

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

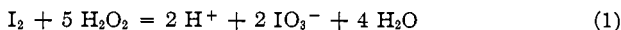
REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION. I. INTRODUCTION

BY WILLIAM C. BRAY AND HERMAN A. LIEBHAFSKY

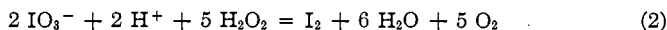
RECEIVED JULY 28, 1930

PUBLISHED JANUARY 12, 1931

Experimental data on the reactions that occur in acid solutions containing hydrogen peroxide, iodine and iodate ion will be presented in a series of papers. The rates of the following reactions have been measured: the oxidation of iodine to iodate



the reduction of iodate to iodine



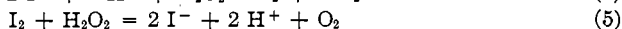
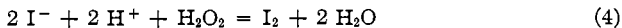
and the catalytic decomposition of hydrogen peroxide



Our investigation was undertaken¹ with the hope of finding an intimate relationship between this catalysis and Reactions 1 and 2, in which the peroxide acts, respectively, as an oxidizing agent and as a reducing agent.

Reactions 1 and 2 were demonstrated by Auger² in 1911, and, independently, by Caulkins¹ in 1916-1917, but no evidence was presented that they could be obtained free, or nearly free, from the catalysis reactions. Recent experiments, however, have shown that under favorable conditions the amount of hydrogen peroxide catalytically decomposed is not over 5% of that used in Reaction 1, or 40% of that used in Reaction 2, though it may be much greater under other conditions.

We shall first consider the experimental conditions for realizing these reactions and also the well-known reactions of hydrogen peroxide with iodide and iodine



The results of a number of qualitative experiments at room temperature are summarized in Table I; observations on catalytic decomposition of the peroxide and on tri-iodide formation are omitted to avoid confusion.

The complete *transformation* of iodide into iodine, Reaction 4, is possible at a sufficiently high concentration of hydrogen ion, as in Expt. *c*; the transformation of iodine into iodide, Reaction 5, may be accomplished without iodate formation by adding iodine (or tri-iodide) to an alkaline peroxide solution as in *d*. Both reactions may be demonstrated at a low concentration of hydrogen ion, as in Expts. *b* and *e*; in each case a steady

¹ Bray and Caulkins, *THIS JOURNAL*, **43**, 1262-1267 (1921).

² Auger, (a) *Compt. rend.*, **152**, 712-713 (1911); (b) *ibid.*, **153**, 1005-1007 (1911); (c) in 1905 Skrabal, *Chem.-Ztg.*, **29**, 554 (1905), reported iodate formation in acid solution as a result of the oxidizing action of hydrogen peroxide.

state is reached, which varies with the concentration of H^+ , I^- and I_2 , and in which Reaction 3 is the main or net reaction. This specific result was pointed out and studied quantitatively by Abel in 1908; his brilliant investigations³ have demonstrated that in this case the catalysis is completely accounted for by Reactions 4 and 5.

TABLE I
REACTIONS OF HYDROGEN PEROXIDE AT VARIOUS CONCENTRATIONS OF HYDROGEN ION

| | Reaction of H_2O_2 with | | | |
|------------------|--|--|---|---|
| | I^- | I_2 | $I_2 + IO_3^-$ | IO_3^- |
| $10^{-13} M H^+$ | a — | $d I_2 \longrightarrow I^-$ very rapid | $g I_2 \longrightarrow I^-$ very rapid | j — |
| $10^{-5} M H^+$ | $b I^- \longrightarrow I_2$ moderate rate | $e I_2 \longrightarrow I^-$ moderate rate | h — | $k IO_3^- \longrightarrow I_2$ and I^- very slow |
| $10^{-1} M H^+$ | $c I^- \longrightarrow I_2$ faster than e | f — | $i I_2 \longrightarrow IO_3^-$ rapid | $m IO_3^- \longrightarrow I_2$ faster than k |

At moderate concentrations of iodate and acid, as in Expts. i and m , another similar steady state is reached, which varies with the concentrations of hydrogen ion, iodate ion, iodine and hydrogen peroxide. In i the transformation of iodine into iodate, Reaction 1, takes place rapidly; while in m the much slower complementary reaction, 2, can be demonstrated easily only by removing the iodine as it is formed, *e. g.*, by extraction with carbon tetrachloride. In the latter case, if the iodine is not removed, the observed reaction is a slow catalytic decomposition of the peroxide. The demonstration of Reaction 2 is more easily accomplished at a somewhat lower concentration of hydrogen ion, since the steady state concentration of iodine is then larger. In alkaline solutions, however, as in Expt. j , the amount of iodate reduced (to iodide) is practically zero;⁴ the relatively rapid decomposition of the peroxide, $HO_2^- = OH^- + \frac{1}{2}O_2$, prevents the detection of the extremely slow reduction of the iodate.

Both iodate and acid are necessary for the immediate and rapid oxidation of iodine to iodate, Expt. i . Thus in the absence of iodate, as in Expt. f , iodine in solution with hydrogen peroxide and acid remains apparently unchanged for several hours before being oxidized. Small initial concentrations of iodate shorten the induction period; but Reaction 1, when once

³ Abel, (a) *Z. Elektrochem.*, **14**, 598-607 (1908); (b) *Monatsh.*, **41**, 405-421 (1920); (c) *Z. physik. Chem.*, **96**, 1-179 (1920); (d) *ibid.*, **136**, 161-182 (1928).

⁴ This is in agreement with the results of Skrabal, *Monatsh.*, **32**, 868 (1911), and of Tanatar, *Ber.*, **32**, 1013 (1899); **33**, 205 (1900). At sufficiently low concentrations of hydroxide ion some reduction to iodide is easily demonstrated. Thus in experiments by Caulkins at 60°, in which the initial concentrations were 0.094 *M* KIO_3 , 0.193 *M* H_2O_2 and (α) 0.022 *M* $NaOH$, (β) 0.0026 *M* $NaOH$, and the colorless solutions were acidified after nearly all the peroxide had decomposed, appreciable amounts of iodine were formed in (β), but not in (α). By assuming the ionization constant $(H^+)(HO_2^-)/(H_2O_2) = 2.5 \times 10^{-12}$, the initial OH^- concentration is found to be approximately 3×10^{-4} *M* in (α) and 3×10^{-5} *M* in (β).

started, proceeds at a rate that is not greatly influenced by changes in the concentrations of iodate, acid and peroxide. Similarly, on lowering the acid concentration in the presence of iodate, induction periods are again encountered; these increase in length until finally Reaction 1 does not take place in the neighborhood of the hydrogen-ion concentration of Expt. *h*.⁵ Reaction 1 is thus seen to be autocatalytic only in the sense that the products, iodate and hydrogen ions, eliminate the induction period.

On account of the speed with which iodide, iodate and hydrogen ions react when all are present at rather low concentrations, it is evident from the above results that Reaction 1 takes place only when the iodide concentration does not exceed an extremely small value. Iodide, when present, as in the work of Abel,³ would react with, or prevent the formation of, intermediate products which are necessary in the oxidation of iodine by hydrogen peroxide. This explanation may not suffice when the solution is alkaline or the concentration of hydrogen ion is very small, but in these cases intermediate products, as hypoiodite, are reduced very rapidly to iodide ion by the peroxide (*cf.* Expts. *g* and *d* in Table I). It is thus not surprising that Abel⁶ found no trace of iodate in any of his experiments with Reactions 4 and 5 and the related catalysis.

The elimination of the induction period in Reaction 1 involves a transition from the iodide to the iodate regions, *e. g.*, from *b e* to *i m* in Table I. The periodic reaction,¹ announced in 1921 as the first example of periodicity in homogeneous solutions, also lies in this transition region, and illustrates its complexity. Rice and Reiff⁷ have questioned this claim of homogeneity, and ascribe the periodicity to the presence of minute dust particles. As we have not repeated the experiments of Rice and Reiff, and our own investigation of the periodicity is by no means complete, we have nothing definite to contribute on this question. We must state, however, that in 1922 Bon repeated and extended Caulkins' measurements on periodic oxygen evolution at 60°. Also in our recent work Liebhafsky has made some incidental observations on periodicity in oxygen evolution at 50° and in iodine formation at 0°. On account of the regularity of the results, and their occurrence in the transition region referred to above, we still believe it possible that the periodicity depends on a system of homogeneous reactions, at least one of which is autocatalytic.

While Brode⁸ seems to have been the first to state clearly the role of hypoiodite as an intermediate step both in the catalytic decomposition of hydrogen peroxide in an initially neutral iodide solution and in Reaction

⁵ An effect of the addition of acid similar to that in the series *d e f*, and the final transition to iodate formation, were noted by Skrabal in 1905; Ref. 2 c.

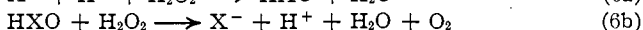
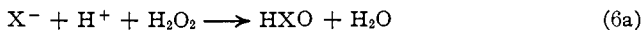
⁶ Abel, Ref. 3 c, p. 30.

⁷ Rice and Reiff, *J. Phys. Chem.*, **31**, 1352 (1927).

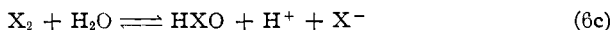
⁸ (a) Brode, *Z. physik. Chem.*, **49**, 208 (1904); (b) *cf.* Bray, *ibid.*, **54**, 485 (1906).

4, we owe to Abel³ the complete demonstration of the *mechanism* of the iodide-iodine reactions with hydrogen peroxide. His conclusions and those of Bray and Livingston,⁹ in the case of the analogous bromide-bromine-peroxide reactions, are in close agreement, and thus support each other. In fact, these investigations furnish two examples in which the proof of mechanism may be regarded as satisfactory. For the mathematical treatment of the results the reader is referred to the original articles, particularly References 9 a, 9 c and 3 d.

All bromide-bromine reactions with hydrogen peroxide in dilute acid solutions depend upon only two rate-determining steps



and the relatively rapid reversible reaction



Corrections in the concentrations of bromide ion and bromine due to

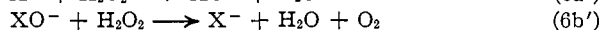
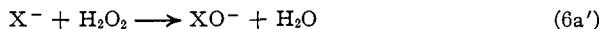


are in general small. The ionization of hypobromous acid can be neglected except in alkaline solutions



In the case of pure catalysis the absolute rates of the two compensating reactions, 6a and 6b, are equal at any instant; but the specific reaction rate of the third order reaction, 6a, is extremely small in comparison with that of the second order reaction, 6b, with the result that the steady state concentration of HXO is always extremely small compared with that of X⁻.

In the iodide-iodine reaction 6a and 6b are each accompanied by a second reaction



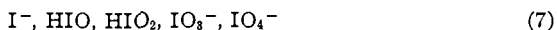
At low concentrations of hydrogen ion Reaction 6a can be neglected in comparison with 6a', but both 6b and 6b', and therefore the equilibrium 6e, must be considered. The concentration of tri-iodide ion is in general much greater than that of iodine, 6d. Finally, and this is the most serious difficulty, the hydrolysis equilibrium, 6c, is not established sufficiently rapidly to prevent the direct and reverse reactions from appearing as rate-determining steps in many of the experiments.^{3d}

The mechanism of the iodine-iodate-hydrogen peroxide reactions undoubtedly involves intermediate substances, such as I⁻, HIO and HIO₂, which are present at very small concentrations. The number of such compounds that may be postulated is very great, and any discussion of inter-

⁹ (a) Bray and Livingston, THIS JOURNAL, 45, 1251 (1923); (b) 2048 (1923); (c) 50, 1654 (1928); (d) Livingston, *ibid.*, 48, 53 (1926).

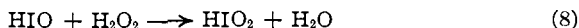
mediate reactions which is qualitative in character or based on incomplete data must be regarded as tentative. The present introduction, accordingly, is intended merely to pave the way for the discussion of mechanism in later papers.

The simplest direct line between iodide and periodate in acid solution is represented by the series



Hypoiodous acid is an extremely weak acid.¹⁰ Iodous acid, which has not been isolated, is to be regarded as a fairly weak acid by analogy with chlorous and nitrous acids, and the remaining three acids are relatively strong electrolytes. While it is practically certain, on the basis of free energy considerations^{1,9a} alone, that hydrogen peroxide is capable of oxidizing each substance in the list (except IO_4^-) and of reducing each (except I^-) in reactions similar to 6a and 6b, the speed of several of these reactions must be concluded to be negligibly small on account of either known stoichiometric results, or the effect of other oxidation-reduction reactions.

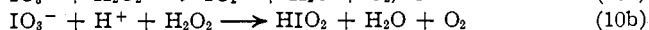
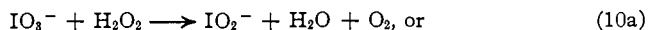
Thus Reaction 5 has been isolated by Abel,^{3c} free from catalysis, Reaction 3; it follows that under his experimental conditions the rate of the reaction



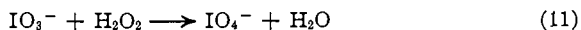
is negligible in comparison with that of



since any HIO_2 formed in 8 would be reduced by H_2O_2 or by $\text{I}^- + \text{H}^+$, thus giving catalytic decomposition as the net result. We shall assume that Reaction 8 remains negligible in comparison with 9 at the higher acid concentration of our experiments, and at all concentrations of HIO and H_2O_2 . Similarly we may conclude, from our evidence as to the isolation of Reaction 2, that the reaction



is more rapid than

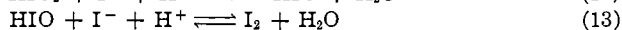
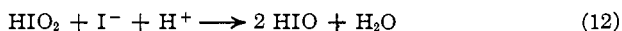


If the formation of periodate were the only primary step in this reaction, as suggested by Tanatar⁴ to account for the catalytic action of iodic acid, then the amount of peroxide decomposed catalytically would be at least 80% in excess of that required by Equation 2, which is much greater than the lowest figures in our experiments. The assumption that HIO_2 and IO_2^- are the primary products in the reduction of IO_3^- by H_2O_2 is in agreement with our rate measurements; and we have, somewhat arbitrarily it is true, omitted IO_4^- from further consideration.

¹⁰ Fürth, *Z. Elektrochem.*, **28**, 57 (1922), gives 10^{-11} as an approximate value for its ionization content at 25°.

The possibility of the oxidation of iodide ion by hydrogen peroxide, Reactions 6a and 6a', must be rejected on account of the presence of acid and iodate. Under these conditions, as has already been indicated in this paper, iodide is oxidized much more rapidly by iodate¹¹ than by hydrogen peroxide.¹² However, this rapid iodate-iodide reaction is probably also relegated to the background (except in induction periods) by the reaction between iodous acid, I⁻ and H⁺, which must have an extremely high specific rate.

Accepting the convention that second and third order reactions are more probable than those of higher orders, we shall write this reaction in two steps

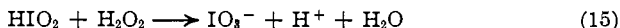


The equilibrium in 13 (*cf.* 6c) is assumed to be maintained except in the very rapid oxidation of iodine to iodate, Reaction 1.

The reduction of HIO₂ by H₂O₂ is also conceivable



but this reaction cannot be considered apart from the oxidation of HIO₂ by H₂O₂



The latter seems to be a necessary step in the very rapid oxidation of I₂ to IO₃⁻, Reaction 1, in the presence of moderate concentrations of H⁺ and IO₃⁻ (*cf.* *i* in Table I). Our evidence on the isolation of Reaction 1, nearly free from catalysis, leads to the conclusion that under these conditions the specific rate of Reaction 15 is very great in comparison with that of 14.

The hydrogen peroxide reactions in acid solution that have not been eliminated by the foregoing conclusions are Nos. 9 and 10 in which the peroxide acts as a reducing agent, and No. 15 in which it acts as an oxidizing agent.

The series of intermediate reactions, 10-12-9-13, is in substantial agreement with our rate data for Reaction 2; Nos. 10 and 15 account partly, but far from completely, for the catalysis, and the following steps are available to explain Reaction 1: the hydrolysis of iodine (the reverse of No. 13), the oxidation of iodide presumably to hypoiodous acid by iodate¹¹ and by iodous acid (No. 12), and the oxidation of iodous acid by hydrogen peroxide (No. 15). It will be noted that in the last series an additional assumption is necessary to account for the rapid oxidation of iodine above the hypoiodite state. Several possibilities are being con-

¹¹ (a) Abel and Stadler, *Z. physik. Chem.*, **122**, 49 (1926); (b) Abel and Hilferding, *ibid.*, **136**, 186 (1928); (c) Dushman, *J. Phys. Chem.*, **8**, 453 (1904); (d) Skrabal, *Z. Elektrochem.*, **28**, 224 (1922); **30**, 109 (1924).

¹² (a) Harcourt and Esson, *Phil. Trans.*, **157**, 117 (1867); (b) Noyes and Scott, *Z. physik. Chem.*, **18**, 118 (1895); (c) *cf.* Bray, *ibid.*, **54**, 486 (1906).

sidered and will be discussed in later papers. At the present time the favored explanation involves the intermediate substance, $\text{H}_2\text{I}_2\text{O}_3$ or I_2O_2 , discussed by Bray in a recent paper.¹³

Summary

The experimental conditions under which the various reactions of hydrogen peroxide in acid solutions containing iodine and iodate or iodide take place have been discussed, and the mechanism of these reactions briefly considered.

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

REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION.

II. THE PREPARATION OF IODIC ACID. PRELIMINARY RATE MEASUREMENTS

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RECEIVED JULY 28, 1930

PUBLISHED JANUARY 12, 1931

On the basis of our first experiments on the oxidation of iodine to iodic acid by hydrogen peroxide (Reaction 1, Part I),¹ a method of preparing iodic acid and iodine pentoxide on a small scale was outlined for use in an undergraduate course. While this method is not as satisfactory as the more recently developed one in which a concentrated solution of chloric acid is the oxidizing agent,² its description affords a convenient way of presenting a number of experimental results.

Materials.—Ten grams of very finely divided iodine (resublimed, crystalline iodine is far less satisfactory than that recovered from an iodide solution by precipitation with an oxidizing agent, as chlorine, or hydrogen peroxide at high acid concentration); 10 cc. of concentrated nitric acid; 300–400 cc. of 3% hydrogen peroxide, which is 1.5 to 2 times the theoretical amount required.

Directions.—Place the iodine, nitric acid and about 50 cc. of the peroxide solution in a 750-cc. flask and heat the mixture in a water-bath at about 70°. To minimize the loss of iodine vapor, place a loosely-fitting glass stopper or small funnel in the mouth of the flask. Shake the flask frequently when the solution does not show a deep color due to dissolved iodine. Observe when the reaction starts, as shown by the first decrease in color. Whenever the solution again becomes deeply colored, add more hydrogen peroxide. Continue until the solid iodine (or the hydrogen peroxide) is consumed. Evaporate the solution rapidly to a small volume.

¹³ Bray, *THIS JOURNAL*, **52**, 3580 (1930).

¹ Part I. Bray and Liebhafsky, *THIS JOURNAL*, **53**, 38 (1931).

² Lamb, Bray and Geldard, *ibid.*, **42**, 1636 (1920).