

weak acid by a strong base. The titer deviation is compared with the titer error due to inaccuracy of e. m. f. measurement.

The absolute titration since it is inherently four times as sensitive as the inflection point titration might advantageously replace the latter when the titer error is above about 1%.

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

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY THE IODINE-IODIDE COUPLE. II AND III. THE RATE OF OXIDATION IN NEUTRAL, AND IN ACID, SOLUTION OF HYDROGEN PEROXIDE BY IODINE

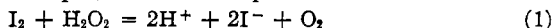
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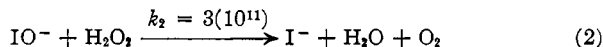
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II. THE RATE OF OXIDATION, IN NEUTRAL SOLUTION, OF HYDROGEN PEROXIDE BY IODINE

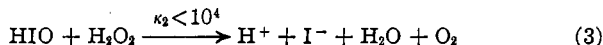
In certain investigations of the catalytic decomposition of hydrogen peroxide by the iodine-iodide couple,¹ it has been postulated that the reaction



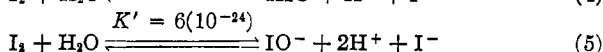
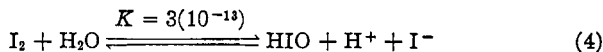
proceeds through the rate-determining steps



and



The concentrations of hypoiodite ion and of hypoiodous acid are governed at the steady state by the equilibria



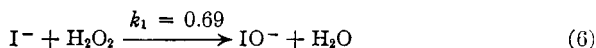
Whether or not the hydrolysis equilibrium of iodine (Reaction 4 or 5) is maintained as the steady state is approached through the progress of Reaction 1 has been questioned by Abel.^{1a,2}

¹ (a) Abel, *Z. physik. Chem.*, **136**, 16 (1928); (b) Liebhafsky, *THIS JOURNAL*, **54**, 1792 (1932). References to earlier work may be found in Ref. 1a. Ref. 1b is the first paper of this series and will be referred to as I. The values of k_2 , κ_2 , and k_1 are taken from I, where references will also be found for the values of K , K' and $(\text{I}_2)(\text{I}^-)/\text{I}_2^-$ given above. ($k_2 = 3(10^{11})$ is an average value deduced from I, Table Ib, Expts. 155-151 incl.; for these experiments the buffer solutions were identical in composition with those employed in the present investigation.) Numerical values of all constants are for 25°. As in other communications, \longrightarrow denotes that the reaction may be rate-determining and () means "concentration of" in moles/liter.

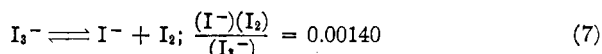
² Cf. also (a) Liebhafsky, *Z. physik. Chem.*, **155**, 289 (1931); (b) *THIS JOURNAL*, **53**, 2074 (1931); (c) *J. Phys. Chem.*, **35**, 1648 (1931).

The study of Reaction 2 at a distance from the steady state might settle this difficulty: if the value of k_2 thus obtained agrees even approximately with the value $3(10^{11})$ calculated from steady state measurements, then—since this equilibrium is established at the steady state—we may regard it as always established in this reaction system.

In order to isolate Reaction 2 it is necessary to choose experimental conditions under which the rates of Reaction 3 and of the reaction



are negligible. Simple calculations employing all the above specific rate and equilibrium constants show that in a saturated iodine solution $[\text{I}_2] = 0.00132]$,³ buffered to maintain a_{H^+} at $10^{-8} M$, and in which (I^-) is 10^{-3} , more than 99% of the peroxide should react with hypoiodite ion. As oxygen is evolved and iodide ion accumulates (*cf.* Reaction 1), the relative rates of Reactions 2 and 3 will decrease (*cf.* Eqs. 4, 5 and 6). The concentration of iodide ion will, however, always be governed by the equilibrium



and, since the tri-iodide ion formed does not react directly with hydrogen peroxide,⁴ this decrease in the relative rates is correspondingly less than would be calculated from Reaction 1 alone.

A series of preliminary experiments indicated the feasibility of measuring k_2 by following the rate of oxygen evolution with the apparatus described in I, provided that (I_2) could be maintained near the saturation value by keeping finely divided iodine in contact with the reaction mixture. This experimental method was accordingly adopted. To maintain a_{H^+} at a (nearly) constant value, the potassium phosphate buffer studied by Cohn⁵ was employed; total phosphate was always 0.2 M .

The rate to be expected for Reaction 2 in a saturated iodine solution may be written as⁶

$$+ \frac{dx}{dt} = k_2' \frac{(\text{I}_2)}{(a_{\text{H}^+})^2 (\text{I}^-)} (a - x) = k_2 6(10^{-24}) \frac{1.32(10^{-3})}{\text{const.} (\text{I}^-)} (a - x) \quad (8)$$

³ Bray and McKay, *THIS JOURNAL*, **32**, 914 (1910); **33**, 1485 (1911).

⁴ Abel's conclusion (Ref. 1a) that tri-iodide ion has no direct kinetic role in this reaction system is completely confirmed by the experiments in I.

⁵ Cohn, *THIS JOURNAL*, **49**, 173 (1927). Values of a_{H^+} were calculated as in I, where this buffer was also used.

⁶ Compare I, Eqs. 9 and 9a. Above, in Eq. 8, x denotes cc. of oxygen evolved at time t ; a is the value of x when reaction is complete. So long as x and $(a - x)$ are expressed in the same units, the value of $k = dx/dt/(a - x)$ is independent of the particular unit employed.

In the first part of all experiments, readings of x were taken at ten-second intervals. If x_1 , x_2 and x_3 are the values of x at $t - 1/6$, t , and $t + 1/6$, then at t minutes k was computed to be $3(x_3 - x_1)/(a - x_2)$. This *differential* method of evaluating $k(\text{I}^-)$ is naturally severe, the more so when x alone determines (I^-) .

We may write

$$\frac{dx}{dt} / (a - x) = k = \frac{\text{const.}}{(I^-)} \quad (9)$$

k thus defined is an apparently first-order "constant" introduced wholly for convenience in obtaining k_2 from the experimental results. This was done in the following manner. A value of the product $k(I^-)$ was calculated for practically every reading of evolved oxygen taken during an experiment; k was calculated as previously explained,⁶ and (I^-) at t minutes was obtained from oxygen evolved⁷ to that time and the initial (I^-) , if iodide had been initially added. These values of this product were plotted against the time as abscissa, and the average value for an experiment taken as the ordinate corresponding to the best horizontal line through the experimental points. From this mean value of $k(I^-)$, k_2 for the experiment is easily calculated (Eqs. 9 and 8).

A series of experiments for which the initial reaction mixture was merely the phosphate buffer solution, containing hydrogen peroxide, in equilibrium with solid iodine gave values of k_2 which were erratic and usually lower than the value $3(10^{11})$ obtained in I. In these experiments the first values of $k(I^-)$ were always much lower than the rest; this fact pointed toward depletion of the dissolved iodine as the most probable cause of the difficulty.⁸ In subsequent experiments, therefore, iodide ion was added initially in order that the reaction mixture might be "buffered" with respect to (I_2) through Reaction 7. The initial (I^-) was never high enough, however, to cause reduction of as much as 10% of the peroxide (Reaction 6).

Detailed results of two such experiments, which could be conveniently plotted together, are given in Fig. 1, which is self-explanatory. Points are plotted for practically every reading taken during each run to the time when only 1 cc. of oxygen remained to be evolved, that is, to within 96% of completion. For the experiments with iodide added to the reaction mixture (Table I, No. 24 *et seq.*), these results are representative, but they are less erratic than are those from reaction mixtures without added iodide (the first four experiments in Table I).

⁷ If a 500-cc. volume of reaction mixture is used (I^-) is changed by unity when $[500/1000 \times 1/2 \times 25,050 \times (1 + 0.00132)/0.00140] = 12,170$ cc. oxygen is evolved; in this calculation, the factor $1/2$ is introduced because 1 mole of oxygen represents 2 moles total iodide (*cf.* Reaction 1); 25,050 is the volume of 1 mole of oxygen under average experimental conditions; the last factor is necessary because part of the total iodide formed is tied up as tri-iodide ion (*cf.* Reaction 7 and Footnote 3).

By omission of the last factor, one calculates that the evolution of 6260 cc. of oxygen corresponds to formation of one mole of acid in a liter of reaction mixture. This figure may obviously be used to calculate the change which takes place in the $H_2PO_4^- - HPO_4^{2-}$ buffer as Reaction 2 proceeds.

⁸ Supersaturation was probably not very serious in these experiments as solid iodine was present and the rate of stirring was always high. (In this connection, *cf.* I.) Duplicate experiments with different rates of stirring gave similar results.

In this table the average $k(I^-)$ values are summarized. For each experiment, the values listed under a_{H^+} and (I^-) are those corresponding to the evolution of half the oxygen from the reaction mixture.⁹ In the last column is entered, for the experiments in which it is appreciable, the percentage of peroxide which one calculates to have been reduced by iodide ion (Reaction 6). The k_2 values were calculated by the substitution of $(a_{H^+})^2$ and $k(I^-)$ in Equations 9 and 8. Only four (Nos. 1-4) of the experiments without added iodide ion have been given; these are entirely representative, and the inclusion of the others would in no wise affect the conclusions drawn below.

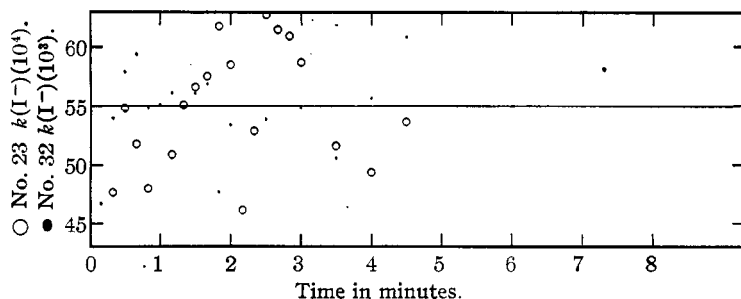
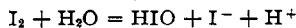


Fig. 1.—Detailed results of two experiments (see Table I).

In Table I the values of k_2 cover a two-fold range while the product $(a_{H^+})^2(I^-)$ which enters into their calculation varies 10^4 -fold. As an average value, $k_2 = 2(10^{11})$ may be taken; and it is probably too low because (I_2) in some of the reaction mixtures fell below that of a saturated solution. Nevertheless, this average value is in satisfactory agreement with the value $3(10^{11})$ deduced in I from the steady state function, F ;¹⁰ the expectation that the rate of Reaction 2 at a distance from the steady state would be given by Equation 8 is thus completely confirmed. Further, the hydrolysis equilibrium of iodine (Reaction 4 or 5) may be regarded as always established in the iodine-iodide-hydrogen peroxide reaction system, and a previous conclusion,^{2a,b} namely, that the specific rate of the reaction



is many times greater than the value 0.25 deduced by Abel, receives strong support from the data in Table I.

⁹ The occurrence of Reaction 6 tends to increase the k_2 values if these are calculated on the assumption that (H_2O_2) is given directly by oxygen evolved. For this reason no measurements were carried out in which the percentage of peroxide reduced exceeded the experimental error in Table I; a correction for the occurrence of this reaction is scarcely necessary, and none was made.

¹⁰ The value $k_2 = 2(10^{11})$ agrees exactly with what one would calculate from steady state experiments at low a_{H^+} in the acetate buffer solutions (I, Table Ia, Nos. 88 and 92); it is even higher than that corresponding to steady state measurements in Sørensen phosphate buffer solutions (*v*, I, footnote 10).

TABLE I

RATE MEASUREMENTS IN POTASSIUM PHOSPHATE BUFFER SOLUTIONS

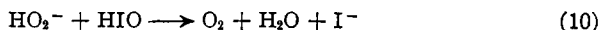
Total phosphate, 0.2 M; temp., 25°; (I₂) = 0.00132; (H₂O₂) = 0.002, approximate initial value.

No.	$a_{H^+}(10^7)^a$	(I ⁻)	$k(I^-)(10^4)$	$k_2(10^{-11})$	% reduction
1	16.8	0.001	6.4	2.3	^b
2	10.9	.001	10.6	1.6	.
3	10.9	.001	9.6	1.4	.
4	9.9	.001	14.6	1.8	.
21	6.93	.012	31.3	1.9	1
22	6.74	.006	29.6	1.7	.
23	5.33	.008	55	2.0	.
24	3.38	.019	143	2.1	2
25	4.17	.022	108	2.3	3
26	4.41	.025	89	2.2	5
27	2.24	.034	311	2.3	3
28	2.52	.037	269	2.1	4
29	2.81	.041	234	2.3	5
30	1.45	.066	588	1.6	5
31	1.65	.070	672	2.7	5
32	1.89	.074	550	2.5	7
33	9.2	.005	10.8	2.0	.
34	16.5	.009	12.9	2.7	.

^a a_{H^+} are average, and (I⁻) approximate average, values.

^b . means that less than 0.5% of the peroxide is reduced.

We shall finally consider why Reaction 2, rather than the reaction



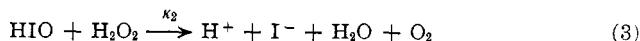
has been assumed as the compensating reaction in the catalysis of hydrogen peroxide by the iodine-iodide couple even though the experimental evidence does not at first sight seem to warrant the assumption of one reaction to the exclusion of the other. (Under the experimental conditions chosen, Reaction 10 would obviously have a rate law identical in form with Equation 8; the numerical value of the equilibrium constant involved would, of course, be different.) In the first place, hydrogen peroxide is at least ten-fold weaker as an acid than is HIO.¹¹ Second, it has not been necessary in many kinetic investigations involving hydrogen peroxide to assume HO₂⁻ as reactant. Finally, it seems logical to assume IO⁻, a product of Reaction 6, as reactant in the compensating reaction in which hydrogen peroxide is oxidized. Bray and Livingston found such a role for hypobromous acid in their investigation of the bromine-bromide catalysis,¹² in which no similar ambiguity involving hydrogen ion exists.

¹¹ The value $(\text{HO}_2^-)(\text{H}^+)/(\text{H}_2\text{O}_2) = 2.4(10^{-12})$ [Joyner, *Z. anorg. Chem.*, **77**, 103 (1912)] is almost exactly one-tenth the value $(\text{H}^+)(\text{IO}^-)/(\text{HIO}) = 2-3(10^{-11})$ [Fürth, *Z. Elektrochem.*, **28**, 57 (1922)]. According to Luther and Sammet [*Z. Elektrochem.*, **11**, 293 (1905)] HIO is an even stronger acid.

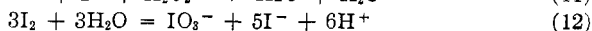
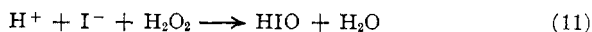
¹² Bray and Livingston, *THIS JOURNAL*, (a) **45**, 1251 (1923); (b) **50**, 1654 (1928).

III. THE RATE OF OXIDATION, IN ACID SOLUTION, OF HYDROGEN PEROXIDE BY IODINE

Two attempts to deduce the specific rate of the reaction¹³



from steady state measurements have yielded the results^{1a} $\kappa_2 = 3.3(10^5)$ and $\kappa_2 < 2(10^4)$ (*cf.* I). The disparity of these values indicates the necessity of isolating Reaction 3 in order that κ_2 may be directly measured. Because of the relative magnitudes of k_2 , the specific rate of Reaction 2, and κ_2 , this isolation can be accomplished only if the reaction mixture is at least moderately acid. Under these conditions it is necessary to minimize the rates not only of Reactions 2 and 6, but of the reactions¹⁴



and



as well.

Calculation and preliminary experiments proved that this could successfully be accomplished in perchloric acid solutions if (I^-) was maintained at a low and (nearly) constant value through the "buffer" action of solid thallous iodide.¹⁵ The rate of Reaction 3 was accordingly measured by

¹³ Even though the specific rate of Reaction 3 is much smaller than that of Reaction 2, its value cannot be obtained directly because hypiodous acid decomposes too rapidly into iodic and hydriodic acids.

¹⁴ (a) Bray, *Z. physik. Chem.*, **54**, 463 (1906); (b) Noyes, *ibid.*, **18**, 118 (1895).

¹⁵ To show that no appreciable conversion of iodine to iodate ion is to be expected in our reaction system, we employ the following data, valid for 25°

(a) $(\text{TI}^+)(\text{I}^-) = 5.52(10^{-9})$, based on the measurements of Jones and Schumb, *Proc. Am. Acad. Arts Sci.*, **56**, 199 (1921).

(b) Solubility of TiNO_3 is 0.433 *M*, Berkeley, *Trans. Roy. Soc. (London)*, **A203**, 211 (1904).

(c) The equilibrium constant for Reaction 12

$$\frac{(\text{H}^+)^6(\text{IO}_3^-)(\text{I}^-)^5}{(\text{I}_2)^3} = 2.8(10^{-47}), \text{ Luther and Sammet, } Z. Elektrochem., \text{ } 11, 293 (1905).$$

In a solution saturated with respect to TiI , TiNO_3 and I_2 , and in which $(\text{H}^+) = 10^{-2}$, the equilibrium (IO_3^-) is approximately 10^{-9} . Iodate formation through hydrolysis alone (Reaction 12) is therefore negligible; in fact, such a reaction mixture might be used to study the induction period preceding Reaction 13 when no iodate is initially added. A set of experiments of this type (Ref. 2b, Table V) has shown that a delay of at least several hours' duration is to be expected before appreciable oxidation of iodine takes place; in this interval the rate of Reaction 3 can be measured.

Unless solid thallous iodide is in equilibrium with the reaction mixture, (I^-) may fall to a value much below 10^{-7} ; then appreciable iodate formation may occur through Reaction 12, or Reaction 13, or both. From a reaction mixture to which no thallous iodide had been added, oxygen was evolved at a rate approximately two hundred times that expected for Reaction 3, and solid TiIO_3 was formed. No such oxidation of iodine was ever encountered when $\text{TiI}(s)$ was known to be present.

following oxygen evolution from reaction mixtures containing thallos nitrate and perchloric acid, and in equilibrium¹⁶ with the solids, iodine and thallos iodide; as in II, the apparatus described in I was employed. It was found that Reaction 3 proceeded so slowly that an accurate value of dO_2/dt could be secured before any great change had occurred in either (TI^+) or (H^+) or (H_2O_2) ; values of κ_2 were therefore calculated from the rates of oxygen evolution by employing for these concentrations their values in the reaction mixture at the mid-point of the time interval over which dO_2/dt was measured.

Evidence obtained in steady state experiments (Ref. Ia and I) warrants the prediction of¹⁷

$$+ \frac{dO_2}{dt} = \kappa_2 \left[K \frac{(I_2)}{(H^+)(I^-)} \right] (H_2O_2) = \kappa_2 \left[3(10^{-13}) \frac{0.00132}{(\text{const.})(\text{const.})} \right] (H_2O_2) \quad (14)$$

as the rate law followed by Reaction 3 at a distance from the steady state in a reaction mixture for which average values of a_{H^+} and (I^-) may be assumed, and which is in equilibrium with solid iodine. Equation 14 may be recast into the more convenient form

$$k = + \frac{dx}{dt} / (a - x) = \left[\frac{3.96(10^{-16})}{(\text{const.})(\text{const.})} \right] \kappa_2 = [\text{const.}] \kappa_2 \quad (15)$$

where a and x are defined as in II, Equation 9. The k there defined was a variable, for (I^-) always changed appreciably in the course of an experiment. Here, however, (I^-) is (practically) constant since no great displacement of the equilibrium

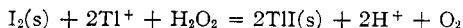


occurs during a run; the k of Equation 15 thus maintains its value for an appreciable time.¹⁸ If k is thus measured for an experiment, the corresponding value of κ_2 may be easily calculated by the substitution of average concentrations in Eq. 15; if the κ_2 values from experiments at 25° over sufficiently large concentration ranges are practically constant, their average may be taken as the value of κ_2 for this temperature.

¹⁶ Blank experiments showed no appreciable oxidation of TI^+ by H_2O_2 .

¹⁷ Compare with I, Eq. 20 and with II, Eq. 8. The quantities bracketed in the above Eqs. 14 and 15 are numerically equal for any one experiment.

¹⁸ Average concentrations may be obtained for an experiment if the net reaction occurring is



From this definite relation between (H^+) and (TI^+) and oxygen, and the known initial concentrations, the values of (H^+) and (TI^+) for the reaction mixture at the mid-point of an experiment are obtained (*cf.* II, Footnote 7); (HIO) corresponding to these average concentrations is the equilibrium concentration in Reaction 4 for $(I_2) = 0.00132$, while (I^-) is calculated from the relation $(TI^+)(I^-) = 5.52(10^{-8})$. Obviously no correction for I_3^- formation is necessary in these calculations. Whether or not k as defined in Eq. 15 changes measurably in the course of an experiment may be used to test the validity of substituting average concentrations, as in Eq. 14: if no such change in k occurs, this procedure is valid. All experiments in Table II meet this test.

The experimental results and average concentrations are summarized in Table II; the lowest value of (I^-) in the table is that of a saturated thallos nitrate solution.^{15b} The values given under κ_2 exp. were calculated directly from the k 's; for experiments at low (H^+) these were corrected for the occurrence of Reaction 2, with the results given in the last column. This correction was made on the assumption that the part of k due to this reaction could be calculated from I, Equation 9; the value $k_2 = 4(10^{11})$ was used. From the remainder of k , which is due only to Reaction 3, the κ_2 values were calculated with the aid of Eq. 15. A comparison of the last two columns in Table II will show that the correction is always small, and negligible at the higher acid concentrations.

TABLE II
RATE MEASUREMENTS IN THALLOUS NITRATE-PERCHLORIC ACID SOLUTIONS
(TI^+) = $5.52(10^{-3})/(I^-)$; (I_2) = 0.00132; temp., 25°

No.	(H^+) ^a	(I^-) (10^3)	(HIO) (10^3)	(H_2O_2)	$k(10^5)$	κ_2 exp. (10^{-3})	$\kappa_2(10^{-3})$
16	0.0219	2.40	0.75	0.821	2.04	2.8	2.4
17	.0231	1.87	0.92	.821	2.78	3.0	2.6
18	.0245	1.16	1.39	.820	3.49	2.5	2.2
19	.0262	0.744	2.03	.820	4.66	2.3	2.0
20	.0287	0.457	2.91	.819	6.60	2.3	2.0
24	.0114	2.55	1.33	.404	2.23	1.7	1.3
25	.0127	1.66	1.88	.403	3.80	2.0	1.5
26	.0139	0.96	2.97	.401	7.16	2.4	1.9
27	.0158	.507	4.94	.400	12.4	2.5	2.0
28	.0183	.204	10.6	.398	26.9	2.5	2.0
46	.0116	.128	26.9	2.05	73	2	2.0
47	.0292	.128	10.7	2.05	32.6	3.0	2.5
48	.0500	.128	6.24	2.05	19.7	3.2	3.0
49	.0800	.128	3.90	2.05	12.3	3.2	3.1
50	.108	.128	2.89	2.05	8.3	2.9	2.8
51	.135	.128	2.31	2.05	5.95	2.6	2.5
52	.161	.128	1.94	2.05	4.53	2.3	2.2
53	.187	.128	1.67	2.05	3.61	2.2	2.2
54	.237	.128	1.32	2.05	2.49	1.9	1.9
55	.309	.128	1.01	2.05	1.76	1.8	1.8

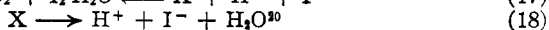
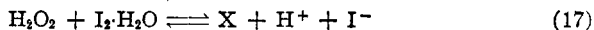
^a All concentrations are average.

The results in Table II require little additional comment. For an average value, we may take $\kappa_2 = 2.2(10^3)$ in complete agreement with the conclusion from I that this specific rate constant must be smaller than $2(10^4)$: Eq. 14 therefore governs the rate of Reaction 3 both at a distance from and at the steady state. The accuracy with which κ_2 is determined is all that could reasonably be expected; indeed, much of the variation in the κ_2 values of Table II is probably due to a salt effect on the equilibrium, Reaction 4. (The kinetic salt effect in Reaction 3 is likely to be very small, since neither of the reacting species is ionic.)

Conclusion

With the completion of the investigations which constitute the first three members of this series, the essential simplicity of the iodine-iodide catalysis of hydrogen peroxide seems well established. Why Abel encountered complications in studying the oxidation of hydrogen peroxide (Reaction 1) at a distance from the steady state is not yet clear; new evidence seems conclusive enough, however, to warrant the statement that in this reaction system there are possible (from $a_{H^+} = 10^{-8}$ to $a_{H^+} = 10^{-3}$) only three rate-determining steps, of which all are compensating reactions in the catalysis. The rate laws which they follow (I, Eq. 6; II, Eq. 9a; III, Eq. 14a) have been deduced at the steady state and verified at a distance from it. The numerical agreement¹⁹ between the specific rate constants obtained under the two conditions is not always as good for our case as for that of Bray and Livingston;¹² this is probably due to several causes, among which may be mentioned that no explicit corrections have been made for salt effect, that this catalysis was investigated over a larger concentration range, and that in this system hydrogen peroxide is oxidized not in one reaction, but in two.

While the rate laws for the reaction system are thus definitely established, the mechanisms of the corresponding reactions are subject to an uncertainty of a type encountered in many kinetic investigations; for we have isolated neither hypoiodous acid nor its anion. Other mechanisms for the compensating reactions are conceivable; thus the mechanism



would formally satisfy the rate law for Reaction 3. A rate law so complex as this can often be interpreted in terms of several mechanisms, of which none can be considered as absolutely established until every intermediate compound it assumes has been isolated and found to react as it prescribes. Unfortunately, both hypoiodous acid and its anion are so unstable that for reactions involving them such proof cannot be obtained. When the absolute establishment of a mechanism is, beyond a certain point, impossible, the most reasonable of the possible mechanisms may be selected as that which best explains the empirically determined rate law; in this choice, the results of analogous kinetic investigations will serve as valuable guides. Further work may then confirm the mechanism selected, or demand its revision. Reactions 2, 3 and 6 have been thus assigned to the three definitely established rate laws for the reaction system comprising hydrogen peroxide, iodine, and iodide ion.

¹⁹ Reaction 6 has been studied at a distance from the steady state by Noyes,^{14b} among others. At higher concentrations of acid, the closely related Reaction 11 is a fourth possible rate-determining step.^{14a}

²⁰ The rate law (Eq. 14) would be formally satisfied had H_2O been placed on the right-hand side of Equation 17, or had it been omitted from both equations.

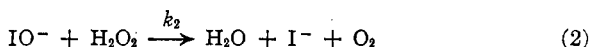
Summary

1. One of the rate-determining steps in the oxidation of hydrogen peroxide by iodine has been isolated; for its rate law the differential equation

$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = 12(10^{-13}) \frac{(\text{I}_2)}{(a_{\text{H}^+})^2(\text{I}^-)} (\text{H}_2\text{O}_2) \text{ at } 25^\circ \quad (8a)$$

has been found valid over a large concentration range.

The most probable mechanism of this rate-determining step involves hypoiodite ion as the oxidizing agent



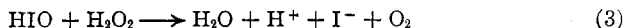
At 25° , $k_2 = 2(10^{11})$. The agreement of this value with the value $3(10^{11})$ previously deduced from steady state measurements seems sufficiently good to warrant the conclusion that the hydrolysis equilibrium of iodine (Reaction 4 or 5) is always established in the iodine-iodide-peroxide reaction system.

2. An alternative mechanism involving hydroperoxide ion has been briefly discussed.

3. A second rate-determining step in the oxidation of hydrogen peroxide by iodine has been isolated; over a large concentration range its rate is given by the differential equation

$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = 6.6(10^{-10}) \frac{(\text{I}_2)}{(\text{H}^+)(\text{I}^-)} (\text{H}_2\text{O}_2), \text{ at } 25^\circ \quad (14a)$$

The most probable mechanism of this step is



At 25° , $\kappa_2 = 2.2(10^3)$, in complete agreement with evidence from steady state measurements.

It has been concluded that the reaction system comprising hydrogen peroxide, iodine and iodide ion can be interpreted in terms of the three compensating reactions within the wide range of experimental conditions over which the corresponding rate laws have been definitely established.

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