

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE,
NEW YORK UNIVERSITY]

THE OXIDATION OF IODIDE ION BY PERSULFATE ION. I. THE EFFECT OF TRI-IODIDE ION FORMATION ON THE REACTION VELOCITY¹

BY ERIC JETTE AND CECIL V. KING

RECEIVED SEPTEMBER 15, 1928

PUBLISHED APRIL 5, 1929

A. Introduction

Thermal and photochemical reactions in which iodine is liberated from iodides by oxidizing agents have been the subject of numerous investigations, in nearly all of which the effect of the equilibrium $I_2 + I^- \rightleftharpoons I_3^-$ has been considered, although not always in an adequate manner. As a general conclusion from such investigations it may be said that one cannot predict with assurance what effect the presence of tri-iodide ion will have on any particular reaction since it depends largely upon the specific properties of the system. In connection with another problem the present writers were forced to investigate in some detail one of these reactions, namely, that between persulfate and iodide ions, a reaction which has been used by Brönsted² as a confirmation of his theory of reaction velocity.

The first to work with this reaction was Price,³ who observed in one of his many experiments that adding iodine to the initial mixture decreased the velocity of the reaction and noted that the probable cause was the formation of tri-iodide ion. The single experiment which Price performed with iodine present in the initial mixture does not supply sufficient information for detailed study of the tri-iodide ion effect. Recently Kiss and his co-workers⁴ have investigated the reaction and found (*cf.* Table IV of ref. 4 c) that the presence of iodine in the initial mixture decreased the reaction velocity, but when the concentration of iodide ion was corrected for the amount of tri-iodide present, the velocity constant was the same as when no iodine was present at the beginning of the experiment. On this basis they concluded that the tri-iodide ion does not react with the persulfate ion. The work of Kiss, Bruckner and Zombory is seriously marred (1) by errors or gross misprints in the equations for the reaction velocity and for the concentration of tri-iodide ion, (2) by so incomplete a statement as to the meaning of their quantitative values and symbols that after

¹ Presented at the Swampscott meeting of the American Chemical Society, September 12, 1928.

² Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

³ Price, *ibid.*, **27**, 474 (1898).

⁴ (a) Kiss and Bruckner, *Z. physik. Chem.*, **128**, 71 (1927); (b) Kiss, *ibid.*, **134**, 26 (1928); (c) Kiss and Zombory, *Rec. trav. chim.*, **46**, 225 (1927); (d) Kiss and Bossányi, *ibid.*, **47**, 619 (1928).

considerable effort the present writers were unable to use the experimental results quoted in the correct equations or to calculate the constants given in the original communication and (3) by the presence of an unknown impurity in the persulfate used for nearly all their experiments, resulting in velocity constants approximately 15% too high; this fact was found and noted by the original experimenters. While all the calculations contained in each one of the papers quoted are presumably made on the same basis, the conclusions regarding the neutral salt effects, agreement with the Brönsted theory and the mechanism of the catalytic effects of iron and copper ions must remain in considerable doubt until the quantitative results are recalculated on a correct basis. More detailed criticisms will be given at various points in the present paper.

B. Materials and Methods

All the salts used in this investigation were "c. p." materials, which were recrystallized at least once from distilled water before using. The potassium persulfate (Baker's "Analyzed") was recrystallized between 50 and 0° and dried over sulfuric acid in a vacuum desiccator. The iodine was a "c. p." grade which was resublimed once with addition of potassium iodide and the product then sublimed once more. The particular purpose of purifying these salts and iodine was for the removal of traces of ferric salts which might have been present, especially in the persulfate, since ferric ion has a very pronounced catalytic effect on the reaction. No observable color was obtained on adding ammonium thiocyanate to any of these salts. Two different lots of each of the three principal substances, potassium iodide, potassium persulfate and iodine were prepared during the course of the investigation. Reaction velocity curves obtained with the first and second lots agreed within experimental error.

The water used in making the solutions was ordinary laboratory distilled water redistilled from potassium permanganate acidified with sulfuric acid and condensed in a block tin condenser, the first portions being rejected.

Most of the solutions, including the potassium persulfate and potassium iodide solutions, were made up by weighing the proper amount of dry salt, dissolving and making up to volume in standardized flasks. The iodine in solutions containing it at the start of the reaction was titrated before use by the method used later in determining the reaction velocity curve. The sodium thiosulfate solution used for the iodine titrations was standardized at frequent intervals against the iodine liberated from potassium iodide solutions by standard potassium permanganate solution, using freshly prepared starch solution as indicator. The concentration of the permanganate solution was determined by means of pure sodium oxalate.

Preliminary experiments carried out in glass-stoppered bottles gave continuously decreasing values for the bimolecular "constant," a result which might have been due to loss of iodine from the solution. In order to eliminate this possibility all the experiments reported in the present article were conducted in sealed pyrex bulbs each containing 50 cc. of the reaction mixture measured from standardized pipets. In most cases the bulbs were of 100-cc. capacity.

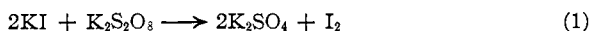
Equal volumes of the two solutions (usually measured from the same flask) were mixed as rapidly as possible, pipetted quickly into the prepared bulbs and sealed. They were then placed in a large thermostat at a temperature of 25.00 \pm 0.01°. After the reaction had proceeded for a given time, the tip of the bulb was removed and the titration of the iodine by means of a standardized sodium thiosulfate solution (approximate

mately 0.01 molar) completed in the shortest possible time, the entire titration taking place without transferring the solution from the bulbs. Since the openings of the bulbs were quite small, and the titrating solution was made to flow over the inner surface of the bulb, and especially since the iodine in the solution was reduced to a very low concentration in less than one-half minute after opening, practically no loss of iodine occurred. Whenever the speed of the reaction was not too great, an excess of thio-sulfate was added and the first titration checked by a back titration with a standard iodine (in potassium iodide) solution. In spite of these precautions, however, the velocity constants still decreased as the reaction proceeded, showing that the effect must be inherent in the reaction, as it has been considered by other investigators from results obtained by methods differing somewhat in details.

In some of the experiments the initial reaction mixture was saturated or nearly so with iodine. In these cases the individual solutions containing potassium persulfate and potassium iodide were saturated separately with iodine and 25-cc. samples of the solutions were titrated immediately to obtain the initial amount of iodine present. Into each reaction bulb 25 cc. of each of the two solutions were pipetted from standardized pipets. The solubility of iodine in the final mixture was unknown but this was not particularly important for the present purpose; if the final solution was not quite saturated just after mixing, it became so very soon due to the iodine formed by the reaction. The minimum time required for these titrations was two minutes, the maximum about five minutes, which accounts for the slight irregularities in the results with saturated iodine solutions. In these experiments also the entire titration was performed in the reaction bulb.

C. Theory and Results of Experiments with Initial Solutions Containing Only Potassium Persulfate and Potassium Iodide

The reaction between $S_2O_8^{--}$ and I^- ions has usually been considered a bimolecular reaction, although the stoichiometric equation for the potassium salts is

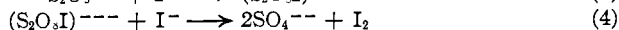
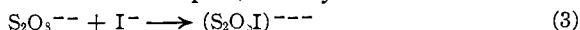


The main reason for so considering it is the fact that the velocity constants as calculated from experimental results⁵ by means of the ordinary bimolecular equation

$$-\frac{dC_{S_2O_8^{--}}}{dt} = kC_{S_2O_8^{--}}C_{I^-} \quad (2)$$

or one of its integrated forms, showed less variation than if the equations for unimolecular or trimolecular reactions were used. The values of k obtained always decreased as the reaction progressed, the decrease being accounted for by the formation of the tri-iodide ion.

Brönsted considers the reaction to take place in two steps, the first of which is the formation of a critical complex, namely:



On the basis of these reactions and his theory of reaction velocity, Brönsted writes the velocity equation

$$-\frac{dC_{S_2O_8^{--}}}{dt} = kC_{S_2O_8^{--}}C_{I^-} \frac{f_{S_2O_8^{--}}f_{I^-}}{f_{(S_2O_8I)^{---}}} = kC_{S_2O_8^{--}}C_{I^-} F \quad (5)$$

⁵ Cf. Price, ref. 3, p. 477.

in which f represents the activity coefficients of the ions indicated and F is called the "kinetic activity factor." Since all the ions in Equation 3 have the same sign, the salt effect is positive and with increasing ionic strength the value of k should increase. If the initial concentration of $K_2S_2O_8$ is a moles per liter and that of KI is $2a$, then the initial ionic strength of the solution is $5a$ while after the reaction has gone to completion it is $6a$ so that the value of k should increase in each experiment. A large amount of data is at hand to show that if the ionic strength of the solution is increased by the addition of ionogens which do not take part in the reaction, the reaction velocity increases. This confirmation of Brönsted's theory has already been pointed out by Kiss and Zombory and Kiss and Bruckner as well as by Brönsted.

Three possible assumptions which may be made in discussing the effect of the tri-iodide ion formation on the speed of reaction are as follows. (1) The tri-iodide ion does not react with the persulfate ion. (2) The tri-iodide ion reacts at the same rate as the iodide ion. (3) The tri-iodide ion reacts but at a rate different from that of the iodide ion. The first assumption was made by Kiss and Zombory and Kiss and Bossányi and will be shown to be incorrect. The second is improbable from the start since the reaction should then proceed just as if no tri-iodide ion was formed and it would be necessary to invoke the aid of unknown inhibitors to account for the actual behavior of the velocity curve. The third assumption will be shown to be correct in the present article. Before proceeding to this point, however, it will be pertinent to demonstrate that correcting the momentary iodide-ion concentration for the presence of tri-iodide ion is quite inadequate and, further, that the apparent constancy of the velocity constant when so corrected reported by Kiss and his co-workers is due to errors in the equations used and in the choice of the equilibrium constant.

The equilibrium



has been the subject of considerable work by Bray and MacKay⁶ and more recently by Jones and Kaplan.⁷ The only true equilibrium constant which can be discussed in this case is the one in terms of the activities of the three substances. The equation is

$$K_a = \frac{a_{I_3^-}}{a_{I_3} a_{I^-}} = \frac{C_{I_3^-} - C_{I_2}}{C_{I_3^-}} \times \frac{f_{I^-} f_{I_2}}{f_{I_3^-}} \quad (7)$$

where a represents activities, C concentrations and f activity coefficients. If it may be assumed that $f_{I_2} = 1$ and that $f_{I^-}/f_{I_3^-} = 1$ or *const.* the ordinary equilibrium equation

$$K = \frac{C_{I_3^-} - C_{I_2}}{C_{I_3^-}} \quad (8)$$

is obtained.

⁶ Bray and MacKay, *THIS JOURNAL*, **32**, 914 (1910).

⁷ Jones and Kaplan, *ibid.*, **50**, 1845, 2066 (1928).

Bray and MacKay fixed a_{I_2} in their experiments by keeping the solution saturated with iodine. By making the assumptions that $f_{I_1^-}/f_{I_3^-} = 1$ and that the concentration of free I_2 in a solution of potassium iodide is the same as in pure water, 0.000136 mole per liter, they found that the values of K in Equation 8 increased steadily from 0.00131 in 0.1 molar potassium iodide to 0.00150 in 0.001 molar potassium iodide and an extrapolated value of 0.00153 for pure water (at 25°). Jones and Kaplan fixed a_{I_2} in the potassium iodide solutions by equilibrating the latter with solutions of iodine in water of known concentration and vapor pressure. Their solutions were not saturated with iodine and they obtained for potassium iodide solutions of concentration from 0.01 to 0.333 molar values of the equilibrium constant in Equation 8 varying slightly around 0.00140 at 25°.

In order to obtain these values for the equilibrium constant K , however, it is necessary for all of these investigators to assume that

$$(C_{I_2})_{H_2O} = (C_{I_2})_{KI \text{ soln.}} \quad \text{or} \quad (f_{I_2})_{H_2O} = (f_{I_2})_{KI \text{ soln.}}$$

While it is thermodynamically true that $(a_{I_2})_{H_2O} = (a_{I_2})_{KI \text{ Soln.}}$ under these conditions, some doubt must rest upon the other assumption, although there is no apparent way at present to avoid making it; no experimental evidence is available for its support.⁸

From the preceding discussion it will be seen that any correction introduced into the reaction velocity equation will in itself involve uncertainties except in those cases where the reaction mixture is saturated with respect to iodine over the entire course of the reaction. Even in the latter case it will still be uncertain that $f_{I_1^-}/f_{I_3^-} = 1$ or a constant. It is worth noting that Lewis and Randall⁹ do not make either assumption, although it is evident that both are approximately true.

As a matter of practical expediency it will be necessary to set aside these theoretical objections, since more exact information on the various terms of Equation 7 is not available, and to assume that over the range of potassium iodide concentrations concerned in the present paper, the series of values for the equilibrium constant K are as determined by Bray and MacKay.¹⁰

⁸ That the present situation is anything but clear may be seen from the fact that the equilibrium constant K in Equation 8 increases as the concentration of potassium iodide decreases from 0.01 to 0.001 molar, while in barium iodide solutions over the same range of concentrations K increases. Cf., footnote 10 and Pearce and Eversole, *J. Phys. Chem.*, **28**, 245 (1924).

⁹ Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 527.

¹⁰ Lewis and Randall, ref. 9, and Jones and Hartmann, *THIS JOURNAL*, **37**, 241 (1915), have applied small corrections to these values or the data which determine them. The differences are immaterial over the range considered. A part of the table given by Bray and MacKay is

$KI + KI_3 =$	0.010	0.005	0.002	0.001	0.000
$C_{I_1^-}/C_{I_3^-} = K'$	1.06	1.08	1.11	1.14	(1.16)
$K = K'C_{I_2}$	0.00140	0.00143	0.00147	0.00150	(0.00153)

Letting the initial concentration of potassium persulfate be a moles per liter and that of potassium iodide be $2a$, then according to the stoichiometric equation, for every x moles per liter of persulfate used in the reaction, $2x$ moles of potassium iodide will also disappear and x moles of iodine be produced. Since the equilibrium constant may then be expressed by the equation

$$K = \frac{C_{I_2}}{C_{I_3^-}} C_{I_2} = \frac{(2a - 2x - C_{I_3^-})(x - C_{I_3^-})}{C_{I_3^-}}$$

we find for the concentration of tri-iodide ion at any time during the reaction

$$C_{I_3^-} = \frac{K + 2a - x}{2} - \sqrt{\left(\frac{K + 2a - x}{2}\right)^2 - 2x(a - x)} \quad (9)$$

If the effect of the tri-iodide ion is merely to reduce the concentration of iodide ion, then the bimolecular reaction velocity equation becomes

$$-\frac{dC_{S_2O_8^{2-}}}{dt} = k_1 C_{I^-} C_{S_2O_8^{2-}} = k_1(2a - 2x - C_{I_3^-})(a - x) \quad (10)$$

The corresponding equations given by Kiss and Zombory^{4c} are

$$C_{I_3^-} = \gamma = \frac{K + 2(b - x) + x}{2} \sqrt{\frac{K + 2(b - x) + x}{2} - 2(b - x)}$$

and

$$2k_1' = k_1 = \frac{dx}{dt} \frac{1}{(a - x)(b - x - \gamma)}$$

where a is the molar concentration of potassium persulfate, $2b$ is the molar concentration of potassium iodide and x is "the amount of I_2 formed." These equations are either grossly misprinted or derived upon some unknown basis. That they are incorrect may be seen in the case of the first by setting $x = 0$, for which it does not yield $C_{I_3^-} = 0$ as demanded by experiment and theory. The second equation can be correct only if $\gamma = C_{I_3^-}$ really means twice the tri-iodide concentration, in which case the first equation becomes still more puzzling.

The equation for the tri-iodide correction given by Kiss and Bruckner^{4a} is

$$C_{I_3^-} = y = \frac{b + K}{2} - \sqrt{\frac{(b + K)^2}{4} - x(b - x)}$$

where b is the equivalent concentration of potassium iodide and x is, presumably, equivalents of iodine formed. This equation results if in Equation 8 we put $C_{I^-} = b - x - y$ and $C_{I_2} = x - y$. The latter, however, means that the equivalent concentration of iodine is inserted into Equation 8, which is unjustified in this case since the equilibrium constant used by these writers is in terms of molar concentrations. The correct equation with b and x as equivalent concentrations is

$$y = \frac{K + b - x/2}{2} - \sqrt{\left(\frac{K + b - x/2}{2}\right)^2 - \frac{x}{2}(b - x)}$$

The experimental results on the reaction between potassium persulfate and potassium iodide in solutions containing initially only these salts are given in Table I and graphically in Fig. 1, Curve 1. Table I summarizes the results of three independent experiments performed at different times with two different samples of each of the salts. The agreement between the results of the three experiments can be seen on the curves. The decrease in the value of k' is evident. These values of k' were calculated by means of the integrated form of Equation 2, which for this case becomes

$$k' = \frac{1}{2at} \frac{x}{a-x} \quad (11)$$

Since k' is only the average value for the reaction between the beginning of the reaction and the time stated, and since several of the velocity equations which will be used cannot be integrated, it will be more convenient for purposes of comparison to use values taken from the single curve representative of all the experimental values. These values are given in Table II. The slope of the curve at each of the various times

TABLE I

THE REACTION BETWEEN PERSULFATE AND IODIDE IONS, AT 25°, WITH NO IODINE PRESENT INITIALLY

KI = $2a = 0.01$; $K_2S_2O_8 = a = 0.005$; $x = I_2$ produced = $S_2O_8^{--}$ consumed in moles per liter.

Time, min.	Expt.	x , moles per liter	k' from Eq. 11	Time, min.	Expt.	x , moles per liter	k' from Eq. 11
100	4	0.000550	0.124	560	4	0.001944	0.114
140	23	.000736	.123	680	24	.002155	.112
160	24	.000825	.124	730	4	.002247	.112
250	4	.001150	.119	785	23	.002318	.110
300	23	.001296	.117	1280	4	.002892	.107
360	24	.001481	.117	1300	24	.002905	.107
420	4	.001640	.116	1580	4	.003122	.105
470	24	.001751	.115	2080	4	.003388	.101
530	23	.001847	.111				

TABLE II

CALCULATION OF THE VELOCITY COEFFICIENTS FROM EQUATIONS 2 AND 10

$C_{KI} = 2a = 0.01 M$. $C_{K_2S_2O_8} = a = 0.005 M$

Time, min.	x , moles per liter	$-\frac{dC_{S_2O_8}}{dt} \times 10^6$	k in Eq. 2	C_{I_2} from Eq. 9	k_1^a in Eq. 10	C_{I_2} from Eq. 9, using $K = 0.0061$	k_1 , Eq. 10, using $K = 0.0061$
0	0	(6.26)	(0.1253)
60	0.000345	5.35	.1234	.000298	0.1275	0.00021	0.1263
100	.000548	4.82	.1214	.000473	.1283	.00032	.1263
200	.000972	3.77	.1162	.000818	.1296	.00054	.1243
400	.001583	2.57	.1101	.001261	.1350	.00079	.1246
800	.002352	1.46	.1040	.001688	.1526	.00098	.1275
1200	.002824	0.945	.0998	.001804	.1707	.00100	.1296
1400	.002994	0.795	.0987	.001811	.1796	.00099	.1314

^a Using interpolated values for the equilibrium constant K .

was determined by finding the difference in the values of x at two times at equal time intervals above and below the desired time and dividing this difference by the total time interval. The velocity constant k in Col. 4 is calculated from the differential Equation 2. Since these values are obtained from the slopes of the curve at the individual points, they represent more nearly than the values of k' in Table I, the actual behavior of the velocity curve at the various times. The decrease in k is therefore very much more marked than that of k' .

The constant obtained in a comparable experiment by Price,¹¹ agrees very well with our value when the results are recalculated to a common basis and the effect of the slight difference in the ionic strengths of the solutions is taken into account.

Column 5 of Table II contains the concentrations of tri-iodide ion as calculated by Equation 9, using interpolated values for the equilibrium at the different concentrations of $KI + KI_3$. When this is taken into consideration by means of Equation 10, the resulting k increases approximately 40% during the first two-thirds of the reaction. Col. 8 contains values for the velocity constant calculated in the same way but setting¹² $K = 0.0061$, the value used by Kiss and his co-workers. This particular value was determined for a special purpose in which a knowledge was desired of the tri-iodide equilibrium in a solution containing 1.65 molar potassium chloride and 0.1 molar hydrochloric acid besides iodine and potassium iodide. It has no significance in solutions such as used in the experiments under discussion¹³ and by Kiss. Therefore, unless we are willing to assume that the values of the equilibrium constant as determined by Bray and MacKay are only about one-quarter of the true values,¹⁴ we must conclude that (1) the constancy of k in Col. 8 is fortuitous,¹⁵ and (2) the correction of the iodide-ion concentration by subtracting the concentration of the tri-iodide is not adequate to account for the experimentally determined velocities. The assumption made by Kiss and his co-workers on the basis of the constancy of k that the tri-iodide ion does not react with persulfate ion is unjustified.

¹¹ Cf. Price, Ref. 3, p. 478, Table 6.

¹² Brønsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922).

¹³ In the present article no account has been taken of the possible effect of the $K_2S_2O_8$ and K_2SO_4 on the equilibrium constants because these substances, at the concentrations involved, have practically no influence on the solubility of iodine.

¹⁴ This is entirely out of the question since their values are in good agreement with those of earlier workers such as Jakowkin and Maitland (for references and summary see Bray and MacKay, ref. 6, p. 915) and those of the very recent work of Jones and Kaplan, ref. 7.

¹⁵ Kiss, Zombory and Bruckner found this constancy using $K = 0.0061$, presumably by applying the equations quoted above given in their articles. The fact that the present writers also obtain constant values for k by applying the correct equations makes the articles by Kiss and his co-workers only more difficult to understand.

The value of $-dC_{S_2O_8^{--}}/dt$ for $t = 0$ in Table II is, obviously, extrapolated. The value of k found from this is in good agreement with values obtained by several other less exact methods. Extrapolation of the values of k' from Table I gave a value somewhere between 0.124 and 0.126. Similar procedures using values of x from the curve and applying Equation 11 gave 0.1251 and again from the plot of k (Table II) 0.1260. From another method, to be described in the next section, also depending upon extrapolations, 0.1285 was obtained. Since the value of k at $t = 0$ represents the velocity constant of the reaction when complicating factors such as the tri-iodide equilibrium are negligibly small, it will be important in several parts of the article. For its value we shall choose $k = 0.125$.

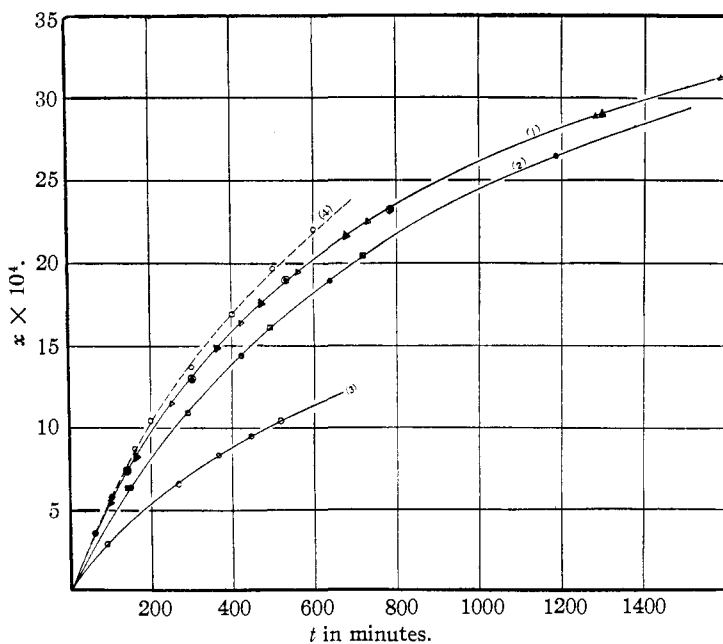


Fig. 1.—Curve 1, $K_2S_2O_8$, 0.005; KI, 0.01; I_2 , 0, initially: Δ , June 19; \odot , July 3; \blacktriangle , July 4. Curve 2, $K_2S_2O_8$, 0.005; KI, 0.01; I_2 , saturated: \odot , June 21; \square , July 3. Curve 3, $K_2S_2O_8$, 0.005; KI, 0.005; KNO_3 , 0.005. Curve 4, I_2 , 0 throughout (extrapolated).

D. Theory and Results of Experiments with Solutions Containing Iodine at the Beginning of the Reaction

All of the experiments by other investigators, as well as those reported above, indicate that the most troublesome factor in studying the reaction between $S_2O_8^{--}$ and I^- ion is the formation of I_3^- ion. The present writers believed that one way of clearing up the situation would be to make it worse. Accordingly, several experiments were performed in

which various amounts of iodine had been added to the initial reaction mixture, in some cases the solutions being saturated with this substance throughout the reaction. The results for solutions saturated with iodine are given in Table III (experimental values) and Table IV (from a smoothed

TABLE III

THE REACTION BETWEEN PERSULFATE AND IODIDE IONS, AT 25°, IN SOLUTIONS SATURATED WITH IODINE

KI = 0.01; K₂S₂O₈ = 0.005; I₂, saturated soln.

Time, min.	Expt.	x_1 , moles per liter	k' , Eq. 11	Time, min.	Expt.	x_1 , moles per liter	k' , Eq. 11
140	20	0.000632	(0.1033)	640	19	0.001900	0.0956
			(discarded)	720	20	.002047	.0960
150	19	.000631	.0963	1185	19	.002644	.0947
290	20	.001088	.0958	2070	19	.003345	.0977
425	19	.001431	.0943				
490	20	.001618	.0975			Av.	.0960

TABLE IV

CALCULATION OF VELOCITY COEFFICIENTS FROM EQUATIONS 11, 2 AND 10

$C_{KI} = 0.01 M = 2a$; K₂S₂O₈ = 0.005 M = a ; C_{I₂} = saturated

Time, min.	x_1 , moles per liter	k' , Eq. 11	$-\frac{dC_{S_2O_8}}{dt} \times 10^4$	k_1 , Eq. 2	C _{I₂} ^a used in Eq. 10	k_1 , Eq. 10
60	0.000275	0.0969	4.35	0.0972	0.00487	0.1892
100	.000440	.0965	4.03	.0969	.00470	.1881
200	.000808	.0964	3.37	.0960	.00432	.1859
300	.001110	.0951	2.85	.0942	.00402	.1823
400	.001378	.0951	2.50	.0952	.00374	.1845
600	.001826	.0959	1.93	.0957	.00328	.1857
800	.002170	.0959	1.52	.0948	.00294	.1828
1000	.002441	.0953	1.25	.0952	.00266	.1838
	Av.	.0959		.0956		.1853

^a Interpolated values of K' were used in obtaining these values.

curve). The results for the unsaturated solutions are included in Table V, which will be discussed in detail later. Experiments 19 and 20 cited in Table III were performed several weeks apart, using different samples of all three substances. Several conclusions follow from these results: (1) the presence of the iodine has decreased the velocity of the reaction; (2) the reaction velocity constant shows a lower value than in Tables I and II but no drift in value regardless of the method of computation; (3) while in saturated solution of iodine in a given concentration of potassium iodide (over this range of concentrations) the actual concentration of iodide ion is only about one-half the amount if iodine were absent, the reaction proceeds at approximately 75% of the initial rate of the reaction without iodine present. The ratio of the two velocity constants and thus of the initial rates of reaction is $0.0958/0.1250 = 0.76$; (4)

if we are not to assume that tri-iodide ion or iodine "catalyzes" the reaction, then the tri-iodide ion must react with persulfate ion.

Before considering the last of these conclusions, it will be pertinent to discuss the reason for the constancy of the values in Cols. 5 and 7 of Table IV. The results of Bray and MacKay (see above) indicate that if the activity of the iodine in a potassium iodide solution is maintained at a constant value by saturating the solution with iodine, the ratio of iodide-ion concentration to tri-iodide-ion concentration remains practically constant over the range of potassium iodide concentrations involved.¹⁶ In solutions in which the iodine activity is changing this is no longer true. Therefore whether iodide ion alone, tri-iodide ion alone, or both ions simultaneously react with persulfate ion, maintaining a constant iodine activity will immediately simplify the entire problem by making, practically, a single factor, that is, the total concentration of iodide plus tri-iodide ions in the solution, responsible for the actual concentration of each one.¹⁷ If we may take the average ratio of the concentrations of these two ions in saturated iodine solutions, setting $C_{I^-}/C_{I_3^-} = K' = 1.07$ for the range involved in Table IV, it can then be shown algebraically that, since

$$C_{I^-} + C_{I_3^-} = 2(a - x) \quad (12)$$

Equation 10 may be transformed into

$$-\frac{dC_{S_2O_8^{--}}}{dt} = \frac{K'}{K' + 1} k_1 2(a - x)^2 \quad (13)$$

By direct comparison of Equations 2 and 13 and inserting the values of K' and k_1 , we get

$$k = \frac{K'}{K' + 1} k_1 = \frac{1.07}{2.07} \times 0.1853 = 0.0958$$

These relationships thus explain the constancy observed among the values in Cols. 5 and 7 of Table IV, for it is evident that taking the tri-iodide concentration into consideration merely modifies Equation 2 by a constant factor when the solution is saturated with iodine throughout the reaction.

Table V summarizes the results of several experiments in which the initial concentrations of iodine were varied.¹⁸ The values of x for each value of t were plotted against the total iodine concentrations ($I_2 + I_3^-$) at the same time and the curve extrapolated to zero iodine concentration

¹⁶ See footnote 10.

¹⁷ In investigations of the HIO_3 -HI reaction Abel and Stadler, *Z. physik. Chem.*, **122**, 49 (1926), found that saturating the solution with iodine simplified the problem.

¹⁸ Only interpolated values are included in Table V. The experimental values on which Col. 3 is based were somewhat erratic, hence the values in this column were given less weight than those in other columns in the subsequent calculations. The values of k' (Equation 11) calculated from the results in Cols. 3 and 4 decrease as the time increases but not quite as much as those given in Table I.

(Col. 6). The iodine concentrations for Col. 2 were obtained from the total iodide concentration ($2a - 2x$) and the solubility table given by Bray and MacKay. The extrapolated values, while not very accurate (see Curve 4, Fig. 1) and becoming more uncertain for the higher values of t , give a constant which is in reasonably good agreement with those found by other methods. The reaction velocity curve obtained in this way is, of course, the result of a purely empirical process which gives merely the curve which would have been obtained from all the experiments cited above, including those in Table I, if the presence of iodine did not interfere with the reaction. By itself this method gives no indication as to the mechanism of the interference. The results in Table V directly contradict the statements made by Kiss and Zombory.¹⁹

TABLE V
THE VELOCITY IN SOLUTIONS CONTAINING IODINE INITIALLY. EXTRAPOLATION TO ZERO IODINE CONCENTRATION

Time, min.	x					k' , Eq. 11
	$I_2 = \text{satd.}$ at $t = 0$	$I_2 = 0.001553$ at $t = 0$	$I_2 = 0.000729$ at $t = 0$	$I_2 = 0$ at $t = 0$	Extrapolated to $(I_2) = 0$ at $t = 0$	
60	0.000275	0.000326	0.000332	0.000345	0.000351	0.126
100	.000440	.000516	.000535	.000548	.000563	.127
160	.000668	.000768	.000780	.000815	.000870	.132
200	.000808	.000922	.000935	.000972	.001042	.132
300	.001110	.001245	.001260	.001306	.001370	.126
400	.001378	.001515	.001537	.001585	.001690	.128
500	.001620	.001702	.001776	.001820	.001930	.126
600	.001826	.001952	.001978	.002022	.002200	.131
					Av.	.1285

Returning to the initial slope of the reaction between iodide and persulfate ions in solutions containing no iodine at the start, it can readily be seen that in a solution of the same ionic strength and concentration of persulfate ion, but with the molar iodide-ion concentration equal to instead of twice that of the persulfate ion, the initial slope of the curve would have been half the limiting value given in Table II, that is, 3.13×10^{-6} . An experiment with a mixture of 0.005 molar $K_2S_2O_8$, 0.005 molar KI and 0.005 molar KNO_3 gave 3.27×10^{-6} as an extrapolated value of $-dC_{S_2O_8}/dt$ at $t = 0$. This agreement is within the errors of experiment and extrapolation. The results of this experiment are plotted on Fig. 1 but not tabulated, since the work of Price is sufficient to establish the proportionality between the velocity and the concentrations of the reactants.

While the possibility that the tri-iodide ion may act as a catalyst for the iodide-persulfate ion reaction cannot be excluded entirely, the probability of such an effect seems to be very low, especially in view of the

¹⁹ Ref. 4 c, pp. 227 and 229,

very satisfactory agreement to be shown below between experimental results and results of calculations based on the hypothesis that the tri-iodide ion itself reacts with the persulfate ion. The possibility that iodine may act as a catalyst must be rejected, however, on the grounds of the agreement just mentioned and because the behavior of the free iodine concentration could not possibly account for the observed results. In order to satisfy the latter, the free iodine concentration must vary in the same way as the tri-iodide ion concentration, that is, the ratio of tri-iodide-ion concentration to free iodine concentration should be constant. In saturated iodine solutions the concentration of free iodine is constant while that of the tri-iodide ion decreases continuously, but in the unsaturated solutions the tri-iodide concentration passes through a maximum during the course of the reaction.

On the other hand, if both iodide and tri-iodide ions react with persulfate ion and if the mechanism of the reaction between tri-iodide ion and persulfate ion is similar to that represented by Equations 3 and 4, the equation for the reaction velocity becomes

$$-\frac{dC_{S_2O_8^{--}}}{dt} = k_{I^-} C_{I^-} C_{S_2O_8^{--}} + k_{I_3^-} C_{I_3^-} C_{S_2O_8^{--}} \quad (14)$$

For saturated iodine solutions the average velocity constant from Tables III and IV may be taken as 0.0958. The initial value for the unsaturated solutions from Table II is 0.125 which is the value of k_{I^-} . Again assuming that over the range of concentrations involved we may call the ratio $C_{I^-}/C_{I_3^-} = K'$ sensibly constant and equal to 1.07 in saturated iodine solutions, by combining this relation with Equation 8, we obtain from Equation 14

$$-\frac{dC_{S_2O_8^{--}}}{dt} = 2 \left(\frac{K'k_{I^-} + k_{I_3^-}}{K' + 1} \right) (a - x)^2 \quad (15)$$

By direct comparison with Equation 2, there results

$$k = 0.0958 = \frac{1.07 \times 0.125 + k_{I_3^-}}{1.07 + 1}$$

from which $k_{I_3^-} = 0.0645$.

For the reactions in which the solutions were not saturated with iodine, Equation 14 becomes

$$-\frac{dC_{S_2O_8^{--}}}{dt} = 2k_{I^-}(a - x)^2 - (k_{I^-} - k_{I_3^-})(a - x) \left[\frac{K + 2a - x}{2} - \sqrt{\left(\frac{K + 2a - x}{2} \right)^2 - 2x(a - x)} \right] \quad (16)$$

The first term on the right is the simple expression for the case where no iodine is present at any point during the reaction; the second represents the effect of the tri-iodide ion. The term in square brackets is the concentration of tri-iodide ion, and for the experiments reported in Tables I and II it is identical with the values in Col. 5 of Table II.

TABLE VI
COMPARISON OF THE FINAL CALCULATED VELOCITY WITH THE OBSERVED VELOCITY
 $C_{KI} = 2a = 0.01 M$; $C_{K_2S_2O_8} = a = 0.005 M$; $C_{I_2} = 0$ initially

Time, min.	$2k_{I^-}(a-x)^2$ $\times 10^4$	2nd term in Eq. 16 $\times 10^4$	Calcd. $\times 10^4$	Obs. $\times 10^4$
60	5.42	-0.084	5.34	5.35
100	4.96	- .127	4.83	4.82
200	4.06	- .199	3.86	3.77
400	2.92	- .261	2.66	2.57
800	1.75	- .270	1.48	1.46
1200	1.184	- .238	0.946	0.945
1400	1.006	- .220	0.786	0.795

$$k_{I^-} = 0.1250; k_{I_3^-} = 0.0645; K' = 1.07$$

Values of the slopes of the velocity curve calculated by Equation 16 are given in Table VI, Col. 4 and for comparison the observed values are included in Col. 5. Col. 2 shows the slopes which would be observed if tri-iodide ions were not formed during the reaction. These calculations demonstrate conclusively that the observed reaction velocity is the sum of the velocities of two reactions, the first involving the iodide ions and the second the tri-iodide ions, and, furthermore, that the tri-iodide ion reacts at approximately one-half the rate of the iodide ion. The conclusion drawn by Kiss and Bossányi^{4d} that the reaction between tri-iodide and persulfate ions is not appreciable at this temperature is unjustified.

Summary

The velocity of the reaction between iodide and persulfate ions is reinvestigated from the standpoint of the effect of tri-iodide ion formation. It is shown that earlier work on this reaction is insufficient and in some cases marred by too serious errors to be used for such a study.

Experiments have been made in solutions containing no iodine in the initial mixture and in solutions saturated with this substance. It is shown that by maintaining a constant iodine activity, it is possible to simplify the theoretical treatment and interpretation of the experimental data so that the observed reaction velocity may be analyzed into two parts, one being due to the iodide ion and the other to the tri-iodide ion.

NEW YORK, N. Y.