

be slightly low. The heat of activation which was found by Schwab and Schmidt at low pressures was 44,000 calories; hence the agreement is good.

The fact that the temperature coefficient is nearly the same for all metals seems to indicate that the mechanism of the ammonia decomposition is the same on each metal. Since experiments on different metals have not been carried out under comparable conditions, it is fruitless to attempt to find a relation between the velocity of decomposition and the heat of reaction.

### Summary

The decomposition of ammonia on platinum gauze has been studied by a flowing method between 772 and 858°. The rate of decomposition is proportional to the ammonia pressure and inversely proportional to the hydrogen pressure. As the pressure of the hydrogen increases, its inhibiting effect reaches a constant value and the reaction proceeds unimolecularly with respect to the ammonia. The heat of activation of the reaction is 40,000 calories per mole. This value is in agreement with those found for a number of other metals.

PRINCETON, NEW JERSEY

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

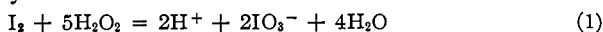
## REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION. IV. THE OXIDATION OF IODINE TO IODATE ION BY HYDROGEN PEROXIDE<sup>1</sup>

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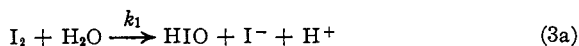
A preliminary study of the reaction



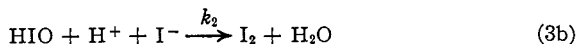
has led Bray and Caulkins (II) to conclude from the rate law

$$-\frac{d\text{I}_2}{dt} = k(\text{I}_2) \quad (2)$$

which it obeys in a rather large region of concentrations, that its principal rate-determining steps are the reactions



and



which taken together constitute the hydrolysis equilibrium of iodine. They found reasonable agreement between their value of  $k$  ( $k = 0.6$  at 25°) and the value of the specific rate for the iodine hydrolysis ( $k_1 = 0.25$  at

<sup>1</sup> The earlier papers of this series are (a) Bray and Liebhafsky, *THIS JOURNAL*, **53**, 38 (1931); (b) Bray and Caulkins, *ibid.*, **53**, 44 (1931); (c) Liebhafsky, *ibid.*, **53**, 896 (1931).

25°), which Abel<sup>2</sup> has deduced from another reaction system. In this paper are presented the results of a more extended investigation of Reaction 1. It was hoped that  $k_1$  could be determined as a maximum limiting value of  $k$ , and that a study of the variation of  $k$  under extreme concentration conditions might cast some light upon the mechanism of the various rapid reactions following the rate-determining steps 3a and 3b.

When hydrogen peroxide and iodine solutions are mixed<sup>3</sup> with the peroxide in moderate excess, no great change in the concentration of iodine occurs even after several weeks, but the hydrogen peroxide gradually disappears. For the oxidation of iodine to iodate, therefore, such a reaction system passes through an infinite induction period. If the mixture is made acid, this induction period may be greatly shortened; if iodate ion is added also, and in sufficient quantity, the initial delay may be eliminated entirely and iodate is formed. The time then required, at room temperature, for half the iodine to be oxidized is approximately one minute.

Accurate measurements of the rate of this reaction are best undertaken at zero degrees for two reasons: first, the rate at that temperature is low enough to permit of careful manipulation, and, second, the concentration of iodine at the steady state is smaller at zero degrees than at room temperature, so that relatively a larger range of iodine concentrations can be covered before catalytic decomposition of hydrogen peroxide complicates the pure oxidation of iodine. The experimental method employed in following the rate of disappearance of iodine in a given reaction mixture consists simply in withdrawing samples of it at known intervals, "freezing" the reaction by shaking the sample with carbon tetrachloride to extract the iodine, and titrating the iodine thus obtained with thiosulfate solution.

**Reagents and Analytical Methods.**—C. P. chemicals not further purified were used in all work. Perchloric and iodic acids were used as sources of hydrogen ion. For certain of the experiments requiring a high concentration of both iodine and iodate ion, a solution of iodine and potassium iodate, saturated with respect to both, was employed.

Sodium thiosulfate solutions were standardized through permanganate against sodium oxalate according to the method of Bray and Miller.<sup>4</sup> Sodium carbonate prepared by fusing the pure bicarbonate was the reference substance for all standard acids. The hydrogen peroxide was determined with permanganate; the iodate solutions were standardized iodimetrically.<sup>5</sup> An iodimetric method was used in the determinations of total oxidizing power.

<sup>2</sup> Abel, *Z. physik. Chem.*, **136**, 161 (1928). Other references are given in 1a.

<sup>3</sup> For a more comprehensive summary of the reactions which may take place in this system see I, Table I.

<sup>4</sup> Bray and Miller, *THIS JOURNAL*, **46**, 2204 (1924).

<sup>5</sup> A method identical in all essential respects with the method of this paper was used by Bray and Livingston [*ibid.*, **50**, 1654 (1928)] to determine hydrogen peroxide.

The determination of the iodine in the reaction mixture was carried out according to a method elsewhere described.<sup>6</sup>

### Experimental Method

The reaction vessel was a 500-cc. glass-stoppered flask placed in the large Dewar flask which served as thermostat. With finely divided ice in the Dewar, the temperature in the flask was  $0.1 \pm 0.1^\circ$ . In all experiments, except in those done to ascertain the effect of the order of mixing the reagents, the peroxide, at  $0^\circ$ , was added to the rest of the reaction mixture, also at  $0^\circ$ , in order to start the reaction. Immediately after the rapid addition of the peroxide, the flask was vigorously shaken; the time of shaking was taken as the initial time for the reaction. Samples were withdrawn in the following manner: fifteen seconds before the minute which was to be the time of the sample, a 20-cc. pipet was placed in the reaction mixture and filled. This volume of reaction mixture was then blown into a separatory funnel having a short, beveled exit tube so that the tip of the pipet was below the surface of the 25 cc. of cold carbon tetrachloride in the funnel. The reaction was "frozen" on the minute by shaking the separatory funnel vigorously enough to insure virtually instantaneous extraction of the iodine. The carbon tetrachloride layer was then run into a 125-cc. glass-stoppered flask containing 50 cc. of distilled water. After the small amount of carbon tetrachloride from a second extraction of the reaction mixture had been added to the flask, it was vigorously shaken in order that the carbon tetrachloride layer might be washed free of iodate and peroxide. After allowing the carbon tetrachloride to settle, the water was carefully poured off, and the washing process twice repeated. Care must be observed in the washing—first, that the flasks are scrupulously clean to prevent adhesion of the carbon tetrachloride; second, that the shaking is not violent enough to emulsify the carbon tetrachloride; and third, that no carbon tetrachloride remains on the surface of the water layer. No correction need be applied for the iodine dissolved in the water since its concentration, assuming equilibrium, will always be proportional to the  $(I_2)$  in the carbon tetrachloride layer: the first order rate constant will thus not be affected so long as the volume of carbon tetrachloride, size of sample, amount of water used for washing and similar factors remain the same.

The samples obtained in this manner were titrated with 0.004 *N* sodium thiosulfate by the method previously mentioned.<sup>6</sup> As the reaction neared completion, the concentration of iodine became so small that samples larger than 20 cc. had to be taken to secure sufficient accuracy in the titration of the iodine; since, at low  $(I_2)$ <sup>7</sup> speed in manipulation is less imperative, this could conveniently be done.

**Detailed Experimental Results.**—The detailed results of several of the rate experiments performed by the above method are shown in Figs. 1 and 2, and Table I. In Fig. 1  $(I_2)$  as ordinate is plotted on *semi-logarithmic* paper against the time  $t$ , in minutes, to give a conventional rate plot for a first order reaction. Zero time for each succeeding experiment is placed further to the right to prevent superposition of the curves. Results as concordant as those shown in the plot were obtained only after long practice had improved the experimental technique. The slope of the steepest line through the experimental points (multiplied by 2.3) was taken for the

<sup>6</sup> Liebhafsky, *THIS JOURNAL*, 53, 165 (1931).

<sup>7</sup> ( ) denotes "concentration of"; thus,  $(I_2)$  is "concentration of iodine." The units, when such are necessary, are moles per liter.

TABLE I  
DATA FOR EXPERIMENTS IN FIGURES 1 AND 2

No.	Fig.	(H <sup>+</sup> )	(IO <sub>3</sub> <sup>-</sup> )	(H <sub>2</sub> O <sub>2</sub> )	k
81	1	0.0268	0.214	0.0038	0.046
82	1	.0134	.214	.0038	.044
83	1 and 2	.0107	.214	.0038	.041
60	1 and 2	.0535	.00022	.103	.0072
78 <sup>a</sup>	1	.0535	.214	.00076	.04
32	2	.148	.0142	.112	.019
71	2	.0535	.214	.103	.037
73	2	.0535	.214	.010	.037
74	2	.0535	.214	.0038	.039

<sup>a</sup> Titrations during the next twenty-four hour period gave no indication of a further change in (I<sub>2</sub>); k is given by the first four points.

value of k as defined in the rate law (Equation 2) previously established for Reaction 1.

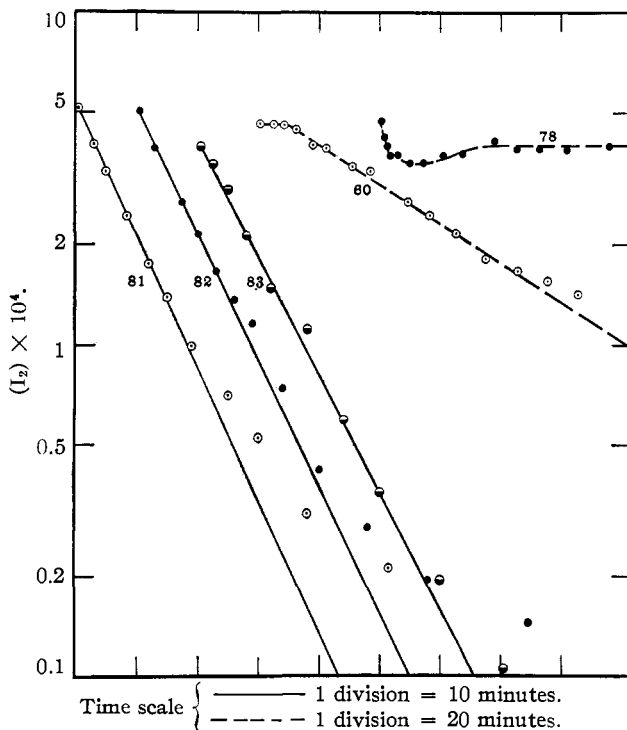


Fig. 1.—Typical experiments. (The plot is on semi-logarithmic paper; for composition of reaction mixtures, see Table I.)

The curves in Fig. 2 represent the dependence of k on (I<sub>2</sub>) (cf. II, Fig. 1) for a number of experiments carried out under various concentration conditions. The values of k for any one experiment were computed from

tangents to a smooth curve drawn through the experimental points plotted as in Fig. 1. Because of the erratic nature of many results at low ( $I_2$ ) (*i. e.*, approximately  $5(10^{-5}) M$ ), this procedure was not generally adopted; even a qualitative interpretation of these results was usually impossible. The behavior of  $k$  as the reaction proceeds is typified by Nos. 74 and 83 rather than by the other experiments: *i. e.*,  $k$  usually remained constant until 50–75% of the iodine had been consumed, and then decreased. This

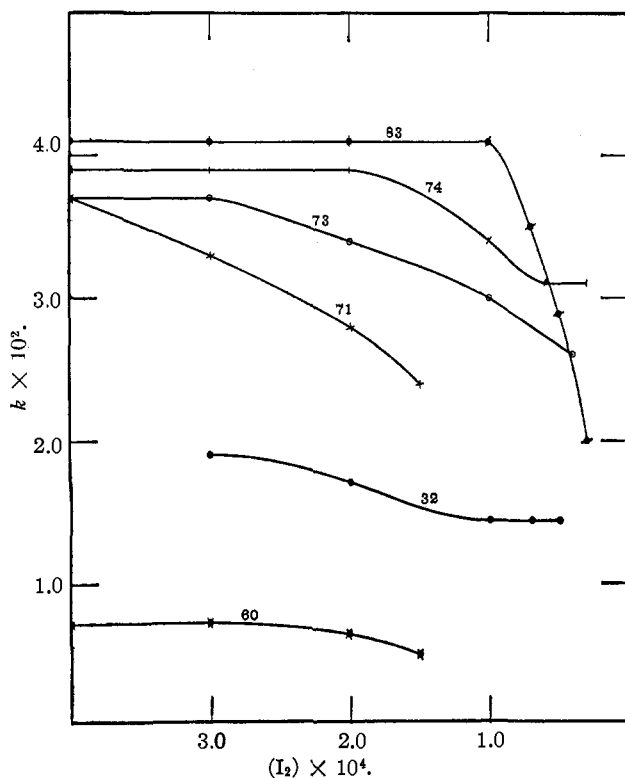


Fig. 2.—Variation of  $k$  with  $(I_2)$  (see Table I).

decrease began at higher values of  $(I_2)$  the higher  $(H_2O_2)$  (as is shown by Nos. 71, 73 and 74), and the higher  $(H^+)$  (as is shown by Nos. 74, 83, 71 and 32). For  $(IO_3^-)$  variation no such conclusion could be drawn. We shall revert to this behavior of  $k$  in a later section.

It follows at once from the conclusion drawn in II—namely, that the *principal* rate-determining steps for Reaction 1 are Reactions 3a and b—that Equation 2 may be written

$$-\frac{d(I_2)}{dt} = k(I_2) = k_1(I_2) - k_2(H^+)(I^-)(HIO) \quad (4)$$

Were our reaction system a simple one, we should accept as conclusive

the close agreement of experiments like Nos. 81, 82 and 83 with a first order rate law, and we should identify the highest (constant) values of  $k$  with  $k_1$ , the specific rate for the iodine hydrolysis. We should say that  $k$  decreases at very low concentrations of iodine because of iodine formation from the Reaction 3b, and that such iodine formation is negligible in the region where  $k$  is truly constant. Unfortunately, the complexity of the reaction system precludes the complete acceptance of this simple explanation, and we shall, in a later section, be forced to examine the possibility that Reaction 3b is of importance throughout the entire range of iodine concentrations.

**Effect of External Factors on the Reaction.**—Experiments designed to reveal any effect on the reaction of either light or glass wool gave conclusive negative results.

Experiments on the effect of different orders of mixing the reagents resulted as follows. If the peroxide was added to an acid iodine solution containing iodate ion (the method of mixing previously described), reproducible results were obtained in all cases where the oxidation of iodine began immediately and was unaccompanied by too much catalytic decomposition of hydrogen peroxide. If an *acid* iodine-peroxide mixture was allowed to stand, and iodic acid added to start the reaction, reproducible results were likewise obtained. If an iodine-peroxide solution is allowed to stand, and iodic acid added as before, there is an increase of iodine (which is caused by oxidation of the iodide ion formed on standing) on mixing; the rate constant in such an experiment was often low. If 30% hydrogen peroxide is added to an iodine solution containing iodic acid, and the reaction mixture is neither stirred nor shaken, the entire rate curve may be altered. (This effect will be mentioned again later.)

**Variation of the Rate Constant with Changes in  $(\text{IO}_3^-)$ .**—The effect on the rate constant of a variation in the iodate concentration is given in Fig. 3 by Curve I for very low, and by Curve II for moderate, concentrations of peroxide. Whether  $k$  has a finite value at zero concentration of iodate ion cannot be settled by our experimental methods for the induction periods at low  $(\text{IO}_3^-)$  are long enough to permit of some iodate formation.

Curve I shows that the value of the rate constant increases from 0.015 to 0.06 as the iodate concentration is increased from a very small value to that for a saturated solution of potassium iodate; Curve II indicates that  $k$  approaches a limiting value,  $k = 0.03$  when the same change is made. If Curve II, which was first established, were the only experimental evidence for the dependence of  $k$  on  $(\text{IO}_3^-)$ , we should conclude—in agreement with II and with Abel's results—that  $k = 0.03$  was the value of the specific rate for the iodine hydrolysis at  $0^\circ$ . Curve I, however, does not agree with this simple conclusion. An inspection of the concentration conditions

obtaining for the curves will show that, although the acid concentrations differ somewhat, the chief difference lies in the concentration of hydrogen peroxide, which is approximately forty times greater for the experiments on Curve II than for those on Curve I. How this difference in peroxide concentrations may explain the difference in the curves will be mentioned in a later section.

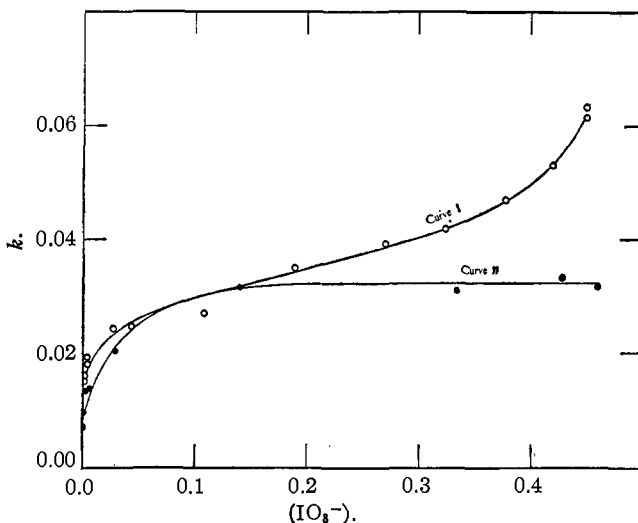


Fig. 3.—Variation of  $k$  with change in  $(\text{IO}_3^-)$ . Curve I,  $(\text{H}^+) = 0.0268$ ;  $(\text{H}_2\text{O}_2) = 0.0039\text{--}0.0018$ ; Curve II,  $(\text{H}^+) = 0.054\text{--}0.071$ ;  $(\text{H}_2\text{O}_2) = 0.10$ .

**The Removal of Iodide Ion.**—We shall now consider evidence for the assumption that the primary function of  $\text{IO}_3^-$  is to assist in the removal of the iodide ion formed by the hydrolysis of iodine. Abel<sup>8</sup> and his co-workers, in revising Dushman's<sup>9</sup> work, have shown that the rate law for the oxidation of iodide ion by iodate ion in acid solution is the following

$$-\frac{d(\text{IO}_3^-)}{dt} = (\text{IO}_3^-)(\text{I}^-)(\text{H}^+)^2[\kappa f^2 + k'F(\text{I}^-) + k''F(\text{I}_3^-)] \quad (5)$$

where, at 25°

$$\kappa = 2.4(10^4); \quad k' = 7.6(10^{10}); \quad k'' = 5.5(10^{10})$$

(The "f" terms involve activity coefficients.) For the very approximate calculation which we shall make,  $\text{I}_3^-$  will be considered simply as  $\text{I}^-$  and the factors involving activity coefficients will be neglected. The 25° values of the constants will be changed to corresponding values for 0° by employing the temperature coefficient 1.3 found by Dushman in a region of  $(\text{I}^-)$  where the fifth order reaction is of primary importance.

<sup>8</sup> (a) Abel and Stadler, *Z. physik. Chem.*, **122**, 49 (1926); (b) Abel and Hilferding, *Z. physik. Chem.*, **136**, 186 (1928).

<sup>9</sup> Dushman, *J. Phys. Chem.*, **8**, 453 (1904).

Equation (5) may now be written

$$-\frac{d(\text{IO}_3^-)}{dt} = (\text{IO}_3^-)(\text{I}^-)(\text{H}^+)^2[3(10^{10})(\text{I}^-) + 1(10^4)] \text{ at } 0^\circ \quad (6)$$

In order to apply this equation to our reaction system, we must write it to give the number of moles of iodide reacting directly with iodate per minute in a liter of reaction mixture. Since two molecules of iodide are involved in the fifth order reaction, the value  $3(10^{10})$  must be doubled. We now have

$$\text{moles of I}^- \text{ reacting with IO}_3^-/\text{min.} = (\text{IO}_3^-)(\text{I}^-)(\text{H}^+)^2[6(10^{10})(\text{I}^-) + 10^4] \quad (6a)$$

The oxidation of iodine through its hydrolysis products to iodate ion requires the oxidation of one mole of  $\text{I}^-$  and of one mole of  $\text{HIO}$  for every mole of iodine consumed in Reaction 1. If we now assume that all the  $\text{I}^-$  which is transformed into iodate reacts first with iodate ion, we may calculate an approximate *upper* limit for the  $(\text{I}^-)$  in our reaction system; for we may then write

$$-\frac{d(\text{I}_2)}{dt} = k(\text{I}_2) = \text{moles I}^- \text{ reacting with IO}_3^-/\text{min.} = (\text{IO}_3^-)(\text{I}^-)(\text{H}^+)^2[6(10^{10})(\text{I}^-) + 10^4] \quad (7)$$

Using this equation and the values of  $k$  given by Curve I, Fig. 3, for different values of  $(\text{IO}_3^-)$ , the last column of Table II was computed.

TABLE II

MAXIMUM $(\text{I}^-)$ IN THE REACTION SYSTEM AT VARIOUS $(\text{IO}_3^-)^*$					
$(\text{IO}_3^-)$	$(\text{H}^+)$	$(\text{H}_2\text{O}_2)$	$(\text{I}_2)$	$k$	$(\text{I}^-)$
$2(10^{-1})$	0.0268	0.0034	$5(10^{-4})$	0.060	$1.8(10^{-6})$
$1(10^{-2})$	.0268	.0034	$5(10^{-4})$	.020	$4.8(10^{-6})$
$1(10^{-3})$	.0268	.0034	$5(10^{-4})$	.015	$1.4(10^{-5})$
$1(10^{-5})$	.0268	.0034	$5(10^{-4})$	.016	$1.3(10^{-4})$

The  $(\text{I}^-)$  values calculated for the two highest iodate concentrations in Table II are of a reasonable order of magnitude; we shall therefore assume that the chief function of iodate ion is to assist in the removal of iodide ion. If iodide is oxidized to a valence above zero by other substances also, the actual  $(\text{I}^-)$  obtaining in the reaction mixture will be less than that calculated from Equation 7.

When  $(\text{IO}_3^-)$  decreases below  $10^{-2}$ , however, the  $(\text{I}^-)$  values of Table II become much too large. The value  $(\text{I}^-) = 1.3(10^{-4})$  calculated for  $(\text{IO}_3^-) = 10^{-5}$  represents an appreciable part of the initial  $(\text{I}_2)$ ; this concentration of iodide could never be established in such a reaction mixture, for the iodide initially present from hydrolysis is less than 0.01% of the iodine with which it was in equilibrium, and the amount of iodine disappearing during an induction period is always relatively small. The maintenance of the concentration of iodide ion at a reasonable value in these reaction mixtures therefore requires the action of another oxidizing agent in addition to iodate ion. Hydrogen peroxide is far too slow;<sup>10</sup> but  $\text{HIO}_2$  remains as a

<sup>10</sup> References 12a, 12b, 12c, from Ref. 1a.



logical possibility. We shall assume that, at low ( $\text{IO}_3^-$ ), iodosic acid reacts first with the major part of the iodide which is converted finally into iodate. The importance of this reaction at higher ( $\text{IO}_3^-$ ) is uncertain; the greater its importance, the farther will the ( $\text{I}^-$ ) of the reaction system be below that calculated from Equation 7.

An examination of the work of Abel and Hilferding<sup>8b</sup> shows that iodate ion cannot to an appreciable extent oxidize HIO. If this reaction were of importance, they could not have found their simple fourth order rate law for the oxidation of iodide by iodate, since the concentration of HIO in their experiments ( $(\text{H}^+)$  and  $(\text{I}^-)$  were sensibly constant) must have undergone a concentration variation parallel to that of iodine.

The relation of the curves of Fig. 3 to the value of the specific rate for the iodine hydrolysis will be discussed later.

**Catalysis in Relation to the Rate Measurements.**—Whenever, in a reaction system involving the action of hydrogen peroxide as an *oxidizing* agent, that substance acts as a *reducing* agent also, the catalytic decomposition of hydrogen peroxide will constitute a side reaction taking place in the system. So long as there is no appreciable decomposition of iodine compounds to liberate oxygen, the decrease in the oxidizing power of our reaction mixture will furnish a quantitative measure of the amount of peroxide reduced, which will be half that catalytically decomposed. This method of determining the amount of such catalysis will cease to be accurate when the total oxidizing power is very much greater than the decrease due to such catalysis.

In Table III some of the catalysis results are given. The seventh column shows the amount of catalysis, expressed as an increment of the peroxide concentration, observed for each reaction mixture during the time interval given in the sixth column. In the last column are given the ratios ( $R$ 's) of this concentration change to the amount of peroxide, equal to  $5(\text{I}_2)$ , which is equivalent in Reaction 1 to the iodine initially present in a liter of reaction mixture.

TABLE III  
CATALYSIS RESULTS

No.	( $\text{H}^+$ )	( $\text{IO}_3^-$ )	( $\text{H}_2\text{O}_2$ ) $10^3$	$k$	Time, hrs.	$\Delta(\text{H}_2\text{O}_2)(10^3)$	$R$
97	0.0268	0.0017	3.9	0.018	20	0.27	0.14
103	.0268	.00108	3.4	(.018)	8	.43	.22
104	.0268	.00053	3.4	.015	8	.33	.17
107	.0677	.0142	110	.023	15	4.4	2.2
108	.0677	.0142	560	.0067	7	77	39

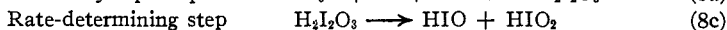
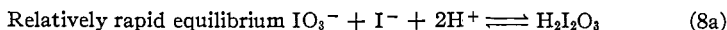
In each case  $2(10^{-3})$  moles of hydrogen peroxide would be required to oxidize the iodine initially present to iodate; the initial ( $\text{I}_2$ ) was approximately  $4(10^{-4})$ .

The titrations of oxidizing power carried on during the course of the two experiments involving the largest absolute amounts of catalysis show

that the rate of this catalysis diminishes markedly as the concentration of iodine decreases. A comparison of Experiment 108 with No. 107 (Table III) shows that a large absolute amount of catalysis brings with it a sharp reduction in  $k$ ; the iodine formation causing this decrease in  $k$  we attribute to the increased rate of Reaction 3b brought about by the higher  $(I^-)$  which obtains in the system when the absolute amount of catalysis is large. These low constants at high  $(H_2O_2)$  were generally observed and will again be mentioned in a later section. Titration of samples from an initially neutral iodine solution, 0.005  $M$  in peroxide, over a period of days showed the catalysis to be proportional to  $(H_2O_2)$ . The  $(I_2)$  of the solution underwent little change during the experiment.

From these facts we conclude that the major part of the catalysis encountered in our reaction system is due to those steady states which Abel<sup>11</sup> has so thoroughly investigated. The fact that this catalytic rate may be made very low shows, according to conclusions presented in Part I, that hydrogen peroxide cannot, in our reaction system, oxidize HIO. Neither can it oxidize the  $I^-$  in this system<sup>12</sup> at a rate comparable with the  $dI_2/dt$  measured. Since changes in  $(H_2O_2)$  do not proportionately alter  $k$  (see the section on variation of  $k$  with  $(H_2O_2)$ ), we conclude that hydrogen peroxide cannot oxidize iodine directly with sufficient speed to explain the removal of iodine. Yet for every mole of iodine disappearing by hydrolysis, one mole of  $I^-$  and one mole of HIO must be removed. We have, therefore, to devise a mechanism by which the oxidation of iodine to iodate can be accomplished in our reaction system *without appreciable direct oxidation of either  $I_2$ ,  $I^-$  or HIO by hydrogen peroxide*, the only oxidizing agent appearing as reactant in the stoichiometric equation for the change.

We have found such a mechanism only by assuming that the fourth order  $IO_3^- - I^-$  reaction proceeds as follows



This formulation of the fourth order reaction indicates that  $H_2I_2O_3$  decomposes the more readily into iodate and iodide ions. In our reaction system hypiodous acid is removed as rapidly as it is formed; we shall assume that this removal is accomplished by the reaction



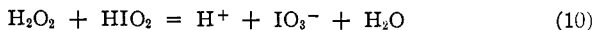
<sup>11</sup> For bibliography see 1a. Two differences between Abel's system and ours must here be observed. In the former, much of the HIO must be formed by the oxidizing action of  $H_2O_2$  on  $I^-$ ; the rate of this step governs the rate of the catalysis. In our system, HIO can be formed from  $I^-$  by the action of  $IO_3^-$ ,  $HIO_2$  and  $H_2I_2O_3$ ; the rate of the catalysis is here governed by the rate at which  $H_2O_2$  reduces HIO at the extremely small concentration obtaining for the latter in this system. Here, also,  $H_2O_2$  may possibly reduce  $IO_3^-$ ,  $HIO_2$  and  $H_2I_2O_3$ ; these reactions may account in part for the catalysis observed.

<sup>12</sup> See 1a, References 12 a, 12 b, 12 c.

which is the reverse of Reaction 8c. Bray,<sup>13</sup> in correlating a number of halogen reactions, has rendered plausible the assumption of Reaction 8b. In order to accomplish iodate formation, the oxidizing action of hydrogen peroxide need now be assumed only in the reactions

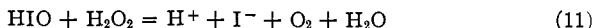


and



If the oxidation of iodine is to proceed, these reactions must be rapid enough to keep  $\text{H}_2\text{I}_2\text{O}_3$  at or below the equilibrium concentration for Reaction 8a; this restriction imposes a lower limit on the values we may assume for the specific rates of Reactions 9 and 10 in order that the oxidation of iodine by hydrogen peroxide may take place in the manner above prescribed. Its applicability to this reaction system is strong additional evidence for the mechanism assigned by Bray to the  $\text{IO}_3^- - \text{I}^-$  reaction.

Using measurements made in Experiments 107 and 108, Table III, on the rates of decrease in oxidizing power, we may, on the assumption that all of the hydrogen peroxide is oxidized according to the equation



calculate a value<sup>14</sup> for  $(\text{HIO})$  in the reaction system; the value  $10^{-8}$ – $10^{-9}$  *M* thus obtained sets an upper limit for the concentration of hypoiodous acid.

**The Induction Period.**—Most of the experiments proceeded without an appreciable induction period; in general, if there was an induction period, it was longer the lower the  $(\text{IO}_3^-)$ , the lower the  $(\text{H}^+)$  (as is shown in Tables IV and V), and the higher the  $(\text{H}_2\text{O}_2)$ . The shape of the induction period curves (Experiment 60, Fig. 1, is an example) shows that it is terminated by an autocatalytic reaction. At low  $(\text{H}^+)$  (Expts. 17, 19 and 21, Table IV), and high  $(\text{H}_2\text{O}_2)$ , it is particularly unreproducible.

A comparison of experiments at low  $(\text{IO}_3^-)$  shows that the concentration of iodate ion in the system is not, other initial concentrations being con-

<sup>13</sup> Bray, *THIS JOURNAL*, **52**, 3580 (1930). For purposes of this paper  $\text{H}_2\text{I}_2\text{O}_3$  and  $\text{I}_2\text{O}_2$  may be considered identical.

<sup>14</sup> In Experiment 108,  $-\text{dH}_2\text{O}_2/\text{d}t$  in moles/min./liter calculated for Reaction 11 from the decrease in oxidizing power is  $4.4(10^{-4})$ ; in Experiment 107, it is  $1.3(10^{-6})$ . Taking the value  $3(10^4)$  for the specific rate of Reaction 11 at  $0^\circ$  [Abel, Ref. 2, gives  $3.3(10^6)$  for this specific rate at  $25^\circ$ ; at our acid concentrations ( $0.01$  *M* and over) the oxidation of  $\text{H}_2\text{O}_2$  by  $\text{IO}^-$  may be neglected], we obtain for 108,  $(\text{HIO}) = 2.6(10^{-8})$ , and for 107,  $(\text{HIO}) = 4(10^{-9})$  on substitution of the  $(\text{H}_2\text{O}_2)$  values from Table III. Using the value

$$K = \frac{(\text{HIO})(\text{I}^-)(\text{H}^+)}{(\text{I}_2)} = 9(10^{-15}) \text{ at } 0^\circ$$

[Grinnell Jones, *THIS JOURNAL*, **37**, 256 (1915)] we find that, at  $(\text{H}^+) = 2(10^{-2})$  and  $(\text{I}_2) = 5(10^{-4})$ , the limiting value of the product  $(\text{HIO})(\text{I}^-)$  is  $2.3(10^{-16})$ . If  $(\text{I}^-)$  is  $10^{-6}$  in order of magnitude, as the previous section would indicate,  $(\text{HIO})$  cannot be above  $10^{-10}$ . This calculation would indicate either that  $(\text{I}^-)$  of the previous section is too high, or that some of the catalysis does not involve  $\text{HIO}$ , or both.

stant, the only factor in determining whether or not the reaction is to suffer an induction period, for the amount of iodine disappearing before smooth oxidation begins is, in an experiment such as 106 or 104, Table IV, far less than the amount initially present in an experiment such as 97, Table IV, which also has an induction period. A comparison of the first group of experiments with the second shows how markedly the induction period is lengthened at low ( $H^+$ ); the experiments in Table V, which were done at room temperature without initial iodate, show this also.

TABLE IV

LENGTH OF INDUCTION PERIOD IN VARIOUS RATE EXPERIMENTS					
No.	( $H^+$ )	( $IO_3^-$ )	( $H_2O_2$ )	$k$	Induction period
57	0.0546	0.00109	0.103	0.0133	8 min.
59	.0540	.00055	.103	.0096	24 min.
60	.0537	.00022	.103	.0081	22 min.
61	.0535	.000035	.103	.0081	31 min.
93, 94, 95, 96	.0268	.135-0.0135	.002-0.004	.039-0.024	Below 2 min. <sup>a</sup>
97	.0268	.0017	.0038	.018	27 min.
104	.0268	.00053	.0034	.015	Approx. 6 hrs.
106	.0268	None initially	.0034	.016	Approx. 9 hrs.
17	.0142	.0142	.112	.017	44 min.
19	.0142	.0142	.112	<sup>b</sup>	8 hrs.
21	.0142	.0142	.112		2 hrs.
35	.0677	.0142	.056	.021	None
30	.0677	.0142	.065	.015	10 min. <sup>c</sup>
28	.0677	.0142	.065	.015	12 min. <sup>c</sup>

<sup>a</sup> The ( $IO_3^-$ ), ( $H_2O_2$ ) and  $k$  values for these experiments are concordant and lie within the limits given. <sup>b</sup> No rate constants obtained in these two experiments. <sup>c</sup> 30% hydrogen peroxide allowed to remain in contact with reaction mixture for several minutes without shaking; irregular induction often encountered at high ( $H_2O_2$ ).

TABLE V<sup>a</sup>

INDUCTION PERIOD EXPERIMENTS WITHOUT INITIAL IODATE ION		
( $H^+$ )	( $H_2O_2$ )	Induction period
0.9	0.005	8 hrs.
.2	.005	9 hrs.
.02	.005	14-21 hrs. <sup>b</sup>
.004	.005	8-11 days <sup>b</sup>
.0004	.005	$\infty$ <sup>c</sup>
Neutral	.005	$\infty$ <sup>c</sup>

<sup>a</sup> These experiments were carried out at room temperature. <sup>b</sup> Induction period within these limits. <sup>c</sup> These experiments will be mentioned in the section on mechanism.

Since an induction period is usually required to establish the necessary concentrations of those intermediate products essential to a reaction, it is logical here also to ascribe the initial delay to this cause. We shall assume that an induction period is necessary to build up the concentration of  $HIO_2$  requisite to the oxidation of iodine. This assumption is entirely in

accord with our previous conclusion that at low ( $\text{IO}_3^-$ )  $\text{HIO}_2$  oxidizes a large part of the iodide ion converted finally into iodate, for every experiment with ( $\text{IO}_3^-$ ) = 0.001  $M$  or less suffered an induction period.

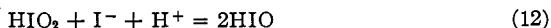
The building up in the reaction system of appreciable concentrations of  $\text{HIO}_2$  entails the lowering of ( $\text{I}^-$ ); for if ( $\text{I}^-$ ) is relatively high, the iodide ion will by reduction remove the first named substance. For this reason any factor tending toward either an increased initial ( $\text{I}^-$ ) (*e. g.*, low  $\text{H}^+$ ), or an incomplete removal of  $\text{I}^-$  (again low ( $\text{H}^+$ ), and low ( $\text{IO}_3^-$ )), or an increased formation of  $\text{I}^-$  (such as increased catalysis in which Reaction 11 is concerned) tends to lengthen the induction period.

In a system so complex that a large number of reactions is possible, the value of the rate constant may depend markedly on what reactions are favored in mixing the reactants. Experiments 35, 30 and 28, Table IV, represent one of two groups in which anomalous results were obtained because the 30% hydrogen peroxide used as a stock solution was left for an appreciable time in contact with the reaction mixture before shaking. Experiments 30 and 28 differ from 35 only in that respect. (The small difference in ( $\text{H}_2\text{O}_2$ ) is unimportant since experiments with ( $\text{H}_2\text{O}_2$ ) above 0.065 also gave constants of 0.02.) The induction period and the decrease in  $k$  which the first two experiments suffered we believe to be due to the large initial catalysis (with its consequent  $\text{I}^-$  formation) brought about by leaving the 30% peroxide in contact with the reaction mixture for several minutes.

Lower values of rate constants usually accompanied induction periods; if, in duplicate experiments, only one went through an initial delay, that one had the lowest  $k$  (*e. g.*, No. 35 as contrasted with Nos. 28 and 30). This behavior was general enough to warrant the belief that the subsequent ( $\text{I}^-$ ) concentration in an experiment with induction period was higher than it would have been had the smooth reaction begun immediately on mixing the reagents.

Because of the extreme unreproducibility of induction periods at high ( $\text{H}_2\text{O}_2$ ), no data are given for induction periods of experiments with ( $\text{H}_2\text{O}_2$ ) above 0.112  $M$ . We shall say only that, if 30% hydrogen peroxide is added to make a reaction mixture concentrated in that substance, it must be so added as to secure thorough initial mixing; for there may otherwise be a long delay before the oxidation of iodine begins.

The autocatalytic reaction terminating the induction period is, we believe, concerned with the removal of  $\text{I}^-$ . While an autocatalytic removal of  $\text{I}^-$  can be accomplished in devious ways, its beginning could well depend on the reaction



which has already been postulated to explain the removal of  $\text{I}^-$  at low ( $\text{IO}_3^-$ ); assigning this function to Reaction 12 harmonizes with the idea

that an induction period is necessary primarily to build up the concentration of  $\text{HIO}_2$ .

$\text{HIO}_2$  formation through Reaction 9 will explain the fact that the oxidation of iodine proceeds at all when  $(\text{IO}_3^-)$  is initially very low; if  $\text{HIO}_2$  formation only through the  $\text{IO}_3^- - \text{I}^-$  reaction is assumed, no such simple explanation is possible. Building up an appreciable  $(\text{HIO}_2)$  by the latter mechanism might take months<sup>16</sup> instead of the ten hours or so actually observed. These considerations furnish further evidence for the existence of  $\text{H}_2\text{I}_2\text{O}_3$ .

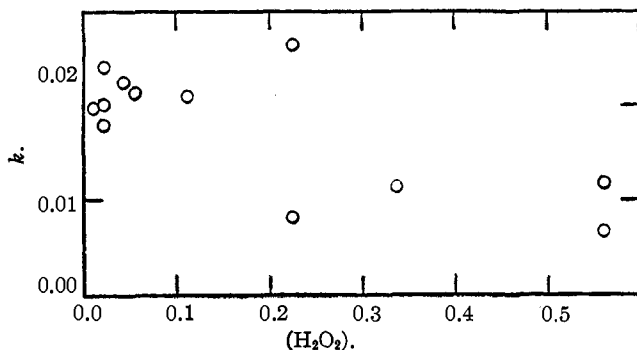


Fig. 4.—Variation of  $k$  with change in  $(\text{H}_2\text{O}_2)$ .  $(\text{H}^+) = 0.0677$ ;  
 $(\text{IO}_3^-) = 0.0142$ .

**Variation of the Rate Constant with  $(\text{H}_2\text{O}_2)$  and  $(\text{H}^+)$ .**—The behavior of  $k$  as  $(\text{H}_2\text{O}_2)$  is changed is shown in Fig. 4, as  $(\text{H}^+)$  is changed, in Fig. 5.

The curves show definitely that, for a rather large concentration range  $((\text{H}_2\text{O}_2)$  from 0.01 to 0.56  $M$ ;  $(\text{H}^+)$  from 0.015 to 0.9  $M$ ) neither hydrogen peroxide nor hydrogen ion exerts on the rate of Reaction 1 an effect proportional to the change in concentration. The figures show, however, that increasing  $(\text{H}_2\text{O}_2)$  or  $(\text{H}^+)$  does result in a lower value of  $k$ . In experiments at the higher

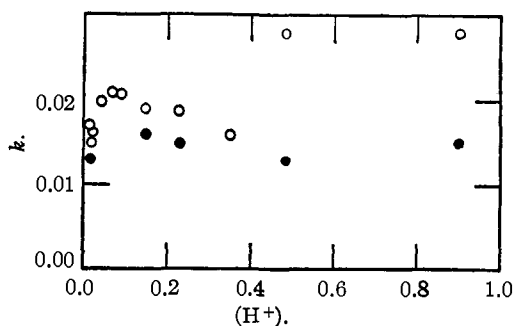


Fig. 5.—Variation of  $k$  with change in  $(\text{H}^+)$ .  $\circ$ , Earlier part of run, or complete run;  $\bullet$ , middle part of run.

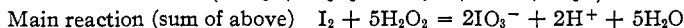
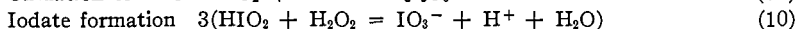
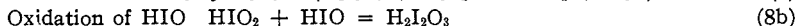
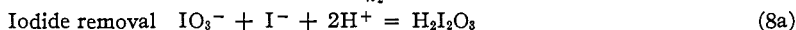
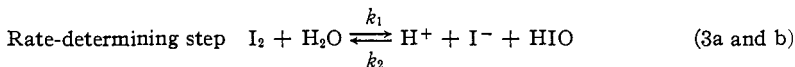
concentrations of acid,  $k$  often fell off to a reasonably constant lower value as the reaction proceeded; for such experiments both the higher and the lower values are plotted in Fig. 5—the lower value is indicated by a dot.

<sup>16</sup> At  $(\text{IO}_3^-) = 10^{-3}$ ,  $(\text{I}^-) = 10^{-2}$ ,  $(\text{H}^+) = 2(10^{-2})$ ,  $d\text{I}^-/dt$  calculated from Equation 6 is  $3(10^{-12})$  moles/liter/min.

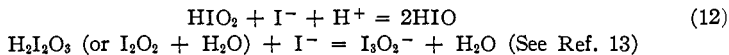
The tendency for  $k$  to decrease in a run, causing the experimental points to diverge from straight lines (*cf.* Figs. 1 and 2, especially Expts. 32, 73 and 71 in the latter figure) is probably related to the lower values of  $k$  obtained at high ( $H^+$ ) and high ( $H_2O_2$ ). Both effects can be explained in terms of iodine formation through Reaction 3b;  $k$  will remain constant as long as this iodine formation remains proportional to  $(I_2)$ , and  $k$  will become smaller when such iodine formation becomes relatively greater. These effects are found at high ( $H^+$ ) because hydrogen ion is involved in Reaction 3b, and at high ( $H_2O_2$ ) because catalytic decomposition of the peroxide brings about iodine formation in a manner already explained (see the section dealing with catalysis).

Results obtained in experiments where the initial ( $H_2O_2$ ) was insufficient for the complete oxidation of  $I_2$  are of interest. Experiment 78, Fig. 1, has a reaction curve typical for such experiments. The fact that the initial portions of the curves for these experiments are straight lines show that  $k$  is independent of ( $H_2O_2$ ) even to very low concentrations of that substance. The peculiar character of the reaction curve after the initial straight line portion is doubtless due to a readjustment of the intermediate iodine compounds in the system.

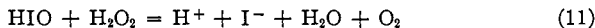
**Mechanism of the Oxidation.**—The foregoing sections have served to indicate certain reactions which may be assumed to explain the oxidation of iodine to iodate ion by hydrogen peroxide. The mechanism which has been devised to explain the empirical fact that iodine is oxidized to iodate ion in our reaction system must explain, qualitatively at least, the diverse experimental results obtained and be in harmony with past work on the chemistry of iodine. This mechanism will now be summarized.



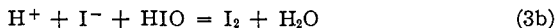
$I^-$  removal is accomplished also by



$I^-$  formation is accomplished also by



$I_2$  formation is accomplished only by



We may explain finally in terms of this mechanism why iodine is reduced to iodide by hydrogen peroxide, in dilute acid solution (below  $4(10^{-3}) N$ )

although that same oxidizing agent will convert it to iodate at concentrations of hydrogen ion greater than this. The two last experiments in Table IV show an infinite induction period with respect to iodate formation because at this low ( $H^+$ ) the iodide formed by the Reaction 11 cannot be effectively removed, and continues to accumulate until the "main" reaction occurring in the system is the catalytic decomposition of hydrogen peroxide by the  $I_2-I^-$  couple. When all the peroxide has been thus decomposed, the system consists of  $I_2$ ,  $\underline{H^+}$ ,  $I^-$  and HIO, with the substances underlined present at higher concentrations than obtain in an aqueous iodine solution.

As ( $H^+$ ) is increased, the formation of  $H_2I_2O_3$  in the second stage of the reaction mechanism is favored. When the ( $H_2I_2O_3$ ) has been thus sufficiently augmented to permit of the establishment of the ( $HIO_2$ ) essential to iodate formation, the iodine will, by the action of hydrogen peroxide, be converted to iodate instead of to iodide ion.

**The Specific Rate of Iodine Hydrolysis.**—Although the preceding sections have yielded a plausible mechanism for the oxidation of iodine by hydrogen peroxide, they have not established definitely the specific rate of the hydrolysis of iodine, the rate-determining step in that mechanism. With regard to the value of that constant, two possibilities, now to be sketched, present themselves.

The first of these, and the simpler, would assign to this specific rate the limiting value 0.03 given by Curve II, Fig. 3; the higher values on Curve I must then be attributed to an unknown reaction which consumes iodine and, directly or indirectly, involves iodate ion. Adopting this conclusion, we bring the investigations of Abel and investigations previously carried out in this Laboratory into complete agreement with the present work. We leave unsettled, however, not only the nature of this reaction, but a more troublesome matter as well, namely, why this reaction did not affect the experiments on Curve II; for these experiments differ essentially from the others only in a higher ( $H_2O_2$ ) 0.1 *M* compared with 0.0034 *M* on Curve I.

The other possibility would say that the limiting rate which should be reached at sufficiently high ( $IO_3^-$ ) had not yet been attained, that iodine formation from Reaction 3b is important at the beginning of an experiment as well as at the end,<sup>16</sup> and that the specific rate of the iodine hydrolysis is, at 0°, much greater than 0.06. The lower results on Curve II would be attributed to iodide formation resulting from the relatively larger amount of catalysis there obtaining. As arguments against this interpretation

<sup>16</sup> The high values calculated for ( $I^-$ ) and (HIO) in this reaction system (see footnote 14) support the conclusion that iodine formation from Reaction 3b is never negligible; but it must be remembered that the ( $I^-$ ) and the (HIO) calculated were both *upper limits*.



we may mention its disagreement with conclusions of other investigators, the excellent agreement of many experiments in this paper with a first order rate law, and the definite character (which may be fortuitous) of the limiting value approached by Curve II. One argument for this interpretation is the simplicity of the resulting mechanism, for then iodine need be assumed to disappear only in the step



and to be formed only in Reaction 3b. Experimental work, principally in other reaction systems, which should eliminate one of these possibilities has been undertaken in this Laboratory. Present indications point to a specific rate for Reaction 3a much greater than 0.6 at 25°, or 0.06 at 0°.

In the course of this investigation, and in the preparation of this paper as well, I have had the benefit of many conferences with Professor William C. Bray, and for these conferences I now wish to thank him.

### Conclusion

From an extensive investigation of the oxidation of iodine by hydrogen peroxide, evidence has been adduced for each step in a mechanism involving  $\text{H}_2\text{I}_2\text{O}_3$  as one of several intermediate products. While the complexities encountered have precluded the mathematical treatment essential to a definite establishment of this mechanism, the fact that it affords a qualitative explanation of these complexities justifies both its adoption and the further use of  $\text{H}_2\text{I}_2\text{O}_3$  as an intermediate step. Since the rate constant for the reaction should approach the specific rate for the iodine hydrolysis as a limit if the latter is the only rate-determining step, its failure to do so at low concentrations of peroxide could not be reconciled with previously measured values of this specific rate.

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