

283. *The Influence of Electrolytic Dissociation upon Rates of Reactions. Part II.* The Thiosulphate-Propyl Bromide Reaction in Aqueous Ethanol.*

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The rate of reaction between various thiosulphates and *n*-propyl bromide in 44% ethanol has been followed. It being assumed that the ion-pairs present in solution do not contribute to the reaction velocity, the velocity constants for the reaction with the free thiosulphate ion are found to be independent of the cations present and of the ionic strengths of the solutions. The constants obtained are considerably higher than those based upon stoichiometric thiosulphate molarities, but over a temperature range the results lead to the same value for the energy of activation. The *isopropyl* bromide reaction is also briefly discussed.

THE reaction $S_2O_3^{2-} + RBr \rightleftharpoons RS_2O_3^- + Br^-$, where R is an alkyl group, is, according to Crowell and Hammett,¹ bimolecular, irreversible, and relatively fast. The resulting alkyl Bunte salt is reasonably stable but, since hydrolysis of the alkyl bromide can render the solutions acidic, buffers such as acetates must be present to prevent decomposition of the thiosulphate ion.

Now in the solvent used by Crowell and Hammett,¹ namely, 44% (w/w) ethanol, the sodium thiosulphate used, from the evidence supplied in the preceding paper, is incompletely dissociated. We have endeavoured to see what is the effect of this by assuming that the essential reaction is between alkyl bromide and free thiosulphate ion. We have examined this feature in detail, using not only sodium but also other thiosulphates. Where bivalent cations M^{2+} were used, the presence of $MRS_2O_3^+$ and MAC^+ also had to be considered. This information was obtained from some solubility studies described below.

Kinetic Measurements.—A typical run in which calcium thiosulphate was used is shown in Table I. The penultimate column records the velocity constants (k) (mole l.⁻¹ sec.⁻¹),

TABLE I. *Reaction of calcium thiosulphate with n-propyl bromide in 44% (w/w) ethanol at 25°.*

<i>t</i> (min.)	Initial concns.: $CaS_2O_3 = 0.05250M$; $Pr^nBr = 0.04431M$; $NaOAc = 0.0050M$.					
	$10^3[Pr^nS_2O_3^-]$	$10^4[CaOAc^+]$	$10^4[CaPr^nS_2O_3^+]$	$10^4[NaS_2O_3^-]$	10^4k	$10^4k/\alpha$
65	2.77	8.9	4.8	8.4	3.83	10.46
115	4.53	9.1	8.9	8.0	3.80	10.50
206	7.93	9.3	14.8	7.3	3.68	10.42
277	9.14	10.0	18.5	6.8	3.64	10.43

calculated on the assumption that ion-pairing is absent. The concentrations of $NaS_2O_3^-$ were calculated from the known dissociation constant (see preceding paper), and those of $CaOAc^+$ and $CaPr^nS_2O_3^+$ from the solubility results reported below. In the final column the ratio k/α represents the velocity constant for the reaction between alkyl bromide and free thiosulphate ion, α being the fraction of total thiosulphate present as $S_2O_3^{2-}$. This

* Part I, *J.*, 1955, 1899.

¹ Crowell and Hammett, *J. Amer. Chem. Soc.*, 1948, **70**, 3444.

was obtained by using the dissociation constant of CaS_2O_3 established by conductivity measurements in the preceding paper. The concentrations of ion-pairs were calculated from the general expression :

$$\log [\text{ion-pair}] = \log [\text{cation}][\text{anion}] - \log K - nf(I)$$

and a form of Davies's activity coefficient expression, *i.e.* :

$$-\log f_i = z_i^2 \times 0.932 \{ I^\dagger / (1 + I^\dagger) - 0.2I \} = f(I)$$

In these, z_i = ion valency, I = ionic strength, and $n = z^2(\text{anion}) + z^2(\text{cation}) - z^2(\text{ion-pair})$.

A series of approximations was needed to establish the true concentrations. A number of runs were analysed in this fashion and are summarised in Table 2. In the runs at the higher concentrations of thiosulphate, k changed slowly with time (see Table 1); the values given in Table 2 are those obtained by extrapolation to $t = 0$.

TABLE 2. Reaction of thiosulphates with *n*-propyl bromide in 44.05% (*w/w*) ethanol at 25°.

Salt	$10^4[\text{thiosulphate}]$	$10^4[\text{Pr}^n\text{Br}]$	$10^4[\text{NaOAc}]$	10^4k	$10^4k/\alpha$
$\text{Na}_2\text{S}_2\text{O}_3$	7.943	4.217	1.25	9.44	10.15
	15.62	8.431	2.5	9.05	10.3
	37.51	19.23	5.0	8.29	10.2
	59.76	24.76	6.1	7.73	10.15
	207.3	111.0	8.4	6.54	10.15
$\text{K}_2\text{S}_2\text{O}_3$	526.2	443.1	50.0	5.73	10.3
	10.26	5.164	1.0	9.12	10.15
	50.13	25.36	4.0	7.52	10.3
	528.1	443.1	50.0	5.13	10.2
MgS_2O_3	6.984	3.423	0.20	6.88	10.3
	10.37	221.5	50.0	4.50	10.0
CaS_2O_3	525.0	443.1	50.0	3.88	10.45
SrS_2O_3	6.023	2.987	0.20	5.92	10.2
	10.47	5.036	0.50	5.35	10.3

Some runs at different temperatures have been similarly interpreted for 0.05M-magnesium thiosulphate. The figures for these are given in Table 3.

TABLE 3. Reaction of magnesium thiosulphate and *n*-propyl bromide in 44.05% (*w/w*) ethanol at various temperatures.

Temp.	15.0°	20.0°	25.0°	30.0°	34.5°
10^4k	1.57	2.64	4.50	7.39	11.14
$10^4k/\alpha$	3.35	5.64	9.62	15.90	24.11

Crowell and Hammett¹ also studied the reaction between the thiosulphate ion and *isopropyl* bromide in 44% ethanol. They used sodium thiosulphate and varying concentrations of sodium acetate in order to vary the ionic strength and thereby study any ion-dipole effects. We have recalculated their data, making allowance for the presence of NaS_2O_3^- ion-pairs, as shown in Table 4.

TABLE 4. Reaction of sodium thiosulphate and *isopropyl* bromide in 44.05% ethanol at 25°.

$[\text{Na}_2\text{S}_2\text{O}_3]$	$[\text{Pr}^i\text{Br}]$	$[\text{NaOAc}]$	10^4k	$10^4k/\alpha$	I
0.10	0.05	0.02	0.294	0.62	0.215
0.10	0.10	0.10	0.25	0.59	0.285
0.15	0.10	0.10	0.22	0.57	0.366
0.20	0.10	0.10	0.18	0.50	0.444

Solubility Measurements.—In order to obtain information about the extent to which the ion-pairs MOAc^+ , MBr^+ , and MRS_2O_3^+ were possible members of the solutions in the kinetic studies, the solubility at 25° of calcium iodate in 44% ethanol solutions of the

² Davies, *J.*, 1938, 2093.

sodium salts of these substances was measured. Davies³ has shown how the dissociation constants of calcium salts can thereby be calculated. The solubility data and consequent calculations are given in Table 5.

Our method of calculation is as follows. Let

$$S = [\text{Ca}^{2+}][\text{IO}_3^-]^2 f_{\text{Ca}}f_{\text{IO}_3}^2$$

where S is the activity solubility product. The form of Davies's activity coefficient expression referred to above was used. The calculation of S required a knowledge of the dissociation constant of the ion-pair CaIO_3^+ . In water this⁴ is 0.13. We have estimated it to be 0.009 here by multiplying the water value by the ratio of the values of NaS_2O_3^- in the two solvents^{5,6} *i.e.*, by 0.0144/0.20. Our reason for doing this is that the ion-pairs are of similar valency types and have about the same dissociation constants in water. The value of S , derived by approximations, is thus 7.93×10^{-11} g.-ion³ l.⁻³.

In the presence of the sodium salts, NaIO_3 ion-pairs are also present. The dissociation

TABLE 5. Solubility of calcium iodate in sodium acetate, sodium bromide, and sodium *n*-propyl thiosulphate solutions (44.0% w/w ethanol; at 25°). (Concn. : 10^{-4} mole l.⁻¹.)

[NaBr]	[Ca(IO ₃) ₂]	[Salt]	[CaIO ₃ ⁺]	[CaX ⁺]	[NaIO ₃]	K (CaX ⁺)
X ⁻ = Acetate						
—	3.100	—	0.172	—	—	—
—	5.172	174.0	0.144	1.60	0.264	0.014
—	5.805	261.1	0.142	1.86	0.408	0.016
—	6.810	435.1	0.141	2.51	0.681	0.017
X ⁻ = Bromide						
—	4.446	139.2	0.155	—	0.196	—
—	5.151	278.3	0.165	—	0.371	—
X ⁻ = Pr ⁿ S ₂ O ₃ ⁻						
462.1	8.194	442.0	0.150	2.28	1.33	0.017
647.1	9.271	617.4	0.151	2.70	1.87	0.019
924.0	10.53	882.1	0.150	3.19	2.64	0.020

constant⁷ of this species in water is 3.0 and our estimate based on the figures for silver acetate in the two solvents is that K (NaIO_3) in 44% ethanol is about 0.4.

The expressions used are :

$$\begin{aligned} \log [\text{Ca}^{2+}] &= -10.1007 - 2 \log [\text{IO}_3^-] + 6 \times 0.932f(I) \\ \log [\text{CaIO}_3^+] &= \log [\text{Ca}^{2+}][\text{IO}_3^-] + 2.046 - 4 \times 0.932f(I) \\ \log [\text{NaIO}_3] &= \log [\text{Na}^+][\text{IO}_3^-] + 0.398 - 3 \times 0.932f(I) \end{aligned}$$

The differences between the measured solubilities and the calculated values of $([\text{Ca}^{2+}] + [\text{CaIO}_3^+])$ represent the concentrations of CaX^+ present.

Discussion.—It is clear from Table 2 that, by assuming that the rate of reaction depends on the concentration of free thiosulphate ion, values of the velocity constant are obtained which are quite different from those based on the total thiosulphate molarity. This is particularly true at higher ionic strengths. Our average value of $k/\alpha = 10.0 \pm 0.2 \times 10^{-4}$ mole l.⁻¹ sec.⁻¹ at 25° is much higher than Crowell and Hammett's value of $k = 4.74 \times 10^{-4}$. In addition, the constancy of k/α for both 2 : 1- and 2 : 2-valent salts and over a range of ionic strengths rules out any significant contribution by the charged ion-pairs NaS_2O_3^- and KS_2O_3^- and also indicates that ion-dipole salt effects are virtually absent.

The activation energy (E) for this reaction was calculated by Crowell and Hammett

³ Davies, *J.*, 1938, 277.

⁴ Wise and Davies, *J.*, 1938, 273.

⁵ Preceding paper.

⁶ Denney and Monk, *Trans. Faraday Soc.*, 1951, 47, 992.

⁷ MacDougall and Davies, *J.*, 1935, 1416.

to be 18.0 kcal. mole⁻¹. Our magnesium figures in Table 3 give a linear plot when $\log k/\alpha$ is plotted against $1/T$, whence from the Arrhenius equation,

$$\log k/\alpha = \log A - E_A/2.303RT$$

$E_A = 18.1 \pm 0.1$ kcal. mole⁻¹ and $A = 1.5 \times 10^{10}$. If k is used instead of k/α , $A = 7.2 \times 10^9$. The former value of A is much the nearer general average⁹ of 2.7×10^{11} that is found for a large number of bimolecular reactions.

Our method of calculation also gives higher figures for the reaction between isopropyl bromide and thiosulphate (Table 4). There is some change with ionic strength which may be due to uncertainties in the calculations or it may be due to an ion-dipole salt effect. The extrapolation of $\log (k/\alpha)$ against I gives 7.2×10^{-5} mole l.⁻¹ sec.⁻¹ for the reaction rate whereas the original workers obtained 2.94×10^{-5} .

EXPERIMENTAL

The preparation of the thiosulphates has been described in the preceding paper. Vogel's method¹⁰ of preparation was used for *n*-propyl bromide. Gravimetric analysis gave 64.92% of bromine (theor., 64.96%). The sample was stored in a dark bottle and refractionated at intervals of not greater than two weeks. The iodine-titration solution was standardised against sodium thiosulphate which itself was standardised against potassium iodate.

For a run, a sample of *n*-propyl bromide was weighed into a graduated flask containing solvent. The volume was made up and the solution siphoned into a burette. A known volume was run into the graduated reaction flask, the desired amount of sodium acetate stock solution added, and the reaction flask placed in the thermostat. A stock solution of thiosulphate was made up by weight after its equivalent weight had been found by titration as described in the preceding paper. The stock solution was placed in a thermostat and the reaction was started by pipetting a portion into the reaction flask. The time of half-delivery was taken as zero. The solution in the reaction flask was made up to the mark, not more than 5 ml. of solvent being required. The whole was well shaken and a volume withdrawn by a lagged pipette stored in the thermostat. The reaction was stopped by running the contents into 100 g. of crushed ice. The time of half-delivery, usually zero plus 1 min., was taken as the time of removal. The titre at zero time was obtained by extrapolating succeeding titres against time. The weighing out of the *n*-propyl bromide was checked by hydrolysing samples with sodium hydroxide in sealed tubes at 100° and analysing the products for bromide. The values agreed with those calculated within 0.04%. In a few cases when sodium thiosulphate was used the reaction was taken to completion; the thiosulphate used was equivalent to 99.5% of the *n*-propyl bromide taken.

For very dilute solutions the end-point with starch was not good. There was a marked end-point error and this was decreased by using 10 ml. of 0.1M-potassium iodide, 5 ml. of 1% starch solution, and sufficient iced water to make the volume up to 150 ml. The colour change was taken to a fixed shade, and corresponding controls of the same colour required 0.02 ml. of 0.01N-iodine to 0.15 ml. of 0.001N-solution. This procedure was also adopted when standardising the thiosulphate against potassium iodate.

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⁸ Davies and Monk, *J.*, 2718, 1951.

⁹ Moelywn-Hughes, "Kinetics of Reactions in Solution," Clarendon Press, Oxford, 1947, p. 70.

¹⁰ Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 277.