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KINETICS OF THE REACTION BETWEEN PERSULFATE AND THIOSULFATE IONS IN DILUTE AQUEOUS SOLUTION

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In the year 1897 Marshall[1] found that if a very slight stoichiometric excess of potassium persulfate were allowed to react with potassium thiosulfate, he could prepare pure tetrathionate. He also found that if excess thiosulfate were used, he could prepare trithionates.[2] These experiments are reviewed by Price,[3] who, however, did not investigate the reactions himself.

Marshall used rather concentrated solutions and did not study the speed of the reaction. No such study has been made until the present time, although the reaction was investigated from a quantitative standpoint by Schwicker.[4]

Schwicker found that in dilute solution in the cold the reaction was very slow, but that if a small amount of persulfate were boiled with excess $N/10$ thiosulfate, titration with iodine showed quantitative oxidation to tetrathionate. With potassium iodide present the oxidation to tetrathionate was also quantitative and much faster.

Experiments in this Laboratory[5] confirmed the fact that in dilute solution, at room temperature, the formation of tetrathionate is quantitative, within a few tenths of one per cent. with either persulfate or thiosulfate in considerable excess, with or without potassium iodide present.

A series of preliminary experiments on the velocity of the reaction in dilute solution[6] showed some interesting results. First, the reaction is catalyzed enormously by copper salts, much less by iron salts, very little by silver salts; other catalysts are quinone, quinhydrone and hydroquinone. Second, impurities in the water or the salts used have a large and uncontrollable catalytic effect. Consequently, most of the experiments reported here were carried out with water redistilled from dilute permanganate. Third, although the uncatalyzed reaction is stoichiometrically trimolecular

$$S_2O_8^{=} + 2S_2O_3^{=} \longrightarrow 2SO_4^{=} + S_4O_6^{=}$$

kinetically it follows the unimolecular law with some tendency in certain solutions to deviate in the direction of a zero or second order reaction.

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[1] Marshall, *J. Soc. Chem. Ind.*, **16**, 396 (1897).

[2] Mackenzie and Marshall, *J. Chem. Soc.*, **93**, 1726 (1908).

[3] Price, "Peracids and Their Salts," Longmans, **1912**, p. 36.

[4] Schwicker, *Z. anal. Chem.*, **74**, 433 (1928).

[5] By Miss Elinor Cook.

[6] Most of the experiments by Mr. Abraham Berkowitz.

Over a considerable range of concentrations, in ordinary distilled water or specially purified water, the velocity is unimolecular with respect to the persulfate ion and almost, though not quite, independent of the thiosulfate concentration.

Materials and Methods

Potassium persulfate was recrystallized from ordinary distilled or redistilled water between 50 and 0° until free from sulfate and dried over sulfuric acid. Standard solutions were made by direct weighing. Sodium thiosulfate was recrystallized two or three times, dried in air and the solutions made up in freshly boiled water; 0.08 *M* solutions in ordinary distilled or redistilled water were standardized by the persulfate-iodide or the permanganate method, and did not change their titer over periods as long as four months.

Potassium iodide, chloride and sulfate were recrystallized similarly, dried in air at suitable temperatures and standard solutions made by direct weighing of the salts. A stock solution of copper sulfate was made from recrystallized $CuSO_4 \cdot 5H_2O$ and standardized by adding potassium iodide and titrating the liberated iodine, as recommended by Fales.[7] The solutions used were made from this by quantitative dilution.

In the preliminary experiments mentioned before, the persulfate and thiosulfate concentrations were varied considerably to establish the character of the reaction. In the experiments reported in detail here the persulfate concentration was always made 0.01 *M* and the thiosulfate 0.02 *M*, these being the correct stoichiometric proportions; the main interest here lies in the catalytic effects, and with these concentrations the unimolecular law is followed closely over two-thirds of the reaction, except in certain solutions, as will be shown later. Suitable standard solutions of the salts used were pipetted from flasks in a large thermostat at 25° (±0.01°), thoroughly mixed and replaced in the thermostat. After suitable time intervals 50-cc. portions were withdrawn and titrated with a 30–40% alcoholic solution of iodine (about 0.01 *M* I_2) containing about 0.02 *M* potassium iodide. An aqueous solution containing more potassium iodide could not be used, since the persulfate oxidizes the iodide too rapidly during the titration; and from an aqueous solution 0.02 *M* in potassium iodide the iodine escapes too rapidly for accurate titration unless special precautions are taken.

The experiments using ordinary distilled water and redistilled water are listed in separate tables for comparison. It will be noted that the velocity in individual experiments is far different, but in spite of this the conclusions with regard to the catalytic effects are changed very little.

The velocity constants were obtained by plotting the logarithm (to the base 10) of the number of cc. of iodine used for the individual titrations, against the time in minutes; the slope of the straight line drawn through these points, multiplied by 2.303, gives the velocity constant. In other words, $\log_{10}(a - x)$ is plotted against t in the equation

$$kt = 2.3 \log \frac{a}{a - x}$$

where a is the initial concentration of persulfate and $a - x$ the concentration at the time t, both expressed in cc. of iodine solution required. The value of k obtained is, of course, the same as if moles per liter of persulfate

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[7] Fales, "Inorganic Quantitative Analysis," The Century Co., New York, 1925.

were substituted; and the method does not even require standardization of the iodine solution. The logarithm of the initial titration is given, if desired, by the extrapolation of the straight line to zero time.

The reproducibility of these experiments is not high, but is, on the whole satisfactory when we consider the ease with which thiosulfate is oxidized and the anomalous character of the persulfate oxidations. It will be recalled that the velocity of the persulfate–oxalate oxidation catalyzed by silver ion is quite uncontrollable.[8] Here we have a very easily oxidized substance (thiosulfate) and a very active oxidizing agent (persulfate, capable even of oxidizing manganese salts to permanganate (with a catalyst)); the system is unstable and extremely sensitive to traces of catalysts. Consequently the highest degree of reproducibility cannot be expected.

1. The Uncatalyzed Reaction.—An example of the actual titrations obtained is given in Table I.

TABLE I

DETAILS OF THE MEASUREMENTS IN ONE EXPERIMENT

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; redistilled water; 25°

Time, min.	0	165	295	445	555	675	800
Iodine, cc.	.	41.90	40.94	39.95	39.19	38.33	37.58

From the plot of log cc. I_2 *vs.* time, k = 0.000177.

Tables II and III summarize a number of experiments with ordinary distilled and redistilled water, and show the effect of an inert salt (potassium chloride) on the reaction velocity.

TABLES II AND III

SUMMARY OF RESULTS FOR THE UNCATALYZED REACTION

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 25°

ORDINARY DISTILLED WATER			REDISTILLED WATER		
k, no. KCl	k, 0.02 M KCl	k, 0.06 M KCl	k, no. KCl	k, 0.02 M KCl	k, 0.06 M KCl
0.000357	0.000444	0.00132	0.000191	0.000262	0.000427
341	437	106	182	270	443
274	374			283	480
255	424			283	
262	460			263	
595	471			296	
606	733			287	
				293	

Discussion

Tables II and III show that the purity of the water has an enormous effect. The experiments in Table II are far from reproducible; this finally led to the use of redistilled water, and the experiments in Table III are much more concordant. Water redistilled in different stills, with glass or tin condensers, from ordinary distilled water from different sources, gave

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[8] King, THIS JOURNAL, 50, 2089 (1928).

fairly concordant results, and it is doubtful whether a very elaborate purification of the water would give much lower velocities. It is just possible that in absolutely pure water no reaction would occur, and that the reaction shown here is catalytic in character. Further experiments are in progress to establish this point.

Another observation from Tables II and III would agree with this. The salt effect is positive, abnormally high and with the ordinary distilled water at least, of an abnormal type—the salt effect increasing as the salt concentration increases. Now according to the well-substantiated theory of Brönsted, no unimolecular reaction could have a positive salt effect, since the salt effect is indicated in the equation

$$k = k_0F$$

where k is the observed velocity constant, k_0 the constant at zero ionic strength and F the "kinetic activity factor," in this case the activity coefficient of the reacting ion. F must decrease as the salt concentration is increased, at least in any usual case at low ionic strengths.

The same is true for a pseudo-unimolecular reaction between an ion and one or more neutral molecules present in constant concentration. The only kind of reaction which will satisfy the observations here is one between the persulfate ion and another negative ion present in constant concentration. A positive ion would mean a negative salt effect. The thiosulfate ion cannot be the negative ion, for its concentration is continually changing and the velocity is independent, or nearly independent of its concentration. The alternate conclusion is that the velocity-determining reaction is between the persulfate ion and an unknown, negative ion present in small amount as an impurity in the water. This mechanism seems untenable too, for the catalyst in ordinary distilled water is apparently some nearly nonvolatile substance and it seems improbable that such impurity would always be present in practically the same concentration in the redistilled water.

2. **The Catalysis by Iodide Ion.**—Since the persulfate–iodide oxidation

$$S_2O_8^{=} + 2I^- \longrightarrow 2SO_4^{=} + I_2$$

is much faster than the reaction

$$S_2O_8^{=} + 2S_2O_3^{=} \longrightarrow 2SO_4^{=} + S_4O_6^{=}$$

and the reaction between thiosulfate and iodine

$$2S_2O_3^{=} + I_2 \longrightarrow S_4O_6^{=} + 2I^-$$

is practically instantaneous, it is reasonable to expect that iodides will catalyze the oxidation of thiosulfate. If the mechanism of the catalysis is entirely as outlined above, it should be possible to measure the velocity of the persulfate–iodide reaction from the catalytic effect on the persulfate–thiosulfate reaction; the two should be additive. Since the iodide is regenerated as fast as it is used up, its concentration is constant, and the total reaction will be unimolecular in character. By subtracting the unimolecular constant for the uncatalyzed from that for the catalyzed reaction (at the same ionic strength), and dividing by the iodide concentration, we will obtain the bimolecular constant for the persulfate–iodide reaction. This can then be compared with the persulfate–iodide constants determined directly with no thiosulfate present.

Similar examples of "induced catalysis" of this type are known, as the catalysis of the persulfate oxidation of phosphorous acid by iodide, measured by Federlin.[9] Here the reactions are

$$S_2O_8^{=} + H_3PO_3 + H_2O \longrightarrow 2SO_4^{=} + H_3PO_4 + 2H^+ \quad (1)$$

$$S_2O_8^{=} + 2I^- \longrightarrow 2SO_4^{=} + I_2 \quad (2)$$

$$H_3PO_3 + I_2 + H_2O \longrightarrow H_3PO_4 + 2I^- + 2H^+ \quad (3)$$

and the net effect is similar, except that (3) is slower than the iodine–thiosulfate reaction; consequently, free iodine makes its appearance in the solution. Federlin concluded that the total rate of oxidation of phosphorous acid could be predicted exactly from the rates of the three reactions; as a mattter of fact, our examination of his data shows that the agreement is by no means good.[10]

In our experimental work we have two series of experiments in each of which the iodide-ion concentration is varied while the ionic strength is kept constant by suitable addition of potassium chloride to take the place of potassium iodide. The first series was run with both ordinary distilled and redistilled water, and it will be noticed that the persulfate–iodide constant is not much different, although the observed velocity is considerably different in the two cases.

Tables IV, V and VI give the results of these experiments. The total observed unimolecular constant is k; with no potassium iodide present, but potassium chloride to keep the ionic strength the same, $k_1 = k$. $k_2 = k - k_1$, *i. e.*, k_2 is the increase in velocity constant caused by the potassium iodide; and k_3 is k_2 divided by the concentration of potassium iodide, *i. e.*, the bimolecular persulfate–iodide constant in the presence of thiosulfate.

TABLE IV

SUMMARY OF EXPERIMENTS ON THE CATALYSIS BY IODIDE

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 0.02 M (KCl + KI); ordinary distilled water; 25°; average value k_1 = 0.000435 (see Table II).

C_{KCl}	C_{KI}	k	k_2	k_3
0.016	0.004	0.00133	0.00090	(0.224)
.012	.008	.00179	.00135	.169
.010	.010	.00214	.00171	.171
.008	.012	.00242	.00198	.165
.004	.016	.00318	.00274	.171
.0	.02	.00399	.00355	.177
			Mean	0.171

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[9] Federlin, *Z. physik. Chem.*, 41, 565 (1902).

[10] A similar example is given by Abel, *Z. Elektrochem.*, 14, 598 (1908).

TABLE V

SUMMARY OF EXPERIMENTS ON THE CATALYSIS BY IODIDE

Concentrations as in Table IV; redistilled water; value of k_1 used determined on same days as k (see Table III).

C_{KCl}	C_{KI}	k	k_3
0.016	0.004	0.000954	0.173
.016	.004	.000937	.163
.012	.008	.00158	.165
.012	.008	.00159	.162
.008	.012	.00227	.168
.008	.012	.00229	.166
.004	.016	.00294	.167
.004	.016	.00294	.167
.0	.02	.00361	.167
		Mean	0.166

The bimolecular constant k_3 is, within experimental error, the same over a considerable range of iodide concentration, and its value is changed but little by the use of ordinary distilled or redistilled water. Table VI shows the effect of a higher salt concentration on the velocity.

TABLE VI

SUMMARY OF EXPERIMENTS ON THE CATALYSIS BY IODIDE

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 0.06 M (KCl + KI); redistilled water; 25°; k_1 determined on same days as k (see Table III).

C_{KCl}	C_{KI}	k	k_3
0.056	0.004	0.00125	0.203
.056	.004	.00130	.205
.052	.008	.00209	.206
.052	.008	.00221	.216
.048	.012	.00294	.208
.044	.016	.00377	.207
.044	.016	.00372	.206
.04	.02	.00477	.216
		Mean	0.208

Discussion

From Tables V and VI it is seen that the salt effect on the persulfate–iodide reaction is positive, as is to be expected for a reaction between two ions of the same sign, and it is also normal in magnitude. We now come to the question of whether the velocities of the two slow reactions concerned are additive; *i. e.*, whether the mechanism of the catalysis is as outlined above and the two independently measurable reactions with the one instantaneous reaction account for the observed velocity. A comparison of the persulfate–iodide constant recorded here with constants recalculated from the data of Price on this reaction,[11] and measurements in this Labora-

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[11] Price, *Z. physik. Chem.*, **27**, 474 (1898).

tory[12] led us to suspect that these constants were somewhat lower than the persulfate–iodide constants determined directly in solutions of the same ionic strength; however, .the authors mentioned did not use solutions of exactly comparable composition. It is not always possible to compare velocities in solutions of the same ionic strength, even if the salts involved are of the same valence type, because of a considerable difference in specific salt effect, unless the concentrations are extremely low.

For this reason, a few experiments were made on this reaction in comparable solutions, replacing sodium thiosulfate with potassium sulfate, a salt of the same valence type. The constants were calculated from measurements made on the first one-fourth of the reaction, to avoid the complicating influence of the iodine formed (see previous work on this reaction). The results are recorded in Table VII.

TABLE VII

BIMOLECULAR CONSTANTS FOR THE PERSULFATE–IODIDE REACTION (NO THIOSULFATE PRESENT)

0.01 M $K_2S_2O_8$; 0.02 M K_2SO_4; redistilled water; 25°

C_{KCl}	C_{KI}	k_2
0.012	0.008	0.213
.008	.012	.216
.052	.008	.262
.048	.012	.268

As expected, these results show that the persulfate–iodide reaction, measured in the presence of thiosulfate, is several per cent. slower than when measured independently. This might be explained in one of three ways: (1) the specific salt effect of sodium thiosulfate is far different from that of potassium sulfate, which seems hardly probable; (2) the iodine–thiosulfate reaction is not as fast as supposed (which would keep the iodide concentration lower than that specified, and would necessitate the appearance of free iodine in the solution; this was never observed even with the aid of the starch test); or (3) one of the reactions, persulfate–iodide or iodine-thiosulfate, takes place in steps, resulting in the accumulation in solution of some colorless intermediate compound. This last seems possible, as both reactions are stoichiometrically trimolecular. We have, however, no way of testing this possibility. Two comments can be made: the agreement observed here is as good as that observed by Federlin in the case of the reaction mentioned before, and work in progress in this Laboratory shows that the velocity of the persulfate–iodide reaction is normal in the presence of extremely small concentrations of thiosulfate (10^{-5}–10^{-6} M).

3. **The Catalysis by Copper Ion.**—Price,[11] in his early work on the persulfate–iodide reaction, found that the velocity was increased enormously by iron and copper salts. The work reported here shows that cop-

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[12] Jette and King, THIS JOURNAL, 51, 1048 (1929).

per salts have also an enormous effect on the persulfate–thiosulfate reaction. Price found a different catalytic effect of iron and copper salts in neutral and acid solution; both were fairly reproducible. Because of the decomposition of thiosulfate in acid solution most of our experiments were in neutral solution; a few, however, were carried out with a low concentration of acid present and are reported in the table.

It has been reported that traces of copper salts greatly accelerate the atmospheric oxidation of thiosulfates.[13] However, we believe this caused little error in the experiments reported here. A more important reaction which occurs in the system is that of cupric ion and thiosulfate.[14] Cupric ion is reduced to cuprous by thiosulfate, and negative complex ions of the type $Cu(S_2O_3)_y^{-x}$ are formed. The importance of this knowledge will be seen in the discussion.

If we assume that the cuprous copper is oxidized to cupric and instantly reduced by thiosulfate to cuprous again, we have a plausible mechanism for the catalysis. The relatively enormous catalytic effect is explained by the great speed of the persulfate–cuprous reaction. In this case again, by subtracting the constant of the uncatalyzed reaction (k_1), we obtain the part of the constant due to the copper catalysis, or, in other words, the constant of the persulfate–cuprous reaction. This reaction is pseudo-unimolecular, since the cuprous-ion concentration remains constant. On dividing this value by the copper-ion concentration, we obtain the bimolecular constant for the persulfate–cuprous reaction (k_4). The agreement of these constants as the copper-ion concentration is varied shows that this reaction is bimolecular, and gives a method of learning the velocity of this reaction, which cannot be measured directly as can the persulfate–iodide reaction.

With copper ion as the catalyst, there was a deviation from the unimolecular law, amounting to as much as 6 or 8% on the logarithmic plot when the reaction was half over. Hence a straight line was drawn as well as possible, tangent to the actual curve at zero time, and the slope of this line was taken as the best measure of the velocity in the first part of the reaction. The deviations were probably caused by the catalysis of side reactions; for instance, if the copper-ion concentration is high enough, sulfur is precipitated in the solution and the odor of hydrogen sulfide is apparent.

Since the copper-ion concentrations were so low, it was unnecessary to add varying amounts of another salt to keep the ionic strength constant. Experiments were run side by side with the catalyzed and uncatalyzed re-

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[13] See Hahn and Clos, *Z. anal. Chem.*, **79**, 11 (1929).

[14] Mellor, Treatise on Inorganic and Theoretical Chemistry, Vol. X, p. 530; Dutoit, *J. chim. phys.*. 11, 650 (1913); Bassett and Durrant, *J. Chem. Soc.*, **123**, 1279 (1923)

TABLES VIII AND IX

SUMMARY OF EXPERIMENTS WITH COPPER ION AS CATALYST

0.01 *M* $K_2S_2O_8$; 0.02 *M* $Na_2S_2O_3$; 25°

ORDINARY DISTILLED WATER

$C_{CuSO_4} \times 10^5$	k	k_4
0	$0.000595 = k_1$	...
0	$.000606 = k_1$	...
2.5	.00926	347
1.25	.00471	329
0.5	.00232	318
.5	.00218	342
.125	.00102	337
.05	.000800	(410)
.05	.000813	(414)
	Mean	334

REDISTILLED WATER

$C_{CuSO_4} \times 10^5$	k	k_4
0	$0.000191 = k_1$	...
0	$.000182 = k_1$	...
2.5	.0114	449
1.25	.00602	466
0.5	.00244	449
.25	.00135	462
.25	.000771	464
.125	.000335	(288)
	Mean	458

TABLES X AND XI

SUMMARY OF EXPERIMENTS WITH COPPER ION AS CATALYST

0.01 *M* $K_2S_2O_8$; 0.02 *M* $Na_2S_2O_3$; 0.02 *M* KCl; 25°

ORDINARY DISTILLED WATER

$C_{CuSO_4} \times 10^5$	k	k_4
0	$0.000471 = k_1$	...
2.5	.0114	436
2.5	.0109	416
1.25	.00607	447
1.0	.00489	432
0.75	.00390	457
.5	.00291	487
.5	.00291	488
.125	.00125	(624)
	Mean	452

REDISTILLED WATER

$C_{CuSO_4} \times 10^5$	k	k_4
0	$0.000283 = k_1$	...
0	$.000283 = k_1$	...
2.5	.0138	540
1.25	.00718	551
0.5	.00285	514
.25	.00166	540
.25	.00155	517
.125	.00100	513
.05	.000549	532
.0125	.000347	512
	Mean	527

TABLES XII AND XIII

SUMMARY OF EXPERIMENTS WITH COPPER ION AS THE CATALYST

0.01 *M* $K_2S_2O_8$; 0.02 *M* $Na_2S_2O_3$; 0.06 *M* KCl; 25°

ORDINARY DISTILLED WATER
(FROM TWO SOURCES)

$C_{CuSO_4} \times 10^5$	k	k_4
0	$0.00132 = k_1$	...
1.25	.00887	604
0.5	.00428	591
.125	.00214	655
0	$0.00106 = k_1$	...
2.5	.0162	605
0.25	.00266	641
.125	.00179	588
	Mean	614

REDISTILLED WATER

$C_{CuSO_4} \times 10^5$	k	k_4
0	$0.000509 = k_1$	...
0	$.000503 = k_1$	...
2.5	.0190	741
1.25	.00966	732
0.5	.00413	730
.5	.00400	698
.25	.00221	691
.25	.00227	704
.05	.000869	721
.0125	.000629	(969)
	Mean	717

TABLE XIV

THE EFFECT OF H^+ ON THE COPPER CATALYSIS

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; 0.02 M KCl; 1.25×10^{-5} M H_2SO_4; ordinary distilled water; 25°

$c_{CuSO_4} \times 10^5$	k	k_4
0	0.000733=k	...
2.5	.0111	414
1.25	.00642	454
1.25	.00662	470
0.5	.00292	436
.25	.00191	470
	Mean	455

actions, to eliminate any effect from different samples of water. The results are given in Tables VIII–XIV.

Discussion

The constancy of the values of k_4 in each table indicates that we are actually measuring the velocity of a definite bimolecular reaction, which probably is, as suggested before, the oxidation of cuprous ion (in a negative complex with the thiosulfate ion) by persulfate. The tables show that in this case the character of the water used has an effect on the persulfate–cuprous reaction, though not as large as on the persulfate–thiosulfate reaction. The salt effect is positive, in complete agreement with the belief that the velocity-determining reaction is between two negative ions. The effect of hydrogen ion is curious; although it increases the velocity of the persulfate–thiosulfate reaction a great deal, its effect on the persulfate–cuprous reaction is negligible. Although cupric ion would be considerably hydrolyzed in pure water solution, evidently in the thiosulfate solution the copper ion is all in the same form whether H^+ is present above its normal value in water or not. This is different from the effect of copper salts on the persulfate–iodide reaction; Price found that acids had a considerable effect on the velocity, presumably because they decrease hydrolysis of the copper ion. Price's data show considerable variation in the value of the persulfate–cuprous constant, chiefly because the straight line obtained by plotting copper-ion concentration against increased velocity constants does not extrapolate to zero effect at zero concentration for some reason.

Inspection of Price's results shows that copper ion does not have as great an effect on the persulfate–iodide reaction as on the persulfate–thiosulfate reaction; 0.0025 M copper ion increases the velocity three to five times in the former case, very much more in the second. The mechanism of the catalysis in the two cases is different; in the first the copper is probably kept in the form of positive cupric ion, in the second by the extremely rapid reaction with thiosulfate, in the form of negative cuprous complex ion.

A point worthy of interest is the possibility of measuring the velocity of extremely rapid reactions by such a catalytic method as this. The iodide catalysis shows that the assumption of additive velocities is not far from true, and, if the same is true in the copper catalysis, we have a means of ascertaining, roughly at least, the velocity of a reaction up to 1000 times as fast (for equal concentrations) as those easily measured by the usual means. Direct measurement of such velocities can be accomplished only by some such scheme as that of Hartridge and Roughton,[15] used later by Saal[16] and by La Mer and Read.[17]

4. **The Combined Catalysis by Iodide and Copper Ions.**—The addition of both copper and iodide ions to the persulfate–thiosulfate system presents interesting possibilities. Price studied the effect of both copper and iron ions together on the persulfate–iodide reaction and found that the two together had practically twice the catalytic effect calculated from adding their separate effects. He was unable to explain this, except rather vaguely as a "promoter" effect.

There is a possibility in this system of at least six reactions, some measurable, some immeasurably fast.

(1)	The persulfate–thiosulfate reaction	measured before
(2)	The persulfate–iodide reaction	
(3)	The persulfate–cuprous reaction	
(4)	The thiosulfate–cupric reaction	"instantaneous"
(5)	The thiosulfate–iodine reaction	
(6)	The cupric–iodide reaction	very fast

The copper salt may catalyze the persulfate–iodide reaction, and so increase the effect of the iodide on the persulfate–thiosulfate reaction; or the iodide may catalyze the persulfate–cuprous reaction, through Reaction 6, and hence increase the effect of the copper salt on the persulfate–thiosulfate reaction; *i. e.*, if the iodide can complete its cycle of iodide–iodine–iodide through the path of Reactions 6–5 faster than through Reactions 2–5, or the copper can complete its cycle cuprous–cupric–cuprous faster through Reactions 3–6 than through Reactions 3–4, there will be an unusually large catalytic effect.

By a process similar to that used in the last section, from a suitable number of experiments we can obtain the constant for either Reaction 2 or 3 in this mixed solution, and compare it with those obtained before. To obtain the most concordant results, it was found necessary to run all experiments used in these calculations simultaneously, since, in general, the velocity constants were reproducible on the same day, with the same materials, but might vary 5–10% on different days. Consequently, experiments were run with no copper or iodide, some with copper, some with io-

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[15] Hartridge and Roughton, *Proc. Roy. Soc.* (London), **104A**, 376 (1923); *Proc. Cambridge Phil. Soc.*, **23**, 450 (1926).

[16] Saal, *Rec. trav. chim.*, **47**, 73, 264, 385 (1928).

[17] La Mer and Read, THIS JOURNAL, **52**, 3098 (1930).

TABLE XV

EXPERIMENTS WITH BOTH IODIDE AND COPPER IONS AS CATALYSTS

0.01 *M* $K_2S_2O_8$; 0.02 *M* $Na_2S_2O_3$; 0.02 *M* (KCl + KI); redistilled water; 25°.

$C_{CuSO_4} \times 10^5$	C_{KCl}	C_{KI}	k	k_3	k_4
0	0.02	0	$0.000287 = k_1$	...	...
			$.000293 = k_1$	...	...
0	.016	0.004	.000937	0.162	...
0	.012	.008	.00159	.162	...
0	.008	.012	.00229	.166	...
1	.02	0	.00555	...	526
1	.016	.004	.00654	.241	560
1	.012	.008	.00724	.214	565
1	.008	.012	.00840	.239	610
0.75	.02	0	.00432	...	538
.75	.016	.004	.00498	.163	538
.5	.02	0	.00297	...	537
			.00289	...	518
.5	.016	.004	.00380	.206	571
.5	.012	.008	.00443	.193	568
.5	.008	.012	.00527	.198	594
.375	.02	0	.00233	...	546
			.00226	...	578
.375	.016	.004	.00313	.198	584
.375	.012	.008	.00385	.191	604
.375	.008	.012	.00461	.196	618
.25	.02	0	.00170	...	556
			.00162	...	529
.25	.016	.004	.00244	.191	602
.25	.012	.008	.00317	.194	632
.25	.008	.012	.00386	.187	625
.125	.02	0	.000980	...	564
.125	.016	.004	.00176	.194	657

TABLE XVI

EXPERIMENTS WITH BOTH IODIDE AND COPPER IONS AS CATALYSTS. HIGHER IONIC STRENGTH

0.01 *M* $K_2S_2O_8$; 0.02 *M* $Na_2S_2O_3$; 0.06 *M* (KCl + KI); redistilled water; 25°

$C_{CuSO_4} \times 10^5$	C_{KCl}	C_{KI}	k	k_3	k_4
0	0.06	0	$0.000480 = k_1$	...	...
0	.056	.004	.00130	0.205	...
0	.052	.008	.00221	.216	...
0.5	.06	0	.00413	...	730
.5	.056	.004	.00512	.246	763
.5	.052	.008	.00615	.252	788
.375	.06	0	.00333	...	761
.375	.056	.004	.00421	.219	776
.375	.052	.008	.00533	.249	834
.25	.06	0	.00221	...	691
.25	.056	.004	.00325	.261	782
.25	.052	.008	.00421	.250	801

dide and some with both, on the same day. Tables XV and XVI show the results of these experiments: k is again the total observed unimolecular constant; k_1 the constant with no catalyst present; k_3 the persulfate–iodide constant, obtained by subtracting k with copper but no iodide present from k with iodide and the same copper-ion concentration and dividing the difference by the iodide-ion concentration. Again, k_4 is the constant of the persulfate–cuprous reaction, obtained by subtracting k with iodide and no copper ion present from k with copper ion present and the same iodide concentration and dividing the difference by the copper-ion concentration.

Discussion

It will be noticed that in these mixed solutions the values of the persulfate–cuprous constants and of the persulfate–iodide constants are not as concordant as in the previous experiments with simpler solutions. This is to be expected since the experimental errors are greater, and the more catalytic effect, the greater the deviation from the unimolecular law for individual reactions (however, the deviation of points in the logarithmic plot never exceeded 8% when the reaction was half over). One consistent variation seems to be that the catalytic effect of the copper, per mole of copper salt, increased with decreasing copper-ion concentration. This is difficult to explain, but is exactly what Price found in the copper-ion catalysis of the persulfate–iodide reaction. When the catalytic effect is plotted against copper-ion concentration, the straight line found does not extrapolate to zero effect for zero concentration.

In these solutions it will be noticed that the persulfate–iodide constant is increased practically to the normal value (see Table VII). We cannot tell whether this is because the additional catalytic effect of this small copper-ion concentration is just sufficient in these solutions to bring the value up fortuitously, or whether the copper prevents some other reaction which has an inhibiting effect on the persulfate–iodide reaction. However, there is by no means the same catalytic effect of copper ion on the persulfate–iodide reaction that would be found if thiosulfate were absent; while there is undoubtedly some effect of the iodide on the persulfate–cuprous reaction, it is not large; there is no large unexplained "promoter" effect such as Price found with two catalysts present. In other words, only few if any copper and iodide ions go through the alternative cycles discussed at the beginning of this section.

5. The Effect of a Non-electrolyte (Cane Sugar) on the Velocity.— Several attempts have been made in recent years to correlate the effect of non-electrolytes on the velocity of ionic reactions, without a high degree of success. If the effect of the non-electrolyte were merely to change the activity coefficients of the reacting ions, then we should be able to make predictions. From the expression

$$\ln f = z^2 \frac{e^2}{2DkT}\sqrt{\frac{4\pi e^2 nz^2}{DkT}}$$

we see that any change in D, the dielectric constant, caused by a non-electrolyte should show a corresponding change in f; in fact

$$\ln f \sim \frac{1}{D^{3/2}}$$

With regard to "neutral salt effect" on ionic reaction velocities, there is no doubt that the activity coefficient is all-important, but the effect of non-electrolytes is by no means merely that of changing the activity coefficients.

By measuring the effect of a non-electrolyte on the persulfate–thiosulfate reaction alone and in the presence of iodide, we can also find the effect on the persulfate–iodide reaction. The latter has been measured before in solutions containing no thiosulfate; hence we can compare the effect in the two cases.

The experimental methods were the same as before. Ordinary distilled water was used, hence Table XVII should be compared with Table IV.

TABLE XVII

THE EFFECT OF SUCROSE ON THE CATALYZED AND UNCATALYZED REACTION

0.01 M $K_2S_2O_8$; 0.02 M $Na_2S_2O_3$; ordinary distilled water; 25°.

c_{Sucrose}	c_{KCl}	c_{KI}	k	k_I
0	0	0	0.000255	
0.35	0	0	.000390	
.70	0	0	.000818	
1.05	0	0	.00120	
0	0.02	0	.000460	
0.35	.02	0	.000620	
.70	.02	0	.00102	
1.05	.02	0	.00142	
0.35	.012	0.008	.00229	0.207
.35	.006	.014	.00348	.203
.35	0	.02	.00469	.203
.70	.012	.008	.00308	.263
.70	.006	.014	.00444	.246
.70	0	.02	.00576	.238
1.05	.012	.008	.00341	.249
1.05	.006	.014	.00493	.250
1.05	0	.02	.00633	.240

Discussion

The constants for both the persulfate–thiosulfate and the persulfate–iodide reactions are increased by the cane sugar; this agrees with the work of Kiss and Hatz[18] on the persulfate–iodide reaction above.

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[18] Hatz, *Magyar Chem. Folyoirat*, **34**, 141, 154, 177 (1928); *C. A.*, **23**, 4872 (1929); Kiss and Hatz, *Rec. trav. chim.*, **48**, 7 (1929).

For these reactions it was noticed that the presence of sugar caused deviations from the unimolecular curve; with the highest sugar concentrations the reaction was practically of zero order over two-thirds of its course. Hence many of the constants in the table were determined on this basis. When iodide is present, however, the curve again becomes unimolecular, as the persulfate–iodide reaction is pseudo-unimolecular and much faster than the uncatalyzed reaction.

It can be seen from the table that the effect of the sugar on the persulfate–iodide reaction appears to have reached a maximum between 0.7 *M* and 1.05 *M* concentrations. This is far different from the results reported by Kiss on the direct reaction, where the sugar has an increasingly greater effect up to a concentration of one molar. The presence of the thiosulfate has apparently modified the character of the reaction.

It is difficult to draw any general conclusions with respect to the effect of the non-electrolyte. For the persulfate–iodide reaction Kiss found that sugar and urea increase the velocity, while methyl and ethyl alcohols and glycerol decrease it. In all these cases the dielectric constant of the medium is decreased; hence the effect is more than that of change in dielectric constant on the activity coefficients.

6. Catalysis by Iron and Silver Salts.—It is well known that ferric salts oxidize thiosulfates, being thereby reduced to ferrous; and that ferrous salts are rapidly oxidized to ferric by persulfate. Hence it might be expected that iron salts would catalyze the persulfate–thiosulfate reaction. Unfortunately it is difficult to run suitable experiments since ferric or even ferrous salts are considerably hydrolyzed in neutral solution; if the solution is acid enough to control this hydrolysis and prevent precipitation of ferric hydroxide, the thiosulfate decomposes too rapidly. The first titrations in a few experiments showed that iron salts are not as effective catalytically as copper salts.

It may be of interest to discuss the similar iron salt catalysis of the persulfate–iodide reaction. The rate of the extremely rapid oxidation of ferrous ion by persulfate ions has been measured directly by Saal.[19] His method of expressing concentrations is obscure and apparently burdened with typographical errors, but if we have interpreted correctly, for a solution containing 0.0005 *M* $S_2O_8^=$, 0.0005 *M* Fe^{++}, 0.01 *M* H^+, 0.1 *M* KCl, at 12.8°, the bimolecular constant for the reaction is approximately 2000.[20] At a lower salt concentration and 25°, to compare with the work of Price on iron salt catalysis of the persulfate–iodide reaction, this value would be increased to perhaps 5000. It is difficult to calculate the velocity of the persulfate–ferrous constant from Price's data; the persulfate–iodide re-

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[19] Saal, *Rec. trav. chim.*, **47**, 385 (1928).

[20] Recalculated according to the scale used here from the equation $(-\mathrm{d}C_{S_2O_8^-})/\mathrm{d}t = kC_{S_2O_8^=}C_{Fe^{++}}$, with concentrations in moles per liter and t in minutes.

action is bimolecular, and if the catalysis by ferrous ion follows the mechanism

$$S_2O_8^{=} + 2Fe^{++} \longrightarrow 2SO_4^{=} + 2Fe^{+++} \qquad (1)$$
$$2Fe^{+++} + 2I^{-} \longrightarrow 2Fe^{++} + I_2 \qquad (2)$$

Reaction 1 will be pseudo-unimolecular if it is the velocity-determining reaction; if (2) is the slower, velocity-determining reaction, it will be pseudo-unimolecular.

Assuming that (1) is the velocity-determining reaction the velocity equation becomes

$$-\frac{dC_{S_2O_8^{=}}}{dt} = k_1 C_{S_2O_8^{=}}\, C_{I^-} + k_2 C_{S_2O_8^{=}}$$

where k_1 is the velocity constant of the uncatalyzed reaction; $k_2 = k_3 C_{Fe^{++}}$, and k_3 is the bimolecular velocity constant of the persulfate–ferrous reaction.

From Price's data, for a solution containing 0.00625 M $S_2O_8^{=}$, 0.025 M I^-, 0.005 M H^+, 25°, we obtain the value 0.147 for k_1. For the same solution $+0.00025$ M Fe^{++}, by reading $-dC_{S_2O_8^{=}}/dt$ from the plotted curve and using the above value of k_1, we calculate for k_3 values ranging from 65 to 40 during the course of the reaction. The complete lack of agreement with the work of Saal indicates that the above mechanism is incorrect; perhaps Reaction 2 is the velocity-determining reaction. If so, values not far different from these above (40–65) become the bimolecular constants for the reaction

$$2Fe^{+++} + 2I^{-} \longrightarrow 2Fe^{++} + I_2$$

In any case, the mechanism of this and similar catalytic reactions is far from clear.

Silver nitrate was also tried as a catalyst, since silver salts are so effective in other persulfate oxidations. However, it was not a good catalyst; the trivalent silver compound described by Yost and others[21] precipitated even with low silver-ion concentrations, and the catalysis was not very great.

Summary

The velocity of the reaction

$$S_2O_8^{=} + 2S_2O_3^{=} \longrightarrow 2SO_4^{=} + S_4O_6^{=}$$

has been measured, (1) alone, (2) with iodide ion as a catalyst, (3) with copper ion as a catalyst, (4) with both iodide and copper ions as catalysts in a mixed solution and (5) in the presence of cane sugar with and without iodide ion as a catalyst.

From these measurements, certain observations about the nature of the several reactions involved have been made.

1. The uncatalyzed reaction is pseudo-unimolecular or nearly so, *i. e.*, independent to a great extent of the thiosulfate concentration; but the salt

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[21] Yost, This Journal, **48**, 374 (1926).

effect indicates the velocity-determining reaction to be between two negative ions.

2. From the iodide catalysis can be calculated a constant for the bimolecular persulfate–iodide reaction; this constant is some 20–30% lower than when the velocity is measured independently, at least in solutions containing 0.02 *M* thiosulfate.

3. From the copper catalysis a constant can be calculated for the persulfate–copper ion reaction; the salt effect on this catalysis shows that the persulfate–copper ion reaction is between two negative ions, as might be expected from the fact that Cu^{++} is reduced and changed into a negative complex cuprous ion by thiosulfate.

4. The effect of sugar is to increase the velocity of the persulfate–thiosulfate reaction, and to increase the velocity of the persulfate–iodide reaction in the presence of thiosulfate in a somewhat abnormal fashion.

Further work on this reaction is in progress.

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[Contribution from the Department of Chemistry, Columbia University, No. 642]

A POTENTIOMETRIC STUDY OF ACID-BASE TITRATION SYSTEMS IN THE VERY STRONGLY ACID SOLVENT FORMIC ACID[1]

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If the ionization of an acid depends upon a reaction of the type

$$HCl + OH_2 \rightleftharpoons OH_3^+ + Cl^-$$

then the effect of the solvent upon the acidity of the solution obtained and upon the extent of the ionization may conveniently be separated into two factors.[2] One of these may be represented as the inherent basicity of the solvent and acts in such a way that a decreased basicity decreases the ionization of the acid but increases the acidity of the solution because the ionization takes place only as a result of the transfer of a proton from a weaker to a firmer binding. Thus hydrochloric acid is a strong electrolyte in water, but is only incompletely ionized in formic acid.[3] Nevertheless, indicator experiments show that the solution in formic acid is more acid than that in water. It is clear that the properties of a base should depend upon the acidity of the solvent in analogous fashion.

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[1] This article is based upon a dissertation submitted by Nicholas Dietz, Jr., to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1930.

[2] Hammett, This Journal, **50**, 2666 (1928).

[3] (a) Schlesinger and Calvert, *ibid.*, **33**, 1924 (1911); (b) Schlesinger and Martin, *ibid.*, **36**, 1589 (1914).