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Activation Parameters of Bromoacetate-Thiosulfate Reaction in Ethylene Glycol-Water Mixtures

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The activation parameters for the reaction between bromoacetate ($\bar{R}$) and $S_2O_3^{2-}$ ions in water and aqueous mixtures of ethylene glycol (5—50% by weight) have been evaluated from the rate constants, corresponding to zero ionic strength, at 15, 25, and 35 °C. The standard free energies of transfer (ΔG°_{tr}) of the reacting ions and hence of the transition state ($\Delta G^{\#}_{tr}$) from water to the mixed media at 25 °C have been determined from the measured solubilities of AgR, TlCl, and $Tl_2S_2O_3$ in the different media, using the reported values of ΔG°_{tr} of Ag^+ and Cl^- ions. Attempts have been made to interpret the kinetic results in the light of solvent properties and free energies of transfer. Although both the reacting ions are destabilized, on adding glycol to the medium, the larger destabilization of the transition state, arising from decreased dielectric constant as well as solvating capacity of the medium, outweighs the combined effects on the reactants leading to reduced reaction rates.

The kinetics of the reaction between bromoacetate and thiosulfate ions

$$BrCH_2COO^- + S_2O_3^{2-} = S_2O_3CH_2COO^{2-} + Br^-$$

has been and is still being used as a probe for studying the effects of various factors influencing reaction rates. Medium effects on the kinetics of the reaction have been studied in different types of water-organic mixtures[1—7] as well as in anhydrous methanol and ethylene glycol.[8] Results of kinetic studies on the reaction in aqueous mixtures of ethylene glycol (5—50% by weight) at different temperatures were reported earlier.[7] The free energies of transfer (ΔG°_{tr}) of the two reacting ions and hence of the transition state from water to the water-glycolic media have now been evaluated from solubility measurements, using TlCl, $Tl_2S_2O_3$, and silver bromoacetate (AgR) in the different media at 25 °C. The medium effects on the rates and activation parameters have been discussed in the light of solvent properties and transfer free energies.

Experimental

Ethylene glycol was purified by a standard procedure.[9] Sodium bromoacetate was prepared by the method of Kappana and Patwardhan.[10] Silver bromoacetate (AgR) was prepared by precipitation on adding $AgNO_3$ to sodium bromoacetate solution followed by filtration and thorough washig with cold water. TlCl and $Tl_2S_2O_3$ were similarly prepared by precipitation on adding NaCl and $Na_2S_2O_3$ respectively to saturated solutions of $TlNO_3$.

The solubilities of the three salts in water and the water-glycolic media at 25 °C were determined by titrating measured volumes of the saturated solutions as described below:

For AgR : The titrant was 0.01 M(1 M=1 mol dm^{-3}) KCNS, and the indicator iron(III) alum,

For TlCl : The titrant was 0.08 M $AgNO_3$, and the indicator K_2CrO_4.

For $Tl_2S_2O_3$: Measured volumes of the saturated solutions were added to measured excess of standard iodine solutions followed by back titration with 0.03 M $Na_2S_2O_3$ using starch as the indicator. The solubilities of TlCl and $Tl_2S_2O_3$ were reproducible within ±2%. For AgR, the solubilities being very low in the glycol-rich media, the errors are higher, but the order of the magnitude is definitely reproducible.

Results and Discussion

The values of the rate constants (k_o) in water and the mixed media[7] at 25 °C corresponding to zero ionic strength, as obtained by extrapolation, and the ratios k_s/k_w are recorded in Table 1, where k_w and k_s are the respective values of k_o in water and any water-glycolic medium. The activation parameters for 25 °C were evaluated from the rate constants (k_o) at 15, 25, and 35 °C, as reported earlier,[7] by the usual method, and recorded in Table 1.

The rate constant decreases with increase in the glycol content in the medium, i.e. with decrease in the dielectric constant, as expected for a reaction between two ions of like charge, $\Delta H^{\#}$ for the reaction is found to increase with increasing glycol concentration, and so does the value of $\Delta S^{\#}$ (which is negative for each medium, as expected). Thus, there occurs a reasonable degree of compensation between $\Delta H^{\#}$ and $T\Delta S^{\#}$, but the larger effect of $\Delta H^{\#}$ predominates leading to a monotonic decrease in the reaction rate.

The medium effect on $\Delta H^{\#}$ may be examined on the basis of the classification of solvents into typically

Table 1. Variation of Rate Constants (dm^3 mol^{-1} min^{-1}) and Activation Parameters (kJ mol^{-1}) at Zero Ionic Strength at 25 °C (Molar Scale)

Wt./% EG	k_0	k_s/k_w	$\Delta H^{\#}$	$T\Delta S^{\#}$	$\Delta G^{\#}$	$m\delta\Delta G^{\#}$	$\Delta G^{\#}_{tr}$
0	0.72	—	50.5	−33.5	84.0	—	—
5	0.69	0.96	52.7	−31.4	84.1	0.1	2.4
20	0.59	0.82	53.3	−31.2	84.5	0.5	5.7
30	0.53	0.74	55.0	−29.8	84.8	0.8	8.2
50	0.43	0.60	56.2	−29.1	85.3	1.3	11.1

aqueous (TA) and typically nonaqueous (TNA) groups.[11,12] The excess functions, G^E and H^E, for aqueous mixtures of ethylene glycol are negative.[12–14] However, ethylene glycol in its aqueous mixtures is considered to form a borderline between the two groups, but leaning more towards TA.[12] On the basis of the model of Caldin and Bennetto,[15,16] the process of the formation of an 'encounter complex' between the reacting ions involves the movement of solvent molecules from the second zone of solvation to the bulk. This second zone is more or less disordered, approximating to an ideal mixture. Hence the excess functions correspond to the changes in the respective thermodynamic quantities occurring in the process of the transfer of the solvent molecules from the second zone to the bulk. If G^E and H^E are negative as for water-glycolic mixtures, this step should tend to decrease $\Delta G^{\#}$ and $\Delta H^{\#}$. The experimental results (Table 1) are, however, just the reverse. Obviously other factors predominate. The electrostatic factor definitely operates, leading to increasing $\Delta H^{\#}$ and $\Delta G^{\#}$, for the reaction between similarly charged ions, with decreasing dielectric constant. Moreover, decreasing solvation of the transition state may also cause its destabilization. The decreasing magnitude of negative value of $\Delta S^{\#}$ (Table 1) may be taken to indicate progressive desolvation of the transition state, in comparison with the reacting ions. The desolvation may arise from an overall reduction in the solvating capacity of the mixed medium, as glycol molecules are gradually substituted for water molecules, because of intramolecular hydrogen bond formation between the adjacent OH groups in the glycol molecule.[17,18]

For a better insight into the medium effect on the rates and activation parameters, the results should be examined in the light of the free energies of transfer of the reactants and the transition state.

The standard free energies of transfer (ΔG°_{tr}) of AgR, TlCl, and $Tl_2S_2O_3$ from water to the mixed media were evaluated from the solubility products (K_{sp}) of the salts (Tables 2 and 3) by Eq. 1.

$$\Delta G^\circ_{tr}(\text{salt}) = RT \ln \frac{K_{sp}(\text{w})}{K_{sp}(\text{s})} \tag{1}$$

where w and s refer to water and any mixed medium respectively. The results are recorded in Tables 2 and 3.

The standard free energies of transfer of the bromoacetate ($\bar{R}$) ion from water to the mixed media at 25 °C were calculated by subtracting from ΔG°_{tr} (AgR) the corresponding literature values[19] for the Ag^+ ion (Table 2).

The ΔG°_{tr} values for the $S_2O_3^{2-}$ ion were obtained as described below. The ΔG°_{tr} (Tl^+) values were first calculated by subtracting from the ΔG°_{tr}(TlCl) values (Table 3) the reported values[18] of ΔG°_{tr} for the Cl^- ion. The ΔG°_{tr} values for the $S_2O_3^{2-}$ ion were then evaluated by subtracting the free energies of transfer of two moles of Tl^+, i.e. $2\Delta G^\circ_{tr}$ (Tl^+) from the corresponding values of ΔG°_{tr} ($Tl_2S_2O_3$), as determined in the present work and recorded in Table 3.

The single ion free energies of transfer for Ag^+ and Cl^-, used above, are based on the familiar extra-thermodynamic TATB assumption that ΔG°_{tr} for the tetraphenylarsonium (TA^+) ion is the same as that for the tetraphenylborate (TB^-) ion for any particular medium. Wells[17,20] has used a different extra-thermodynamic assumption for evaluating single ion free energies of transfer, and his values are in general appreciably different. The TATB assumption is, however, considered to be more sound.[21] Although uncertainties are unavoidably involved in the ΔG°_{tr} values for the single ions because of the extra-thermodynamic assumption, some conclusions of a semiquantitative nature can definitely be drawn

Table 2. Solubility Products (K_{sp}) of Silverbromoacetate (AgR) and Standard Free Energies of Transfer (kJ mol^{-1}) of AgR, Ag^+, and R^- at 25 °C (Molar Scale)

Wt./% EG	K_{sp}(AgR) × 10^8	ΔG°_{tr} (AgR)	ΔG°_{tr} (Ag^+)$^{a)}$	ΔG°_{tr} (R^-)
0	13.3	—	—	—
5	7.0	1.6	−0.10	1.7
20	3.9	3.0	−0.40	3.4
30	2.7	3.9	−0.70	4.6
50	1.3	5.8	−1.40	7.2

a) Ref. 19.

Table 3. Solubility Products (K_{sp}) of TlCl and $Tl_2S_2O_3$ and Standard Free Energies of Transfer, ΔG°_{tr} (kJ mol^{-1}) of the Salts and Single ions at 25 °C (Molar Scale)

Wt./% EG	K_{sp}(TlCl) × 10^4	ΔG°_{tr}(TlCl)	$\Delta G^{\circ\, a)}_{tr}$($Cl^-$)	ΔG°_{tr}(Tl^+)	K_{sp}($Tl_2S_2O_3$) × 10^7	ΔG°_{tr}($Tl_2S_2O_3$)	ΔG°_{tr}($S_2O_3^{2-}$)
0	4.58	—	—	—	4.36	—	—
5	3.99	0.3	0.3	0	3.33	0.6	0.6
20	3.00	1.1	1.0	0.1	1.96	2.0	1.8
30	2.72	1.3	1.4	−0.1	1.54	2.6	2.8
50	2.40	1.6	1.1	0.5	1.03	3.6	2.6

a) Ref. 18.

therefrom in respect of the medium effect.

The medium effect on the free energy of activation ($m\delta\Delta G^{\#}$) is given by Eq. 2.

$$m\delta\Delta G^{\#} = \Delta G^{\#}(\mathrm{s}) - \Delta G^{\#}(\mathrm{w}) \qquad (2)$$

where w and s denote water and any mixed medium respectively. The standard free energy of transfer of the transition state ($\Delta G^{\#}_{\mathrm{tr}}$) is given by Eq. 3.

$$\Delta G^{\#}_{\mathrm{tr}} = m\delta\Delta G^{\#} + \Delta G^{\circ}_{\mathrm{tr}}(\overline{\mathrm{R}}) + \Delta G^{\circ}_{\mathrm{tr}}(\mathrm{S_2O_3}^{2-}) \qquad (3)$$

The values of $m\delta\Delta G^{\#}$ and $\Delta G^{\#}_{\mathrm{tr}}$ are shown in Table 1.

From Tables 1—3 it will be seen that for both the reacting ions as well as the transition state, $\Delta G^{\circ}_{\mathrm{tr}}$ values are positive, increasing with the proportion of glycol in the medium. The effect on the $\overline{\mathrm{R}}$ ion (Table 2) is distinctly larger than that on the $\mathrm{S_2O_3}^{2-}$ ion (Table 3). For the transition state (Table 1), however, the transfer free energy ($\Delta G^{\#}_{\mathrm{tr}}$) is not only larger than the corresponding value of either of the reacting ions, but preponderates over the combined effect on the two reactants taken together, leading to a reduced rate. Thus, basically it is the large destabilization of the transition state which dictates the resultant medium effect on the reaction rate. The effect, however, is not as pronounced as it might have been, because of the simultaneous destabilization of the reacting, ions, although occurring to a smaller extent.

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