

Ion Pair Formation Studies: Part IV—Effect of Ion Pairs on the Kinetics of the Reaction between Potassium Peroxydisulphate & Potassium Iodide

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The present rate data show that I^- ion is oxidized not only by the $S_2O_8^{2-}$ ion but also by the ion-pair KS_2O_8 simultaneously. The rate constants at zero ionic strength for the $S_2O_8^{2-}+I^-$ and $KS_2O_8+I^-$ reactions have been separated from the observed rate constants and found to be 0.089 litre $mol^{-1} min^{-1}$ (k_1^0) and 0.514 litre $mol^{-1} min^{-1}$ (k_2^0) respectively at 25° . The extent of participation of the ion-pair in the oxidation increases with increase in the ionic strength of the solution and in the present work it is found to be 19% over the ionic strength range studied (0.025-0.10M).

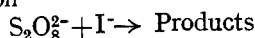
EARLIER investigations¹⁻⁷ on the peroxydisulphate and iodide ions reaction have shown that Brönsted-Bjerrum equation⁸ is applicable below ionic strength of 0.025M. The deviations at high ionic strength in many reactions^{9,10a} have been interpreted as due to the possible participation of ion pairs. In our earlier work¹¹ it was shown that the ion pair KS_2O_8 exists in aqueous solution of $K_2S_2O_8$ and its stability constant was found to be 13.16 litre mole⁻¹ at 25° . There is likelihood of either $S_2O_8^{2-}$ or the ion pair KS_2O_8 alone acting as an oxidant in the $S_2O_8^{2-}+I^-$ reaction. Also it is possible that both the species might be involved in the oxidation of I^- ion simultaneously. In the present paper, the oxidation of I^- ion by peroxydisulphate was studied at high ionic strengths with a view to recognizing the possible species involved in the oxidation of I^- ion.

Materials and Methods

All the chemicals used were AR grade and the solutions were prepared always fresh in conductivity water (sp. cond. $<1 \times 10^{-6}$ mhos). The concentration of $K_2S_2O_8$ and KI were 0.01N each and KCl was employed to adjust the ionic strength. The reaction was followed at $25.0^\circ \pm 0.02^\circ$ by titrating the liberated iodine at different intervals with standard hypo.

Results and Discussion

Since the reaction obeyed second order kinetics it is quite likely that the rate determining step involves reaction



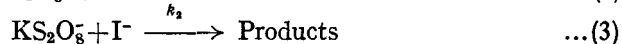
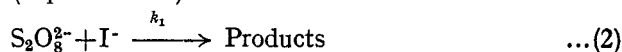
According to Brönsted-Bjerrum equation⁸ for aqueous systems at 25°

$$\log k = \log k_0 + 1.02 Z_A Z_B \sqrt{\mu} \quad \dots(1)$$

The slope of the plot $\log k$ vs $\sqrt{\mu}$ should be 2.04 for the above reaction. At low ionic strengths King and Jacobs², and Indelli and Prue⁶ obtained a slope

of 2.0 (Fig. 1). Here it must be pointed out that when one excludes the last two values of Indelli and Prue at low concentrations, viz. 0.00338 and 0.00838M (Table 1), the slope comes out to be 1.77. In the present work we have reinvestigated the reaction over the ionic strength range of 0.025 to 0.10M and the least square slope of the plot of $\log k_{obs}$ vs $\sqrt{\mu}$ comes out to be 1.62 (Fig. 1). However, Chlebek and Lister⁹ who studied the reaction between potassium hexacyanoferrate(II) and potassium peroxydisulphate concluded that the reactive species are $KFe(CN)_6^{3-}$ and KS_2O_8 since a slope of 3.0 was obtained for the plot of $\log k$ vs $f(\mu)$. Therefore the possible participation of KS_2O_8 appears likely, in $S_2O_8^{2-}+I^-$ reaction also. Hence we have interpreted the observed deviation of the experimental slopes from the theoretical values in terms of the involvement of the ion pair KS_2O_8 as outlined below.

First it was assumed that either $S_2O_8^{2-}$ or KS_2O_8 is reacting with I^- ion in the rate determining step (Eqs. 2 and 3).



If K_0 is the association constant of the ion pair at zero ionic strength, then k_1 and k_2 in terms of k_{obs} could be written in terms of Eqs. (4) and (5) respectively.

$$k_1 = k_{obs} (1 + K_0 [K^+] f_2) \quad \dots(4)$$

$$k_2 = k_{obs} (1 + K_0 [K^+] f_2) / K_0 [K^+] f_2 \quad \dots(5)$$

The rate constants k_1 and k_2 were calculated from Eqs. (4) and (5) respectively. The value of K_0 was taken from our earlier work¹¹. If the reaction proceeds solely by path (2), the slope of the Brönsted-Bjerrum plot should be 2.04. But slope of $\log k_1$ vs $\sqrt{\mu}$ was found to be 2.8. If the reaction proceeds solely by path (3), then the slope should be 1.02. But k_2 did not show any regular trend with the change in ionic strength (μ). Since neither k_1 nor

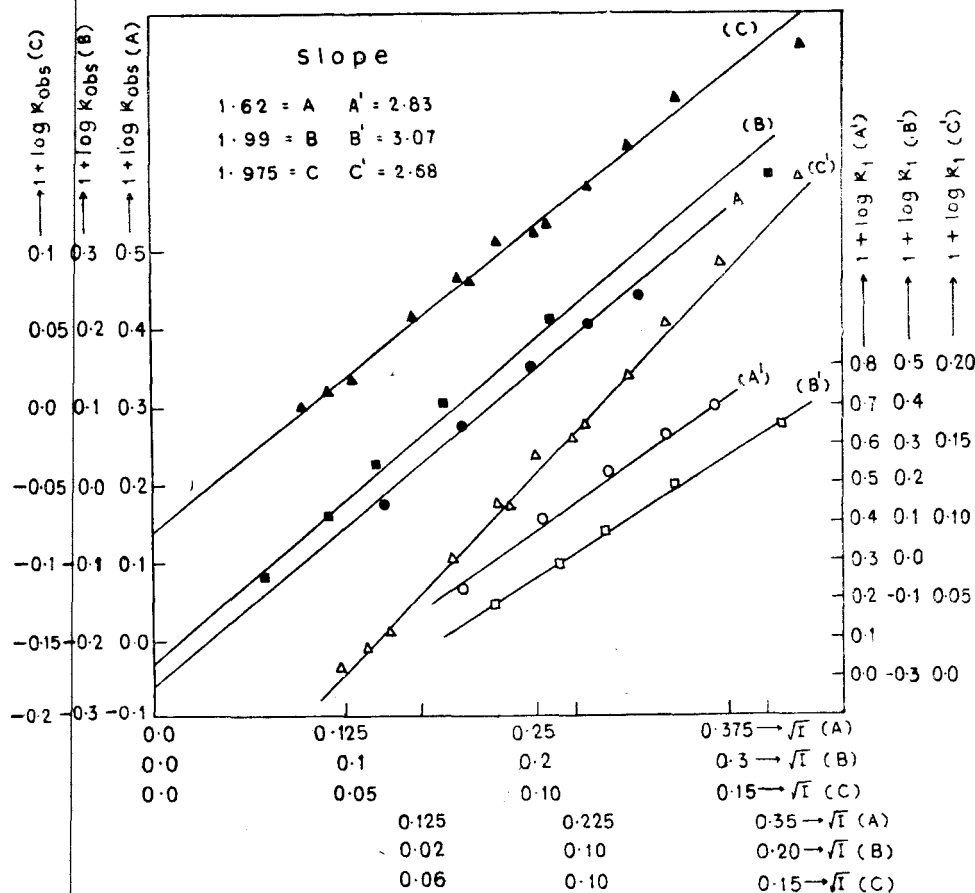


Fig. 1 — Plots of $1 + \log k_{obs}$ versus $\sqrt{\mu}$ (curves A, B and C) at 25° and of $1 + \log k_1$ versus $\sqrt{\mu}$ (curves A', B' and C') at 25° [Curves A, A' for the present data; B, B' for Indelli and Prue; and C, C' for King and Jacobs]

TABLE 1 — RATE CONSTANT AND ACTIVITY COEFFICIENT VALUES AT VARIOUS IONIC STRENGTHS FOR $K_2S_2O_8 + KI$ REACTION AT 25°

$\mu(M)$	k_{obs} (litre mole ⁻¹ min ⁻¹)	f_2	f_1	k_1° (litre mole ⁻¹ min ⁻¹)	k_2° (litre mole ⁻¹ min ⁻¹)
PRESENT WORK					
				$k_1^\circ = 0.089$	$k_2^\circ = 0.514$
0.0234	0.1500	0.7460	0.8630	0.1826	0.7362
0.0423	0.1875	0.7400	0.8310	0.2338	0.8331
0.0616	0.2250	0.6720	0.8094	0.2856	0.9207
0.0810	0.2550	0.6436	0.7935	0.3388	1.0029
0.1005	0.2750	0.6321	0.7812	0.3945	1.0822
INDELLI AND PRUE					
				$k_1^\circ = 0.0648$	$k_2^\circ = 0.415$
0.00388	0.0756	0.8966	0.9387	0.0851	0.4757
0.00888	0.0912	0.8603	0.9090	0.0996	0.5145
0.01388	0.1062	0.8145	0.8898	0.1116	0.5446
0.02388	0.1278	0.7574	0.8630	0.1329	0.5943
0.04388	0.1624	0.6964	0.8296	0.1724	0.6769
0.10388	0.2470	0.6112	0.7797	0.2934	0.8830
KING AND JACOBS					
				$k_1^\circ = 0.093$	$k_2^\circ = 0.4885$
0.00154	0.1000	0.9413	0.9571	0.1118	0.5356
0.00215	0.1021	0.9239	0.9501	0.1156	0.5447
0.00275	0.1040	0.9100	0.9442	0.1190	0.5525
0.00456	0.1140	0.8790	0.9301	0.1277	0.5724
0.00635	0.1210	0.8585	0.9192	0.1352	0.5891
0.00696	0.1200	0.8498	0.9160	0.1376	0.5942
0.00815	0.1279	0.8380	0.9101	0.1421	0.6039
0.00996	0.1291	0.8226	0.9023	0.1486	0.6175
0.01057	0.1309	0.8180	0.8999	0.1507	0.6219
0.01295	0.1380	0.8013	0.8912	0.1587	0.6382
0.01538	0.1459	0.7869	0.8835	0.1664	0.6535
0.01893	0.1581	0.7685	0.8735	0.1775	0.6749
0.02515	0.1698	0.7435	0.8597	0.1959	0.7090

k_2 varied in accordance with the Brönsted-Bjerrum equation, it is concluded that the assumption of only one species participating in the reaction is not valid. Alternatively it was assumed that both the species are participating in the reaction simultaneously. In such a case the rate law for the reaction could be represented by Eq. (6)

$$\frac{d[I_2]}{dt} = k_1^0[I^-][S_2O_8^{2-}] \frac{f_1 f_2}{f_3} + k_2^0[I^-][KS_2O_8] \frac{f_1^2}{f_2} \quad \dots(6)$$

where k_1^0 and k_2^0 are the rate constants for the reactions (2) and (3) respectively and f_1 , f_2 and f_3 are the activity coefficients of uni-, bi- and tri-valent (activated complex) species present in solution. The observed rate law and the association constant for the ion pair (K_0) may be represented by Eqs. (7) and (8).

$$\frac{d[I_2]}{dt} = k_{obs} [I^-]_{total} [S_2O_8^{2-}]_{total} \quad \dots(7)$$

$$K_0 = \frac{[KS_2O_8]}{[K^+][S_2O_8^{2-}]} \quad \dots(8)$$

From Equations (6), (7) and (8), we get

$$k_{obs} (1 + K_0[K^+]f_2) = k_1^0 \frac{f_1 f_2}{f_3} + k_2^0 K_0 [K^+] f_1^2 \quad \dots(9)$$

The concentration of free K^+ , $S_2O_8^{2-}$ and activity coefficients were calculated as follows:

If m_1 is the molar concentration of potassium peroxydisulphate and α the degree of dissociation of the ion pair formed, then the ionic strength of the $K_2S_2O_8$ is given by the relationship (10)

$$\mu = (1 + 2\alpha)m_1 \quad \dots(10)$$

and the total ionic strength of the solution is given by Eq. (11)

$$\mu = (1 + 2\alpha)m_1 + m_2 + m_3 \quad \dots(11)$$

where m_2 and m_3 refer to the concentrations of KI and KCl respectively. Activity coefficients were calculated using Davies equation^{10b}

$$-\log f = AZ_A Z_B \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3\mu \right) \quad \dots(12)$$

where $A = 1.8246 \times 10^6 / (\epsilon T)^{3/2}$. The activity coefficient of KCl and KI are almost the same^{12a} and hence, were considered together as one constituent and $K_2S_2O_8$ as another in the calculation of activity coefficient $f_{2\pm}$ by Guggenheim's equation^{12b} (Eq. 13) for the mixed electrolytes:

$$\ln f_{2\pm} = \ln f_1^0 + X (\ln f_{2\pm}^0 + \ln f_1^0) \quad \dots(13)$$

where X is the mole fraction and $f_{2\pm}^0$ is the activity coefficient of the pure $K_2S_2O_8$ solution. Using the relation (14), f_2 was calculated.

$$\ln f_2 = 2 \ln f_{2\pm} \quad \dots(14)$$

The degree of dissociation of the ion pair, α is related to the association constant (K_0) by the expression (15).

$$K_0 = \frac{(1 - \alpha)}{\alpha(1 + \alpha)m_1 + m_2 + m_3} f_2 \quad \dots(15)$$

To start with α was assumed to be unity and the corresponding value of μ was calculated from Eq. (10). This value of μ was then substituted in Eq. (12) from which $f_{2\pm}^0$ was calculated. The value of f_1^0 was also calculated from Eq. (12). Using these values of

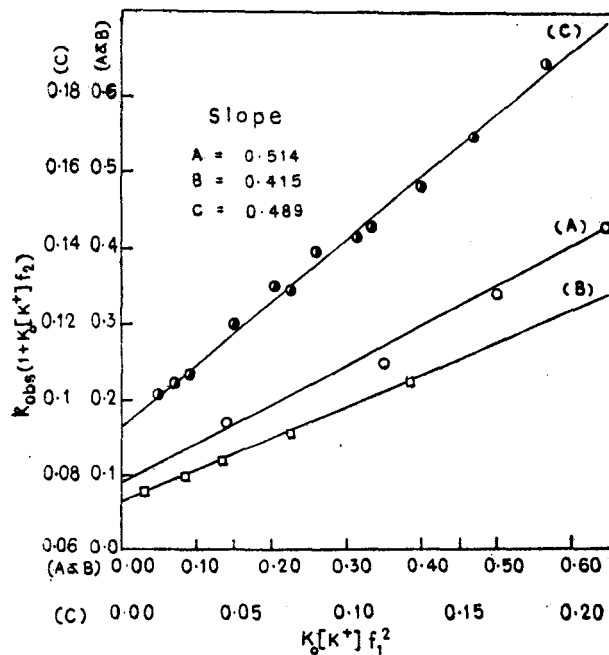


Fig. 2 — Plots of $(1 + K_0[K^+]f_2)$ versus $K_0[K^+]f_1^2$ [(A) for the present data at 25°; (B) for the data due to Indelli and Prue; and (C) King and Jacobs at 25°]

$f_{2\pm}^0$ and f_1^0 , the value of $f_{2\pm}$ (Eq. 13) and f_2 (Eq. 14) were calculated. The f_2 value was substituted in Eq. (15) to get an improved value of α . This procedure was repeated several times till constant values for α and f_2 were obtained.

The values of μ , f_1 , f_2 , $[K^+]$ and k_{obs} are tabulated in Table 1. According to Eq. (9), plot of $k_{obs} (1 + k_0[K^+]f_2)$ vs $K_0[K^+]f_1^2$ should be linear with an intercept. Such a plot was obtained (Fig. 2) in the present work suggesting that the assumption made earlier, viz. that both the species are participating in the oxidation of I^- ion simultaneously is correct. The slope was found to be 0.514 (k_2^0) and intercept 0.089 (k_1^0). Their standard errors are also presented in Table 2. King and Jacobs² and Indelli and Prue⁶ reported only the second order rate constants (k_{obs}) at different ionic strengths. We have analysed their data also for comparison and calculated the activity coefficients (Table 1), k_1^0 and k_2^0 values (Table 2) by the method discussed above. The expected rate constants (k_1^0 and k_2^0) at various ionic strengths were calculated using Brönsted-Bjerrum equation⁸. The value of the observed rate constant (k_{obs}) does not agree with the calculated values of either k_1^0 or k_2^0 . So k_{obs} was considered as a linear combination of k_1^0 and k_2^0 with appropriate coefficients A and B (Eq. 15).

$$k_{obs} = Ak_1^0 + Bk_2^0 \quad \dots(16)$$

The values of A and B were calculated using least square bivalent regression procedure¹³. From the values of A and B (Table 2), the percentage contribution of the ion pair to the overall reaction was calculated to be 19% over the ionic strength range 0.025 to 0.10M. Similar values for King and Jacob's and Indelli and Prue's data were also computed for comparison (Table 2).

TABLE 2 — VALUES OF k_1^0 (SLOPE) AND k_2^0 (INTERCEPT) OF EQ. 9 AND OF COEFFICIENTS A AND B (EQ. 16)

Author	Ionic strength range M	k_1^0 (litre mole ⁻¹ min ⁻¹)	k_2^0 (litre mole ⁻¹ min ⁻¹)	A	B	Reaction (%) with	
						$S_2O_8^{2-}$	$KS_2O_8^-$
Present work	0.025-0.10	0.089 (0.011)	0.514 (0.019)	0.4270	0.1050	81.0	19.0
Indelli and Prue	0.003-0.10	0.0629 (0.017)	0.415 (0.010)	0.7190	0.0450	94.0	6.0
King and Jacobs	0.010-0.10	0.0629	0.415	0.6280	0.0730	89.5	10.5
	0.0015-0.025	0.093 (0.0012)	0.4885 (0.011)	0.8260	0.0130	98.5	1.5

Values in the parentheses are standard errors.

From these results one can conclude that at high ionic strengths both $S_2O_8^{2-}$ and the ion pair $KS_2O_8^-$ participate in the oxidation of I^- ion simultaneously and the high value for k_2^0 can be attributed to electrostatic forces of repulsion which would be expected to be less for the $KS_2O_8^- + I^-$ reaction compared to $S_2O_8^{2-} + I^-$ reaction. However, the extent of participation of the ion pair appears to depend on the ionic strength range employed.

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References

1. JETTE, E. & KING, C. V., *J. Am. chem. Soc.*, **51** (1929), 1034.
2. KING, C. V. & JACOBS, M. B., *J. Am. chem. Soc.*, **53** (1931), 1704.
3. KING, C. V. & KUNDSEN, O. M., *J. Am. chem. Soc.*, **60** (1938), 687.
4. SOPER, F. G. & WILLIAMS, E., *Proc. R. Soc.*, **140A** (1933), 59.
5. HOWELLS, W. J., *J. chem. Soc.*, (1939), 463; (1941), 641; (1946), 203; (1964), 5844.
6. INDELLI, A. & PRUE, J. E., *J. chem. Soc.*, (1959), 107.
7. PRICE, TH. SL., *Z. phys. Chem.*, **27** (1898), 474.
8. MOELWYN HUGHES, E. A., *The chemical statics and kinetics of solutions* (Academic Press, London & New York), 1971, 162.
9. CHLEBEK, R. W. & LISTER, M. W., *Can. J. Chem.*, **44** (1966), 437.
10. DAVIES, C. W., *Ion association* (Butterworths, London), 1962, (a) 138; (b) 426.
11. ANANTHASWAMY, J., SETHURAM, B. & NAVANEETH RAO, T., *Indian J. Chem.*, **15A** (1977), 9.
12. ROBINSON, R. A. & STOKES, R. H., *Electrolyte solutions* (Butterworths, London), 1955, (a) 479; (b) 426.
13. MARGENAU, H. & MURPHY, G. M., *The mathematics of physics and chemistry*, Vol. I (Affiliated East-West Press, New Delhi), 1971, 517.