

1114. *The Persulphate-Iodide Reaction. The Basic Rate, Salt Effects, and Solvent Influence.*

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The rate of the reaction has been determined in aqueous solutions of various iodides, and in aqueous solutions of ethyl alcohol in the presence, separately, of sodium and potassium chloride. The velocity constants for the reaction have been estimated at different temperatures in water and in several mixed solvents; they decrease in the series: $\text{H}_2\text{O} > \text{CH}_3\cdot\text{CO}_2\text{H} > \text{C}_2\text{H}_5\cdot\text{OH} > \text{n-C}_3\text{H}_7\cdot\text{OH}$, when the added substances are present in equal molecular concentrations.

THE influence of various ions on the rate of the persulphate-iodide reaction has been recorded in previous Papers. The rate increases in the series $\text{H} < \text{Li} < \text{Na} < \text{NH}_4 < \text{K} < \text{Rb} < \text{Cs}$, and an explanation for this has been suggested in terms of their electric fields.¹ One might expect the electrolyte effects of the same series of cations on a reaction between cations to be in the reverse order, because of repulsion forces of differing magnitude exerted by the added cations. It is of interest to record in this connection that Alina Ulinska, in her investigation of the rate of the reaction between ferric and stannous ions,² found that the cation effect decreases in the series $\text{Li} > \text{Na} > \text{NH}_4 > \text{K} > \text{H}$; this effect is related to the radius of the ion and its electrical field. The only divergence from the reverse order is that of the hydrogen ion, complicated possibly because it is really H_3O^+ and H_5O_2^+ .

In the present work, the reaction rate of the persulphate-iodide reaction has been determined in water and in solutions of mixtures of water and, separately, dextrose, acetic acid, ethyl alcohol, and n-propyl alcohol, some of which contained chlorides as well.

EXPERIMENTAL

The general procedure is described in the previous papers,¹ where the bimolecular velocity constants are expressed in l. equiv.⁻¹ min.⁻¹ units. In the present paper they are in l. mole⁻¹ sec.⁻¹ units and derivable from the equation $k = x/[2at(a-x)]$, where the initial concentrations of persulphate and iodide are respectively a and $2a$ moles l.⁻¹, and x is the number of moles of iodine liberated and persulphate consumed per litre in time t . When the appropriate unit changes are made, this equation and the one previously used yield the same numerical value for the velocity constants.

The alcohols were refluxed over calcium oxide: the ethyl alcohol distilled at 78.0—78.3° at standard pressure, and the propyl alcohol at 96.9—97.3°. The dextrose was AnalaR grade, and the glacial acetic acid and the chlorides were recrystallised AnalaR products. To avoid

¹ Howells, *J.*, 1939, 463; 1941, 641.

² Ulinska, *Roczniki Chem.*, 1951, 25, 69.

contraction effects on mixing, the two reactant solutions contained equal concentrations of these substances. The rate constants in the dextrose and acetic acid solutions are extrapolated initial rates, while all the others are mean values. The reaction solution always contained 0.0025M-H₂SO₄, because slightly acid solutions were found to give more consistent results.

TABLE 1.

Values for bimolecular velocity constants (l. mole⁻¹ sec.⁻¹) for the reaction between persulphate and iodide at 25° in the presence of 0.0025M-H₂SO₄.

	10 ⁵ <i>k</i>	10 ⁵ <i>k</i> ⁰
(a) 0.00833M-Na ₂ S ₂ O ₈ + 0.01666M-NaI	183	83.6
(b) 0.0125M-Na ₂ S ₂ O ₈ + 0.0250M-NaI	205	84.7
(c) 0.01665M-Na ₂ S ₂ O ₈ + 0.0333M-NaI	232	88.9
(d) 0.0125M-K ₂ S ₂ O ₈ + 0.0250M-KI	278	115
(e) 0.0125M-K ₂ S ₂ O ₈ + 0.0250M-RbI	300	124
(f) 0.0125M-K ₂ S ₂ O ₈ + 0.0250M-CsI	328	136

The rate constants in Table 1 are taken from a previous paper,¹ and show that the total electrolyte effects due to potassium, rubidium, and caesium ions are considerably larger than for sodium ions. The *k*⁰ values have been calculated from Brönsted's equation: $k = k^0 f_B / f_{AB}$. Since the Debye-Hückel expression holds only for solutions of very low ionic strengths, the activity coefficients were calculated from Davies's equation, which holds up to an ionic strength of about 0.2M:

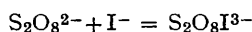
$$-\log f = \frac{1.825 \times 10^6}{(DT)^{3/2}} \cdot z^2 \left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - B\mu \right) = z^2 A \phi(\mu).$$

where μ is the ionic strength and ϕ signifies function.

The *B* term is an empirical parameter included to account for specific ion effects when these are small. Davies and his co-workers³ have frequently use *dB* as 0.2, but Davies's revised value⁴ of *B* as 0.3 has been used in the present calculations. *A* is approximately 0.51 for water at 25°; the *A* values for the mixed solvents were obtained from dielectric constants computed from Åkerlof's tables,⁵ and the International Critical Tables. Combining the above equations:

$$\log k = \log k^0 + 2z_A z_B A \phi(\mu),$$

where the last term becomes 2.04 $\phi(\mu)$ for the persulphate-iodide reaction in water at 25°, since the reaction involved is



The antilogarithm of this term may be regarded as a measure of the primary salt effect.

The *k*⁰ value, although itself a composite term, is ideally a constant for a given reaction. The calculated *k*⁰ figures in Tables 1 and 2 for the solutions containing potassium, rubidium, and caesium salts are much higher than the basic *k*⁰ for the reaction, and signify that the total electrolyte effects in them greatly exceed those expected from a primary salt effect. The gap between the calculated and the basic value provides some indication of the magnitude of the additional salt effect.

Working with a solution of very low concentration, 1.25 × 10⁻⁴M-potassium persulphate, 2.5 × 10⁻³M-potassium iodide, and 5 × 10⁻⁴M-hydrochloric acid, Indelli and Prue⁶ obtained *k* = 0.00126, from which the Brönsted-Davies equation yields a *k*⁰ value of 0.00098 for the reaction. This is in close agreement with the extrapolated estimation of *k*⁰, 0.00100, recorded elsewhere.¹ But since the specific salt effect for sodium ions is much less than for potassium ions, the value of 0.00084 for *k*⁰ in Table 1 (a) is probably a closer approach to the basic rate constant for the persulphate-iodide reaction in water at 25°, and its use in the expression $k_{\text{obs.}}/k^0$ would yield the overall electrolyte effect.

Table 2 gives the experimental and the calculated velocity constants for the reaction in water, aqueous ethanol, and in these in the presence of the specified chlorides.

³ Davies, James, and Monk, *Trans. Faraday Soc.*, 1952, **48**, 921; Davies and Williams, *ibid.*, 1958, **54**, 1549.

⁴ Davies, "Ion Association," Butterworths, London, 1962, p. 41.

⁵ Åkerlof, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

⁶ Indelli and Prue, *J.*, 1959, **1**, 107.

TABLE 2.

Experimental and calculated velocity constants (l. mole⁻¹ sec.⁻¹ units) for the reaction between persulphate and iodide at 25° in water, aqueous ethanol, and n-propanol, and in the presence of chlorides.

(a) 0.01665M-K ₂ S ₂ O ₈ + 0.0333M-KI + 0.0025M-H ₂ SO ₄ ; <i>D</i> = 78.5			
Chloride concn.	0	0.1000M-NaCl	0.1000M-KCl
Ionic strength (M)	0.09075	0.19075	0.19075
10 ⁵ <i>k</i>	312	393	508
10 ⁵ <i>k</i> ⁰	120	123	159
10 ⁵ <i>k</i> (calc.)	312	383	383
(b) = (a) with 3.467M-C ₂ H ₅ ·OH; <i>D</i> = 69			
10 ⁵ <i>k</i>	144	187	283
10 ⁵ <i>k</i> ⁰	44.8	45.7	69.1
10 ⁵ <i>k</i> (calc.)	144 (385)	183 (491)	183 (491)
(c) = (a) with 4.285M-C ₂ H ₅ ·OH; <i>D</i> = 66.5			
10 ⁵ <i>k</i>	122	167	272
10 ⁵ <i>k</i> ⁰	35.6	37.7	61.4
10 ⁵ <i>k</i> (calc.)	122	158	158
(d) = (a) with 3.348M-n-C ₃ H ₇ ·OH; <i>D</i> = 64			
10 ⁵ <i>k</i>	133	—	—
10 ⁵ <i>k</i> ⁰	36.1	—	—

The velocity constants calculated from the Brönsted–Davies equation will depend upon the *k*⁰ value chosen. The adoption of *k*⁰ = 0.00120 throughout Table 2 would yield calculated rate constants that would be higher for the mixed solvents than for water, because of their smaller dielectric constant. A few calculations based on this are given in parentheses in Table 2 (b); they illustrate this point, and disclose the presence of a strong solvent influence. The use of the more basic *k*⁰ = 0.00100 for the aqueous solutions would indicate a substantial specific ion effect, even in the sodium chloride solution, one due largely to the potassium ions present.

However, the calculated rate constants in Table 2 were derived from the specific *k*⁰ values calculated for each solvent in the absence of chloride, and are included since they reveal more clearly the relative salt effects due to the addition of the two chlorides, effects that are superimposed by these chlorides on the reaction described at the head of Table 2.

For the same set of experiments, the *k*⁰ values in the first two columns are in fair agreement despite the presence of 0.1M-sodium chloride; so also are the experimental and calculated rate constants. Those in the first column are of course equal by definition. Thus, it seems that the salt effects in the three sodium chloride solutions can be attributed largely to a primary salt effect.

The velocity constants in the potassium chloride solutions are evidently much too large to be accounted for by a primary salt effect alone. Indelli and Prue have recorded similar results for the reaction in aqueous solutions of these chlorides.⁶ These high reaction rates may be the result of an ion-pair side-reaction induced by the relatively large potassium-ion concentration: $\text{KS}_2\text{O}_8^- + \text{I}^- = \text{KS}_2\text{O}_8\text{I}^{2-}$. On electrostatic grounds, one would expect a faster basic rate for this reaction, because the repulsion between the reactants would be less than for persulphate and iodide ions. Ion-pairing is more likely to happen with potassium than with the smaller sodium ions, although both are known to pair with sulphate and thiosulphate ions.⁷ Similar ion-pairing might occur in the solutions containing rubidium and caesium ions, and account for the relatively high velocity constants in Table I, (e) and (f).

Such pairing of ions of unlike sign might be expected to be more pronounced in mixed solvents because of their smaller dielectric constants. This view finds some support from the fact that the ratio *k*:*k*(calc.) in the potassium chloride solutions is appreciably greater in experiments (c) and (b) than in water; they are 1.72, 1.55, and 1.33, respectively, indicating the relative increase of some specific effect from (a) to (c).

But the influence of such ion-pairing in the mixed solvents is evidently subordinated to some other solvent effects, for the values in Tables 2 and 3 show that the rate constants in them are very much lower than the corresponding ones in water. Brönsted⁸ refers to the tendency towards incomplete dissociation in solvent media of smaller dielectric constant than water. This would

⁷ Davies, "Ion Association," Butterworths, London, 1962, pp. 78, 89.

⁸ Brönsted, *Trans. Faraday Soc.*, 1927, **23**, 431.

decrease the reaction rate by reducing the concentrations of the reactants. Another possibility is that the larger forces of repulsion in such mixed solvents reduce the collision frequency of the reacting ions.

TABLE 3.

Velocity constants (l. mole⁻¹ sec.⁻¹) for the reaction between persulphate and iodide at various temperatures in aqueous solutions of dextrose, acetic acid, ethanol, and n-propanol.

(a) 0.01665M-K ₂ S ₂ O ₈ + 0.0333M-KI + 0.0025M-H ₂ SO ₄ ; <i>D</i> = 78.5						
Temp.	28°	25°	20°	15°	<i>E</i> (g. cal.)	10 ⁻⁷ <i>PZ</i>
10 ⁵ <i>k</i>	383	312	217	148	12700	0.657
(b) = (a) with 0.5000M-dextrose; <i>D</i> = 67						
10 ⁵ <i>k</i>	450	362	263	168	12640	0.691
(c) = (a) with 1.745M-CH ₃ ·CO ₂ H						
10 ⁵ <i>k</i>	312	253	178	120	12590	0.445
(d) = (a) with 3.489M-CH ₃ ·CO ₂ H						
10 ⁵ <i>k</i>	270	215	153	103	12710	0.460
(e) = (a) with 1.711M-C ₂ H ₅ ·OH; <i>D</i> = 74						
10 ⁵ <i>k</i>	255	207	146	100	12430	0.277
(f) = (a) with 3.467M-C ₂ H ₅ ·OH; <i>D</i> = 69						
10 ⁵ <i>k</i>	177	144	99.7	67.5	12570	0.244
(g) = (a) with 6.857M-C ₂ H ₅ ·OH; <i>D</i> = 59						
10 ⁵ <i>k</i>	105	81.8	55.8	36.3	13740	1.007
(h) = (a) with 3.348M-n-C ₃ H ₇ ·OH; <i>D</i> = 64						
10 ⁵ <i>k</i>	165	133	91	61.7	13030	0.497

Von Kiss and Hatz⁹ determined the rate of the persulphate-iodide reaction in aqueous solutions of glycerol, methyl alcohol, and ethyl alcohol and found the rate constant diminished in the order glycerol > methyl alcohol > ethyl alcohol.

Table 3 records the rate constants at different temperatures in several aqueous mixtures. The salt effect of acetic acid is probably small and has not been considered. The activation energies for the reaction were computed by plotting $\ln k$ against $1/T$ (°K) and approximately straight lines were obtained, showing conformity with the Arrhenius equation. The *PZ* values, at 25°, were calculated from the collision equation: $k = PZ e^{-E/RT}$. The persulphate was not easily soluble in the 6.857M-alcohol solution, and the *E* and *PZ* values, which at best are only approximate, may be less reliable in this solution.

The results show that the solvent influence on the reaction rate is considerable, and that the rate constants generally diminish as the dielectric constant of the solvent mixtures decreases.

The velocity constants in the dextrose solutions indicate that there are instances when some other solvent effect plays the dominant rôle, since, despite a smaller dielectric constant, the reaction rate is greater than in water. Fairclough and Hinshelwood¹⁰ suggest that a large molecule such as dextrose may "hem in" reactant pairs to bring about a higher incidence of repeated collisions, which together may be more effective in producing chemical change than a series of fresh encounters.

DISCUSSION

The activation energy of the reaction is relatively small, and possible reasons for this have been suggested elsewhere.¹¹ The superior electrolyte effect of potassium, rubidium, and caesium ions may be caused by ion-pairing followed by a more rapid side-reaction. The solvent influence on the activation energy of the reaction does not appear to be large. The reaction rate, excepting that in the dextrose solution, is much greater in water than in the mixed solvents, which are media of smaller dielectric constant. The rate diminishes in

⁹ Von Kiss and Hatz, *Rec. Trav. chim.*, 1929, **48**, 7.

¹⁰ Fairclough and Hinshelwood, *J.*, 1939, 593.

¹¹ Howells, *J.*, 1946, 206.

the order $\text{H}_2\text{O} > \text{CH}_3\cdot\text{COOH} > \text{C}_2\text{H}_5\text{OH} > \text{n-C}_3\text{H}_7\cdot\text{OH}$, when the added substances are present in equal molecular concentrations. Except in experiments (b) and (g), the *PZ* value is highest in water.

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