

Medium Effect on Rates & Activation Parameters of Bromacetate-Thiosulphate Reaction in Aqueous Mixtures of Dimethyl Sulphoxide

PRASANTA KUMAR BISWAS & MIHIR NATH DAS*

Department of Chemistry, Jadavpur University,
Calcutta 700 032

Received 4 December 1986; revised and accepted 14 May 1987

The rates of reaction between the bromacetate (\bar{R}) and thiosulphate ions have been measured at 15°, 25° and 35°C in water and aqueous dimethyl sulphoxide (DMSO) mixtures. The activation parameters have been evaluated. The rate increases with mol fraction (x_2) of DMSO, but ΔH^\ddagger and ΔS^\ddagger pass through minima around $x_2 = 0.3$, the enhanced rates being due to decreased ΔH^\ddagger . The standard free energies of transfer of the reacting ions and hence of the transition state from water to the mixed media at 25°C have been obtained from the solubilities of AgR, TlCl and Tl₂S₂O₃ in the different media.

Reactions between two singly charged anions have been found to occur faster in aqueous mixtures of dimethyl sulphoxide (DMSO) than in water¹⁻⁴. The present work was undertaken to investigate the effect of aqueous mixtures of DMSO of varying compositions on the rates and activation parameters of the thiosulphate-bromacetate (\bar{R}) reaction. This reaction involves a dianion and a monoanion and is still being extensively used for investigating the effects of various factors influencing kinetic parameters⁵⁻¹⁴. The transfer free energies of the reacting anions and hence of the transition state have also been determined, and attempts have been made to correlate the activation parameters with the transfer quantities and solvent properties.

DMSO (E. Merck, India) was purified by a stand-

ard procedure¹⁵. The preparation and standardisation of different solutions as well as the procedure for kinetic measurements were described earlier¹³.

Rates were measured at 15°, 25° and 35°C, using each reactant at an initial concentration of 0.01 mol dm⁻³. Ionic strengths were varied from 0.04 to 0.10 mol dm⁻³ by adding requisite amounts of standard NaCl solution. The second order rate constants (k), obtained graphically, were reproducible within $\pm 2\%$. The rate constants at zero ionic strength (k_0) were obtained by extrapolation of the linear plots of log k against the $\sqrt{\mu}$.

The silver salt of bromoacetic acid (AgR) was prepared and its solubilities at 25°C in water and the mixed media were determined by the procedure described earlier⁴. Thallium(I) thiosulphate was obtained by adding Na₂S₂O₃ to a solution of TlNO₃, followed by filtration of the precipitate and its thorough washing with cold water. Thallous chloride was prepared similarly by adding NaCl to a solution of TlNO₃. The solubilities of Tl₂S₂O₃ at 25°C were determined by adding measured volumes of saturated solutions to measured excess of standard iodine solutions and back titrating with standard sodium thiosulphate. The solubilities of TlCl at 25°C were determined by titrating aliquots of the saturated solutions with standard AgNO₃ solution using K₂CrO₄ as the indicator. The solubility measurements were done in duplicate and some in triplicate, the reproducibility being better than $\pm 2\%$.

The rate constant (k_0) at zero ionic strength increases with increase in the mol fraction (x_2) of DMSO, a rapid change occurring beyond $x_2 \approx 0.2$ (Table 1). This increase in rate is in sharp contrast to the results reported for the same reaction in a number of aquo-organic media⁵⁻¹⁴. For the reaction of

Table 1—Rate Constants, Activation Parameters and Free Energies of Transfer (kJ mol⁻¹) of the Transition States at 25°C (Molar Scale)

Mol fra of DMSO (x_2)	k_0 (dm ³ mol ⁻¹ min ⁻¹)			ΔH^\ddagger (kJ mol ⁻¹)	$T\Delta S^\ddagger$ (Jk ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)	ΔG_r^\ddagger (kJ mol ⁻¹)
	15°C	25°C	35°C				
0	0.37	0.72	1.51	51	-34	85	—
0.05	0.41	0.77	1.59	49	-35	84	8.0
0.10	0.46	0.87	1.78	47	-36	83	16
0.15	0.90	1.67	3.42	46	-36	82	20
0.20	1.08	2.09	4.07	45	-36	81	21
0.25	2.14	4.37	8.09	45	-35	80	29
0.30	2.97	5.50	9.55	42	-38	80	41
0.35	3.68	7.15	13.6	44	-34	78	49
0.40	4.74	8.91	15.9	44	-34	78	54

$S_2O_3^{2-}$ with an uncharged species like benzyl chloride¹⁶ as well, the rate increases with increase in DMSO concentration in the medium, as generally expected for a S_N2 reaction of such charge type². Addition of acetone or dioxane, however, slows down the rate. The reaction between $S_2O_3^{2-}$ and benzyl bromide also becomes slower on addition of alcohols, acetone and dioxane to water¹⁷.

On adding DMSO to the medium, ΔH^\ddagger and $T\Delta S^\ddagger$ for the bromacetate-thiosulphate reaction first decrease, reaching a minimum around $x_2 \approx 0.3$, and then increase (Table 1). The variation in ΔH^\ddagger is markedly large, but changes in $T\Delta S^\ddagger$, which also follow more or less a similar trend, are substantially smaller. There is however only partial compensation between ΔH^\ddagger and $T\Delta S^\ddagger$, and the enhanced rates of the bromacetate-thiosulphate reaction in aqueous DMSO largely arise from reduced ΔH^\ddagger . On the basis of excess thermodynamic functions, G^E , H^E and S^E of its aqueous mixtures, DMSO has been classified as typically nonaqueous with negative G^E (TNAN)^{18,19}. The pronounced decrease in ΔH^\ddagger (Table 1) can be explained on the basis of the model of Caldin and Bennetto²⁰ according to which negative G^E should lead to a decrease in the energy of ac-

tivation²¹. There is ample evidence¹⁹ to indicate the occurrence of strong intercomponent association in water-DMSO solvent system leading to the formation of a 2:1 complex ($x_2 = 0.33$), and the minima in ΔH^\ddagger and $T\Delta S^\ddagger$ for the reaction around this composition (Table 1) presumably arise from this fact.

Further insight into the medium effect may be obtained from the standard free energies of transfer (ΔG_{tr}^0) of the reacting ions from water to the mixed media. For this purpose, the ΔG_{tr}^0 values at 25°C of silver bromacetate (AgR) and thallium(I) thiosulphate and chloride were first obtained from the respective solubility products (K_{sp}) in water and aqueous mixtures of DMSO in the usual manner⁴ (Table 2). The ΔG_{tr}^0 values for the bromacetate (\bar{R}) ion were calculated by subtracting from ΔG_{tr}^0 (AgR) the corresponding values of ΔG_{tr}^0 (Ag^+) as reported in the literature²² (Table 2). The ΔG_{tr}^0 ($S_2O_3^{2-}$) values were obtained as described below. The ΔG_{tr}^0 (Tl^+) values were obtained using the experimental ΔG_{tr}^0 (TlCl) values, and subtracting therefrom the corresponding values of ΔG_{tr}^0 (Cl^-) obtained by interpolation from the reported values²³. The values of ΔG_{tr}^0 ($S_2O_3^{2-}$) were then determined by subtracting the calculated values of the free energy of transfer for 2 mol of Tl^+ from the corresponding values of ΔG_{tr}^0 of $Tl_2S_2O_3$ as experimentally determined in the present work (Table 3). The literature values in the mol fraction scale were converted into the molar scale. The single ion free energies of transfer for Ag^+ and Cl^- ions as used above are based on the well known extra thermodynamic TATB assumption that ΔG_{tr}^0 for the tetraphenylarsonium (TA^+) ion is equal to that for the tetraphenylboride (TB^-) ion for any particular medium^{22,23}. The ΔG_{tr}^0 values for the bromacetate (\bar{R}) ion are positive and progressively increase with x_2 (Table 2). The solubilities of thallium(I) thiosulphate do not decrease monotonically with increase in x_2 , as might be expected (Table 3), but the reason for such anomaly is not clear. The ΔG_{tr}^0

Table 2—Solubility Products (K_{sp}) of AgR and Transfer Free Energies of AgR, Ag^+ and \bar{R} at 25°C (Molar Scale)

Mol fra of DMSO (x_2)	K_{sp} (AgR) $\times 10^8$	G_{tr}^0 (AgR) (kJ mol ⁻¹)	G_{tr}^0 (Ag^+) (kJ mol ⁻¹)	G_{tr}^0 (\bar{R}) (kJ mol ⁻¹)
0	13	—	—	—
0.05	7.5	1.4	-1.9	3.3
0.10	4.8	2.5	-4.0	6.5
0.15	4.0	3.0	-5.9	8.9
0.20	3.4	3.4	-8.0	11
0.25	2.7	4.0	-11	15
0.30	2.1	4.5	-14	19
0.35	1.6	5.2	-17	22
0.40	1.2	6.0	-19	25

^aRef. (22)

Table 3—Solubility Products (K_{sp}) of $Tl_2S_2O_3$ and Transfer Free Energies of $Tl_2S_2O_3$, TlCl, Cl^- , Tl^+ and $S_2O_3^{2-}$ at 25°C (Molar Scale)

Mol fra of DMSO (x_2)	K_{sp} ($Tl_2S_2O_3$) $\times 10^8$	G_{tr}^0 ($Tl_2S_2O_3$) (kJ mol ⁻¹)	K_{sp} (TlCl) $\times 10^5$	G_{tr}^0 (TlCl) (kJ mol ⁻¹)	G_{tr}^0 (Cl^-) (kJ mol ⁻¹)	G_{tr}^0 (Tl^+) (kJ mol ⁻¹)	G_{tr}^0 ($S_2O_3^{2-}$) (kJ mol ⁻¹)
0	43	—	46	—	—	—	—
0.05	9.4	3.5	32	0.90	2.0	-1.1	5.7
0.10	4.4	5.7	20	2.0	4.6	-2.6	11
0.15	4.9	5.5	13	3.2	7.3	-4.1	14
0.20	15	2.7	9.2	4.2	10	-5.8	14
0.25	15	2.6	6.5	4.8	13	-8.2	19
0.30	6.0	4.9	5.3	5.3	16	-11	27
0.35	4.9	5.5	5.0	5.5	19	-14	34
0.40	4.4	5.8	4.5	5.8	21	-15	36

^a Ref. 23

($S_2O_3^{2-}$) values are positive and increase with x_2 , being much larger than the corresponding values for the bromacetate ion.

The standard free energy of transfer (ΔG_{tr}^\ddagger) of the transition state is given by relation⁴ (1)

$$\Delta G_{tr}^\ddagger = \Delta G^\ddagger(s) - \Delta G^\ddagger(w) + \Delta G_{tr}^0(\bar{R}) + \Delta G_{tr}^0(S_2O_3^{2-}) \quad \dots (1)$$

where w and s respectively denote water and any mixed medium. The values of ΔG_{tr}^\ddagger are given in Table 1. The transfer free energies of the triply charged transition state indicate that it is destabilized to a larger extent than either of the reacting ions (Tables 2 and 3), but the combined destabilization of the two reacting anions outweighs the destabilization of the transition state. The enhanced rates are thus basically caused by the higher reactivities of the reactants obviously arising from progressive desolvation of the anions on the addition of DMSO to water. The strong desolvation and the consequent destabilization of the transition state, however, make the increase in rate much less than it would otherwise be.

We thank the UGC, New Delhi for the award of a teacher fellowship (to PKB) and the authorities of the R.B.C. College, Naihati, West Bengal, for granting him leave of absence.

References

- 1 Alexander R, Ko E C F, Parker A J & Broxton T J, *J Am chem Soc*, **90** (1968) 5049.
- 2 Parker A J, *Chem Rev*, **69** (1969) 1.
- 3 Dantzenberg H & Philipp B, *Z phys Chem (Leipzig)*, **260** (1979) 260.
- 4 Biswas P K & Das M N, *J chem Soc Faraday Trans 1*, (1986) 1973.
- 5 Kappana A N, *J Indian chem Soc*, **6** (1929) 419.
- 6 LaMer V K & Kamner M E, *J Am chem Soc*, **57** (1935) 2669.
- 7 Straup D & Cohn E J, *J Am chem Soc*, **57** (1935) 1794.
- 8 Eagle S & Warner J C, *J Am chem Soc*, **58** (1936) 2335.
- 9 LaMer V K, *J Franklin Inst*, **225** (1938) 225.
- 10 Davis H G & LaMer V K, *J chem Phys*, **10** (1942) 585.
- 11 Burris C T & Laidler K J, *Trans Faraday Soc*, **51** (1955) 1497.
- 12 Clements (Jr) L D, *Ind Eng Chem Process Des Develop*, **10** (1971) 401.
- 13 Maula Anwarul, *Indian J Chem*, **16A** (1978) 1049.
- 14 Biswas P K, Maula A & Das M N, *Bull chem Soc Japan*, (In press).
- 15 Coetzee J F & Ritchie C D, *Solute-solvent interactions*, (Marcel Dekker, New York) 1969.
- 16 Kalliorinne K & Tommila E, *Acta Chem Scand*, **23** (1969) 2567.
- 17 Punnaiah G & Sundaram E V, *Z phys Chem (Frankfurt am Main)*, **89** (1974) 188.
- 18 Blandamer M J & Burges J, *Chem Soc Rev*, **4** (1975) 55.
- 19 Blandamer M J, in *Advances in physical organic chemistry*, Vol. 14, edited by V Gold & D Bethel (Academic Press, New York), 1977, pp 203-352.
- 20 Caldin E F & Bennetto H P, in *The physical chemistry of aqueous systems*, edited by R L Kay (Plenum, New York), 1973, pp 129-131.
- 21 Tejeda P P, Velasco J R & Burgos F S, *J chem Soc Dalton Trans*, (1983) 2679.
- 22 Kundu K K & Parker A J, *J soln Chem*, **12** (1981) 847.
- 23 Das A K & Kundu K K, *J soln Chem*, **8** (1979) 289.