

sidered and will be discussed in later papers. At the present time the favored explanation involves the intermediate substance, $H_2I_2O_3$ 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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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).

To remove the nitric acid and the organic substances introduced with the peroxide, evaporate the solution to dryness in a small porcelain dish; heat the residue in a drying oven for at least two hours, at first at 140–150° and later at 170–180°; extract the iodic acid with boiling water, filter off and reject the dark-colored residue. Evaporate the solution to dryness, and partially dehydrate the solid by heating it in a drying oven at 150–200°, carefully avoiding overheating.

If the product is still dark-colored, add some concentrated nitric acid and treat the mixture again as described in the preceding paragraph, or proceed as follows.

To prepare crystalline iodic acid, HIO_3 , dissolve nearly all of the partially dehydrated solid in the minimum amount of hot water, filter, cool the filtrate, place the clear solution in a crystallizing dish in a vacuum desiccator over anhydrous calcium chloride and seed with a crystal of iodic acid if this is necessary. Finally, reject the mother liquor when only a small portion remains, and wash the crystals with a few drops of cold water.

Notes.—While in 0.1 *N* acid at 25° the reaction between iodine and hydrogen peroxide will not start for several hours, it starts rapidly at a temperature of 70–80° when the acid concentration is molal or greater. When once started the reaction in the solution is rapid even at a low temperature, and the limiting factor is the rate of solution of the solid iodine. For this reason the high temperature is maintained, finely divided iodine is used, and the mixture is shaken frequently. Since hydrogen peroxide reacts also with iodic acid (*cf.* Expt. *m*, Part I), catalytic decomposition is unavoidable; a 50% excess of peroxide is required in the procedure as here outlined, but much more may be used if the shaking is neglected.

The process would be much more satisfactory if hydrogen peroxide were available at higher concentration and free from preservative. The organic material is partially decomposed and rendered insoluble in the evaporation and subsequent heating, presumably on account of the presence of the nitric acid; but the product is not as white as that obtained with chloric acid.²

The yield with respect to iodine is practically quantitative. There is danger of loss by decomposition during the heating of the solid product only if the temperature is not properly controlled, but the permissible temperatures are lower than for material prepared by the chloric acid method,³ and our product is thus less completely dehydrated.

The Rate of Oxidation in Homogeneous Solution.—In agreement with the observation, noted above, that the reaction proceeds rapidly when once started, it was found that the reaction also starts rapidly when *iodate* and acid are present initially. The kinetic investigation of this reaction in homogeneous solution was then undertaken. Nearly all the measurements were made at 25°.

³ *Cf.* Ref. 2, pp. 1644–1645.

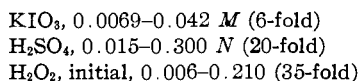
A large quantity of a nearly saturated solution of iodine in conductivity water was kept in a thermostat in contact with finely divided iodine, and portions were withdrawn through an asbestos filter. Standardized stock solutions of potassium iodate, sulfuric acid and hydrogen peroxide were also suspended in the thermostat. In each experiment known amounts of iodate and acid were added to a known volume of the iodine solution, the mixture was shaken, after ten minutes a measured volume of the peroxide solution was added rapidly and the mixture was again shaken. The rate was followed by determining the concentration of iodine in samples pipetted out of the reaction mixture. On account of the high speed of the reaction the first samples were withdrawn as rapidly as possible. The first order rate constant was calculated for successive pairs of results by means of the formula

$$k = \frac{2.3}{t_{n+1} - t_n} \log \frac{(I_2)_n}{(I_2)_{n+1}} \quad (1)$$

The units are moles per liter and minutes. The time at which half the peroxide had been added was recorded as t_0 . The initial concentration of iodine, $(I_2)_0$, was calculated from the concentration of the stock solution and the volumes of the various solutions taken. A reasonable check was furnished by the analysis of the first sample in a few cases in which there was a noticeable induction period.

The reaction was stopped by adding each sample withdrawn for analysis to carbon tetrachloride and shaking the mixture at once. The time of shaking was recorded as t_n . The corresponding concentration of iodine, $(I_2)_n$, was determined by carefully separating the phases as soon as was convenient, adding the carbon tetrachloride layer to a solution of potassium iodide, and titrating with thiosulfate. Sources of error and further experimental details will be discussed in a later paper. At the present time it is sufficient to note that fairly definite results were obtained by increasing the number of identical or similar experiments.

Thirteen sets of experiments were performed at 25°, with enough duplicates to bring the total to twenty-eight. The range of concentrations covered was as follows



Typical results are shown in Fig. 1. Values of k are plotted against the concentration of iodine, each concentration being the mean of the initial and final values used in calculating k . To show the high speed of the reaction, the successive time intervals in Expt. A are recorded, in minutes: 1.08, 0.58, 0.59, 0.67, 1.25, 1.02, 28.17. The half time is approximately one minute.

All the experiments were in accord with the following conclusions: the

values of k are nearly constant at concentrations of iodine from $1 \times 10^{-3} M$ to $3 \times 10^{-4} M$ (and in some cases to $1.5 \times 10^{-4} M$), but always fall off markedly at lower concentrations; the "constant" is independent of the concentrations of iodate, acid and peroxide within the ranges investigated. The average, $k = 0.6 \pm 0.1$, was chosen at the time; but single values sometimes deviated from this by as much as ± 0.3 , and the possibility of a gradual decrease of k during a run was not excluded.

Four experiments at 0° , in which the concentrations of iodate and acid were close to $0.018 M$ and $0.12 N$ and that of the peroxide was varied between 0.033 and $0.093 M$, gave an average value of k of 0.027 ± 0.002 ; but this should be neglected for the present, since the iodate and acid were not varied.

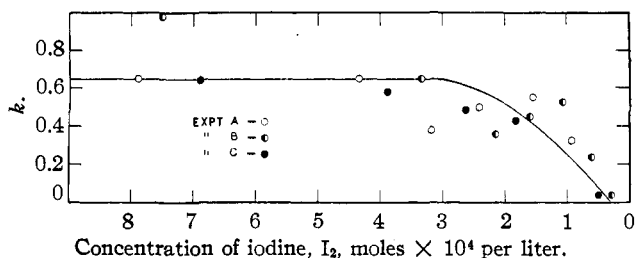


Fig. 1.—Values of the specific reaction rate in three experiments. Initial concentrations: in Expts. A and B, $0.010 M$ KIO_3 , $0.130 N$ H_2SO_4 , $0.106 M$ H_2O_2 ; in Expt. C, $0.031 M$ KIO_3 , $0.130 N$ H_2SO_4 , $0.042 M$ H_2O_2 .

In 1920 similar measurements were made at 25° by Bray and Dr. Harry East Miller, to determine whether the earlier results could be checked, and whether traces of chloride ion played an important role in the reaction. The accelerating effect of chloride had been stressed by Auger (Ref. 2 a, Part I). The only difference in procedure was that the iodine was dissolved in an iodic acid solution instead of in distilled water.

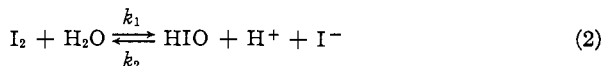
In several experiments with $0.045 M$ HIO_3 and 0.013 to $0.042 M$ H_2O_2 , k was again found to be 0.6 , and the variations were within ± 0.1 or less, down to a concentration of iodine between 1 and $2 \times 10^{-4} M$.

In two experiments with higher peroxide concentration, $0.086 M$ and $0.045 M$ HIO_3 , a decrease of k from 0.6 to about 0.4 was observed in the iodine range where constancy had been observed in other cases. Also, when the iodate concentration was decreased to $0.0090 M$, lower values of k were obtained: approximately 0.3 with iodic acid alone, and 0.5 when enough sulfuric acid was added to make the acid concentration $0.045 N$. The earlier statement as to the constancy of k must therefore be regarded as approximate rather than exact.

The effect of the presence of chloride is shown by the results of experiments with $0.045 M$ HIO_3 and $0.013 M$ H_2O_2 , in which the initial concentra-

tions of chloride due to added potassium chloride were 0.0, 0.268×10^{-4} and $1.34 \times 10^{-4} M$; the corresponding values of k were 0.6, 0.66 (constant), and 1.0 (decreasing to 0.8). It is evident that the amount of chloride impurity present in our solutions was too small to influence the results.

The simplest interpretation of our results is that the first order reaction is the rate of hydrolysis of iodine, and that the rapid decrease of k at low iodine concentration is due to the effect of the reverse reaction as the hydrolysis equilibrium is being approached. From a consideration of the equations



$$-d(I_2)/dt = k(I_2) = k_1(I_2) - k_2(HIO)(H^+)(I^-) \quad (3)$$

it is evident that k , calculated from the experimental data by means of Equation 1, will be equal to k_1 , when $k_2(HIO)(H^+)(I^-)$ is negligible in comparison with $k_1(I_2)$ provided that (2) is the only reaction in which iodine is being consumed.

The probability of a direct relation to the rate of iodine hydrolysis was recognized from the first; but we hesitated to publish this conclusion before additional evidence was available. This has now been supplied by the recent work of Abel, referred to in Part I (Ref. 3 d), on the reaction of iodine and iodide with hydrogen peroxide (in the absence of iodate); and our results in turn furnish a confirmation of the mechanism he proposes. By means of a mathematical analysis of these reactions, and his own experimental data at 25° for 0.4 M sodium acetate solutions, he concluded that $k_1 = 0.25$. Higher values 0.38-1.1 were obtained from less extensive data for more concentrated acetate solutions, but were considered less reliable. The agreement between our "constant," 0.6 and Abel's values of k_1 , is very striking.

We have concluded that the oxidation of iodine by hydrogen peroxide furnishes a direct method of investigating the rate of hydrolysis of iodine, Equation 2.

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