[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE CATALYTIC INFLUENCE OF FERRIC IONS ON THE OXIDATION OF ETHANOL BY HYDROGEN PEROXIDE

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Although solutions of hydrogen peroxide containing ferrous salts (Fenton's reagent) have long been used for oxidizing sugars, alcohols and other organic compounds,[1] there is comparatively little information on the conditions influencing such oxidations. Much confusion exists concerning the applicability of ferric salts and, further, little attention has been paid to the control of the acidity of the solution, a factor that recent investigation has shown to be of utmost importance.[2]

The object of this investigation was to study the conditions under which Fenton's reagent may best be used and at the same time to throw some light upon the mechanism of the reaction.

Experimental Part

The Reaction.—It was shown by Bohnson[3] that hydrogen peroxide oxidizes ethanol in the presence of ferric salts. Preliminary experiments showed that while hydrogen peroxide and ethanol undergo no appreciable reaction without a catalyst, in the presence of ferric salts the ethanol is completely oxidized to acetic acid without perceptible formation of aldehyde.

Materials.—The ethanol was dehydrated by the usual methods. A specific-gravity test showed it to be practically absolute. All salts were recrystallized at least once. "Perhydrol" (30% by volume hydrogen peroxide) was used as the source of hydrogen peroxide.

Method.—The reaction was followed by titrating the acetic acid formed during various time intervals using phenolphthalein as the indicator, with standard alkali solution. Since hydrogen peroxide is catalytically decomposed by iron salts[3] the active mass present at any given time could not be calculated from this titration; consequently, it was necessary to parallel the acetic acid titrations with permanganate titrations for the peroxide.

In all of the following experiments the volume of the solution was 172 cc. This contained 2 cc. of pure ethanol (0.2 millimole per cc.) and concentrations of hydrogen peroxide, catalyst and acid recorded in the tables. The temperature of all experiments was 35°.

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[1] Fenton, *Chem. News*, **33**, 190 (1876); **43**, 110 (1881); *J. Chem. Soc.*, **65**, 899 (1894); **75**, 1 (1899); **77**, 69 (1900); *Proc. Chem. Soc.*, **15**, 224 (1899).

[2] Hatcher, *Trans. Royal Soc. Canada*, **47**, 119 (1923). Hatcher and Holden, *ibid.*, **48**, 231 (1924).

[3] Bohnson, *J. Phys. Chem.*, **25**, 19 (1921).

Before the reaction started, all of the solutions used contained an original concentration of acid, this being furnished in part by the hydrolysis of the catalyst and in part by acid added to the solution. As a consequence it was necessary to correct the acid titration's values for the concentration of acid present before the oxidation of ethanol began. A correction was also made for the alkali used to precipitate the catalyst as ferric hydroxide.

A sharp end-point was obtained in the acid titration at the beginning of the reaction, but near the end, when practically all the alcohol had been oxidized, the end-point was indistinct and the acid value less than it should be. This was shown to be due to the oxidation of acetic acid to carbon dioxide, a reaction that does not take place, however, until the ethanol is almost completely oxidized, as will be shown later. As a consequence of this reaction, the titrations made near the end of the reaction are untrustworthy.

From the titration values it was possible to calculate at any given time (1) the total number of millimoles of active oxygen given up by the peroxide and (2) the millimoles of ethanol oxidized to acetic acid. If all of the oxygen thus liberated were used to oxidize the ethanol, the number of millimoles of ethanol oxidized in a given period would equal the number of millimoles of oxygen liberated. Since some of the peroxide is decomposed catalytically by the iron salts, the above-mentioned conditions are never realized. The ratio of ethanol oxidized to the decrease in the hydrogen peroxide concentration will be called the "efficiency" of the reaction, or Efficiency = (millimoles of ethanol oxidized)/(millimoles of oxygen evolved).

Reaction Velocities.—According to evidence to be given later, the two reactions, decomposition of the peroxide and oxidation of ethanol, tend to be unimolecular. This is not strictly true under all conditions, however; hence for purposes of comparison first order constants are calculated for the second 25% of the oxidation of the ethanol, during which period the reactions were most free from disturbing factors. The time for the second 25% of the two reactions was determined by plotting the curve for the reaction and interpolating for the time (t) over the region specified. A simple calculation shows that the first-order velocity constant can be obtained by dividing 0.406 by this time for the second 25% of the reaction. Mention has been made of the fact that the reactions measured are not strictly first order. This was made very apparent by plotting the logarithm of the concentration of ethanol against the time. In unimolecular reactions the resulting curve should be a straight line. In those solutions in which the acid added was present in rather high concentration (0.324) this was found to be true. The divergence from unimolecularity probably bears some relation to the increase in acid concentration resulting from the oxidation of ethanol. In those solutions that were strongly acid at the beginning of the experiment, the change in acidity would be relatively less than in the weakly acid solutions.

Effect of Acids on the Reaction.—The speed of oxidation of ethanol and the catalytic decomposition of the hydrogen peroxide in the presence of fixed concentrations of iron salts was measured in solutions containing various amounts of the hydrochloric, nitric, sulfuric and acetic acids. The data for the oxidation of ethanol in the presence of several iron salts are given in Table I and shown graphically in Fig. 1. In all tables the velocity constant K is 1000 times the value calculated. In those solutions to which no acid was added a small amount of basic salt always separated. This precipitate does not catalyze the reaction and its formation decreases the concentration of the ferric ions; consequently, these experiments are slower than the others. In all cases increase in acid concentration decreases the speed of the oxidation of ethanol to acetic acid. In solutions of the same normality, sulfuric acid shows the greatest retarding effect, followed by hydrochloric, nitric and acetic in the order given. From these data the most favorable condition for the rapid oxidation of the ethanol is to have just enough acid in the solution to keep the iron salt from precipitating as a result of hydrolysis.

TABLE I

EFFECT OF ACIDS ON THE REACTION

Concn. of catalyst in each case, 0.005 mole of iron per liter; that of ethanol, 0.2 N. The concentrations of the acids are expressed as normality.

1. $FeCl_3$ and HCl. Initial concn. of H_2O_2 = 0.61 mole per liter.

Concn. acid	0	0.0054	0.016	0.027	0.054	0.081	0.162	0.324
K (C_2H_5OH)	47.7	72.5	48.4	33.3	15.5	9.7	4.5	1.0
K (H_2O_2)	34.6	60.5	41.8	25.6	12.9	8.1	5.1	4.1

2. Fe $(NO_3)_3$ and HNO_3. Initial concn. of H_2O_2 = 0.67 mole per liter.

Concn. acid	0.021	0.042	0.063	0.084	0.104	0.167
K (C_2H_5OH)	50.7	27.0	18.5	13.1	11.7	6.4
K (H_2O_2)	38.0	21.4	13.7	9.2	8.1	5.4

3. $FeSO_4$ and H_2SO_4. Initial concn. of H_2O_2 = 0.55 mole per liter.

Concn. acid	0	0.005	0.0059	0.0273	0.0496	0.104
K (C_2H_5OH)	12.2	24.4	20.1	9.5	5.0	2.5
K (H_2O_2)	10.4	22.0	18.3	7.8	4.5	2.2

4. $FeCl_3$ and CH_3COOH. Initial concn. of H_2O_2 = 0.67 mole per liter.

Concn. acid	0.029	0.074	0.118	0.191
K (C_2H_5OH)	67.8	50.2	38.7	26.2
K (H_2O_2)	50.8	36.0	28.4	22.0

5. $Fe_2(SO_4)_3$ and H_2SO_4. Initial concn. of H_2O_2 = 0.63 mole per liter.
For 0.0164 N acid: K (C_2H_5OH) = 11.8; K (H_2O_2) = 9.4.

6. $FeSO_4.(NH_4)_2SO_4$ and H_2SO_4. Initial concn. of H_2O_2 = 0.61 mole per liter.
For 0.0114 acid: K (C_2H_5OH) = 16.5; K (H_2O_2) = 12.6.

Efficiency of the Reaction.—Table II gives the efficiency of the oxidation of ethanol using different catalysts in equivalent concentrations and different concentrations of acid. The results are expressed as "per cent. efficiency" which is the ethanol actually oxidized compared with the ethanol that would have been oxidized if there had been no catalytic decomposition of hydrogen peroxide.

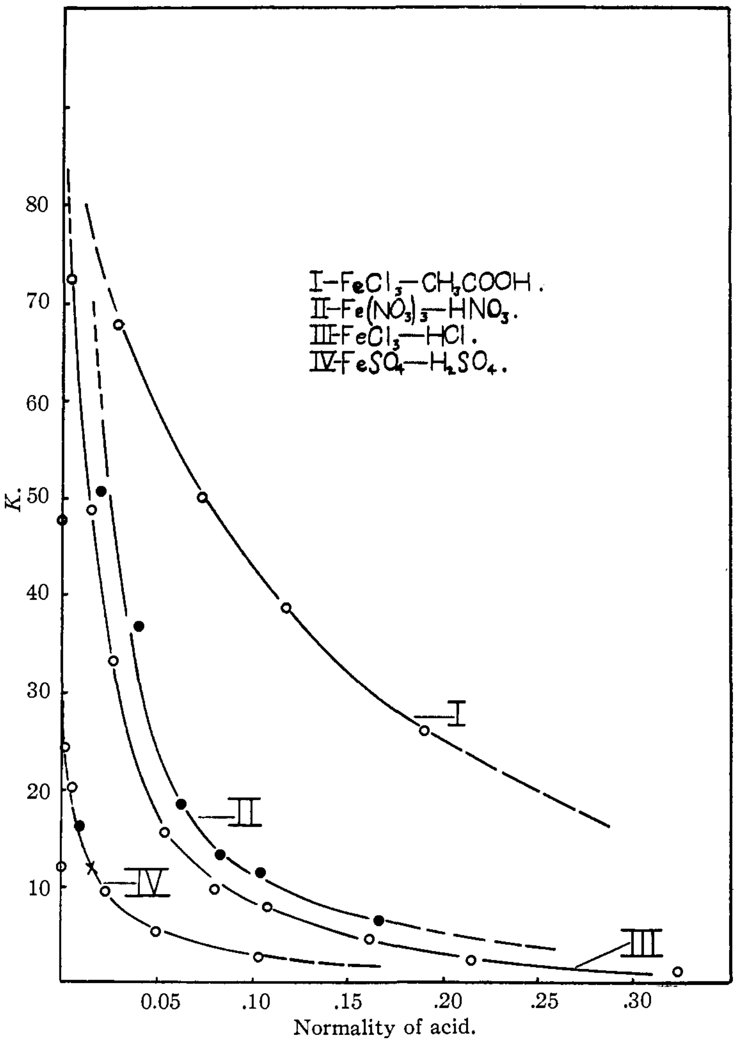

Fig. 1.—Effect of acids on velocity of oxidation of ethanol.

Hydrochloric Acid with Ferric Chloride.—The efficiency drops off when the concentration of the acid is greater than 0.027 *N*. This is undoubtedly due to the fact that hydrochloric acid is a catalyst for hydrogen

Table II

Efficiency of the Reaction

Catalyst[a]	Acid	Acid, *N*	Moles of H_2O_2 per liter	Per cent. efficiency for First 10 millimoles of oxygen evolved	Per cent. efficiency for First 20 millimoles of oxygen evolved	Per cent. efficiency for First 35 millimoles of oxygen evolved
$FeCl_3$	HCl	0 to 0.027	0.61	58	64	71
		0.054	.61	49	57	66
		.081	.61	40	47.5	56
		.108	.61	33	40	44
		.162	.61	25	30	41
		.324	.61	20	25	30
$Fe(NO_3)_3$	HNO_3	0 to 0.167	.67	47.5	58.8	71
$FeSO_4$	H_2SO_4	0 to 0.109	.55	60.0	71.0	79
$FeCl_3$	$HC_2H_3O_2$	0 to 0.191	.67	50.0	61.0	70
$Fe(NO_3)_3$	HNO_3	0.024	1.79	60.0	59.0	60.7

[a] Concentration of catalyst in each case 0.005 mole of iron per liter.

peroxide[4] and this substance is being decomposed by both the ferric chloride and the hydrochloric acid. The ferric salt, however, is the only catalyst for the oxidation of the ethanol. The catalytic influence of hydrochloric acid is further evident in Fig. 2, where the catalytic decomposition of hydrogen peroxide is slightly more rapid in the nitric acid than the hydrochloric acid solutions of low acid concentration. As the concentrations of the acids increase, however, the speeds of the reactions in the two solutions approach each other and there is little doubt that at higher concentrations the speed in the hydrochloric acid would exceed that in the nitric acid solution. No such relationship is seen in the oxidation of ethanol, Fig. 1; the curves parallel each other over the entire range.

Nitric Acid with Ferric Nitrate.—While an increase in the concentration of this acid cuts down the rate of the two reactions, the efficiency is constant throughout the range of concentrations, and approximates the efficiency of hydrochloric acid systems of 0.027 *N*.

Sulfuric Acid with Ferric and Ferrous Salts.—The salts used were ferrous sulfate, ferric sulfate and ferrous ammonium sulfate. The two types of salts were used because of the statement that the ferrous salts only are effective in Fenton's reagent. If the assumption is made that the ferrous salt is at once oxidized by the hydrogen peroxide according to the equation $2FeSO_4 + H_2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O$, it is evident that in comparing the effect of acid in the presence of the two salts a correction must be made for the acid used up in the oxidation of the ferrous salt. The data given have been corrected accordingly. The lower curves of Figs. 1 and 2 show that the velocity constants for these three salts are in agreement, for they all fall on the same general curve; in other words, in

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[4] Maass and Hiebert, This Journal, **46,** 290 (1924). Livingston and Bray, *ibid.*, **47,** 2069 (1925).

this reaction the state of oxidation of the iron in Fenton's reagent is immaterial. The efficiency of the system is independent of the concentration of the sulfuric acid and is of the same order as the nitric acid though the table shows a slightly higher value. This is undoubtedly due to the fact that the initial concentration of hydrogen peroxide is lower than that in the nitric acid solutions. This effect will be considered later.

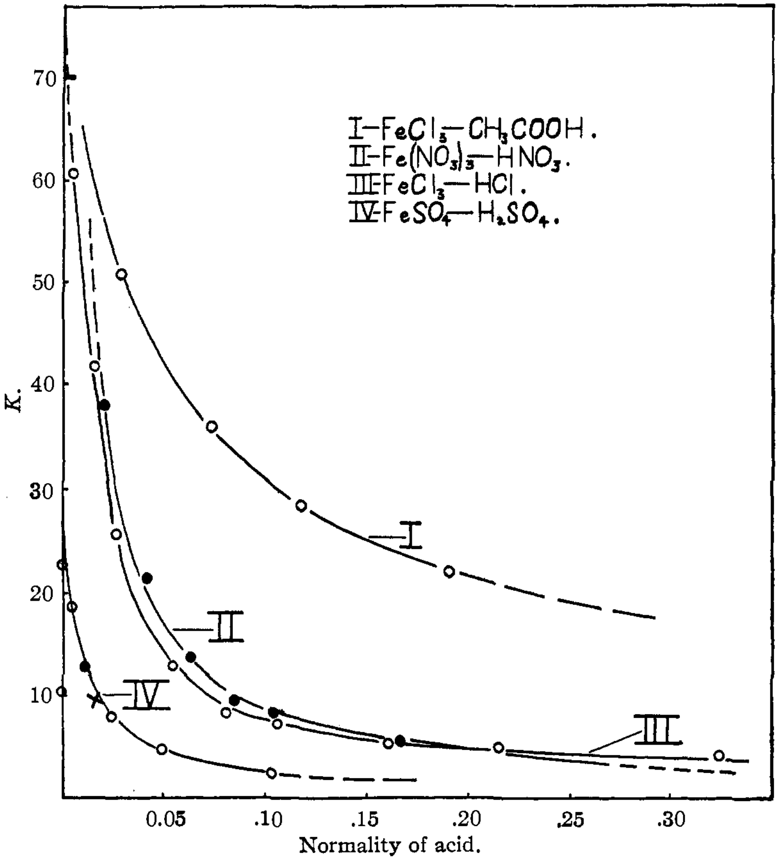

Fig. 2.—Effect of acids on velocity of decomposition of hydrogen peroxide.

Acetic Acid and Ferric Chloride.—Acetic acid does not retard the two reactions as much as the other acids, but the efficiency is about the same as that of the sulfuric and nitric acid solutions.

Comparison of the Different Acids.—The data in Table II show that the efficiency of this reaction increases as the concentration of the hydrogen peroxide decreases. Further, the efficiency, except in the case of the solutions of hydrochloric acid above 0.027 *N*, is independent of the acid, the acid concentration and the iron salt used as a catalyst.

In a study of the catalytic decomposition of hydrogen peroxide by ferric salts Bohnson found that increasing the acidity of the solution decreased the activity of the iron salts. This has been explained as follows. The hydrogen peroxide oxidizes the ferric salt to ferric acid, which is then reduced to ferric iron by the excess of hydrogen peroxide as follows.

$$2FeR_3 + 3H_2O_2 + 2H_2 \rightleftharpoons H_2FeO_4 + 6HR \qquad (1)$$
$$2H_2FeO_4 + 3H_2O_2 \longrightarrow 2Fe(OH)_3 + 2H_2O + 3O_2 \qquad (2)$$
$$2Fe\,(OH)_3 + 6HR \rightleftharpoons 2FeR_3 + 6H_2O \qquad (3)$$

The existence of the ferric acid has been conclusively demonstrated by Bohnson and Robertson[5] by means of spectrographic studies. From Equation 1, it is evident that an increase in the concentration of the acid would decrease the concentration of ferric acid, thus explaining the retarding effect of acids.

The fact that both oxidation of ethanol and decomposition of peroxide are retarded by acids suggests ferric acid as the same intermediate in both cases. In this case one would expect that change in the concentration of the intermediate would affect the two reactions in a similar manner. That this is the case will be seen by comparing the curves in Fig. 1 with those in Fig. 2. With the exception of the $FeCl_3$-HCl solutions, whose discrepancy has been explained, these curves parallel each other throughout. It is therefore concluded that the ferric acid is the intermediate in the oxidation of ethanol by Fenton's reagent. Whether or not this holds in other oxidations by Fenton's reagent will be the subject of further investigation.

Effect of Concentration of Catalyst.—Using ferric nitrate in nitric acid as a catalyst, the data given in Table III were obtained. The constancy of the values in the last two columns shows that the speed of the two reactions is directly proportional to the concentration of the catalyst used.

TABLE III

RELATION BETWEEN THE CONCENTRATION OF CATALYST ($Fe(NO_3)_3$) AND SPEED OF THE REACTION

Acid concentration: 0.0417 N HNO_3. H_2O_2 concentration: 0.60 mole per liter

Concn. of $Fe(NO_3)_3$, moles per liter	$K(C_2H_5OH)$	$K(H_2O_2)$	$\frac{K(C_2H_5OH)}{\text{Concn. } Fe(NO_3)_3}$	$\frac{K(H_2O_2)}{\text{Concn. } Fe(NO_3)_3}$
0.001	5.7	4.2	0.0057	0.0042
.005	36.9	25.4	.0074	.0051
.010	72.5	58.0	.0073	.0058
.015	109.8	88.4	.0073	.0059
.020	156.1	119.5	.0073	.0060

Effect of Increasing the Concentration of Hydrogen Peroxide.—The concentration of the peroxide was almost thrice that used in the

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[5] Bohnson and Robertson, THIS JOURNAL, **45**, 2493 (1923).

previous experiments. Ferric nitrate was used as a catalyst. The value of K for oxidation of ethanol was 162 compared with 50.7 in the dilute solutions of the peroxide. After the ethanol was completely oxidized to acetic acid a large excess of peroxide still being present, the acidity of the solution began to decrease due to oxidation of acetic acid to carbon dioxide and water. The carbon dioxide was swept out of the solution by the oxygen that was continuously evolved, so that the end-point obtained while following the reaction by titration with alkali was sharp at all times. Plotting the logarithm of the concentration of the acid against the time gave a curve with a very sharp break, which showed that the oxidation of the acetic acid follows the oxidation of the ethanol. This break is indicated in the following data obtained from duplicate experiments in which the oxidation of the ethanol and subsequent oxidation of acetic acid were followed by titrating samples of the solution with approximately 0.1 N potassium hydroxide solution.

t, min.	29	62	97	132	167	198	230	328	443	879
KOH, cc.	3.0	6.5	9.9	10.1	9.1	8.4	8	7	6.5	5.5

The efficiency of this experiment is constant (Table II). The data in Table II show that in experiments with very dilute solutions of hydrogen peroxide the efficiency approaches 100%, but at higher concentrations of peroxide it remains constant at about 60%.

Effect of Copper as a Promoter.—Bohnson and Robertson[5] have shown that copper ions promote the decomposition of hydrogen peroxide by ferric ions. Robertson[6] has shown that the copper ions function as follows. Ferric acid is formed which reacts with the copper thus: $3CuO + 2FeO_3 = 3CuO_2 + Fe_2O_3$. The CuO_2 (cupric acid), a new intermediate formed only in the presence of ferric acid, reacts very much more energetically in a mutual reduction with hydrogen peroxide, than the ferric acid. In view of these facts it was of interest to investigate the effect of copper salts on the oxidation of ethanol by Fenton's reagent. In no case was promoter action observed in the oxidation of ethanol but the decomposition of hydrogen peroxide was greatly accelerated.

Other Salts as Catalysts.—A number of other salt catalysts were used in place of the iron salt in the application of hydrogen peroxide in oxidizing ethanol but no one of them approached the iron as a catalyst. Of those tried, sodium vanadate was the best, with potassium chloroplatinate a close second. The other substances used were cobalt chloride, nickel chloride, sodium molybdate, uranium nitrate, manganese chloride, manganese acetate, chloroplatinic acid, sodium tungstate, cerium chloride, potassium dichromate and sodium borate. Certain experimenters have stated that manganese salts are good catalysts in oxidations with atmos-

[6] Robertson, This Journal, **47**, 1299 (1925).

pheric oxygen. With the hydrogen peroxide, however, they are comparatively ineffective.

Summary

1. Hydrogen peroxide in the presence of ferric salts (Fenton's reagent) oxidizes ethanol to acetic acid. The reaction is quantitative. This reaction is paralleled by the catalytic decomposition of the hydrogen peroxide by the ferric ions. The two reactions are approximately unimolecular.

2. Acids retard the speed of these reactions. In solutions of equivalent concentrations the order of increasing effectiveness is acetic, nitric, hydrochloric, sulfuric.

3. The speed of the two reactions is directly proportional to the concentration of the catalyst.

4. The reaction velocity increases with the concentration of the hydrogen peroxide.

5. Ferrous salts have been shown to be just as effective as ferric salts, inasmuch as they are immediately oxidized to the trivalent condition.

6. Evidence has been obtained that the ethanol is oxidized through the formation of ferric acid as an intermediate.

7. The oxidation of the ethanol to acetic acid is followed by the oxidation of the acetic acid to carbon dioxide and water.

8. Other salts substituted for the ferric compounds in Fenton's reagent have been found to be unsatisfactory.

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[Contribution from the Chemical Laboratory of the Johns Hopkins University]

CATALYSIS IN BUFFER SOLUTIONS. I

By Martin Kilpatrick, Jr.[1]

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The general purpose of this work was to study the velocity of various reactions in small concentrations of hydrogen and hydroxyl ions. The study necessitated the use of buffer solutions and a consideration of the effect of neutral salts. A preliminary study indicated that with certain limitations several reactions are suitable for the purpose: (1) the decomposition of nitrosotriacetoneamine; (2) the decomposition of diazoacetic ester; (3) the reaction between acetone and iodine as catalyzed by hydrogen ion; (4) the mutarotation of sugars; (5) the hydrolysis of the esters. The last two reactions are catalyzed by both hydrogen and hydroxyl ions and permit a study of the catalytic minimum point.

The present paper deals with the decomposition of nitrosotriacetoneamine, catalyzed by hydroxyl ions. The reaction has been studied by

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[1] National Research Fellow.