23. *Kinetic Salt Effects in the Reaction between Persulphate and Iodide Ions.*

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The second-order reaction between persulphate and iodide ions can be accurately and conveniently studied in dilute solution by using a polarised electrode to determine the times of reappearance of iodine after the injection of successive quantities of sodium thiosulphate. The kinetic salt effects of a variety of added salts of various valency types have been studied. Over a range of ionic strengths above 0·0034 mole l.$^{-1}$ the effects are very specific; there is some correlation with the concentration of ions of charge opposite to that of the reactants, but none with the ionic strength. The effects cannot be satisfactorily interpreted with Debye–Hückel-type equations for the activity coefficients of the reactant ions and the activated complex, even with the additional assumption of ion association. The theory of kinetic salt effects is discussed.

In 1949 Olson and Simonson,[1] discussing the effect of addition of inert salts on the rates of ionic reactions, asserted that for reactions between ions of like charge the effect is almost exclusively due to the concentration and character of ions of charge opposite to that of reactants, and that the rate is not simply dependent on the ionic strength of the solutions. Kilpatrick [2] pointed out that in Brönsted's original formulation [3] of the theory of kinetic salt effects, before the advent of the Debye-Hückel theory,[4] the importance of specific interactions between ions of opposite charge was clearly recognised. There can be little doubt that the fundamental equation of Brönsted's theory of kinetic salt effects is correct, *viz.*, for reaction between two ions of charges z_A and z_B respectively, $k = k^\circ f_A f_B / f_{AB}$ where

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[1] Olson and Simonson, *J. Chem. Phys.*, 1949, **17**, 1167.
[2] Kilpatrick, *Ann. Rev. Phys. Chem.*, 1951, **2**, 255.
[3] Brönsted, *Z. phys. Chem.*, 1922, **102**, 169.

k° is a constant for the solvent and f_A, f_B, and f_{AB} are activity coefficients which tend to unity as the total concentration of ions in solution tends to zero; f_{AB} is the activity coefficient of the activated complex, and Brönsted's theory can be regarded [5] as a special application of the transition-state theory of reaction kinetics. Brönsted [3] tested the equation with experimental results for the activity-coefficient factor derived from solubility measurements. Barrett and Baxendale [6] recently showed that at sufficiently low ionic strengths ($<4 \times 10^{-3}$ mole l.$^{-1}$) the variation with ionic strength of the rate constant of a reaction between two ions of opposite charge, *viz.*, $Fe^{2+} + Co(C_2O_4)_3{}^{3-}$, is close to that predicted by substituting the Debye–Hückel limiting-law values for the activity coefficients in the Brönsted equation; the correlation of the rate constant with ionic strength is good, and only small specific effects appear. In other cases, results can be quantitatively described [7] up to an ionic strength of 0·1 mole l.$^{-1}$ by the equation $\log k = \log k^\circ + 2z_Az_BAI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) + BI$ where A is a constant of the Debye–Hückel theory and B is an empirical parameter which takes account of small specific effects. However, the repeated reproduction in text-books of a diagram published by Livingston [8] in 1930, in which the rate constants for six reactions of different charge types are shown to vary approximately as predicted by the limiting-law, even when the ionic strengths increase to 0·04—0·07 mole l.$^{-1}$, has perhaps led to an attitude which underestimates the specific effects which can occur. Data for the reaction between bromoacetate and thiosulphate ions were used in Livingston's diagram, but when bivalent cations are present as well as alkali-metal cations large specific effects arise [9] which have been quantitatively interpreted [10] in terms of ion association. Olson and Simonson [1] concluded that, even for univalent cations, the cation concentration was more significant than the ionic strength. Scatchard [11] has discussed the effects observed for this reaction and concludes that they are in accord with Mayer's treatment [12] of electrolyte solutions.

A reaction of the same charge type is that between persulphate and iodide ions to produce iodine and sulphate ions. It is of the first order with respect to both reactants and King and Jacobs [13] and King and Knudsen [14] obtained results that followed the limiting-law prediction up to an ionic strength of 0·025 mole l.$^{-1}$; Soper and Williams [15] found a greater increase of rate constant with increasing ionic strength than predicted by the limiting law. In most of these experiments the ionic strength was varied by changing the reactant concentrations. Specific salt effects have been observed at much higher concentrations by Howells,[16] Rolla and Carassiti,[17] and Carassiti and Dejak,[18] who interpreted the results in terms of a theory due to Bonino.[19] We have found that accurate results for this reaction can conveniently be obtained in dilute solution by using a polarised electrode [20] to determine the times of reappearance of iodine in the solution after the injection of successive small quantities of sodium thiosulphate solution with a micro-syringe. In this way we have studied the kinetic salt effects of a variety of added salts of various valency types. Large specific effects were observed and it is not possible to

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[4] Debye and Hückel, *Physik. Z.*, 1923, **24**, 185.

[5] Eyring and Wynne-Jones, *J. Chem. Phys.*, 1935, **3**, 492.

[6] Barrett and Baxendale, *Trans. Faraday Soc.*, 1956, **52**, 210.

[7] Guggenheim and Prue, "Physicochemical Calculations," North-Holland Publishing Co., Amsterdam, 1956, p. 466.

[8] Livingston, *J. Chem. Educ.*, 1930, **7**, 2899.

[9] LaMer and Fessenden, *J. Amer. Chem. Soc.*, 1932, **54**, 2351.

[10] Wyatt and Davies, *Trans. Faraday Soc.*, 1949, **45**, 774; Davies and Williams, *ibid.*, 1958, **54**, 1547.

[11] Scatchard, "Electrochemical Constants," National Bureau of Standards Circular 524, 1953, p. 185.

[12] Mayer, *J. Chem. Phys.*, 1950, **18**, 1426.

[13] King and Jacobs, *J. Amer. Chem. Soc.*, 1931, **53**, 1704.

[14] King and Knudsen, *J. Amer. Chem. Soc.*, 1938, **60**, 687.

[15] Soper and Williams, *Proc. Roy. Soc.*, 1933, *A*, **140**, 59.

[16] Howells, *J.*, 1939, 463; 1941, 641; 1946, 203.

[17] Rolla and Carassiti, *Boll. Fac. Chim. Ind., Bologna*, 1949, **7**, 37.

[18] Carassiti and Dejak, *Atti. Accad. Sci. Inst. Bologna*, 1955, **11**, 1.

[19] Bonino, *Mem. R. Accad. ital.*, 1933, **4**, 415.

[20] Sully, *Chem. and Ind.*, 1955, 1146.

describe the results over the ionic strength range 0·004—0·1 mole $l.^{-1}$ in terms of Debye–Hückel-type equations for the activity coefficients. There is some correlation of the rate constants with the concentration and character of ions of charge opposite to that of the reactants.

EXPERIMENTAL

Materials.—" AnalaR " reagents were used, except for sodium tri- and tetra-metaphosphates ($Na_3P_3O_9$ and $Na_4P_4O_{12}$), prepared and purified as described elsewhere,[21, 22] and sodium iodide, lithium and lanthanum chlorides, potassium perchlorate, tetramethyl- and tetraethyl-ammonium bromide, and hexamminocobalt trichloride which were B.D.H. laboratory reagents. All solutions were prepared with water of conductivity less than 10^{-6} ohm^{-1} $cm.^{-1}$ from an ion-exchange column. Potassium iodide and sodium thiosulphate solutions were standardised against " AnalaR " potassium iodate. Potassium persulphate solution was standardised by adding a sample to a large excess of potassium iodide and a trace of ferrous sulphate, leaving the solution for a day, and titrating the liberated iodine against the standard thiosulphate solution. Magnesium chloride solutions were standardised against EDTA, and lithium and lanthanum chloride solutions against silver nitrate.

Procedure.—Most experiments (Table 1) were carried out with 200 ml. of a solution containing 0·0025M-potassium iodide, 0·000125M-potassium persulphate, 0·0005M-hydrochloric acid, 5×10^{-6}M-EDTA (as disodium salt), and an added electrolyte. The reaction vessel was in a thermostat at 25° ± 0·02° and was completely shielded from light.

Successive accurately known additions of 0·01 ml. of 0·01M-sodium thiosulphate solution were made from an " Agla " micrometer syringe. On each occasion, the time at which the thiosulphate had been completely consumed by the iodine produced was determined by a polarised electrode method. Two platinum wires, each 1″ long, dipped into the solution and were connected in series with a 27v dry battery and a 20 megohm resistance as a constant-current source; a Tinsley 4500 LS galvanometer with a 1·8 megohm resistance in series was used as a voltmeter. The solution was stirred by an electric motor whose speed was maintained constant with a manually controlled resistance and a stroboscope. Both the thiosulphate and iodine depolarise the electrodes and the potential difference between the electrodes rises to a maximum when neither is present. It was found convenient to treat as the end-point a time when the galvanometer deflection had fallen a small but definite amount below the maximum.

TABLE 1. *Second-order rate-constants,* 10^3k *(l. mole^{-1} sec.$^{-1}$), for the reaction of* $S_2O_8^{2-}$ *with* I^- *at 25°.*

$[K_2S_2O_8] = 1{\cdot}25 \times 10^{-4}$, $[KI] = 2{\cdot}50 \times 10^{-3}$, $[HCl] = 5 \times 10^{-4}$, $[EDTA] = 5 \times 10^{-6}$ mole $l.^{-1}$, $10^3k = 1{\cdot}26$ l. $mole^{-1}$ $sec.^{-1}$.

Equiv. $l.^{-1}$ Added salt	0·005	0·01	0·02	0·04	0·1
KCl(1)	1·52	1·77	2·13	2·70	4·12
$KClO_4$(2)	—	1·75	2·11	2·67	—
KNO_3(3)	1·56	1·86	2·21	2·79	4·24
K_2SO_4(4)	1·53	1·75	2·11	2·65	3·82
NaCl(5)	—	—	1·77	2·12	2·84
$NaClO_4$(6)	—	—	1·90	2·28	3·05
Na_2SO_4(7)	1·44	1·54	1·76	2·08	2·73
$Na_3P_3O_9$(8)	—	—	1·80	2·11	2·73
$Na_4P_4O_{12}$(9)	—	1·54	1·72	2·03	—
LiCl(10)	—	—	1·67	1·91	2·43
NMe_4Br(11)	—	—	—	1·89	2·22
NEt_4Br(12)	—	—	—	1·48	1·40
$MgCl_2$(13)	1·74	2·06	2·44	2·89	3·58
$LaCl_3$(14)	—	4·35	5·32	—	—
$Co(NH_3)_6Cl_3$(15)	13·85 *	25·2	—	38·7	—

* 0·0025 equiv. $l.^{-1}$.

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[21] Indelli, *Ann. Chim.* (*Italy*), 1953, **43**, 845.

[22] *Idem, ibid.*, 1957, **47**, 586.

Usually 15 to 20 points were determined on the reaction curve for each solution. Iodide ions are constantly regenerated by the reaction of the iodine produced with the added thiosulphate and the reaction under these conditions behaves as a first-order one. Fig. 1 shows a typical first-order plot for a reaction in 0·1M-sodium chloride, in which C_0 and C_t are the persulphate-ion concentrations at times 0 and t. Because of the sensitivity of the polarised-electrode method of end-point determination and the use of the microsyringe, we believe that we have been able to determine rate constants accurate to within 1—2% by a study of only about 4% of the reaction; the deviations of the individual points from the first-order plots correspond to 10^{-8} mole/l of I_2. The good first-order plots and the very small change in the composition of the solutions during a measurement support the necessary assumption that throughout a measurement the concentration of thiosulphate (or iodine) at each potential maximum is the same even if not exactly zero.

All solutions were 0·0005M in hydrochloric acid because preliminary experiments showed that the acid eliminated an induction period. The solutions were also 5×10^{-6}M in EDTA because otherwise the reaction rates were higher and less reproducible; presumably EDTA removes traces of heavy-metal ions with a strong catalytic effect. A tenfold increase in the concentration of EDTA did not affect the rates. No complications could arise from the presence of I_3^- ions, for their concentration is always negligible compared with that of iodide ions. Ordinarily the thiosulphate was only present for a very short time, but the possibility that reaction between thiosulphate and persulphate ions was a source of error was eliminated by performing some experiments in which the concentrations of thiosulphate and persulphate were both increased tenfold and the thiosulphate was added immediately after the appearance of iodine; the observed rates did not differ by more than 4% from those ordinarily obtained.

TABLE 2. *Second-order rate-constants for the reaction of* $S_2O_8^{2-}$ *with* I^- *at* 25°

Except in last entry $[K_2S_2O_8] = 1{\cdot}25 \times 10^{-3}$, $[KI] = 2{\cdot}50 \times 10^{-3}$, $[HCl] = 5 \times 10^{-4}$ mole l.$^{-1}$, $[EDTA] = 5 \times 10^{-6}$ mole l.$^{-1}$.

Added salt	—	NaCl	NaCl	$NaClO_4$	$NaClO_4$	$Na_3P_3O_9$	$Na_3P_3O_9$	$Na_4P_4O_{12}$	NaI *
Concn. (equiv. l.$^{-1}$) ...	—	0·02	0·10	0·02	0·10	0·02	0·10	0·02	0·0025
10^3k (l. mole^{-1} sec.$^{-1}$)...	1·30	1·78	2·85	1·80	2·86	1·81	2·83	1·72	1·19

* KI omitted, $[K_2S_2O_8] = 1{\cdot}25 \times 10^{-4}$ mole l.$^{-1}$.

If there were any appreciable reaction between persulphate and tetrathionate ions one would not expect linear first-order plots.

The results of a few experiments with a concentration of potassium persulphate ten times greater than usual, or with sodium iodide replacing potassium iodide, are given in Table 2.

DISCUSSION

The logarithms of the second-order rate-constants in Table 1 have been plotted in Fig. 2 against the square-root of the ionic strength. The numbering of the added salts in Table 1 corresponds to that in Figs. 2 and 3. For clarity the experimental points are not shown; none deviates by more than 2% from its curve. Fig. 2 also shows the Debye–Hückel limiting-law slopes for reactions of various charge types. The primary kinetic salt effects observed are positive but very specific, and seldom even approximate to the behaviour predicted by the limiting law for a reaction between singly- and doubly-negatively charged ions. For most salts, attempts to describe the results up to an ionic strength of 0·1 by the equation previously found successful [7] for the reaction between potassium bromoacetate and potassium thiosulphate also fail. It is also clear that association of the activated complex with cations cannot alone adequately explain the results both because many of the salt effects are much less than the Debye–Hückel equation predicts, and also because of the pronounced specific effects of anions. Although the results for potassium chloride and potassium sulphate can be described to within 5% by assuming that there are two reaction paths, in the second of which the activated complex contains a potassium ion as well as the persulphate and iodide ions, yet attempts to extend this treatment to other salts by postulating the association of reactant ions fail.

The magnitude of the specific effects of the cations is evident both from the very large influence of the triply charged cations and from the observation that even when the ionic strength is as low as 0·0034 mole $l.^{-1}$, replacement of the 0·0025M-potassium iodide by sodium iodide reduces the rate by 5%. If the rate constant is plotted against the equivalent concentration of cations (Fig. 3), the curves for the various sodium and potassium salts fall in sheafs corresponding to the cation and to this extent there is a better correlation of the rate constants with the concentration and character of ions of charge opposite to that of the reactants than with the ionic strength, but we note also the differences between the curves for uni-univalent salts of the same cation. We conclude that over the ionic strength range studied, the specific effects exerted by both cations and anions on the large triply charged activated complex with unknown charge distribution outweigh completely the long-range interactions described by the Debye–Hückel equations; nor does the additional assumption of ion association seem capable of providing a satisfactory interpretation of the results.

Fig. 1.

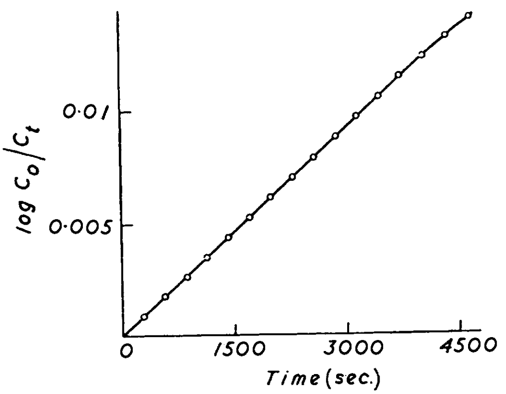


Fig. 2.

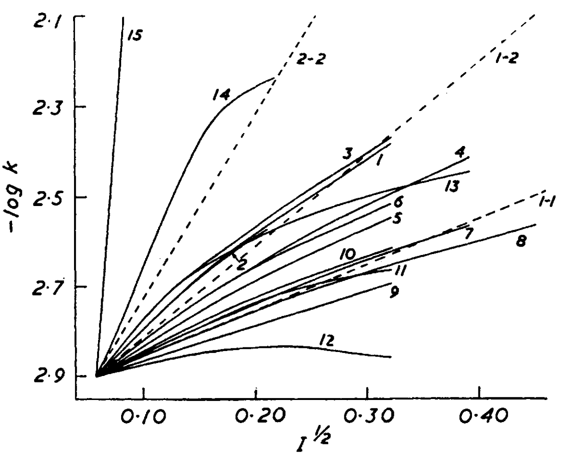
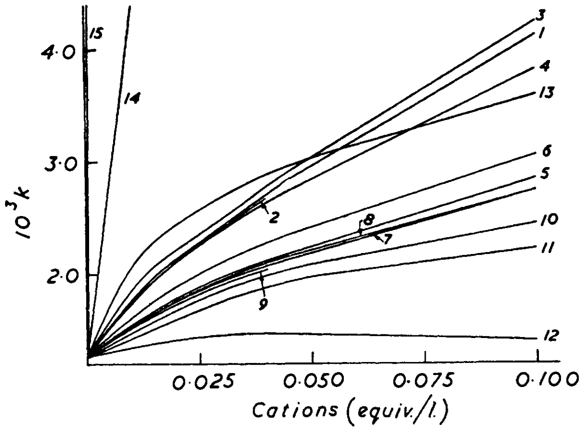


Fig. 3.



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