constant and 1/D1/2 values for the reaction as is shown in Fig. 3.

The relationship is also found valid in case of other ionic reactions carried out in the medium of dielectric constant 40 to 80. [11].

References

1. S.A.H. Zaidi, *Zh.Obschie Khimii*, 51(9), 1936 (1981).
2. C.H. Bamford, and C.F.H. Tipper, "Comprehensive Chemical Kinetics", Vol. 6, Elsvier Publishing Co. p. 388 (1972).
3. L.K. Sharp, "Inorganic Chemistry," Bailiere, Tindall and Dox, p. 286 (1962).
4. K.J. Laidler, and P.A. Landskroner, *Trans.Faraday Soc.*, 52, 200 (1956).
5. J.C. Kirkwood, *J.Chem.Physics*, 2, 351 (1934).
6. K.Hiromi, *Bull.Chem.Soc.Jpn.*, 33, 1251 (1960).
7. E.S.Amis, *J.Chem.Educ.*, 29, 337 (1952).
8. J.R. Pertington, An Advanced Treatise in Physical Chemistry, Vol. 5, p. 428, Longman and Green, London, 1954.
9. S.G. Entelis, R.P. Tiger and E.Ya. Nevelskii, *Izv. Akad.Naukk* USSR *Otd. Khim Nauk.*, p. 429 (1963).
10. S.G. Entelis, Kinetika reacktsii Zhidkoi faze, Izdatel'stvo "Khimiya" p. 187 (1973).
11. S.A.H.Zaidi (accepted for publication).