

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

The Reaction between Ferrous Iron and Peroxides. II. Reaction with Hydrogen Peroxide, in the Presence of Oxygen¹

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In the preceding paper of this series,² the course of the reaction between ferrous iron and hydrogen peroxide, in the absence of oxygen, but in the presence of various other compounds, was described. Evidence was given that several compounds react with active intermediates formed in the course of this reaction; thus, ethanol is believed to form the hydroxyethyl radical, and acetic acid, the acetate radical. It is known^{3,4} that organic radicals are extremely reactive toward oxygen. It is shown in the present paper that not only quantitatively, but also qualitatively, quite different results are obtained in the presence of oxygen than in its absence.

Experimental

Many of the experiments described in this paper were carried out with the reaction vessel and technique described in the preceding paper,² but flushing the vessel with oxygen or air, in place of nitrogen, for at least ten minutes before mixing, as well as between mixing and titration. This technique will be referred to as the "shaking" procedure. Other experiments were carried out by a "stirring" procedure, described below.

"Stirring" Procedure.—The ferrous sulfate solution was added from a 10-ml. "Exax" pipet to 45 ml. of hydrogen peroxide solution in a 125-ml. erlenmeyer flask. The contents of the flask was stirred vigorously during addition of the ferrous solution by means of a flattened twisted stirring rod rotating at 1800 r. p. m. In many experiments the reverse order of mixing was used. With either order of mixing, the solution originally in the flask contained acid as well as any added substances other than the primary reactants; the ferrous sulfate solution was always acid. After standing for a short time, the entire content of the flask was titrated with ceric sulfate solution. The reaction mixtures of duplicate experiments were allowed to stand for different lengths of time (generally ten and twenty minutes) before titrating.

Reagents.—The following reagents were used in the experiments described in this paper in addition to those described in the preceding one.

<i>t</i> -Butyl alcohol	Laboratory supply, distilled through a fractionating column with a reflux ratio of 2:1, in all-glass apparatus
Perchloric acid	J. T. Baker C. P. (20%)
Ferrous perchlorate	Prepared by solution of pure iron wire (B and A reagent) in perchloric acid
Oxygen	Air Reduction Co. (99.5%), filtered through glass wool

Results and Discussion

Reaction in the Presence of Sulfuric Acid and Ethanol.—Results of experiments carried out by the "shaking" procedure are given in Table I. If desirable, before titration with ceric sulfate, small portions of the reaction mixtures were tested for hydrogen peroxide by addition of titanous sulfate solution. The column headed "gas" indicates the gas with which the solutions and gas space were flushed before and after mixing.

TABLE I

EXPERIMENTS IN 1.5 *N* SULFURIC ACID, WITH VARIOUS CONCENTRATIONS OF ETHANOL

Each figure is an average obtained with aliquots from a single reaction mixture after 15 and 30 minutes reaction time. Experiments carried out by "shaking" technique.

Initial concentrations Ethanol, <i>M</i>	Initial Fe ⁺⁺ (<i>M</i> × 10 ³)	Molar ratio, initial (Fe ⁺⁺) / (H ₂ O ₂) taken	Gas	Molar ratio, (Fe ⁺⁺) reacted / (H ₂ O ₂) taken	Titanium sulfate test	Induction factor
..	0.51	3.92	Oxygen	2.06	0.03
10 ⁻⁴	.51	3.92	Oxygen	2.74	Negative	0.37
10 ⁻²	.51	3.92	Oxygen	2.69 ^a , 10.4 ^b	Positive	4.2 ^b
10 ⁻²	.51	7.84	Oxygen	7.46	Negative	2.73
10 ⁻⁴	1.0	3.60	Air	2.42, 2.44	0.21
10 ⁻²	1.0	15.7	Oxygen	6.71	Negative	2.35
..	2.2	4.38	Oxygen	2.04	0.02
10 ⁻⁴	2.0	3.64	Air	2.20	0.10
10 ⁻⁴	2.0	3.64	Oxygen	2.34	0.17
10 ⁻²	2.2	4.38	Oxygen	4.16 ^a , 4.89 ^b	Positive	1.45 ^b
10 ⁻²	2.2	7.30	Oxygen	5.15	Negative	1.57
10 ⁻²	2.2	10.95	Oxygen	5.46	Negative	1.73
10 ⁻¹	2.2	10.95	Oxygen	5.51	Negative	1.75
10 ⁻²	2.2	4.38	Air	2.92	Negative	0.46
10 ⁻²	2.2	7.30	Air	3.39	Negative	0.70
..	13.1	4.38	Oxygen	2.00	Negative	0.00
10 ⁻⁴	13.1	4.38	Oxygen	2.06	Negative	0.03
10 ⁻²	13.1	4.38	Oxygen	2.08	Negative	0.04
10 ⁻²	9.5	3.76	Air	0.79	Negative	..

^a These values are calculated on the incorrect assumption that all the hydrogen peroxide has been consumed by reaction with ferrous iron. ^b Calculated on the assumption that all the ferrous iron has been consumed by reaction with hydrogen peroxide.

The results given in Table I show that considerable induced oxygen oxidation of the ferrous iron can take place during the reaction between hydrogen peroxide and ferrous iron in the presence of ethanol and oxygen. The induction factor for this reaction is $(R - 2)/2$, where R is the reaction ratio

(1) This work was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Synthetic Rubber Program of the United States Government. From a thesis submitted by A. I. Medalia to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of the degree of Doctor of Philosophy (1948).

(2) I. M. Kolthoff and A. I. Medalia, *THIS JOURNAL*, **71**, 3777 (1949).

(3) F. A. Bovey and I. M. Kolthoff, *Chem. Rev.*, **42**, 491 (1948).

(4) W. A. Waters, "The Chemistry of Free Radicals," Clarendon Press, Oxford, England, 1946.

given in the fifth column of the table. In dilute solutions (0.001 *M*) saturated with oxygen, induction factors greater than 2 may be found. Even when the concentration of ethanol is only one-twentieth as great as that of the ferrous iron, an appreciable induced reaction is found. The mechanism of the induced oxidation of ferrous iron is discussed in the following section.

Under certain circumstances the extent of induced air oxidation of ferrous iron may be so great that hydrogen peroxide rather than ferrous iron is left after completion of the reaction. This was found to be the case in the experiments reported in the third and seventh lines of Table I. Since hydrogen peroxide can be titrated with ceric sulfate in the same manner as ferrous iron, titration values are obtained which might be mistaken as corresponding to the amount of iron present, if no test is made for hydrogen peroxide.

With higher concentrations of ferrous iron and hydrogen peroxide, lower induction factors or reaction ratios are found at the same ethanol concentrations. Comparison of the results obtained in oxygen and in air suggests that the magnitude of the reaction ratio is limited by the amount of oxygen available to the system, with initial concentrations of ferrous iron of 2×10^{-3} *M* or greater. The ratio of the amount of dissolved oxygen to the amount of ferrous iron becomes smaller, of course, as the concentration of ferrous iron is increased. The concentration of oxygen in a solution of 1.5 *N* sulfuric acid, saturated with oxygen at 25° at atmospheric pressure, is 1.07×10^{-3} *M*.⁵ Also as the concentrations of ferrous iron and of hydrogen peroxide are increased, the ferrous iron-hydrogen peroxide reaction goes to completion more rapidly, so that less oxygen can enter the solution from the gas phase during the course of the reaction. For both reasons it is not surprising that a very low induction factor is found with 0.013 *M* ferrous iron and 0.0029 *M* peroxide in the presence of oxygen, while in the presence of air, the reaction ratio is actually lower than the stoichiometric value, with 0.0095 *M* ferrous iron and 0.0025 *M* peroxide. Apparently both induced reduction of the peroxide (*cf.* preceding paper²) and induced air oxidation of the ferrous iron can take place in the course of a given experiment; if relatively little oxygen is present, the reduction may predominate over the oxidation.

In Table II are given data obtained by the "stirring" technique. Hydrogen peroxide was added to ferrous iron ("reverse" addition), to prevent the error which would result, even in the absence of ethanol, from induced decomposition of hydrogen peroxide in solutions containing a large excess of hydrogen peroxide over ferrous iron.⁶ All results are averages of duplicate experiments, titrated after different times, which checked

closely. When more than one result is given for a given experiment each figure is the result of a single determination. In all the experiments reported, ferrous iron was in excess to hydrogen peroxide at the time of titration with ceric sulfate.

TABLE II
EXPERIMENTS IN 1.5 *N* SULFURIC ACID WITH VARIOUS CONCENTRATIONS OF ETHANOL IN THE PRESENCE OF AIR, USING THE "STIRRING" TECHNIQUE

Concentration of ethanol, <i>M</i>	Initial concentration of Fe ⁺⁺ (<i>M</i> × 10 ³)	Molar ratio Initial (Fe ⁺⁺) / (H ₂ O ₂) taken	Molar ratio (Fe ⁺⁺) reacted / (H ₂ O ₂) taken
.....	1.0	4.16	2.04
3×10^{-6}	1.0	3.38	2.07
10^{-6}	1.0	3.38	2.12
3×10^{-5}	1.0	3.38	2.20
10^{-4}	1.0	4.16	2.19
10^{-3}	1.0	4.16	2.77, 2.94
.....	2.0	4.24	2.04
10^{-4}	2.0	4.24	2.22
10^{-3}	2.0	4.24	2.32
10^{-2}	2.0	4.24	2.06, 2.11, 1.95
10^{-1}	2.0	4.24	2.05 (single expt.)
1	2.0	4.24	2.07, 2.18
10	2.0	4.24	3.10
.....	10.5	4.38	1.99
2×10^{-4}	10.5	4.38	1.98
2×10^{-3}	10.5	4.38	1.44 ..
2×10^{-2}	10.5	4.38	0.91, 0.95
.....	17	3.74	2.00 ^a
10^{-2}	17	3.74	0.66 ^a
.....	172	3.70	2.00
10^{-2}	172	3.70	1.45

^a In 0.046 *N* sulfuric acid.

Qualitatively, the deviations from the stoichiometric reaction ratio correspond to those given in Table I. With low concentrations of ethanol, ferrous iron, and hydrogen peroxide, the error is due mainly to induced air oxidation of the ferrous iron. When the concentrations of ferrous iron and peroxide are high relative to the concentration of oxygen in the solution, the induced reduction of hydrogen peroxide becomes of greater importance, leading to values of *R* less than the stoichiometric value of 2. Thus under typical analytical conditions, in the presence of air and ethanol, peroxide values may be found which are low, high, or by chance approximately correct, depending on the concentrations of peroxide and ferrous iron.

With an initial concentration of ferrous iron of 2×10^{-3} *M*, results within 5% of the stoichiometric are found over a wide range of concentrations of ethanol, due to compensation of the induced oxygen oxidation of ferrous iron and the induced reduction of the peroxide. The high values of *R* found with 10 *M* (46% by weight) ethanol may be partly due to the increased solubility of oxygen in this solvent as compared to dilute aqueous solutions.

Reaction in the Presence of Sulfuric Acid and Organic Compounds Other than Ethanol.—In

(5) G. Geffcken, *Z. phys. Chem.*, **49**, 257 (1904).

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

the preceding paper² it was shown that acetic acid suppresses the induced reaction between hydrogen peroxide and ethanol in the absence of oxygen. It seemed of interest to investigate the behavior of acetic acid in the presence of oxygen. Results of experiments carried out by the "shaking" procedure are given in Table III.

TABLE III

EXPERIMENTS IN 1.5 *N* SULFURIC ACID, USING THE "SHAKING" TECHNIQUE, WITH OXYGEN-SATURATED SOLUTIONS

Acetic acid, <i>M</i>	Initial concentrations		Molar ratios	
	Ethanol, <i>M</i>	Fe ⁺⁺ (<i>M</i> × 10 ³)	Initial (Fe ⁺⁺) (H ₂ O ₂) taken	(Fe ⁺⁺) reacted (H ₂ O ₂) taken
..	..	0.51	3.92	2.02
10 ⁻²	..	0.51	3.92	2.60
10 ⁻²	..	0.51	7.84	2.47
..	..	2.0	3.76	2.04
1	10 ⁻³	2.0	3.76	3.44

The data of Table III show that, like ethanol, acetic acid also gives rise to induced oxygen oxidation of ferrous iron in the peroxide-iron reaction. This confirms the hypothesis that acetic acid reacts with the active intermediates which are formed in the ferrous iron-hydrogen peroxide reaction. Since acetic acid itself can give rise to induced oxygen oxidation of ferrous iron, acetic acid would not be expected to suppress the induced oxygen oxidation caused by ethanol; this is brought out by comparison of the data of Tables I and III.

TABLE IV

EXPERIMENTS IN 1.5 *N* SULFURIC ACID, IN THE PRESENCE OF AIR AND VARIOUS ORGANIC SUBSTANCES, USING THE "STIRRING" TECHNIQUE

Substance added	Concentration, moles/liter	Initial concn. Fe ⁺⁺ <i>M</i> × 10 ³	Molar ratio	
			Initial (Fe ⁺⁺) H ₂ O ₂ taken	(Fe ⁺⁺) reacted H ₂ O ₂ taken
Nothing	..	1.0	3.75	2.04
Methanol	10 ⁻⁵	1.0	3.75	2.06
Methanol	10 ⁻⁴	1.0	3.75	2.22
Methanol	10 ⁻³	1.0	3.75	2.46
Methanol	10 ⁻²	1.0	3.75	2.10
Methanol	10 ⁻¹	1.0	3.75	2.16 ^a , 2.51 ^a
Nothing	..	1.3	4.64	2.02
Methanol	10 ⁻³	1.3	4.64	2.49
Methanol	10 ⁻²	1.3	4.64	2.37
Methanol	10 ⁻²	1.3	9.28	3.21
Methanol	10 ⁻¹	1.3	4.64	2.31
Acetic acid	10 ⁻⁴	1.0	3.75	2.07
Acetic acid	10 ⁻³	1.0	3.75	2.11
Acetic acid	10 ⁻²	1.0	3.75	2.41
Acetic acid	1	1.3	4.64	3.00
Acetone	10 ⁻⁴	1.0	3.75	2.09
Acetone	10 ⁻³	1.0	3.75	2.38
Acetone	2 × 10 ⁻³	1.0	3.75	2.59
Acetone	10 ⁻²	1.0	3.75	3.04
<i>t</i> -Butyl alcohol	10 ⁻⁴	1.0	3.66	2.11
<i>t</i> -Butyl alcohol	10 ⁻³	1.0	3.66	2.46
<i>t</i> -Butyl alcohol	10 ⁻²	1.0	3.66	2.45

^a Single experiments.

Results obtained by the "stirring" technique, in air-saturated solutions, in the presence of various organic substances, are given in Table IV. The "reverse" mode of addition was used throughout. All results (except as noted) are averages of duplicate experiments titrated after different times, which checked closely.

The reaction between ferrous iron and hydrogen peroxide leads to induced oxygen oxidation of ferrous iron when carried out in the presence of dissolved oxygen and any of the five organic compounds tested, as shown in the preceding tables: namely, ethanol, methanol, acetic acid, acetone and *t*-butyl alcohol. It is of particular interest that even relatively stable substances such as acetic acid and *t*-butyl alcohol can bring about considerable induced reaction. As was observed with ethanol (Table II), the extent of the induced oxidation found with a given initial concentration of ferrous iron and peroxide may vary irregularly with increasing concentrations of the added organic compound. In many of the present experiments in Table IV the extent of the induced air oxidation is limited by the amount of oxygen present, while the extent of induced decomposition of the peroxide increases with increasing concentrations of the organic compound. Thus it is seen qualitatively that the net extent of induced oxidation may be expected to pass through a maximum with increasing concentrations of the organic compound. A more exact treatment of the complex reactions involved cannot be given (*v. i.*).

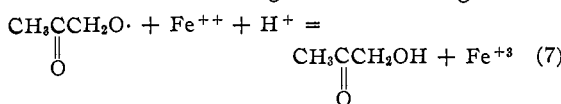
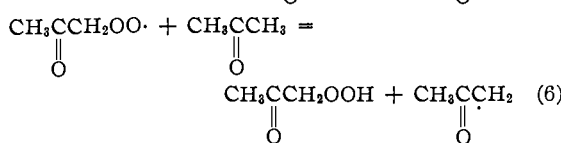
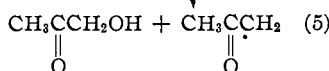
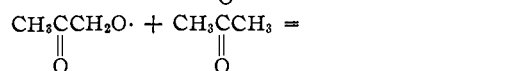
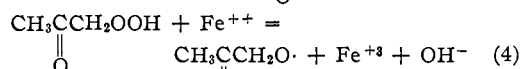
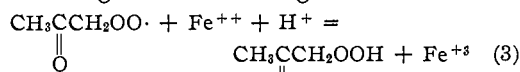
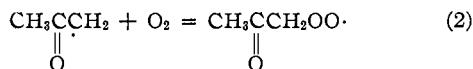
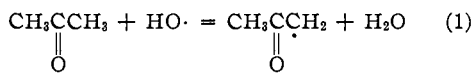
Mechanism of the Induced Oxygen Oxidation of Ferrous Iron.—When the reaction between ferrous iron and hydrogen peroxide is carried out in the presence of various organic compounds, organic radicals apparently are formed, which can react with oxygen (if present in the system), forming peroxide radicals. These can in turn react with molecules of the organic compound present, leading to a chain autoxidation of this compound, with the formation of considerable quantities of peroxides^{7,8}; or the peroxide radicals may react with ferrous iron or with hydrogen peroxide; or they may decompose spontaneously. The steps which are possible in the presence of oxygen are much more numerous than in the absence of oxygen, and a detailed analysis of the results does not seem possible. As an illustration, some of the reactions which may take place are given below. For simplicity, the formation of hydroxyl radical in the primary step of the peroxide-iron reaction will be assumed.²

In the case of acetone, the hydrogen atoms are labilized by the keto group, so that autoxidation is facilitated. We would expect the following reactions to be possible.

Steps (3), (4) and (7) predict the oxidation of three ferrous ions by each peroxide radical formed

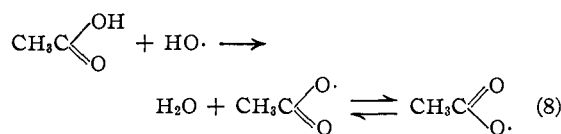
(7) J. L. Bolland, *Proc. Roy. Soc. (London)*, **A186**, 218 (1946).

(8) E. H. Farmer and D. A. Sutton, *J. Chem. Soc.*, 119 (1943).



in step (1); however, since the initial formation of the peroxide radical (step (1)) consumes a hydroxyl radical which would otherwise oxidize a ferrous ion, only two *additional* ferrous ions are oxidized by the peroxide radical formed in this manner; so that, barring autoxidation (steps (5) and (2), or (6) and (2)), the highest possible induction factor should be unity. Induction factors greater than unity are accounted for by the chain autoxidation reactions, in which a very large number of peroxide radicals can be formed, each of which oxidizes two additional ferrous ions.

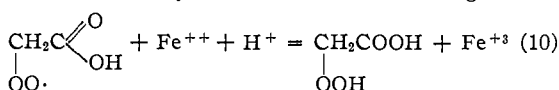
With acetic acid, removal of a hydrogen atom from the hydroxyl group leads to formation of a radical (acetate radical) which is stabilized by resonance.



Another mode of interaction between the hydroxyl radical and acetic acid would be



this radical could add molecular oxygen to form a peroxide radical, which would oxidize ferrous iron as shown in step (10). Formation of the radical, $\cdot\text{CH}_2\text{COOH}$, by intramolecular rearrangement of



the acetate radical, or by reaction of the acetate radical with acetic acid, also appears possible.

The hydroperoxide formed in step (10) could react further, in a manner similar to steps (4)–(7).

Reaction in the Presence of Various Inorganic Compounds, in the Presence and Absence of Ethanol.—Experiments have been carried out by the “stirring” technique in 1.5 *N* sulfuric acid solutions in the presence of air, with various inorganic compounds present in low concentrations, but in the absence of organic compounds. None of the inorganic compounds investigated gave rise to induced oxygen oxidation of ferrous iron in the reaction between the latter (10^{-3} *M*) and hydrogen peroxide (3×10^{-4} *M*); these compounds include NaHCO_3 (1.5×10^{-4} *M*), CuSO_4 (5×10^{-5} *M*), $(\text{NH}_4)_2\text{SO}_4$ (up to 10^{-3} *M*), KCl (10^{-4} *M*), MnSO_4 (5×10^{-5} *M*), and SnCl_4 (up to 10^{-4} *M*); C.P. or reagent grade salts were used.

A study of the effects of various common inorganic acids or salts upon the reaction in question, in the presence and absence of ethanol, has been carried out, using the “shaking” technique, with oxygen-saturated solutions. The data, given in Table V, show that with the exception of phosphoric acid, none of the compounds studied leads to any significant induced reaction, in the absence of organic compounds. The small effect found with phosphoric acid may be due to traces of impurities in the sample used, as indicated from the data obtained in the absence of oxygen,² or to direct reaction between oxygen and ferrous iron.

TABLE V

EFFECT OF SOME INORGANIC COMPOUNDS ON THE INDUCED OXYGEN OXIDATION. EXPERIMENTS IN OXYGEN-SATURATED SOLUTIONS, BY THE “SHAKING” TECHNIQUE

H- ClO ₄ , <i>M</i>	Eth- anol, <i>M</i>	Initial concentrations		Molar ratios	
		Fe ⁺⁺ (<i>M</i> × 10 ³)	Other compound	Initial (Fe ⁺⁺) (H ₂ O ₂) taken	(Fe ⁺⁺) reacted (H ₂ O ₂) taken
1.0	..	1.5	6.5	2.05
1.0	10 ⁻²	1.5	6.5	7.19
..	..	1.5	H ₂ SO ₄ (1.5 <i>N</i>)	6.7	2.04
..	10 ⁻²	1.5	H ₂ SO ₄ (1.5 <i>N</i>)	6.7	6.08
..	..	1.5	HCl (1 <i>N</i>)	6.7	1.95
..	10 ⁻³	1.5	HCl (1 <i>N</i>)	6.7	2.12
..	10 ⁻²	1.5	HCl (1 <i>N</i>)	6.7	2.18
0.14	..	1.5	KNO ₃ (1 <i>M</i>)	6.5	2.02
0.14	10 ⁻²	1.5	KNO ₃ (1 <i>M</i>)	6.5	4.76
..	..	1.5	H ₃ PO ₄ (1 <i>M</i>)	6.5	2.12
..	10 ⁻²	1.5	H ₃ PO ₄ (1 <i>M</i>)	6.5	11.7

In the presence of ethanol, the extent of induced oxygen oxidation of ferrous iron depends markedly upon the anion present. This behavior may be correlated with the suppressing action in nitrogen, except for phosphoric acid. The strong suppressing action of chloride ion in the presence of oxygen is particularly striking and may be of practical importance in the determination of peroxides by re-

action with ferrous iron; it is planned to investigate whether chloride ion exerts this suppressing action in the presence of oxygen in the reaction between ferrous iron and organic hydroperoxides. Evidently atomic chlorine, formed from the chloride ion during the course of the peroxide-iron reaction, does not react with oxygen to form reactive peroxides under the experimental conditions used. Neither do the chlorine free radicals formed activate the organic compounds present in the reaction mixture. The above reactions may be possible, but under our experimental conditions the chlorine free radicals apparently react faster with ferrous iron than with other constituents of the reaction mixture.

It is evident that traces of organic impurities in the reagents used may give rise to considerable induced reactions, especially when the concentration of the primary reactants is small (of the order of $10^{-3} M$). In a previous paper² it has been shown that various samples of reagent grade perchloric acid from different sources contained impurities which caused considerable induced reduction of hydrogen peroxide. Even traces of organic impurities in the water used may exert a considerable effect on the ferrous iron-hydrogen peroxide reaction. When the present work was started we used twice-distilled water; however, no permanganate was present in the still. When this water was used reaction ratios greatly deviating from 2 were found, as shown in Table VI.

TABLE VI

EXPERIMENTS WITH IMPURE WATER IN THE PRESENCE OF AIR (EXCEPT AS NOTED). "STIRRING" TECHNIQUE

Acid and concentration, <i>N</i>	Initial concentration of Fe ⁺⁺ (<i>M</i> × 10 ³)	Molar ratios	
		Initial (Fe ⁺⁺) (H ₂ O ₂) taken	(Fe ⁺⁺) reacted (H ₂ O ₂) taken
1.5 <i>N</i> H ₂ SO ₄	0.42	4.0	2.64
0.15 <i>N</i> H ₂ SO ₄	.42	4.0	2.26
1 <i>N</i> HClO ₄	.46	4.5	2.72
0.1 <i>N</i> HClO ₄	.46	4.5	2.28
0.005 <i>N</i> HClO ₄	.46	4.5	2.12
1 <i>N</i> HClO ₄	.46	4.5	1.54 ^a
0.005 <i>N</i> HClO ₄	.46	4.5	1.72 ^a

^a Nitrogen was passed through the solutions before mixing; however, oxygen was only partially removed by the technique employed.

The impure water gave results similar to those found with pure water in the presence of small amounts of various organic compounds. Systematic investigation showed that the induced reaction could be almost completely eliminated by distillation of the water from alkaline permanganate, whereas no significant change in the extent of the induced reaction was found upon changing any of the other ingredients. Thus, similar results were found in impure water with ferrous solutions from two different sources (reagent grade FeSO₄·7H₂O and pure iron wire dissolved in perchloric acid); with three different brands of hydrogen peroxide (Merck, Baker, and Buffalo Electrochemical Co.); and with perchloric or sulfuric acid. While in the experiments of Table VI, increasing concentrations of acid led to increasing induced reaction, this effect cannot be due to impurities in the acids used, since no induced reaction was found when these same acids were used in purified water. The deviations from stoichiometric results found with the impure water must be attributed to the presence of traces of organic impurities in the water.

Summary

The reaction between hydrogen peroxide and ferrous iron in dilute solutions in the presence of oxygen and organic compounds leads to induced oxygen oxidation of ferrous iron. The extent of the induced oxidation may be quite large, particularly in oxygen-saturated solutions of the order of $10^{-3} M$ in peroxide and iron, in which the concentration of oxygen is relatively high. The amount of ferrous iron oxidized by the induced reaction may be two to three times as great as the amount oxidized by the stoichiometric reaction, under certain circumstances. It appears that the organic radical formed can add molecular oxygen, forming a peroxide radical, which can react with three ferrous ions, or can lead to autoxidation of the organic compound by a chain reaction. In the presence of oxygen, all the organic compounds tested show qualitatively similar behavior, without distinction between "promoting" and "suppressing" compounds. On the other hand, chloride ion is a suppressor in the presence as well as the absence of oxygen.

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