105. *The Persulphate–Iodide Reaction. Specific Effects of Cations. Part I.*

By W. J. Howells.

The velocity of the persulphate–iodide reaction has been determined in the presence of cations of the alkali series. The salt effect increases as we pass from solutions containing hydrogen ions to solutions containing cæsium ions and is greatest in the presence of the cation of least activity coefficient. The influence of ionic radius is discussed. It is suggested that there is some evidence of a correlation between the observed velocities and the viscosities of the solutions in which they are determined.

The persulphate–iodide reaction in the presence of potassium ions has been studied by many workers; *e.g.*, Price (*Z. physikal. Chem.*, 1898, **27**, 474), Jette and King (*J. Amer. Chem. Soc.*, 1929, **51**, 1034), King and Steinbach (*ibid.*, 1930, **52**, 4779), King and Jacobs (*ibid.*, 1931, **53**, 1704), Knudsen and King (*ibid.*, 1938, **60**, 687), Soper and Williams (*Proc. Roy. Soc.*, 1933, *A*, **140**, 59).

Price, working with solutions of moderate ionic strength, followed the course of the reaction by titrating the liberated iodine with thiosulphate solution in the presence of starch. King and his co-workers, using a photo-cell method, studied the reaction in solutions of low ionic strengths, and showed that the Debye–Hückel law is obeyed up to $\sqrt{I} = 0{\cdot}16$ when the ionic strength is increased by addition of neutral univalent salts. In solutions of higher ionic strengths, the values for the velocity constants show a negative deviation from those calculated by means of the equation $\ln k = \ln k_0 + 2\alpha z_a z_b \sqrt{I}$. The deviations would be still more marked if reference were made to the more complete equation

$$\ln k = \ln k_0 + 2\alpha z_a z_b \sqrt{I} + (\beta_1 + \beta_2 - \beta_x)I$$

which may be deduced from the relation $-\ln f = \alpha z^2 \sqrt{I} - \beta I$. This equation has, nevertheless, theoretical significance. The β terms are specific terms partly dependent on the nature of all the ions present in solution. In solutions of low ionic strengths the βI terms are negligible, and the k values are independent of the nature, in this instance, of the cations present. In the present work the persulphate–iodide reaction has been studied in the presence of hydrogen, lithium, sodium, ammonium, potassium, rubidium, and cæsium ions. Since the object of the work was to compare the specific effects of the cations, it was necessary to observe reaction velocities in solutions of moderate ionic strengths.

EXPERIMENTAL.

" AnalaR " Potassium and ammonium persulphates were recrystallised between 50° and 0°, and the fine crystals were pressed between filter-papers and dried in a vacuum over sulphuric acid. In one case, recrystallised potassium persulphate was washed free from water first with alcohol and then with ether, and dried at 30°. This product gave results identical with those obtained with potassium persulphate dried in the usual way. The purity of the sodium persulphate was estimated by the iodide method and also by the ferrous sulphate method. " AnalaR " Potassium iodide was recrystallised and dried in a vacuum over sulphuric acid, and also by heating out of contact with air. This iodide and the other iodides used—which were the purest obtainable—were estimated before use by titration with standard potassium iodate solution in the presence of acetone. This method gave a sharper end-point and more consistent results than titration with standard silver nitrate in the presence of di-iododimethylfluorescein as adsorption indicator. The chlorides used, with the exception of lithium chloride, were " AnalaR " reagents, and were further purified by the usual methods.

Tests showed that the materials used were free from salts of copper and iron—which act as catalysts—and from iodate. Whenever necessary, *k* values were corrected for salt effects due to presence of impurities. For example, two different lots of rubidium iodide were estimated to contain 99·30% and 99·47% of rubidium iodide severally; the foreign substance was regarded as potassium chloride, and an appropriate salt-effect correction applied.

The temperature of the thermostat was maintained at 25° ± 0·02° by means of a spiral-shaped toluene–mercury gas regulator, used in conjunction with an electrically-driven stirrer. All glass-ware was standardised, and solutions were made up in freshly distilled water at thermostat temperature. The reacting solutions were freshly made for each velocity determination. At observed intervals, 24·95 c.c. of the reacting mixture were withdrawn and added to 400 c.c. of distilled water in order to arrest the reaction. The liberated iodine was estimated by titration with 0·01N-sodium thiosulphate solution, standardised for each determination, starch solution being added towards the end of the titration. There was no need to apply corrections to the iodine titration values since the liberated iodine was seldom much less than 10^{-4} M (see Knudsen and King, *loc. cit.*). Moreover, only comparison of *k* values was involved.

A few complications arise in connexion with the persulphate–iodide reaction : (i) The reaction is retarded slightly by the formation of tri-iodide, but the velocities compared in the present work are diminished to the same extent. (ii) The oxidation of iodide to iodate is possible, but takes place appreciably only in concentrated persulphate solutions (Marshall, *Proc. Roy. Soc. Edin.*, 1898, **22**, 388).

Results.—In order that the cations might be readily interchanged, equivalent initial concentrations of persulphate and iodide were used in all the experiments. Most of the determinations were made in slightly acid solutions (0·005N-sulphuric acid) as such solutions appear to give more consistent results than neutral solutions.

The velocity constants were calculated from the equation $k = x/at(a - x)$, a being the initial concentrations of persulphate and iodide in g.-equivs./l., and x the number of g.-equivs./l. of iodine liberated in t minutes.

TABLE I.

(*a*) 0·0333N-$K_2S_2O_8$ + 0·0333N-NH_4I + 0·005N-H_2SO_4.

t.	$x \times 10^5$.	$k \times 10^3$.	t.	$x \times 10^5$.	$k \times 10^3$.
13·7	246	175	58·9	850	174
23·9	412	177	68·8	956	175
34·9	563	175	77·8	1038	174
45·9	709	177		Mean	175

(*b*) 0·0333N-$(NH_4)_2S_2O_8$ + 0·0333N-KI + 0·005N-H_2SO_4.

t.	$x \times 10^5$.	$k \times 10^3$.	t.	$x \times 10^5$.	$k \times 10^3$.
14·0	255	178	70·9	982	177
28·9	486	177	80·0	1063	176
38·0	608	176	88·2	1136	176
53·9	814	180		Mean	177

(*c*) $K_2S_2O_8$ + NaI + 0·005N-H_2SO_4 : $a = 0{\cdot}0250$, $k = 0{\cdot}145$.
(*d*) $Na_2S_2O_8$ + KI + 0·005N-H_2SO_4 : $a = 0{\cdot}0250$, $k = 0{\cdot}146$.

All determinations recorded were made at 25°. A few determinations were made in solutions containing salt-pairs. Allowance being made for experimental error, the results, given in Table I, indicate that the velocity constants have, as one would expect, the same value in corresponding solution-pairs, *i.e.*, in those of the same ionic strength. These results serve to establish the purity of the materials and the uniformity of the experimental conditions.

Specific effects of cations. In order to ascertain the specific effects of different cations on the velocity of the reaction, experiments were carried out in solutions containing separately equivalent concentrations of potassium, ammonium, and sodium ions, and usually 0·005N-sulphuric acid. The velocity constants observed are given in Table II. The values in parentheses are those for neutral solutions. For solutions of the same ionic strength the values are highest in the presence of potassium ions and lowest in that of sodium ions. Similar results have been found for the monobromoacetate–thiosulphate reaction (LaMer, *Chem. Reviews*, **1932**, **10**, 199) and for the thiocyanate–monoiodoacetate reaction (Holmberg, *Z. physikal. Chem.*, **1921**, **97**, 134).

TABLE II.

Concn.	0·0125N.	0·01666N.	0·0250N.	0·0333N.
$K_2S_2O_8 + KI$	0·125	0·143	0·167 (0·160)	0·188 (0·186)
$(NH_4)_2S_2O_8 + NH_4I$	0·113	0·125	0·147 (0·141)	0·167 (0·163)
$Na_2S_2O_8 + NaI$		0·110	0·123	0·139

Observations were extended to include the cations of other alkali metals and of ammonium by the addition of equivalent amounts of their iodides to an equivalent amount of potassium persulphate. The velocity constants observed are given in Table III (*a*) : values in parentheses are for neutral solutions. The *k* values decrease in the series from cæsium to lithium :

$$\mathrm{Cs}^{\cdot} > \mathrm{Rb}^{\cdot} > \mathrm{K}^{\cdot} > \mathrm{NH_4}^{\cdot} > \mathrm{Na}^{\cdot}, \mathrm{Li}^{\cdot}.$$

TABLE III.

(*a*) 0·0250N-$K_2S_2O_8$ + 0·0250N-RI + 0·005N-H_2SO_4.

R =	$\mathrm{Cs}^{\cdot}$.	$\mathrm{Rb}^{\cdot}$.	$\mathrm{K}^{\cdot}$.	$\mathrm{NH_4}^{\cdot}$.	$\mathrm{Na}^{\cdot}$.	$\mathrm{Li}^{\cdot}$.
k	0·197	0·180	0·167 (0·160)	0·157 (0·152)	0·145 (0·142)	0·146
F	3·28	3·00	2·78	2·62	2·42	2·43

(*b*) 0·01666N-$K_2S_2O_8$ + 0·01666N-KI + 0·005N-H_2SO_4 + 0·0333N-RCl.

R =	$\mathrm{K}^{\cdot}$.	$\mathrm{NH_4}^{\cdot}$.	$\mathrm{Na}^{\cdot}$.	$\mathrm{Li}^{\cdot}$.	$\mathrm{H}^{\cdot}$.
k	0·191	0·182	0·163	0·162	0·158
F	3·18	3·03	2·72	2·70	2·63

Table III (*b*) gives the *k* values for solutions of potassium persulphate and potassium iodide in the presence of various chlorides. In order to settle more definitely the relative effects of sodium and lithium ions, velocity determinations were carried out in solutions 0·3000N with respect to the two chlorides separately. The velocity constants were 0·287 and 0·262 respectively, showing that sodium ions are more effective than lithium ions in increasing the velocity of the reaction.

Table III (*b*) shows that the influence of cations involved is in the same direction as that indicated in Table III (*a*).

DISCUSSION OF RESULTS.

The velocity constant–ionic strength curves plotted from data given in Table II converge at low ionic strength. The extrapolated value for *k* at zero ionic strength, *i.e.*, k_0, is approximately 0·06. As was to be expected, this value differs from that obtained by King and Jacobs, since they worked at low ionic strengths, but it may be used for calculating the relative kinetic activity factors. In the equation $k = k_0 f_{S_2O_8''} f_{I'} / f_{S_2O_8I'''} = k_0 F$ (see Brönsted, *Z. physikal. Chem.*, **1922**, **102**, 169), k_0 has the same value whatever cations are present. The values of *F*, the kinetic activity factor or salt effect, are given in Table III, and show that the salt effect is greatest in the presence of cæsium ions. Now, the sequence for the activity coefficients of the salts involved is HCl > LiCl > NaCl > KCl, etc., so in the reaction under consideration the salt effect—a primary salt effect—is greatest in the solution containing the cation of lowest activity coefficient, and *vice versa.*

Ordinary theory does not lead one to expect this, since $f_{I'}$ decreases in aqueous chloride solutions in the order HCl > LiCl > NaCl > KCl (Harned, *Trans. Faraday Soc.*, **1927**, **23**, 468). Also, since the S_2O_8'' ion, though complex, is symmetrical, $f_{S_2O_8''}$ is greatest in hydrochloric acid solution. On the other hand, $f_{S_2O_8I'''}$ (in aqueous lithium chloride) may be less than $f_{S_2O_8I'''}$ (in aqueous potassium chloride) because S_2O_8I''' is an unsymmetrical ion. Thus, on this theory alone, we might expect the kinetic activity factor to be greatest in solutions containing hydrogen ions, and least in those containing cæsium ions. It appears difficult to find an explanation for the relative specific effects on the basis of the activity concept alone, unless we assume, probably unjustifiably, that $f_{S_2O_8I'''}$ decreases very rapidly as we pass from a solution containing lithium to one containing cæsium ions.

Since the velocity of the reaction depends upon the rate of formation of the complex ion, which has a short life, one important factor determining the velocity is the ease with which the reacting anions can move about in the solution. The smaller lithium ions exert a stronger attractive force on the anions than do the larger cæsium ions. In this way it may be that the movement of the anions in the presence of lithium ions is slower than in the presence of cæsium ions. For a similar reason, Fajans (*ibid.*, p. 359) observes that the cation with strongest electric field has the strongest lowering effect on the refractivity of an anion.

There is also some evidence of correlation between the reaction velocities, in solutions of equal ionic strength, and the viscosities of the solutions in which they are determined. It is known that the viscosities of solutions of alkali-metal salts increase in the sequence cæsium to lithium : Applebey (J., 1910, **97**, 2021) gives the following values for the specific viscosities of 0·1N-solutions of cæsium, potassium, sodium, and lithium nitrates at 18° : 0·9933, 0·9941, 1·0044, and 1·0113, respectively; and the viscosities of chloride solutions increase in the sequence cæsium, rubidium, potassium, sodium, lithium and hydrogen (Castell-Evans, " Physico-Chemical Tables," 1911, Vol. 2, 610).

The velocities observed in the present work decrease in this sequence. In view of the fact that these velocities are dependent on the movement of the two anions concerned, this is partly to be expected, since Stokes's law states that the velocity of a particle varies inversely with the viscosity of the medium.

PORTH, GLAM.

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