[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Reaction between Ferrous Iron and Peroxides. I. Reaction with Hydrogen Peroxide in the Absence of Oxygen[1]

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In a previous paper[2] the mechanisms which have been proposed for the reaction between ferrous iron and hydrogen peroxide have been reviewed. Two mechanisms which appear equally satisfactory are those of Bray and Gorin[3] and of Haber and Weiss.[4,5] In both mechanisms the primary step is assumed to be unimolecular in ferrous iron and hydrogen peroxide, and to result in the formation of a highly active intermediate. This intermediate is ferryl iron, FeO^{++}, in the former mechanism, and the hydroxyl radical, $HO\cdot$, in the latter. For simplicity, attention is focused in the present paper upon the more familiar mechanism of Haber and Weiss. The steps proposed by Haber and Weiss are

$$Fe^{++} + H_2O_2 = Fe^{+3} + OH^- + HO\cdot \quad (1)$$

$$HO\cdot + H_2O_2 = H_2O + HO_2\cdot \quad (2)$$

$$HO_2\cdot + H_2O_2 = O_2 + H_2O + HO\cdot \quad (3)$$

$$HO\cdot + Fe^{++} = Fe^{+3} + OH^- \quad (4)$$

The active intermediate ($HO\cdot$) can react with ferrous iron, hydrogen peroxide or other components contained in the reaction mixture. Reaction with ferrous iron leads to the stoichiometric over-all reaction (sum of steps (1) and (4))

$$2Fe^{++} + H_2O_2 + 2H^+ = 2Fe^{+3} + 2H_2O \quad (I)$$

while reaction with hydrogen peroxide leads to induced decomposition of hydrogen peroxide (sum of steps (2) and (3))

$$2H_2O_2 = 2H_2O + O_2 \quad (II)$$

If the reaction mixture contains only ferrous iron, hydrogen peroxide, water and sulfuric acid, the free radical reaction with ferrous iron predominates, unless hydrogen peroxide is present in large excess over ferrous iron. Under the latter circumstances some of the intermediates decompose hydrogen peroxide. Consideration of the reaction in this simple system, on the basis of either mechanism mentioned above, leads to the following expression for the instantaneous consumption ratio, n

$$n = \frac{d(H_2O_2)}{d(Fe^{++})} = 0.5 + \frac{k_a}{k_b}\frac{(H_2O_2)}{(Fe^{++})} \quad (5)$$

where k_a and k_b represent the rate constants for reaction of the active intermediate with hydrogen peroxide or ferrous iron, respectively. This expression was derived theoretically and confirmed experimentally by Haber and Weiss; the value of k_a/k_b is of the order of 2×10^{-2} at 20°, depending somewhat upon the acidity.

The rate law for the *stoichiometric* reaction (I) which would be expected on the basis of either of the above mechanisms

$$-\frac{d(Fe^{++})}{dt} = \frac{2d(H_2O_2)}{dt} = k_4(Fe^{++})(H_2O_2) \quad (5a)$$

was established experimentally by Baxendale, Evans and Park,[6] who found an average value of k_4 of 62 liters $mole^{-1}$ $sec.^{-1}$ at 25°.

The reaction between hydrogen peroxide and ferrous iron becomes of special interest when carried out in the presence of other compounds with which the active intermediate can react. The polymerization of vinyl monomers may be initiated in this way,[6] the free radical reacting with the monomer and thus initiating the polymerization. The oxidation of many organic compounds by hydrogen peroxide is induced by the ferrous iron–hydrogen peroxide reaction; this is known as a Fenton reaction. For example, it is shown in the experimental part that ethanol is oxidized to acetaldehyde when it is present in the reaction mixture of hydrogen peroxide and ferrous iron.

The reaction between ferrous iron and organic hydroperoxides is widely used for the determination of these compounds, especially when they are present in very small amounts. This reaction results in a ratio of moles of ferrous iron to hydroperoxide reacted which may be much smaller or much larger than the stoichiometric ratio dependent on whether oxygen is absent or present. Similar deviations from the stoichiometric ratio are found in the reaction between hydrogen peroxide and ferrous iron in the presence of various organic substances. The present paper deals with a study of these deviations in the absence of oxygen; in a subsequent paper the results of a similar study in the presence of oxygen will be presented. These studies have yielded insight into the side reactions which occur in the reaction between ferrous iron and organic hydroperoxides, which will be reported in a future paper.

Experimental

In adopting a technique for the study of the re-

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(1) This investigation was started under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Synthetic Rubber Program of the United States Government.

(1a) From a thesis submitted by A. I. Medalia to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the doctor's degree (July 1948).

(2) A. I. Medalia and I. M. Kolthoff, *J. Polymer Sci.*, **4**, 377 (1949).

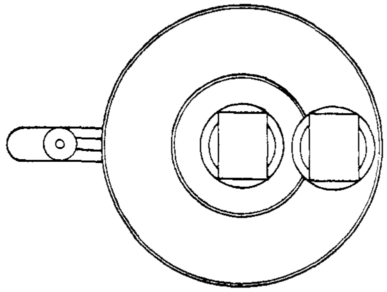
(3) W. C. Bray and M. H. Gorin, THIS JOURNAL, **54**, 2124 (1932).

(4) F. Haber and J. Weiss, *Naturwiss.*, **20**, 948 (1932).

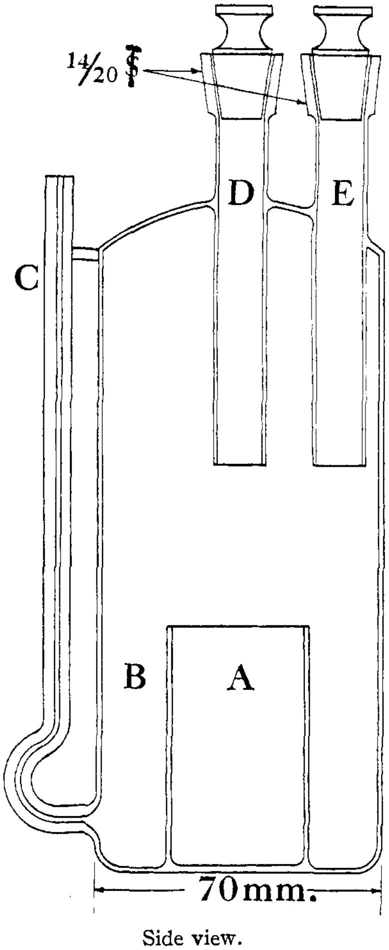
(5) F. Haber and J. Weiss, *Proc. Roy. Soc.*, **A147**, 332 (1934).

(6) J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).

action between hydrogen peroxide and ferrous iron in the absence of oxygen, the following factors were considered: (1) exclusion of oxygen must be thorough, (2) mixing should be rapid, (3) the reaction vessel should be free from contamination by organic matter, such as stopcock grease. Reaction vessels were constructed as shown in Fig. 1. Experiments in the absence of oxygen have been carried out as follows.



Top view.



Side view.

Fig. 1.—Reaction vessel.

Procedure.—Purified nitrogen is passed through the capillary side-tube C, and through inlet tubes inserted through the tubes D and E, for at least ten minutes. The solutions which are to be added are flushed with nitrogen, in vessels provided with tubes similar to D and E, for at least thirty minutes. Aliquots are withdrawn with nitrogen-filled pipets, which are then inserted all the way through tubes D and E before draining. Solutions are introduced into compartment A through inlet tube D, and into compartment B through inlet tube E. The nitrogen inlet tube is removed from D or E immediately before inserting the pipet; however, nitrogen is continually passed through the other of these tubes, and through the capillary side-arm. When the solutions have all been added, the tubes D and E are flushed with nitrogen by keeping one tube stoppered tightly and the other loosely (alternately) while passing nitrogen through the capillary. The tubes are then stoppered tightly and the vessel is shaken vigorously for about fifteen seconds. One stopper is then loosened and nitrogen is passed through the side-arm. Aliquots are removed with a pipet, and the ferrous iron is titrated. Evidently the total volume of solution added to the vessel must be known accurately.

When the above procedure is followed, complete mixing appears to be brought about in one second (three strokes). Calculation on the basis of the rate law[4] and rate constant given above shows that in a solution initially $2 \times 10^{-3}\ M$ in ferrous iron and $5 \times 10^{-4}\ M$ in hydrogen peroxide (typical conditions used in the present work), the stoichiometric reaction is 11.4% complete in one second. Thus under the experimental conditions, only a minor portion of the reaction can take place before mixing is complete.

In the experiments reported in this paper, 25 ml. of acid (generally 1.5 N sulfuric) was placed in A and 75 ml. in B. Solutions of the organic substance and ferrous iron were placed in B and of hydrogen peroxide in A. The total volumes of solution were 120–130 ml., and 50-ml. aliquots were titrated ten and twenty minutes (or fifteen and thirty minutes), respectively, after mixing, with ceric sulfate solution of the proper concentration, using ferrous *o*-phenanthroline perchlorate as indicator. Good end-points were obtained with 0.001321 N cerate solution, which was the most dilute cerate solution used, using comparison flasks in the detection of the end-point. No interference in the titration of iron was found in the presence of ethanol or acetaldehyde. All experiments were carried out at room temperature (25–30°).

To test completeness of removal of oxygen by the above procedure, solutions of ferrous iron and alkali pyrophosphate were flushed with nitrogen in the separate compartments of the reaction vessel, then mixed and allowed to stand for fifteen minutes. Titration of aliquots showed that the extent of air oxidation of ferrous iron was negligible.

Reagents.—Water: Twice-distilled water was redistilled from alkaline permanganate in an allglass still; the middle three-fifths portion was used. Sulfuric acid was du Pont (Grasselli) reagent grade; ferrous sulfate heptahydrate, Merck reagent grade; hydrogen peroxide, Merck Superoxol (30%), C.P.; sodium perchlorate, G. F. Smith Co. Other inorganic compounds were C.P. or reagent grade. Ethanol, absolute ethanol was refluxed with aluminum and sodium hydroxide, then distilled; acetic acid, du Pont (Grasselli) reagent grade; acetone, C.P., freshly distilled; acetaldehyde, Eastman Kodak Co. "White Label" grade; methanol, C.P., freshly distilled; nitrogen, pre-purified nitrogen, obtained from Air Reduction Co. (Seaford works) and from Linde Air Co.

The dilute cerate solutions for titration were made up daily by dilution with 1 *N* sulfuric acid of a 0.1321 *N* stock solution (standardized against Bureau of Standards arsenious oxide). Both the ferrous solution and the hydrogen peroxide solution were standardized daily against the dilute cerate solution. The ferrous *o*-phenanthroline end-point was not sharp in the titration of dilute hydrogen peroxide with dilute cerate, and for this reason a known amount of ferrous solution was added after the approximate end-point, and the excess ferrous iron was back-titrated with cerate.

Results and Discussion

Results Obtained in the Presence of Sulfuric Acid and Ethanol.—In the present experiments attention is focused upon the stoichiometry of the reaction between ferrous iron and hydrogen peroxide in the presence of various other compounds, while in a later section there is described a brief study of the products formed. The stoichiometry was determined simply by titration of the ferrous iron remaining after carrying out a reaction under conditions such that the hydrogen peroxide taken was completely consumed; completeness of reaction was tested by titration of aliquots taken after two different reaction times; qualitative tests (with titanic sulfate or potassium ferricyanide) established whether ferrous iron or hydrogen peroxide remained in the mixture after completion of the reaction.

Results obtained for the reaction in sulfuric acid solutions in the presence of various concentrations of ethanol are shown in Table I. This table, as well as all other tables in this paper, gives analytical data obtained for the reaction between ferrous iron and hydrogen peroxide, in the absence of oxygen, according to the above procedure. The initial concentrations of ingredients given are those which would be present immediately after mixing if no reaction had taken place during mixing. The column headed "Molar ratio, (Fe^{++}) reacted/(H_2O_2) taken" gives the results of the titrations. Each figure given in this column is an average obtained with aliquots from a single reaction mixture after reaction times differing by a factor of two. Since in all experiments, therefore, the concentration of hydrogen peroxide taken was equal to the concentration of hydrogen peroxide reacted, this column gives the values of the over-all reaction ratio, which may be designated as

$$R = \frac{\text{moles } (Fe^{++}) \text{ reacted}}{\text{moles } (H_2O_2) \text{ reacted}} = \frac{\Delta(Fe^{++})}{\Delta(H_2O_2)} = \frac{1}{\bar{n}}$$

The stoichiometric value of R is 2. The significance of the induction factor is discussed below.

TABLE I

REACTION IN 1.5 *N* SULFURIC ACID IN THE PRESENCE OF ETHANOL

Initial concentrations		Molar ratios		
Ethanol, M	Fe^{++} ($M \times 10^3$)	Initial $\frac{(Fe^{++})}{(H_2O_2)}$ taken	$\frac{(Fe^{++}) \text{ reacted}}{(H_2O_2) \text{ taken}}$	Induction factor
....	0.52	3.8	1.98	0.01
1.0×10^{-4}	.52	3.8	1.64	0.22
1.0×10^{-3}	.52	3.8	0.54	2.7
1.0×10^{-3}	.52	7.6	.56	2.6
1.0×10^{-3}	.52	1.9	.58	2.5
1.0×10^{-2}	.52	3.8	.15	12.3
1.0×10^{-1}	.52	3.8	.18	10.1
1.0×10^{-2}	.90	0.85	.19	9.5
....	2.0	4.1	1.96	0.02
1.0×10^{-4}	2.0	4.1	1.64	0.22
1.0×10^{-3}	2.0	4.1	0.70, 0.71	1.86
1.0×10^{-2}	2.0	4.1	0.19, 0.24, 0.23	8.5
1.0×10^{-2}	2.0	2.0	0.21	8.5
1.0×10^{-1}	2.0	4.1	0.11	17.2
5.0×10^{-5}	4.4	3.5	1.90	0.05
1.0×10^{-2}	2.0	8.2	0.21	8.5
1.0×10^{-4}	8.7	8.2	1.88	0.064
....	9.5	3.8	1.99	0.005
1.0×10^{-3}	9.5	3.8	1.16	0.72
1.0×10^{-2}	9.5	3.8	0.36	4.56
1.3×10^{-4}	23	3.5	1.94	0.03
1.0×10^{-3}	2.0	3.8	0.89[a]	1.25
1.0×10^{-3}	2.0	3.8	0.49[b]	3.08

[a] In 2.1 *N* sulfuric acid. [b] In 0.045 *N* sulfuric acid.

The above data show that in the presence of ethanol, less ferrous iron is oxidized than would correspond to the hydrogen peroxide initially present, on a stoichiometric basis. Thus hydrogen peroxide must be consumed by some reaction which is induced by the ferrous iron–hydrogen peroxide reaction. It is shown further in this paper that this induced reaction is principally the oxidation of ethanol to acetaldehyde; that is, a Fenton reaction. The extent of this induced reaction increases with increasing concentrations of ethanol, when the initial concentrations of iron and peroxide are kept constant. With given concentrations of ethanol and iron (10^{-3} and 0.52×10^{-3} *M*, respectively), the reaction ratio was found to be independent of the initial concentration of peroxide, over a fourfold range; while with a given concentration of ethanol and a given initial ratio of iron to peroxide, the reaction ratio increased (*i. e.*, the extent of the induced reaction decreased) with increasing concentrations of iron. The effect of the concentration of sulfuric acid is discussed later. The slight deviations from the stoichiometric reaction ratio found in the absence of ethanol may be due to traces of organic impurities.

The induction factor is defined as the number of equivalents of the induced reaction divided by the number of equivalents of the primary reaction.[7] In the present experiments, R equivalents (or moles) of ferrous iron react per mole (or per 2 equivalents) of hydrogen peroxide. Thus the number of equivalents of hydrogen peroxide consumed in the primary reaction is R, and the number consumed in the induced reaction is $2 - R$; so that the induction factor is $(2 - R)/R$. The large values of the induction factor are significant from an analytical standpoint. If a determination of hydrogen peroxide with ferrous iron were attempted in the presence of ethanol, the percentage error (based on the amount of hydrogen peroxide found) would be given by 100 times the induction factor. It is seen that the error in the presence of sufficient ethanol would be over one thousand per cent.

The Fenton oxidation of ethanol may be interpreted either on the basis of the Haber and Weiss[4,5] mechanism or the Bray and Gorin[3] mechanism. On the former basis, the mechanism would be

$$Fe^{++} + H_2O_2 = Fe^{+3} + HO\cdot + OH^- \quad (1)$$

$$HO\cdot + CH_3CH_2OH = CH_3\underset{\cdot}{C}HOH + H_2O \quad (6)$$

$$CH_3\underset{\cdot}{C}HOH + Fe^{+3} = CH_3CHO + H^+ + Fe^{++} \quad (7)$$

$$Fe^{++} + HO\cdot = Fe^{+3} + OH^- \quad (4)$$

Steps (1), (6) and (7) form a chain mechanism for the reaction between hydrogen peroxide and ethanol, with ferrous iron, hydroxyl radical and hydroxyethyl radical as chain-carriers; step (4) is the termination step. The sum of steps (1), (6) and (7) gives the over-all induced oxidation of ethanol by hydrogen peroxide

$$CH_3CH_2OH + H_2O_2 = CH_3CHO + 2H_2O \quad (8)$$

In a qualitative interpretation of the results, termination by reaction between the organic radical and ferrous iron, though possible, need not be assumed for compounds, such as ethanol, which are oxidized during the course of the peroxide–iron reaction. Termination by reaction with the organic radical is found with acetic acid, as shown in step (15). Direct reaction between hydrogen peroxide and the hydroxyethyl radical may also take place, as shown in step (9), which is equivalent to the sum of steps (7) and (1).

$$CH_3\underset{\cdot}{C}HOH + H_2O_2 = CH_3CH(OH)_2 + HO\cdot = CH_3CHO + H_2O + HO\cdot \quad (9)$$

On the basis of the mechanism of Bray and Gorin, the pertinent steps would be

$$Fe^{++} + H_2O_2 = FeO^{++} + H_2O \quad (10)$$

$$FeO^{++} + CH_3CH_2OH = Fe^{+3} + CH_3\underset{\cdot}{C}HOH + OH^- \quad (11)$$

$$CH_3\underset{\cdot}{C}HOH + Fe^{+3} = CH_3CHO + H^+ + Fe^{++} \quad (7)$$

$$Fe^{++} + FeO^{++} + 2H^+ = 2Fe^{+3} + H_2O \quad (12)$$

Steps (10), (11) and (7) form a chain reaction with the ferryl ion as a chain-carrier; the chain is terminated by step (12). It is also possible that hydrogen peroxide is consumed by steps (16) and (17) discussed later in this paper. We are indebted to Professor M. S. Kharasch of the University of Chicago for the suggestion that acetaldehyde is the reaction product.

We have attempted to derive expressions for the stoichiometry of the reaction in the presence of ethanol, based on the above mechanisms[8]; however, agreement of any of these expressions with the experimental data of Table I is only fair. A complicating factor is the induced oxidation of acetaldehyde to acetic acid, as shown below; that is, as soon as some acetaldehyde is formed by oxidation of ethanol, it will compete with both ethanol and ferrous iron for reaction with the active intermediate (ferryl iron or hydroxyl radical), so that the kinetic treatment becomes very complicated and difficult to test experimentally.

Results Obtained in the Presence of Sulfuric Acid and Organic Compounds other than Ethanol.—Some experiments have been carried out using the apparatus and technique described above, but with acetic acid, acetone or acetaldehyde in place of ethanol. The data are given in Table II.

TABLE II

REACTION IN 1.5 N SULFURIC ACID IN THE PRESENCE OF VARIOUS ORGANIC COMPOUNDS

Initial concentrations				Molar ratios		
Acetic acid, M	Acetone, M	Acetaldehyde, M	Fe^{++} ($M \times 10^3$)	Initial $(Fe^{++})/(H_2O_2)$ taken	(Fe^{++}) reacted $/(H_2O_2)$ taken	Induction factor
...	..	..	0.51	3.9	1.99	0.005
10^{-4}	..	..	.51	3.9	1.97	.015
10^{-2}	..	..	.51	3.9	1.91	.047
10^{-1}	..	..	.51	3.9	1.92	.042
10^{-1}[a]	..	..	.51	3.9	1.91	.047
10[a]	..	..	2.0	3.8	1.97	.015
...	10^{-2}	..	2.0	3.8	1.95	.025
...	..	10^{-3}	8.7	3.5	1.54	.30

[a] In 0.045 N sulfuric acid.

The behavior of acetaldehyde, as indicated in Table II, is qualitatively similar to that of ethanol; that is, a significant deviation from the stoichiometric reaction is found in the presence of a small concentration of acetaldehyde. In preliminary experiments with a less refined experimental technique, methanol was also found to behave similarly.

In contrast, even relatively high concentrations of acetic acid or acetone give rise to practically no deviation from the stoichiometric reaction. In terms of the mechanisms given above, this means that these compounds either fail to react with the active intermediates, or that, if reaction does oc-

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[7] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942.

[8] A. I. Medalia, Ph.D. Thesis, University of Minnesota, 1948.

cur, the organic radicals thus formed react with ferrous iron in preference to ferric iron or hydrogen peroxide; this is illustrated in equations (13)–(15), with acetic acid.[9a]

$$HO\cdot + CH_3COOH = CH_3COO\cdot + H_2O \quad (13)$$

$$FeO^{++} + CH_3COOH = Fe^{+3} + CH_3COO\cdot + OH^- \quad (14)$$

$$CH_3COO\cdot + Fe^{++} = CH_3COO^- + Fe^{+3} \quad (15)$$

The sum of steps (1), (13) and (15) or of steps (10), (14) and (15), gives the stoichiometric reaction (I), which in the absence of added organic compounds results from the combination of steps (1) and (4), or (10) and (12). Thus, while the reaction between ferrous iron and hydrogen peroxide is stoichiometric in either the presence or absence of acetic acid (or acetone), the reaction may proceed through a different path in the two cases. Strong evidence that this is the correct interpretation is derived from the work described in the second paper of this series, in which it is shown that both acetic acid and acetone give rise to considerable induced oxygen oxidation of ferrous iron when the peroxide–iron reaction is carried out in the presence of dissolved oxygen. Additional evidence is given in the following section. Independent evidence that acetic acid reacts with the hydroxyl radical comes from a study of the hydrogen peroxide–ozone system, by Taube and Bray.[9b] Using the values of relative rate constants for the reaction of hydroxyl radical with acetic acid, hydrogen peroxide and ferrous iron, as determined by Taube and Bray and by Haber and Weiss, a simple kinetic treatment shows that in the experiments of Table II with 0.1 M acetic acid, where a reaction ratio of 1.91 was found, a reaction ratio of only 0.59 would be expected if the acetate radicals reacted with ferric iron or hydrogen peroxide rather than with ferrous iron; this is of significance, of course, only if the Haber and Weiss mechanism is adopted rather than that of Bray and Gorin.

Results Obtained in the Presence of Sulfuric Acid and Mixtures of Organic Compounds.—As shown above, it appears that when the active intermediates which are formed in the ferrous iron–hydrogen peroxide reaction react with acetic acid, then the over-all reaction is stoichiometric, while if these intermediates react with ethanol, then induced reduction of hydrogen peroxide takes place. In a mixture containing both ethanol and acetic acid, competition between these compounds (and ferrous iron) for reaction with the active intermediates would be expected to result in a reaction ratio intermediate between that found with the same concentrations of either organic compound separately. Data illustrating this are shown in Table III.

TABLE III

REACTION IN SULFURIC ACID IN THE PRESENCE OF A MIXTURE OF ACETIC ACID AND ETHANOL

Initial concentrations				Molar ratios		
H_2SO_4, N	Acetic acid, M	Ethanol, M	Fe^{++} ($M \times 10^3$)	Initial $\frac{(Fe^{++})}{(H_2O_2)}$ taken	$\frac{(Fe^{++})\text{ reacted}}{(H_2O_2)}$ taken	Induction factor
2.1	..	10^{-3}	2.0	3.8	0.89	1.25
2.1	10^{-1}	10^{-3}	2.0	3.8	1.27	0.57
1.5	..	10^{-3}	2.0	3.8	0.71	1.86
1.5	1	10^{-3}	2.0	3.8	1.79	0.12
0.045	..	10^{-3}	2.0	3.8	0.49	3.09
.045	10^{a}	..	2.0	3.8	1.97	0.015
.045	10^{a}	10^{-3}	2.0	3.8	1.95	.025
.045	10^{a}	10^{-4}	2.0	3.8	1.97	.015

[a] Reaction medium approximately 60% acetic acid.

These data strongly support the view that acetic acid and ethanol compete for the active intermediates formed in the reaction between ferrous iron and hydrogen peroxide. The acetate free radicals do not give rise to decomposition of hydrogen peroxide (equations (13) to (15)), while the hydroxyethyl free radicals do. Thus acetic acid suppresses the induced oxidation of ethanol observed in the reaction between ferrous iron and hydrogen peroxide. Interaction between a hydroxyethyl radical and acetic acid, or an acetate radical and ethanol, while possible, need not be considered in the qualitative interpretation.

On a purely experimental basis, ethanol may be said to promote the decomposition of hydrogen peroxide during the course of the ferrous iron–hydrogen peroxide reaction, while acetic acid suppresses the promoting action of ethanol. The classification of compounds as "promoting" or "suppressing" is of great utility in considering chain reactions such as those between ferrous iron and hydrogen peroxide, organic hydroperoxides or persulfate. From an analytical standpoint, the above results are significant as indicating the use which can be made of the suppressing action of certain compounds in overcoming the induced decomposition caused by other compounds. Application of this principle to the determination of organic peroxides may be of considerable importance, as will be shown in a subsequent paper.

Reaction in the Presence of Inorganic Compounds other than Sulfuric Acid.—The experiments described above were carried out in the presence of sulfuric acid. This acid is convenient to use, since it is available in pure form and is quite stable, and extensive previous study of the ferrous iron–hydrogen peroxide reaction has been carried out in sulfuric acid medium. However, some study of the reaction in the presence of perchloric rather than sulfuric acid seemed desirable in view of the comparatively slight tendency of

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[9a] If the acetate radical would decompose appreciably (to $CH_3\cdot$ and CO_2) before reacting with ferrous iron, the stoichiometry would require oxidation of ferrous iron by the methyl radical:

$$CH_3\cdot + Fe^{++} + H^+ = CH_4 + Fe^{+3} \quad (15a)$$

Because of the low concentrations of peroxide and ferrous iron used in the present experiments, no attempt was made to detect the presence of methane or carbon dioxide. Reaction between hydroxyl radical and acetic acid might form the radical $\cdot CH_2COOH$ instead of the acetate radical (step (13)); *cf.* the following paper.

[9b] H. Taube and W. C. Bray, THIS JOURNAL, 62, 3357 (1940).

perchloric acid to form complexes with ferrous and ferric iron. Some difficulty was encountered in these experiments, apparently as a result of impurities present in several of the samples of perchloric acid which were used. In selecting a sample of perchloric acid for use in further experiments, the criterion of purity which was used was the reaction ratio of ferrous iron to hydrogen peroxide found in the presence of perchloric acid (1 *M*) in nitrogen, in the absence of other added substances. The sample which gave the reaction ratio closest to the theoretical (J. T. Baker C.P. vacuum distilled, 20%) was used in subsequent work. The reaction ratio obtained with this sample was 1.94 (theoretical, 2.0); other ratios obtained are as follows: Merck 60%, two different lots, 1.03 and 1.23; Baker and Adamson 60%, 1.82.

The reaction has also been studied in the presence of sodium perchlorate, sodium chloride, potassium nitrate and phosphoric acid. Experiments with each compound were carried out both in the absence and presence of ethanol. The data are given in Table IV.

TABLE IV

REACTION IN THE PRESENCE OF VARIOUS INORGANIC COMPOUNDS IN THE PRESENCE AND ABSENCE OF ETHANOL

Initial concentrations				Molar ratios		
$HClO_4$, *M*	Ethanol, *M*	Fe^{++} (*M* × 10^3)	Other compound	Initial $(Fe^{++})/(H_2O_2)$ taken	(Fe^{++}) reacted$/(H_2O_2)$ taken	Induction factor
1.0	..	1.6	....	2.69	1.94	0.03
1.0	10^{-3}	1.6	....	2.69	0.55, 0.53	2.70
0.14	10^{-3}	1.6	....	2.69	0.51	2.92
.02	..	1.9	....	3.28	1.98	0.01
.02	10^{-3}	1.9	....	3.28	0.50	3.00
.02	..	1.9	$NaClO_4$, 1 *M*	3.28	1.89	0.06
.02	10^{-3}	1.9	$NaClO_4$, 1 *M*	3.28	0.51	2.92
.14	..	1.6	NaCl, 1 *M*	2.69	1.96	0.02
.14	10^{-3}	1.6	NaCl, 1 *M*	2.69	1.95	.03
.14	10^{-2}	1.6	NaCl, 1 *M*	2.69	1.87	.07
.14	..	1.6	KNO_3, 1 *M*	3.25	1.95	.03
.14	10^{-3}	1.6	KNO_3, 1 *M*	3.25	0.79	1.53
..	..	1.6	H_3PO_4, 1 *M*	3.25	1.93	0.04
..	10^{-3}	1.6	H_3PO_4, 1 *M*	3.25	0.67	1.99
..	10^{-3}	2.0	H_2SO_4, 1.5 *N*	4.1	.70	1.86
..	10^{-3}	2.0	H_2SO_4, 0.045 *N*	3.8	.49	3.08

The above data show definitely that with perchloric acid the extent of the induced reaction in nitrogen is practically independent of the amount of acid over a fifty-fold range. The coincidence of the value obtained in perchloric acid with that obtained in dilute (0.045 *N*) sulfuric acid makes it appear that these values are limiting values, without interference by the anions. The data obtained with sodium perchlorate substantiate the conclusion that there is no salt effect upon the reaction ratio with perchlorate as the anion. The extent of the induced reaction depends upon the competition between ethanol and ferrous iron for reaction with the active intermediates. Absence of a salt effect indicates that the active intermediate is uncharged; this supports the free-radical mechanism. If ferryl iron were the active intermediate, then a salt effect would be expected for the reaction of ferryl iron with ferrous iron, but not for the reaction of ferryl iron with ethanol; thus the reaction ratio would be expected to depend upon salt concentration. It is, however, possible that hydrolysis or complex formation may obscure the expected salt effect.

Chloride ion is seen to act as a powerful suppressor, comparable with acetic acid. Reaction of hydroxyl radical with chloride ion, to form atomic chlorine, was described by Taube and Bray.[9b] From our results it follows that atomic chlorine must react more readily with ferrous iron than with ferric iron, hydrogen peroxide or ethanol.

With high concentrations of sulfuric acid, phosphoric acid or potassium nitrate, slightly higher values are found for the reaction ratio in the presence of 10^{-3} *M* ethanol than are found in dilute sulfuric acid or in perchloric acid. The effect of these compounds may be regarded as mild "suppression," either by the mechanism assumed for suppression by acetic acid, acetone and chloride ion, namely, by reaction of these compounds with the active intermediate; or possibly by protection of the ferrous ion by complex formation, resulting in a decreased rate of reaction between ferrous iron and the active intermediate.

Detection of Acetaldehyde Formed from Ethanol.—In the above presentation it has been assumed that the role of ethanol in the ferrous iron–hydrogen peroxide reaction is to reduce hydrogen peroxide. It also appeared possible that ethanol could serve simply as a chain-carrier, without itself being oxidized. A mechanism for this behavior, based on the mechanism of Haber and Weiss, would include steps (1) and (6) followed by (16) and (17).

$$CH_3\underset{\cdot}{C}HOH + H_2O_2 = CH_3CH_2OH + HO_2\cdot \quad (16)$$

$$HO_2\cdot + H_2O_2 = H_2O + O_2 + HO. \quad (17)$$

It has been reported by Goldschmidt and Pauncz[10] that acetaldehyde, acetic acid and a small amount of oxygen are formed upon slow addition of ferrous iron to relatively concentrated solutions of hydrogen peroxide and ethanol. The conditions under which these experiments were carried out are quite different from those described in this paper. In order to decide by which mechanism hydrogen peroxide disappears when ethanol is present in the reaction mixture it was decided to determine the amount of acetaldehyde formed. It was assumed that if acetaldehyde were formed in the presence of a large amount of ethanol, ethanol would be attacked by the active intermediates rather than the small amounts of acetaldehyde. The experimental results show that the assumption is justified. The most suitable method for the detection and determination of acetaldehyde

[10] S. Goldschmidt and S. Pauncz, *Ann.*, **502**, 1 (1933).

in the presence of ferrous and ferric iron appeared to be that based on reaction with Schiff reagent.

A solution of Schiff reagent was prepared by dissolving 0.50 g. of basic fuchsin (National Aniline Co.) in 1 l. of water, together with 0.31 ml. of 6 *N* sulfuric acid and 0.58 g. of sodium sulfite. The solution was still pink, and sulfur dioxide was passed through very slowly until the color just turned to yellow. The solution was thus 1.5×10^{-3} *M* in the fuchsin reagent. Tests were carried out with various buffer solutions, using the following procedure: 5 ml. of buffer solution was mixed with 1 ml. of Schiff reagent solution, and the colors developed in various solutions after five to fifteen minutes were compared visually. At a *p*H of greater than 3.0, a rose color of fuchsin was visible in the absence of aldehyde. The sensitivity of the test for acetaldehyde decreased with decreasing *p*H below 3.0. A biphthalate buffer of *p*H 3.0 was unsuitable, owing to the formation of orange hydrous ferric oxide upon addition of ferric iron in a concentration of 10^{-3} *M*. In a phosphate buffer, at a *p*H of 3.0 or 2.4, a white turbidity was formed on addition of ferric iron (ferric phosphate) which did not, however, interfere with the Schiff test under the present conditions. In a phosphate buffer of *p*H 2.0, no precipitate was formed on addition of ferric iron, but the sensitivity of the test was lower than at the higher values of *p*H. Ferrous iron did not interfere with the test in the *p*H range 2–3. The procedure which was adopted for testing reaction mixtures was as follows.

Procedure.—To 5 ml. of reaction mixture, containing up to 0.05 *N* acid (sulfuric or perchloric), was added sufficient sodium dihydrogen phosphate to give a *p*H of 3.0 (calculated). One ml. of the solution of Schiff reagent was added and the color was observed after fifteen minutes.

By means of this test, acetaldehyde could be detected in concentrations as low as 10^{-4} *M*. By visual comparison with controls containing various amounts of acetaldehyde, the concentration could be estimated to $\pm 10^{-4}$ *M* in the range between 2 and 5×10^{-4} *M*. More concentrated solutions were diluted before carrying out the test.

Reactions were carried out as described previously. The conditions and results are given in Table V.

TABLE V

ALDEHYDE DETERMINATIONS

	Initial concentrations		Molar ratios		
Acid[a]	Ethanol, *M*	Fe^{++} (*M* × 10^3)	Initial (Fe^{++}) / Initial (H_2O_2)	(Fe^{++}) reacted / Initial (H_2O_2)	Acetaldehyde found, *M*
Sulfuric	10^{-1}	2.9	2.1	0.13	1×10^{-3}
Perchloric	10^{-3}	2.0	3.3	.50	4×10^{-4}
Perchloric[b]	10^{-3}	2.0	3.3	.51	3×10^{-4}

[a] The sulfuric acid was 0.05 *N*; the perchloric acid was 0.02 *N*. [b] With sodium perchlorate (1 *M*) in addition to perchloric acid (0.02 *N*).

The concentration of hydrogen peroxide consumed by reaction with ethanol in the first experiment of Table V is 1.3×10^{-3} *M*, and in the last two experiments, 0.45×10^{-3} *M*. It is seen that the concentrations of acetaldehyde found correspond to the concentrations of hydrogen peroxide consumed by the induced reaction. Thus the induced reaction is, at least principally, induced oxidation of ethanol to acetaldehyde.

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Summary

An apparatus and procedure are described with which the reaction between ferrous iron and hydrogen peroxide has been investigated, with rapid mixing, in the absence of oxygen. Ethanol, in concentrations of 10^{-4} to 10^{-1} *M*, has been added to reaction mixtures in acid solution, with concentrations of the primary reactants generally of the order of 10^{-3} *M*; in these mixtures, the primary reaction between ferrous iron and hydrogen peroxide induces the reaction between hydrogen peroxide and ethanol, with the formation of acetaldehyde; this is known as a Fenton reaction. Mechanisms for this reaction are presented. No induced reaction is found between hydrogen peroxide and acetic acid; but when acetic acid is added to a mixture containing ethanol, the extent of the induced reduction of hydrogen peroxide by the latter is decreased. Apparently there is competition between acetic acid and ethanol for reaction with the active intermediates formed in the primary reaction; the radicals formed from the two organic compounds differ in their subsequent reactions. Ethanol is termed a promoter, and acetic acid a suppressor.

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