

54. *The Persulphate-Iodide Reaction. Part III. Specific Effects of Univalent and Bivalent Cations. The Activation Energy of the Reaction.*

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The gradients of the $\log k-\sqrt{I}$ curves for the reaction in solutions containing corresponding chlorides and sulphates are compared and are found to be higher for the chloride solutions. A comparison is made between the salt effects of cations in relation to their size and valency. These effects decrease in the sequence $K^+ > Zn^{2+} > Mg^{2+} > Be^{2+} > Na^+ > Li^+ > H^+$. The activation energy of the reaction has been determined in the presence, separately, of chlorides of potassium, sodium, and hydrogen, and appears to increase in this sequence. The relation between the activation energy and the collision factor is discussed, and the relatively low values of both are considered.

RESULTS recorded in Part I (Howells, *J.*, 1939, 463) show that the velocity of the persulphate-iodide reaction varies with the nature of the cations present in the reaction solution. That there should be velocity variation in the presence of different ions is suggested by the extended Debye-Hückel equation given in Part I, *viz.*,

$$\ln k = \ln k_0 + 2\alpha Z_a Z_b \sqrt{I} + (\beta_1 + \beta_2 - \beta_3)I$$

where the β terms are specific terms partly dependent upon the nature of all the ions in the reaction solution.

When the cations were present, separately, in equivalent concentrations, it was found that the velocity constant decreased in the series $Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+ > H^+$. The investigation has now been extended to include some bivalent cations, but calcium, strontium, and barium could not be included owing to the formation of sulphate ions.

A further object of the present work was to determine and compare the collision factors of the reaction in the presence, separately, of potassium, sodium, and hydrogen ions.

EXPERIMENTAL.

The general procedure has been described in Part I. The velocity constants were calculated from the bimolecular equation $k = x/at(a-x)$, a being the initial concentrations of persulphate and iodide in g.-equiv./l., and x the number of g.-equiv./l. of iodine liberated in t minutes. The iodine liberated was estimated by titration with 0.01N-sodium thio-sulphate solution, the reaction being sufficiently arrested by dilution of 25 c.c. of the reaction mixture in 250 c.c. of distilled water. Starch solution was added towards the end of each titre. The experimental conditions brought about a premature end-point, and the blue colour returned; this was therefore discharged by a few additional drops of thio-sulphate solution, and the titration considered completed. This procedure was consistently followed throughout.

The velocity of the persulphate-iodide reaction is increased slightly by light (von Kiss, *Rec. Trav. chim.*, 1927, 46, 230; Soper and Williams, *Proc. Roy. Soc.*, 1933, A, 140, 59), so the reaction vessel was only weakly illuminated by artificial light.

Specific Ion Effect.—The velocity constants for the reaction, at 25°, were determined in the presence, separately, of potassium, sodium, lithium, cadmium, zinc, magnesium, and beryllium sulphates. The reaction solutions contained

in each case 0.01666*N*-iodide and 0.01666*N*-persulphate, together with 0.005*N*-sulphuric acid. The lithium and beryllium sulphates used were the purest obtainable. All other materials used were "AnalaR," and these, with the exception of sodium and cadmium sulphates, were further purified by recrystallisation. The sulphates were, where necessary, dehydrated, and weighed in the anhydrous state.

Satisfactory bimolecular velocity constants were obtained, and these are recorded in Table II. Those for the reaction in the presence of chlorides were obtained by intrapolation, using data given in Part II (*J.*, 1941, 643). The velocity constants recorded for the sulphate solutions are mean values, and a detailed example is given in Table I(a).

TABLE I.

(a) 0.01666 <i>N</i> -K ₂ S ₂ O ₈ + 0.01666 <i>N</i> -KI + 0.005 <i>N</i> -H ₂ SO ₄ + 0.1000 <i>M</i> -BeSO ₄ ; 25°.						(b) 0.01666 <i>N</i> -K ₂ S ₂ O ₈ + 0.01666 <i>N</i> -KI + 0.3500 <i>M</i> -HCl; 15°.					
<i>t.</i>	<i>x</i> × 10 ⁵ .	<i>k</i> × 10 ³	<i>t.</i>	<i>x</i> × 10 ⁵ .	<i>k</i> × 10 ³	<i>t.</i>	<i>x</i> × 10 ⁵ .	<i>k</i> × 10 ³ .	<i>t.</i>	<i>x</i> × 10 ⁵ .	<i>k</i> × 10 ³ .
37.4	214	237	77.3	384	232	40.6	137	132	105.0	302	126
49.1	270	237	85.4	415	233	62.1	197	130	120.3	335	125
63.3	330	234	93.2	446	235	85.5	256	128	126.4	346	125
<i>k</i> × 10 ³ (mean) = 235.						<i>k</i> × 10 ³ (initial value) = 135.					

DISCUSSIONS OF RESULTS.

Results recorded in Part I (*loc. cit.*) show that the velocity constant for the persulphate-iodide reaction, in the presence of different univalent cations, decreases in the series caesium to lithium, *i.e.*, with decreasing ionic radius. Table II shows that this is true also for the Group II cations involved, with the exception of that of cadmium. That the velocity rates are related to the radii of the ions present is to be expected, since the electric field within the reaction solution depends to some extent upon the radii of the ions present. The radii of zinc and magnesium ions do not differ much, and neither do the corresponding rates. The radius value given for the beryllium ion is considered doubtful.

The relatively low velocity in the cadmium sulphate solution is due to the fact that the cadmium forms complex ions with the iodide in the reaction solution, thus removing part of one of the reactants: $2\text{CdI}_2 \rightleftharpoons \text{Cd}(\text{CdI}_4) \rightleftharpoons \text{Cd}^{2+} + \text{CdI}_4^{2-}$. That this is so is indicated also by the lower velocity in 0.1000*M*- than in 0.0333*M*-cadmium sulphate solution, since an increase in ionic strength is usually accompanied by an increase in the rate of the reaction.

Table II, (c) and (e), shows that the rate of the reaction in the presence of 0.1*M*-potassium chloride exceeds the rate in the presence of 0.05*M*-potassium sulphate, although the total ionic strength of the reaction solution is considerably higher in the latter case. Both reaction solutions contain the same concentration of potassium ions. Similar observations apply to the reaction in the presence of 0.2*M*-potassium chloride and 0.1*M*-potassium sulphate, and to the reaction in the presence, separately, of equivalent concentrations of sodium chloride and sulphate.

It follows that the $\log k - \sqrt{I}$ curves for the reaction have steeper gradients in solutions containing the chlorides than in those containing the corresponding sulphates. It is evident that the specific effects of the ions present, represented by the β terms in the extended Debye-Hückel equation, are of considerable significance in their bearing upon the reaction rate.

The gradients of the $\log k - \sqrt{I}$ curves are, at the concentrations concerned, nearly the same for the solutions containing zinc, magnesium, sodium, and beryllium sulphates.

Table II, (a) and (b), records the rates of the reaction in the presence of equimolecular amounts of sulphates. It being borne in mind that the added concentration of univalent cations is double that of bivalent ones, a comparison may be made between the salt effects of the two types of cations. Excluding the case of potassium, the superior effect of the bivalent cations, with their double charge and more powerful electric fields, is apparent. The relatively low reaction rate in the cadmium sulphate solution is due to causes already stated.

The data for solutions containing 0.05*M*-potassium sulphate and 0.1*M*-zinc, magnesium, and beryllium sulphates, severally, Table II, (b) and (e), enable a comparison to be made between the salt effects due to the addition of equal concentrations of the cations involved. The largest salt effect is caused by the potassium ion, and this is due, probably, to the fact that its ionic radius is a dominating factor. A numerical example will illustrate this for the solutions concerned.

The Debye-Hückel equation, in its extended form, for the iodide-persulphate reaction in aqueous solutions, may be written: $\log k = \log k_0 + 2\sqrt{I} + \beta I$, since, in this case, $2\alpha Z_a Z_b / 2.303 = 2$, approximately.

The value of k_0 , the velocity constant at zero ionic strength, is taken as 0.06 (see Part I, *loc. cit.*). Using the appropriate values of k and I , it may be shown that the values of the β terms are -1.31, -1.61, -1.65, and -1.66, respectively, for the solutions containing potassium, zinc, magnesium, and beryllium ions. The β term is a composite one, but it, nevertheless, represents in part the contribution made by the cations present. The β values are negative since a gradient of 2 applies to the $\log k - \sqrt{I}$ curve for this reaction only when the ionic strength is low.

In Table II, k = the observed velocity constant; I = the total ionic strength of the reaction solution concerned; F = an arbitrary kinetic activity factor = k/k_a , where $k_a = 0.142$, the velocity constant in the absence of neutral salt.

Activation Energies.—The activation energy of the reaction has been taken as equivalent to its critical increment, and an attempt has been made to ascertain whether it increases with ionic strength and whether

TABLE II.

0.01666N-K₂S₂O₈ + 0.01666N-KI + 0.005N-H₂SO₄ + neutral salt; 25°.

		Concn. of neutral salt : (a) 0.0333M, (b) 0.1000M.						
Salt.		K ₂ SO ₄ .	Na ₂ SO ₄ .	Li ₂ SO ₄ .	CdSO ₄ .	ZnSO ₄ .	MgSO ₄ .	BcSO ₄ .
(a)	<i>k</i>	0.221	0.171	0.160	0.156	0.194	0.188	—
	<i>I</i>	0.1491	—	—	0.1824	—	—	—
(b)	<i>k</i>	0.347	0.223	—	0.148	0.248	0.239	0.235
	<i>F</i>	2.44	1.57	—	1.04	1.74	1.70	1.65
	<i>I</i>	0.3492	—	—	0.4492	—	—	—

Concn. of neutral salt : (c) 0.1000M, (d) 0.2000M, (e) 0.0500M.

Total ionic strength : (c) 0.14916, (d) 0.24916, (e) 0.19916.

Salt.		KCl.	NaCl.	LiCl.	HCl.		K ₂ SO ₄ .	Na ₂ SO ₄ .
(c)	<i>k</i>	0.280	0.191	0.182	0.179	(e) <i>k</i>	0.257	0.182
	<i>F</i>	1.97	1.35	1.28	1.26	<i>F</i>	1.81	1.28
(d)	<i>k</i>	0.387	0.239	0.225	0.216			
	<i>F</i>	2.73	1.68	1.58	1.52			
<i>r</i> × 10 ⁸ , cm.		K ⁺ . 1.33	Na ⁺ . 0.95	Li ⁺ . 0.70	Cd ⁺⁺ . 0.99	Zn ⁺⁺ . 0.83	Mg ⁺⁺ . 0.75	Be ⁺⁺ . 0.30(?)

it is dependent upon the cations present in the reacting solution. Velocity constants for the reaction, at two different initial concentrations and in the presence, separately, of potassium, sodium, and hydrogen ions, were determined at four different temperatures. All glassware and thermometers were standardised, and solutions were made up at thermostat temperatures, which were constant to ±0.02°. The reaction rates in solutions containing neutral salts decreased as the reactions proceeded, the rates being relatively fast (see Part II, *loc. cit.*). The velocity constants recorded in Table III for these solutions are, therefore, extrapolated initial rates, and a detailed example is given in Table I(b). Those given for the other two solutions are mean values and have been re-determined; they differ only slightly from the values given in Part II.

All reaction solutions, excepting those containing hydrochloric acid, contained 0.005N-sulphuric acid. Determinations were made in slightly acid solutions because they appear to give more consistent results than neutral solutions. In order to avoid heating and contraction effects on mixing, the two reactant solutions contained equivalent chloride concentrations.

TABLE III.

Salt and concn.	28°.	25°	20°.	15°.	<i>E</i> .	<i>PZ</i> × 10 ⁻⁷ .
(a) 0.01666N-K ₂ S ₂ O ₈ + 0.01666N-KI + 0.005N-H ₂ SO ₄ + RCl.						
—	0.174	0.142	0.0984	0.0683	12,500	0.361
0.3500M-KCl	0.673	0.551	0.390	0.270	12,430	1.222
0.3500M-NaCl	0.425	0.343	0.238	0.160	13,010	2.028
0.3500M-HCl	0.366	0.290	0.199	0.135	13,150	2.179
(b) 0.0333N-K ₂ S ₂ O ₈ + 0.0333N-KI + 0.005N-H ₂ SO ₄ + RCl.						
—	0.230	0.187	0.130	0.088	12,700	0.657
0.2000M-KCl	0.528	0.430	0.298	0.205	12,680	1.453
0.2000M-NaCl	0.373	0.298	0.205	0.141	12,900	1.476
0.2000M-HCl	0.338	0.272	0.185	0.127	13,090	1.856

The velocity constants, in g.-equiv./l./min., are recorded in Table III beneath the corresponding temperatures; *PZ* values are in l./sec. The activation energies, in cal./g.-mol., were computed by plotting ln *k* against 1/*T*, and straight lines were obtained in all cases. The velocity constants have the same numerical value whether expressed in terms of g.-equiv. or g.-mols. They were reduced from minute to second units, and were then used in calculating the *PZ* values from the equation $k = PZe^{-E/RT}$.

Table III shows that neutral salts, even in moderate concentrations, have a marked effect upon the velocity constant of the reaction. Since the experimental error in the estimation of *k* is approximately 1%, the variations in *E* values are too small to permit of any definite conclusions concerning the specific effects of different cations, but there is some evidence that both *E* and *PZ* increase with increasing ionic strength. This is predicted by the following considerations. One may write the Debye-Hückel equation in the form :

$$\ln k = \ln k_0 + 2\alpha_1 Z_a Z_b \sqrt{I} \times (RT)^{-1.5},$$

where *D* is the dielectric constant, whence one obtains

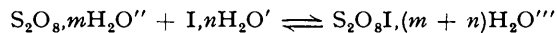
$$E = E_0 - 3\alpha Z_a Z_b \sqrt{I} \times (RT)^{-1.5} \left\{ RT^2 \cdot \frac{d}{dt} \ln D + RT \right\}$$

which, since $\alpha_1 = \alpha(RDT)^{1.5}$, is the expression given by Moelwyn-Hughes ("Kinetics of Reactions in Solution," 1933, p. 199), who points out that, for water at 25°, the two terms $RT^2(d \ln D/dt)$ and *RT* are, approximately, -930 and 590 cal., respectively. The activation energy for the persulphate-iodide reaction should therefore increase with increase in ionic strength, since the reacting ions are of like sign.

If *E*, the activation energy, for such a reaction increases with increase in ionic strength, it follows, from the

equation $k = PZe^{-E/RT}$, that PZ , the collision factor, must do so also, since the bimolecular constant for a reaction between ions of like sign increases rapidly with increase in ionic strength. Furthermore, PZ must increase with increase in E , and this agrees with most of the examples in Table III. That there is such a functional relationship between PZ and E has been shown by Fairclough and Hinshelwood (*J.*, 1937, 539) for a reaction in a series of solvents.

The PZ and E values for the reaction are relatively low. Since the reactants, the critical complex, and the products are polar, solvation of all three occurs, and the complex, being the most polar, is solvated to a greater degree than the reactants :



Employing the transition-state theory, Bell (*J.*, 1943, 632) has shown that such solvation leads to low values for both PZ and E . The factor E is, evidently, the more effective in the case of the persulphate-iodide reaction and accounts for its relatively rapid rate.

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