

We wish to thank Dr. George Walden for placing his electrical instruments at our disposal.

III. Summary and Conclusions

1. An electrometric method is described for titrating acids and bases in benzene using quinhydrone electrodes.

2. The curve obtained when trichloroacetic acid is titrated electrometrically with diethylamine has the same characteristics that are observed in aqueous solution on titrating a strong acid with a strong base.

3. The difference in hydrogen electrode potential (proton escaping tendency) between the trichloroacetic acid system and the diethylammonium acid system is of the order of 400 millivolts.

4. Conductivity titrations of acids and bases in benzene exhibit the anomalous behavior similar to that reported by Paul Walden for salts in benzene. The equivalence points correspond to minima regions in the conductance titration curves.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION.

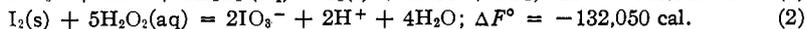
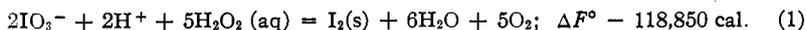
III. THE REDUCTION OF IODATE ION BY HYDROGEN PEROXIDE¹

BY HERMAN A. LIEBHAFSKY

RECEIVED NOVEMBER 29, 1930

PUBLISHED MARCH 6, 1931

The equations and the free energy data² for the reactions



make it evident that the $\text{I}_2\text{-IO}_3^-$ couple is capable of catalytically decomposing hydrogen peroxide. The present investigation was begun with an extensive series of experiments on the iodine-iodate catalysis, but the results obtained proved to be so complex that no definite conclusions concerning the mechanism of the catalysis could be drawn from them alone. These data showed, however, that the catalysis was the result of several compensating reactions, of which two—the oxidation of iodine by hydrogen peroxide and the reduction of iodate ion by that same substance—gave hope of being suitable for separate study. In the second paper of this series there have been presented some experimental results on the former

¹ The preceding papers of this series are Part I, Bray and Liebhafsky, *THIS JOURNAL*, **53**, 38 (1931), and Part II, Bray and Caulkins, *ibid.*, **53**, 44 (1931).

² Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, pp. 607-608.

reaction (Equation 2). To determine, in so far as is possible by chemical and kinetic methods, the character of the steps underlying the reduction of iodate ion by hydrogen peroxide (Equation 1) is the purpose of this paper.

A reaction system corresponding entirely to the "pure" reduction of iodate ion according to Equation 1 has never been experimentally realized. When peroxide and iodate are mixed in acid solution, the initial formation of a small amount of iodine is followed by the establishment of a "steady state" in which the main reaction is the catalytic decomposition of hydrogen peroxide (cf. Part I). The amount of such catalysis is a complicated function of the concentration of iodine in the system; it seemed almost certain, that by maintaining this iodine concentration as low as possible, the rates of the reactions resulting in catalysis could be reduced. The minimizing of the amount of this catalysis is the first requirement which any experimental method for the study of the reduction of iodate ion must fulfil.

An effective means for meeting this requirement is provided by placing the reaction mixture in contact with carbon tetrachloride and shaking the whole at a rate sufficient to insure rapid extraction of the iodine. Part of the carbon tetrachloride can be withdrawn and replaced immediately by an equal volume of fresh solvent at convenient time intervals; the rate of formation of iodine may be followed by titrating the samples withdrawn. That dI_2/dt thus determined can measure accurately the rate of reduction of iodate ion by hydrogen peroxide will be shown in a later section. Since small amounts of iodine can be determined with relatively high accuracy, and since the reaction is not extremely rapid at the temperatures employed, an accurate value of dI_2/dt can be obtained before the concentration of any of the reacting substances has changed enough to affect this rate beyond the experimental error. The order of the reaction with respect to any substance may be obtained, therefore, from a series of measurements in which only the concentration of that substance is varied.

Experimental Part

C. P. reagents not further purified were used. Permanganate solution standardized against sodium oxalate served for the analysis of peroxide solution, and for the standardization of the thiosulfate solution used in all iodimetric work. The potassium iodate solution was analyzed iodimetrically. Perchloric acid standardized against sodium carbonate was used as the source of hydrogen ion.

Two-hundred cc. glass flasks with conical bottoms were used as reaction vessels; to the acid iodate solution in these flasks 25 cc. of carbon tetrachloride was added, and the whole shaken in an oil thermostat in a dark room at the rate of 120-130 double shakings a minute. The hydrogen peroxide was added from a reservoir in the thermostat with a pipet after the attainment of temperature equilibrium; the initial time was taken as that at which the pipet was half emptied; 20-cc. samples of the carbon tetrachloride in the reaction mixture were withdrawn as follows. The shaker was stopped at

a time taken as the time of the sample. After a twenty-second interval,³ allowed to insure a complete separation of the two layers, the sample was pipetted into a glass-stoppered flask containing water which served both to wash the carbon tetrachloride and to prevent its loss by volatilization. After two further washings in a separatory funnel, the carbon tetrachloride containing the iodine was transferred into a flask containing weakly acid potassium iodide solution, and then titrated with thiosulfate solution of convenient concentration; the most dilute solution of sodium thiosulfate practicable was found to be 0.002 *N*. For purposes of calculation, all results were expressed in terms of 0.1 *N* sodium thiosulfate. Experiments in dilute solutions depended upon the titration of amounts of iodine equivalent sometimes to 0.01–0.02 cc. of 0.1 *N* thiosulfate. These titrations were carried out according to a method previously outlined.⁴

Measurements of dO_2/dt were carried out in the usual manner with the aid of gas burets; the time intervals for the readings were so chosen that the presence of the carbon tetrachloride had no disturbing effect due either to the establishment of the equilibrium vapor pressure of carbon tetrachloride, or to the saturation of the carbon tetrachloride with oxygen. The same dO_2/dt was obtained initially from experiments of the same composition when the one reaction mixture was in contact with carbon tetrachloride while the other was not. Since such agreement was obtained repeatedly without considering the vapor pressure of carbon tetrachloride in calculating the volume of oxygen evolved in the first case, all later results were calculated in this way. Accurate measurements of the gas evolution could not be obtained for the experiments in very dilute solutions.

The above experimental method of determining dI_2/dt is subject to several possible inaccuracies; among the most obvious are loss of carbon tetrachloride by vaporization, irregularities in the transfer of iodine from the aqueous to the carbon tetrachloride layers, excessive heat losses due to the vaporization of carbon tetrachloride and of water, inaccuracies incident to the extremely rapid use of pipets, losses of iodine during washings, and iodate contamination in the iodine titrations. The loss of carbon tetrachloride by vaporization was shown to be negligible at 50°, small at 60° and so large at 70° that the temperature of a reaction mixture containing carbon tetrachloride and immersed in a thermostat at 70° could not be maintained above 68°. Accurate experiments at 70° were therefore impossible. Irregularities, for which no better reason could be given than that they were due to corresponding irregularities in the transfer of iodine from the aqueous to the carbon tetrachloride layer, sometimes appeared in the values of dI_2/dt obtained in the course of a run; the value of the over-all average dI_2/dt for such a run was almost always satisfactory, so that these fluctuations could be neglected. Pipet inaccuracies cancel out almost entirely if several samples are taken in the course of an experiment. Iodine losses by contact with aqueous layers, both during reaction and in the subsequent washing, were approximately compensated by an addition of 3% to the volume of thiosulfate solution used. Iodate contaminations

³ In experiments requiring a sample to be taken every minute, this interval was shortened to five seconds.

⁴ Liebhafsky, *THIS JOURNAL*, **53**, 165 (1931).

were practically eliminated by three careful washings. No correction was made for concentration variations occurring during a run. The induction period⁵ was never included in the time interval over which the over-all rate for an experiment was calculated.

The detailed data for a regular experiment (No. 023) and for an irregular experiment (No. 09) are given in Table I.

TABLE I

THE CALCULATION OF RATE CONSTANTS FROM EXPERIMENTAL OBSERVATIONS
 Experiment 023 Table III. Concentrations: (H⁺) = 0.0357; (IO₃⁻) = 0.1001; (H₂O₂) = 0.0228

Time, min.	0.1 N Na ₂ S ₂ O ₃ , cc.	Cc. of 0.1 N Na ₂ S ₂ O ₃ /min
1	0.0123	0.0154
2.5	.0045	.0017
6	.0067	.0020
10	.0080	.0020
28	.0416	.0028
61	.0626	.0020

$$\text{Over-all average: } \frac{0.0067 + 0.0080 + 0.0416 + 0.0626 + \frac{0.0626 - 0.0045}{4}}{58.5}$$

$$= 0.1334/58.5 = 0.00228 \text{ cc. of } 0.1 \text{ N Na}_2\text{S}_2\text{O}_3/\text{min.}$$

$$dI_2/dt = 5(10^{-5}) \times 2.28(10^{-3}) = 1.14(10^{-7}) \text{ moles of } I_2/\text{min.}$$

Experiment 09, Table IV. Concentrations: (H⁺) = 0.1438; (IO₃⁻) = 0.1001; (H₂O₂) = 0.746

Time, min.	0.1 N Na ₂ S ₂ O ₃ , cc.	Cc. of 0.1 N Na ₂ S ₂ O ₃ /min.
0-0.75	0.15	0.27
0.75-4	.36	.13
4-7	.58	.21
7-10	.84	.30
10-14	.98	.26

$$\text{Over-all average: } 2.97/13.25 = 0.224 \text{ cc. of } 0.1 \text{ N Na}_2\text{S}_2\text{O}_3/\text{min.}$$

$$dI_2/dt = 11.2(10^{-6}) \text{ moles } I_2/\text{min.}$$

In this table and throughout this paper all concentrations will be given in moles/liter at room temperature, and will be indicated by (). All rates will be given in moles/min. for a 150-cc. reaction mixture. The temperature of all experiments was 50°, unless otherwise noted. The calculations of the rates for the first two intervals in Experiment 023 were made in the following manner

$$0-1 \text{ min. } \frac{0.0123 + \frac{0.0123}{4}}{1} = 0.0154; \quad \frac{0.0045 + \frac{0.0045 - 0.0123}{4}}{1.5} = 0.0017$$

⁵ The initial deficiency of iodine during the induction period will be discussed later. In several experiments at very low (H₂O₂), such as Experiment 023, Table I, formation of a relatively large amount of iodine was observed shortly after mixing the reagents; since this abnormality was variable and unreproducible, it was also disregarded in computing the over-all average.

The factor $\frac{1}{4}$ which appears in the numerator is necessary because 5 cc. of carbon tetrachloride always remained in the reaction vessel when 20 cc. was withdrawn for analysis of the iodine content.

Calculation of the Rate Constants.—Experiments, of the kind just outlined, were carried out to determine the order of the reaction with respect to (H^+) , (IO_3^-) and (H_2O_2) . Since two of these three concentrations were kept constant in each of the three series, it is possible to obtain three average values of the specific reaction rate by plotting the experiments of each of the three series. The constant concentrations used were (with a few exceptions): $(\text{H}^+) = 0.0357$, $(\text{IO}_3^-) = 0.1001$, $(\text{H}_2\text{O}_2) = 0.514$. The data are summarized in Tables II, III and IV; the concentrations and the corresponding values of $d\text{I}_2/dt$ are given in the first portions of the tables. The other data will be discussed later.

TABLE II (SEE FIGURE 1)
VARIATION OF RATE WITH CHANGE IN (IO_3^-)
 $(\text{H}_2\text{O}_2) = 0.514$; $(\text{H}^+) = 0.0357$; $T = 50^\circ$

Expt.	(IO_3^-)	$d\text{I}_2/dt$ (10^6)	"Defect" moles I_2 (10^6)	$d\text{O}_2/dt$ (10^6)	Ratio $\frac{d\text{O}_2}{dt} / \frac{d\text{I}_2}{dt}$
027	0.00192	0.045	0.16
026	.0100	.270	1.6	0.90	33
012	.1001	2.73	10.8	2.01	7.4
025	.2301	6.29	33.5	4.61	7.0

TABLE III (SEE FIGURE 1)
VARIATION OF RATE WITH CHANGE IN (H_2O_2)
 $(\text{H}^+) = 0.0357$; $(\text{IO}_3^-) = 0.1001$; $T = 50^\circ$

Expt.	(H_2O_2)	$d\text{I}_2/dt$ (10^6)	"Defect" moles I_2 (10^6)	$d\text{O}_2/dt$ (10^6)	Ratio $\frac{d\text{O}_2}{dt} / \frac{d\text{I}_2}{dt}$
038	0.00217	0.011
024	.00874	.0473
023	.0228	.114	..	0.21	18.0
019	.0459	.243	..	.25	9.6
018	.250	1.40	2.7	.98	7.0
012	.514	2.73	10.8	2.01	7.4
061	.746	4.39	38.8
017	1.246	7.18	10.8	4.96	6.9
060	1.760	10.2	101.0
021	2.498	15.6	32.4	13.7	8.8

In Fig. 1, $d\text{I}_2/dt$ of Tables II and III is plotted logarithmically against (IO_3^-) , and against (H_2O_2) : the logarithmic plot is used in order that the entire concentration range may be included in a plot of convenient size, and in order that the fundamental nature of relative, rather than absolute, changes in the concentrations of reacting substances may be emphasized. The radius of the circles used is equivalent to a 5% change in $\log d\text{I}_2/dt$.

the approximate magnitude of the average experimental error. The upper limit of the IO_3^- concentration range is fixed by the solubility limit of potassium iodate. The two straight lines show that the reduction of iodate ion is accurately first order with respect to (IO_3^-) over a 120-fold concentration range, and with respect to (H_2O_2) over a 1200-fold concentration range. In a plot of this kind, a set of experimental results must meet *two* requirements in order that the reaction involved may be first order with respect to the reactant considered: (1) the points must lie on a straight line; (2) the line must have a slope of 45° .⁶ The lines in Fig. 1 meet both requirements.

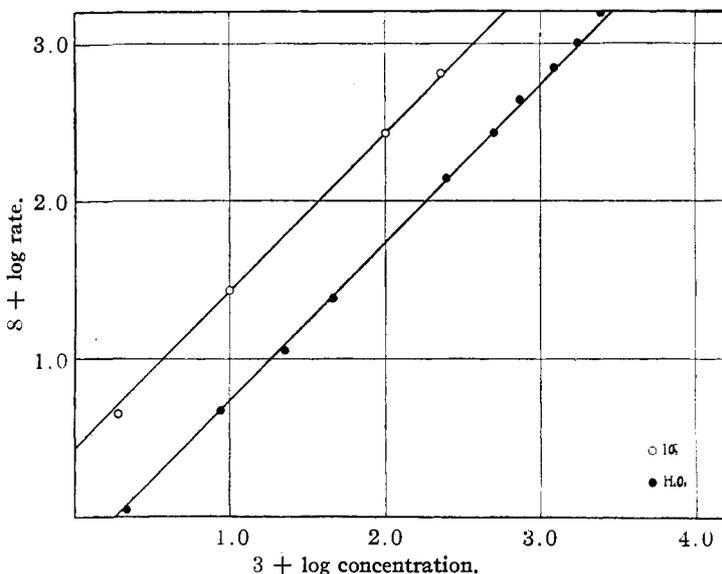


Fig. 1.—Variations of $\log d\text{I}_2/dt$ with $\log (\text{IO}_3^-)$ and with $\log (\text{H}_2\text{O}_2)$ (see Tables II and III).

In Fig. 2, $d\text{I}_2/dt$ from Table IV for the various temperatures employed is plotted directly against (H^+) . The radius of the circles now corresponds to a 5% error, only at $(\text{H}^+) = 0.05$ for the 50° experiments. Given the results from Fig. 1, it is evident that at the constant values of (H_2O_2) and (IO_3^-) employed, $d\text{I}_2/dt$ obeys the following rate law at all hydrogen-ion concentrations below $0.14 N$

$$d\text{I}_2/dt = k_1 (\text{H}_2\text{O}_2) (\text{IO}_3^-) + k_2 (\text{H}^+) (\text{H}_2\text{O}_2) (\text{IO}_3^-) \quad (3)$$

The value of k_1 is obtained by dividing the intercept by $(\text{H}_2\text{O}_2)(\text{IO}_3^-) = 0.0514$; the result at 50° is $k_1 = 1.00(10^{-6})/0.0514 = 19.4(10^{-6})$. Simi-

⁶ The logarithmic method employed in this paper is useful in determining the order of a reaction with respect to any reactant so long as the concentrations of all other substances are (sensibly) constant; the slope of the line in such a plot is numerically equal to the quantity sought.

TABLE IV (SEE FIGURE 2)

VARIATION OF RATE WITH CHANGES IN (H^+) AT DIFFERENT TEMPERATURES

Expt.	(H^+)	(IO_3^-)	(H_2O_2)	$\frac{dI_2}{dt}$ (10^6)		"Defect" moles I_2 (10^6)	$\frac{dO_2}{dt}$ (10^6)	Ratio $\frac{dO_2}{dt} / \frac{dI_2}{dt}$	% Yield of I^-
				Meas.	calcd.				
053	Initially neutral	0.1001	0.514	1.18		22
05	0.00716	.1001	.514	1.33		6.5	1.25	9.4	
011	.0214	.1001	.514	2.02		7.0	1.39	6.9	
012	.0357	.1001	.514	2.73		10.8	2.01	7.4	
013	.0439	.1001	.514	3.03		11.9	2.05	6.7	
014	.0572	.1001	.514	3.42		12.4	2.48	7.3	
04	.0715	.1001	.514	4.43		10.8	3.14	7.1	
016	.0929	.1001	.514	4.88		15.1	3.81	7.8	
08	.1072	.1001	.514	6.74		..	4.20	6.2	
015	.1438	.1001	.514	5.52	8.14	..	10.5	19	
06	.7144	.1001	.514	.465	36.4	..	41.4	890	
09 ^a	.1438	.1001	.746	11.2	11.8	..	46.9	39	
010	.3564	.1001	2.498	33.1	90.9	..	375	113	
028	.2134	.2406	.746	8.77	40.4	

^a Since the rate is proportional to (H_2O_2) , $dI_2/dt = 11.2 (10^{-6})$ at $(H_2O_2) = 0.746$ corresponds to $dI_2/dt = 7.74 (10^{-6})$ at $(H_2O_2) = 0.514$; this is the value plotted in Fig. 2.

(b) At 60°: $(IO_3^-) = 0.1001$; $(H_2O_2) = 0.514$

Expt.	(H^+)	$\frac{dI_2}{dt}$ (10^6)	% Yield of I^-
049	Initially neutral	4.22	38
051	0.0214	6.93	
052	.0357	9.47	
050	.0715	14.7	

(c) At 40°: $(IO_3^-) = 0.1001$; $(H_2O_2) = 0.514$

056	Initially neutral	0.298	8.8
055	0.0214	.613	
054	.0357	.793	
039	.0715	1.32	

(d) At 30°: $(IO_3^-) = 0.1001$; $(H_2O_2) = 0.514$

058	Initially neutral	0.064	8.5
041	0.0357	.200	
057	.0572	.264	

larly the value of k_2 is obtained by dividing the slope of the line by (H_2O_2) (IO_3^-) ; at 50°, $k_2 = 48.7(10^{-6})/0.0514 = 947(10^{-6})$.

Values of k_2 can be computed from Fig. 1 only if k_1 is known; the calculation for the series in which (H_2O_2) varies will be given. Equation 3 after transposing and after substituting the numerical values of $k_1(IO_3^-)$ and (H^+) becomes: $(dI_2/dt)/(H_2O_2) = [19.4(10^{-6}) + k_2(0.0357)]/1001$. For any point on the lower line in Fig. 1, the difference between ordinate and abscissa is simply $(\log dI_2/dt) - \log (H_2O_2) = \log (dI_2/dt)/(H_2O_2)$;

its numerical value is 0.743-6. The antilogarithm of this number, 48.7-(10⁻⁶), is the ratio (dI₂/dt)/(H₂O₂). Solving the above equation for *k*₂, we obtain *k*₂ = 1005(10⁻⁶).

From the (IO₃⁻) plot (dI₂/dt)/(IO₃⁻) = 27.3(10⁻⁶), whence the value *k*₂ = 934(10⁻⁶) is calculated.

Since the values of *k*₂ are in substantial agreement, *k*₂ = 965(10⁻⁶) may be taken as a reliable mean, and the value *k*₁ = 19.4(10⁻⁶) may be regarded as satisfactory; *k*₁, however, is less accurate than *k*₂.

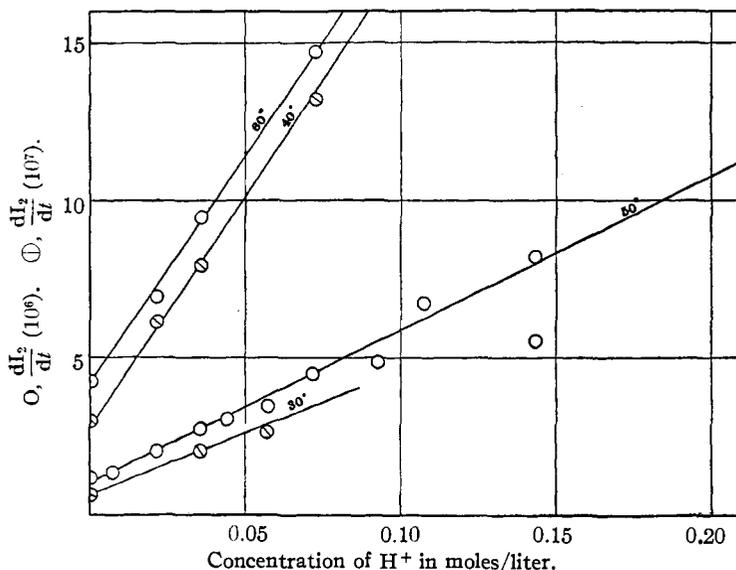
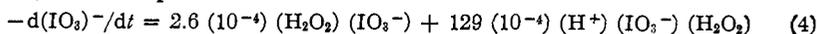


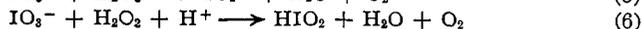
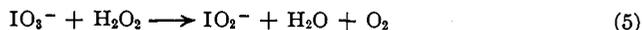
Fig. 2.—Variation of rate with (H⁺) (see Table IV).

These constants must finally be multiplied by 2 to change from dI₂/dt to -dIO₃⁻/dt, and by 6²/3 to change from moles/min./150 cc. to moles/min./liter. Equation 3 now becomes



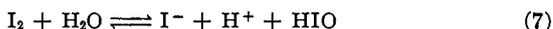
-d(IO₃⁻)/dt thus calculated is probably accurate to ±5%.

Mechanism of the Reaction.—Equation 3 shows that the first step in the reduction of iodate may occur in the following ways



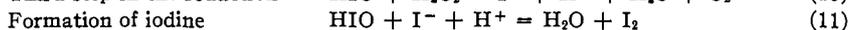
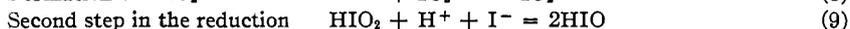
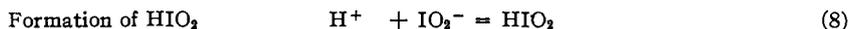
The formation of IO₂⁻ and HIO₂ as intermediate products resulting from two simultaneous reactions appears to be the only simple explanation of the empirically determined rate law. This mechanism is not intended to exclude the possibility of the formation of intermediate complexes, such as H₂O₂·IO₃⁻ in Equation 5; there is thus no contradiction between this formulation and that of Brönsted for similar reactions.

The relatively rapid follow reactions cannot be postulated with certainty. As guides in selecting them we have the following. (1) Characteristic of iodine chemistry is the relatively rapid establishment of the equilibrium



(2) Reactions involving the oxidation of hydrogen peroxide are generally first order with respect to that substance. (3) The oxidations of hydrogen peroxide by the hypo-halites and their acids are known to be rapid reactions.^{8,9} (4) The end-product of the reduction of iodate ion is iodine in acid, iodine and iodide ion in neutral, and iodide alone in basic solution.⁷ (5) The reduction of iodic acid by hydrogen peroxide, if it occurs at all, is not very rapid.⁸ Reaction between HIO_2 and I^- is very probable.

The reactions in acid solution following those in Equations 5 and 6 may therefore be the following



Equation 1 is the sum of 6 (or 5 and 8) counted twice, 9 counted twice, 10 counted three times and 11. If the iodine concentration is permitted to build up in the hydrolysis equilibrium, the concentration of intermediate products increases, and the catalytic decomposition of hydrogen peroxide, which depends on the intermediate products such as I^- , also increases.

The relative rates of the above reactions as individuals cannot be established. A comparison of their velocity as a group with the velocity of the first step is possible if the combined concentration of all iodine compounds intermediate between iodate and iodine is known; for, in a series of consecutive reactions which has reached a steady state, the concentration of an intermediate product is inversely proportional to the specific rate constant for the step in which this intermediate product is consumed.

⁷ The percentages of iodine obtained as I^- in the various experiments in neutral solution are given in Table IV. An experiment in which the initial (H^+) was 3×10^{-12} yielded only I^- ; quantitative work here was futile because of the large loss of hydrogen peroxide due to catalysis decomposition. Since, however, the reaction mixtures initially neutral were distinctly basic at the end of the run, their agreement with the rate law may be taken as an indication that this rate law is valid in moderately basic solution.

While the percentages of I^- at the different temperatures cannot be correlated because (H^+), (I_2) and (HIO) were not always the same, it may be pointed out that larger percentages of I^- at the higher temperatures are to be expected if the hydrolysis equilibrium, Equation 7, is realized, from the sign of ΔH for this reaction.

⁸ The reduction of iodic acid by hydrogen peroxide and by I^- has been discussed in Part I; it was there concluded that in moderately acid solution the former must be negligible. While this is probably true also for solutions of low acid concentration, there is always the possibility that hydrogen peroxide may begin to reduce either HIO_2 or IO_2^- as the acid concentration is further decreased.

The Induction Period.—At the beginning of every experiment there exists a time interval during which the rate of formation of iodine differs from that given by Equation 3; this time interval is presumably necessary to establish the concentrations of intermediate products required for the reduction of iodate ion. The length of this induction period in acid solution⁹ is roughly independent of the concentrations of hydrogen and iodate ions, and inversely proportional to the concentration of hydrogen peroxide; in many experiments it approximates seven minutes. Ordinarily dI_2/dt begins with a small initial value and gradually increases until the expected rate is reached.

This induction period furnishes a means for calculating the maximum amount of iodine stored up as intermediate products in the course of any experiment. If the mechanism of the first step in the reduction of iodate is the simple one advanced above, then the rate of this first step is presumably always that calculated from Equation 3; the reduction of iodate ion according to this equation begins as soon as peroxide and iodate are mixed. If this simple picture is correct, the amount of intermediate products—the iodine “defect”—should be the difference between the average dI_2/dt for the experiment, multiplied by the time in minutes of the entire experiment, and the total amount of iodine actually obtained. The “defect” thus calculated is given in Tables II, III and IV, and is plotted against the rate in Fig. 3. Since the values of these “defects” depend upon the determination of very small amounts of iodine, the accuracy obtained is not very great. The legend shows, for any experiment, that substance the variation of whose concentration was principally responsible for the change in rate.

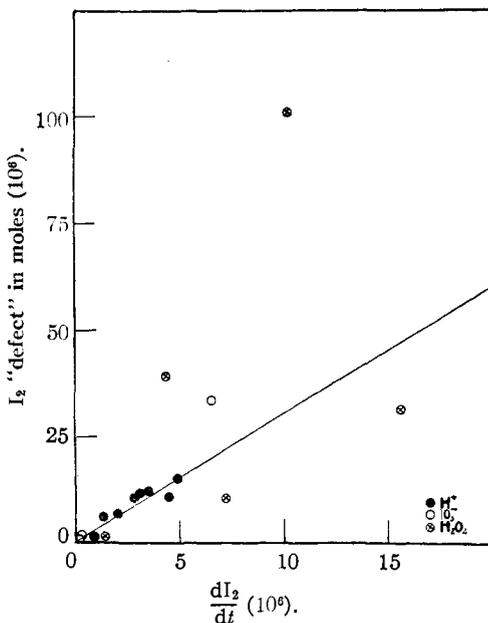


Fig. 3.—Variation of intermediate products with rate.

The calculations show, first of all, that the approximate percentage of

⁹ In neutral solution the induction period lengthened with decreasing iodate. The formation here of amounts of I^- very large as compared with the amounts formed in acid solution is the explanation.

iodate stored up as intermediate products is 0.1%; the great speed of the follow reactions as compared to that of the first step in the reduction is thus established. The graph shows further that at low rates, the "defect" is proportional to the rate when (H^+) and (IO_3^-) are varied; the relationship expressed by the straight line is "defect" = $3 \times$ rate. For variations in (H_2O_2) no such definite statement can be made; it may be concluded, however, that the "defect" is not independent of (H_2O_2) variations. The proportional increase of the concentration of intermediate products with the rate is to be expected as the result of any concentration change which increases the rate of the first step in the reduction of iodate without directly affecting the rate of the following reactions. The necessary increase of the absolute rate of the latter must then be brought about by an increase in the concentration of those intermediate products concerned. That the same proportionality which exists for (H^+) and (IO_3^-) does not exist¹⁰ for (H_2O_2) justifies the selection of a reaction between HIO_2 and I^- as the second step in the reduction (Equation 9). If each step in the reduction involved one molecule of hydrogen peroxide, the "defect" should be unaltered when (H_2O_2) is changed.

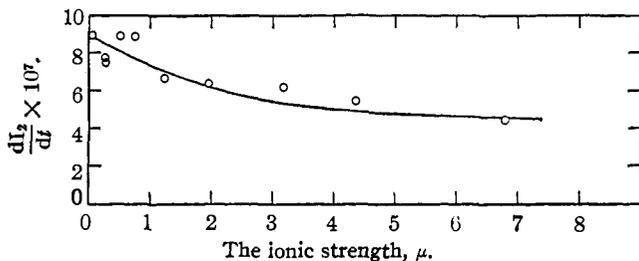


Fig. 4.—The salt effect.

The Salt Effect.—In Fig. 4 the result of a series of experiments on the salt effect at 60° is given. The experiments were carried out at $(\text{H}^+) = (\text{IO}_3^-) = 0.038 M$ and $(\text{H}_2\text{O}_2) = 0.115 M$; changes in the ionic strength, μ , were produced by adding sodium nitrate.

We do not wish here to discuss the application of any "activity" theory of reaction rate. That there is a relatively small salt effect which disappears at higher μ is quite apparent; it is apparent further that no simple function of the activity coefficients involved is likely to yield a curve like that in Fig. 4. We must bear in mind, also, that this curve represents two salt effects, superimposed one upon the other, because the reaction has two rate-determining steps. One of these, the one involving only H_2O_2 and IO_3^- , should have a "linear" salt effect, but for the other the effect should be¹¹

¹⁰ Experiment 012 serves as a point for all three cases.

¹¹ See Brönsted "The Velocity of Ionic Reactions," Contemporary Developments in Chemistry, Columbia University Press, 1927.

“exponential.” The matter is complicated further by the change in solvent which occurs as the higher ionic strengths are reached, and by uncertainty of the value of activity coefficients under the experimental conditions. As evidence in dilute solution, where the activity rate applications have been most successful, the line in Fig. 1 representing (IO_3^-) variations might be used. There is a change in from 0.038 to 0.267 because of the change in (IO_3^-) ; but, as the graph shows, there is no salt effect greater than the experimental error.

Variation of Rate Constants with Temperature.—The effect on the rate constants of temperature variation in the interval from 30 to 60° is shown in Fig. 5; the line of greater slope represents the value of k_1 as de-

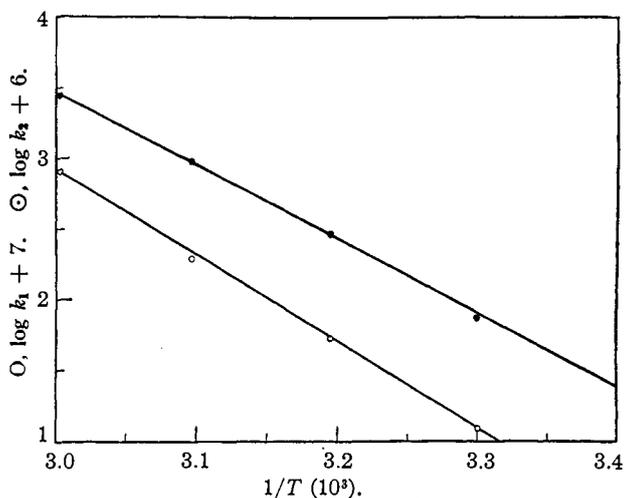


Fig. 5.—Variation of rate constants with temperature.

termined from the values of the intercepts in Fig. 2; the other line represents the values of k_2 as calculated from the slopes in that figure. From Fig. 5

$$\frac{d \log k_1}{d(1/T)} = -6.07(10^3); \quad \frac{d \log k_2}{d(1/T)} = -5.20(10^3)$$

the corresponding values of the heats of activation are $Q_1 = 27,500 \pm 1500$ calories, and $Q_2 = 23,500 \pm 500$ calories. These values have been obtained by subtracting $RT/2$ calories (*ca.* 300 cal.) from the value calculated directly from the temperature coefficients, to correct for the variation of the root mean square velocity of the molecules with temperature. The estimated errors are the differences between the mean value of Q given above and the heats calculated from the lines of greatest and least slopes consonant with each set of experimental results in Fig. 5. Using the value of k_1 at 50° and the value of Q_1 , the average of the diameters of H_2O_2 and IO_3^- may be calculated by the application of an equation given

by Tolman;¹² for a heat of activation within the limits given above for Q , the value of the molecular diameter lies between $1(10^{-7})$ and $1(10^{-6})$ cm.

This average diameter is considerably larger than the values, 10^{-8} in order of magnitude, obtained from x-ray measurements; although a hydrated molecule in aqueous solution is probably larger than an ion in a crystal, the above result is larger than we should expect even for such a hydrated molecule. The simplified calculation we have made is, however, only very approximate. The number of moles colliding has been calculated for a gaseous system; if this number is greater for an equally concentrated aqueous solution of the reactants, then a smaller average diameter would be obtained. If, on the other hand, all collisions between molecules whose combined energies equal or exceed the minimum energy required for reaction are not effective, and an "orientation factor" must be introduced, the calculation would lead to an even larger molecular diameter. However, these difficulties will not vitiate the comparison to be made below, since the reactions to be compared are part of the same reaction system.

Using $5(10^{-7})$ as the average diameter, the rate may be calculated at which a bimolecular reaction involving IO_3^- and H_2O_2 with a heat of activation equal to Q_2 should proceed. A comparison of the rate thus calculated with that observed for Reaction 6 shows that the former rate is only about ten times the latter. This reaction, therefore, is too rapid to be the result of ordinary triple collisions;¹³ it can be regarded simply as a bimolecular reaction in which the substance reacting with H_2O_2 is a complex, $\text{H}^+\cdot\text{IO}_3^-$,¹⁴ resulting from loose coupling, perhaps of an electrostatic nature, between the ions. Thus HIO_3 , although completely dissociated in a thermodynamic sense, might act as a unit in chemical reactions involving both H^+ and IO_3^- .

The fact that the values of Q_1 and Q_2 are so nearly equal indicates that the activation processes in the two reactions are closely related. The dif-

¹² Tolman, "Statistical Mechanics, Etc.," Chemical Catalog Co., 1927, p. 242, Equation 543; no. of mols. colliding/cc./sec. = $10^{28} \cdot 4427 \sigma^2 C_1 C_2 \sqrt{T \frac{M_1 + M_2}{M_1 M_2}}$; C_1 and C_2 are concentrations in moles/cc.; σ is the average diameter of the colliding molecules, T the absolute temperature and M_1 and M_2 are the ordinary molecular weights. This total number of moles colliding multiplied by the factor $e^{-Q/RT}$ which is the probability that any collision will have the minimum energy required for reaction, is equated to the experimentally measured rate; the equation is then solved for the value of σ .

¹³ Since orientation is assumed to be of relatively greater importance in a triple collision, the introduction of orientation factors into the calculations would strengthen this conclusion.

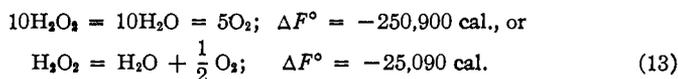
¹⁴ Another possibility would be complex formation of the type $\text{H}_2\text{O}_2\cdot\text{H}^+$; this oxonium compound, however, can be present only at very low concentrations, since preliminary transference and freezing point experiments failed to show any evidence for its existence.

ference in the heats of activation, however, exceeds the estimated error. If we postulate the addition compounds, $\text{H}_2\text{O}_2 \cdot \text{IO}_3^-$ and $\text{H}_2\text{O}_2 \cdot \text{HIO}_3$, as intermediate steps in Reactions 5 and 6 it is evident that the presence of H^+ in the addition compound lowers the critical energy necessary for the reduction of iodate by 4000 calories. This is equal in order of magnitude to the heat of dissociation of a weak acid, such as HIO_2 by analogy appears to be. The products assumed in Reactions 5 and 6 are IO_2^- and HIO_2 , respectively, and the difference in critical energies may thus be related to the energy of the $\text{H}^+ - \text{IO}_2^-$ bond. Whether this suggestion is of value can be determined by applying it, whenever accurate data for temperature coefficients are available, to other similar pairs of reactions, such as those involved in the oxidation of iodide ion by H_2O_2 (cf. Part I, Equations 6a' and 6a).

Catalysis and the Rate Measurements.—Equation 1 suggests that the rate of the reduction involved might be followed by measuring either the rate of formation of iodine, or the rate of evolution of oxygen. In the ideal case

$$-\frac{d\text{IO}_3}{dt} = 2 \frac{d\text{I}_2}{dt} = \frac{2}{5} \frac{d\text{O}_2}{dt} = -\frac{2}{5} \frac{d\text{H}_2\text{O}_2}{dt} \quad (12)$$

If, however, hydrogen peroxide *oxidizes* any iodine compound present in the reaction system, Equation 3 will no longer be strictly valid; should such oxidation increase until one molecule of hydrogen peroxide reacted thus for every molecule *reducing* an iodine compound, the main reaction occurring in the system would be the sum of 1 and 2



and a steady state analogous in principle to that in the simpler bromine-bromide catalysis¹⁵ would then have been reached. In this event

$$-\frac{d\text{IO}_3^-}{dt} = 2 \frac{d\text{I}_2}{dt} = 0 \text{ (very nearly); } \frac{d\text{O}_2}{dt} = \frac{1}{2} \frac{d\text{H}_2\text{O}_2}{dt} \quad (14)$$

The criterion for pure stoichiometric reduction of iodate is therefore $(d\text{O}_2/dt)/(d\text{I}_2/dt) = 5$, while for pure catalytic decomposition of hydrogen peroxide this ratio approaches an infinite value. Any system composed initially of iodate ion and hydrogen peroxide in acid solution must have for its rate-ratio a value included within the above limits. While the pure reduction of iodate has never been experimentally realized, pure catalysis will take place in every reaction system as soon as the steady state concentration of iodine has been built up by the reduction of iodate ion. Since, in moderately acid solution and at low (H_2O_2), this steady state iodine concentration is less than $10^{-6} M$, it is experimentally impossible to study the reduction of iodate ion under such conditions.

¹⁵ Bray and Livingston, THIS JOURNAL, 45, 1251 (1923).

As long as appreciable catalysis does occur, dO_2/dt can never accurately measure $-dIO_3/dt$, for a measurement of oxygen evolved must necessarily include oxygen produced by catalysis. That it is possible to have catalysis and still measure accurately $-dIO_3/dt$ by following dI_2/dt will now be shown. Experimental evidence proves that the reactions underlying Equation 1 must form a consecutive series which depends for its existence upon a series of intermediate iodine compounds; the slowest member of this series (*i. e.*, the one with the smallest specific rate) is the one directly involving iodate ion. If catalysis involving the oxidation of an intermediate compound back to iodate occurs, then some iodate will of necessity take part more than once in this slowest step. Under such conditions no measure of the absolute rate of reduction of iodate is possible, for there is no way of measuring how much of this substance, once reduced to a lower valence, is returned to its original state by the oxidizing action of hydrogen peroxide. Catalysis in which no iodate ion is re-formed, such as that resulting from the oxidation of I^- by H_2O_2 , will not sensibly affect dI_2/dt , for it does not affect the *slowest reaction* taking place in the system.

A direct proof that no iodate is formed in the system is impossible. If, however, the amount of catalysis taking place as measured by the ratio $(dO_2/dt)/(dI_2/dt)$ changes from experiment to experiment, then the amount of oxidation involved in this catalysis must also change, as must the concentrations of all the intermediate products concerned. Thus, if the catalysis involves the re-formation of iodate ion, a change in the amount of catalysis will effect a change in the amount of iodate ion formed in the system, with the result that dI_2/dt (which must always measure the net amount of iodate reduced, since the concentration of intermediate products is small) will no longer follow a simple law.

A measure of the relative amount of catalysis in an experiment is the difference between the experimental value of $(dO_2/dt)/(dI_2/dt)$ and 5, its value for the pure reduction of iodate ion. In Tables II, III and IV these ratios are given wherever dO_2/dt was measured; with two exceptions, the values lie between 6.2 and 9.6 for all experiments with $(H^+) < 0.14$. (In the experiments on the salt effect three ratios between 5.9 and 6.6 were obtained.) In this region of acid concentrations, the amount of catalysis varies while dI_2/dt obeys the simple rate law in Equation 3; we conclude, therefore, that in this region the catalysis does not involve the re-formation of iodate ion.

In Table IV, the results of several experiments in more acid solutions are presented; the ratios for these experiments were always larger, 19 to 890, and calculations showed that the experimental values of dI_2/dt were always below those calculated from the simple rate law (see Columns 5 and 6, Table IV). The only simple explanation seems to be that catalysis at these higher acid concentrations involves some re-formation of iodate.

In Experiment 06 (Table IV), in which $(H^+) = 0.7144$, the value 890 for the ratio was obtained in the usual way with carbon tetrachloride; the value 160 was obtained by using mercury to extract the iodine. Since the extraction by means of mercury is more complete, the experiment definitely indicates that, other things being equal, the amount of catalysis depends on (I_2) .

In the series of experiments at 50° plotted in Fig. 2, the low results can all be explained as due to catalysis involving IO_3^- . The most striking case is furnished by the two experiments at $(H^+) = 0.1438$ (Experiments 09 and 015, Table IV) which differ only in the magnitude of (H_2O_2) . From unpublished work on the catalytic decomposition of hydrogen peroxide by iodic acid, it is known that the steady state (I_2) is proportional to (H_2O_2) . That the experiment at the higher (H_2O_2) gives a value of dI_2/dt in agreement with the rate law is thus due to the effective elimination of IO_3^- formation made possible by the higher value of the steady state (I_2) . Attempts further to extend the range of (H^+) for which Equation 3 is valid by increasing (H_2O_2) and (IO_3^-) , failed.

The close relation of the reduction of iodate ion to the general problem of the catalytic decomposition of hydrogen peroxide by the iodine-iodate couple must now be apparent. A knowledge of the mechanism and the rate of this reduction will be of value first of all in interpreting the induction period for the catalysis, for the reduction of iodate was studied merely by prolonging this induction period indefinitely through the addition of carbon tetrachloride to remove the iodine formed.

In conclusion I desire to thank Professor William C. Bray for his assistance in this investigation.

Summary

1. The rate of reduction of iodate ion by hydrogen peroxide has been measured and found to be given by the expression $-d(IO_3^-)/dt = 2.6(10^{-4})(H_2O_2)(IO_3^-) + 129(10^{-4})(H^+)(IO_3^-)(H_2O_2)$ to within $\pm 5\%$.
2. A plausible mechanism for the reaction has been suggested.
3. The induction period has been studied and discussed.
4. A relatively small salt effect has been found for the reaction.
5. The reaction has been studied from 30 to 60° , and the data thus obtained were used to calculate the average diameters of H_2O_2 and IO_3^- ; the resulting value was of the correct order of magnitude.
6. The relation of this reaction to the catalytic decomposition of hydrogen peroxide by the iodine-iodate couple has been discussed.

BERKELEY, CALIFORNIA