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

A STUDY OF THE OXIDATION OF SOME DICARBOXYLIC ACIDS BY HYDROGEN PEROXIDE IN THE PRESENCE OF CERTAIN CATALYSTS[1]

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In an investigation by Christensen and the senior author[2] of this paper, it was shown that ethanol is completely oxidized to acetic acid by hydrogen peroxide in the presence of iron salts (Fenton's reagent). The effect of temperature and of hydrogen ion concentration as well as concentrations of reactants and catalysts were investigated at that time. The present paper is a continuation of the above mentioned work, and deals with the oxidation of certain dicarboxylic acids of the paraffin series.

Methods.—The solutions to be used were placed in a thermostat and allowed to come to the temperature at which the reaction was to be studied. Known quantities of the catalyst were then pipetted into 100 cc. volumetric flasks, together with the acid under investigation and the requisite amount of hydrogen peroxide. The flasks were then filled to the mark with distilled water at the temperature of the reaction and placed in a thermostat. The progress of the reaction was followed by titration of samples withdrawn at definite time intervals. The acid strength was followed by titration with standard alkali, while a permanganate titration furnished an index of the concentration of the hydrogen peroxide. The dicarboxylic acids so studied were oxalic, succinic, malic, lactic and tartaric acids, with iron and copper salts as catalysts. Similar studies were made on glycerol, formic acid and ethylene glycol.

Results

Oxalic Acid.—The oxidation of oxalic acid by comparatively concentrated solutions of hydrogen peroxide, about 10 per cent. by weight, was studied by Hatcher,[3] and Hatcher and Holden,[4] who investigated the effect of acids on the reaction in the absence of catalysts. No appreciable oxidation of the oxalic acid by solutions of hydrogen peroxide of a concentration of less than 6% was observed. From these results and the fact that oxalic acid is rather easily oxidized by a number of the more common oxidizing agents, it was expected that it would be easily oxidized by dilute solutions of hydrogen peroxide in the presence of a

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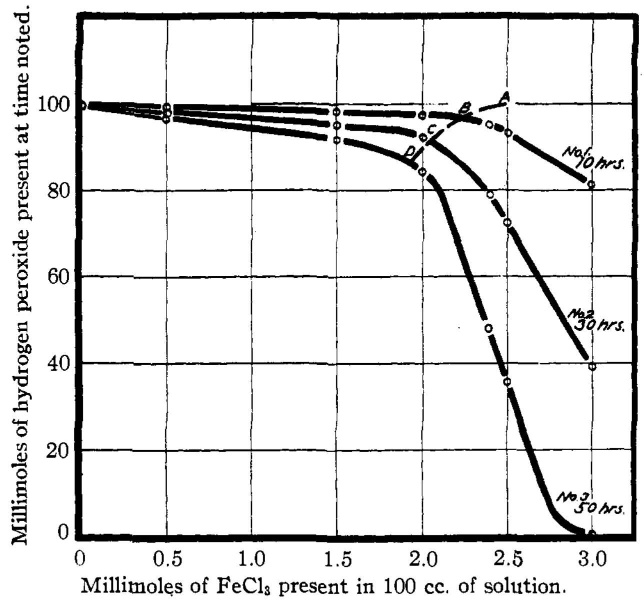
[1] This investigation was made possible by a grant from the Research Committee of the University of Wisconsin, Dean C. S. Slichter, Chairman.

[2] Walton and Christensen, THIS JOURNAL, **48**, 2083 (1926).

[3] Hatcher, *Trans. Roy. Soc. Canada*, **17**, 119 (1923).

[4] Hatcher and Holden, *ibid.*, **18**, 231 (1924).

catalyst. With this acid, the catalyst used was ferric chloride. It was impossible to study satisfactorily the reactions in the presence of the copper salts as catalysts due to the fact that a precipitate was formed. It was noted that with ferric chloride the oxidation efficiency[5] was low and that the hydrogen peroxide was completely decomposed before more than a small fraction of the oxalic acid had been oxidized. (This is shown in Fig. 1.) It was difficult to follow the changes in acidity when the temperature was above 25° due to the rapidity of the decomposition of the hydrogen peroxide, which increased with increase in temperature more rapidly than did the rate of oxidation of the oxalic acid.



Dotted curve, millimoles of oxalic acid present in 100 cc. of solution.

Fig. 1.—The oxidation of oxalic acid (graph indicating formation of complex).

The most interesting and perhaps the most important observation resulting from this work was the tendency of the oxalic acid to inhibit the decomposition of hydrogen peroxide by ferric chloride. A similar property of oxalic acid was observed by Colin and Senechal[6] in their study of the effect of acids on the catalytic oxidation of phenols by hydrogen peroxide in the presence of ferric salts as catalysts. These investigators

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[5] The term oxidation efficiency is applied to the ratio of the oxygen actually used to that available from the hydrogen peroxide. This function is used only qualitatively.

[6] Colin and Senechal, *Compt. rend.*, **153**, 76–79, 282–283 (1911).

postulated the formation of a complex between the ferric ion and the oxalate ion. As further substantiation of the existence of this complex, they advance the fact that when an excess of oxalic acid is added to a solution containing a little ferric salt, neither potassium ferrocyanide nor potassium thiocyanate shows a test for iron. Their data do not indicate the possible composition of the complex. They indicate the formation of similar complexes of ferric ion with acetic acid, lactic acid, malic acid, tartaric acid and citric acid, in the order of increasing stability, the ferrioxalate complex being the most stable of all.

In the present study the rate of decomposition of hydrogen peroxide by ferric chloride in the presence of oxalic acid was found to be extremely slow when the molar concentration of ferric chloride was less than that of the oxalic acid. It increased rapidly, however, as the ferric chloride concentration increased beyond that of the oxalic acid. This indicated the formation of a definite and stable complex consisting of equimolecular quantities of ferric ion and oxalate ion.

This relationship is shown by the data in Table I and is illustrated graphically in Fig. 1, in which the concentration of the hydrogen peroxide in solutions containing various concentrations of ferric chloride is given at the time intervals, 10, 30 and 50 hours, respectively. In the three curves a change takes place in the reaction when the molar concentration of the ferric chloride exceeds that of the oxalic acid. For curve 1 the break occurs at the point at which the concentration of ferric chloride is 2.2 millimoles. In curves 2 and 3 it will be noticed that the break takes place at a concentration somewhat below this value. This is due to the fact that even in the lower concentrations of ferric chloride, oxidation of the oxalic acid is slowly taking place, so that after ten hours slightly less than 2.5 millimoles of the acid is present.

Table I

The Oxidation of Oxalic Acid

Catalyst concn. $FeCl_3$, mmls.	Start		After 10 hours		After 20 hours		After 30 hours		After 40 hours		After 50 hours	
	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.	H_2O_2, mmls.	$C_2H_2O_4$, mmls.
0.500	100.0	2.500	99.5	..	99.0	..	98.3	..	97.6	..	97.0	..
1.500	100.0	2.500	98.5	2.41	96.7	2.34	95.2	2.27	93.5	2.22	91.5	2.15
2.000	100.0	2.500	97.7	2.39	95.7	2.33	92.3	2.22	87.5	2.12	84.2	2.05
2.400	100.0	2.500	95.2	2.16	88.0	2.10	79.0	1.88	65.0	1.77	48.0	1.73
2.500	100.0	2.500	93.7	2.22	84.6	2.10	72.2	1.99	57.0	1.88	36.0	1.67
3.000	100.0	2.500	81.2	2.36	59.5	2.27	39.0	2.16	19.0	2.10	0.0	2.05

The dotted curve A-D represents this variation of acid concentration, expressed in the units denoted in the abscissa legend, point "A" representing the concentration of oxalic acid (2.5 millimoles) corresponding to a ferric chloride concentration of 2.5 millimoles, at the beginning of the run. Point "B" is the catalyst concentration at which the oxalic acid concentration is reduced to its equivalent (2.2 millimoles) in ten hours. Point "C" is the catalyst concentration at which the oxalic acid is reduced in concentration to its equivalent in thirty hours, and point "D" the catalyst concentration at which the oxalic acid is reduced to its concentration in fifty hours. In other words, curve A-D is a line passing through those points on the isotemporal curves at which the oxalic acid concentration equals, molecularly, the ferric chloride concentration. These values were obtained by interpolation of the accompanying oxalic acid data.

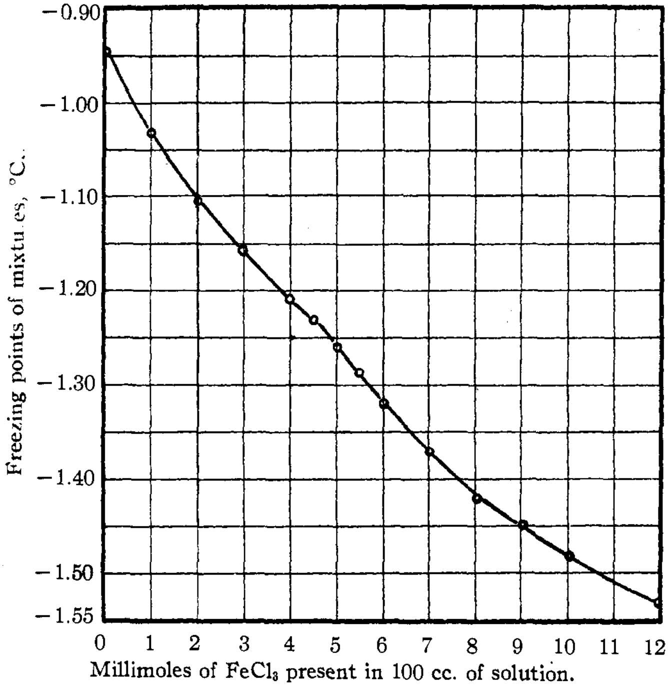

Fig. 2.—Freezing point–composition curve for solutions containing 50 cc. of 3% H_2O_2, 5 mmls. of oxalic acid, and varying quantities of $FeCl_3$ as noted.

Since runs made at temperatures of 25, 35 and 45° show the same relationship, the temperature of the reaction does not in any way alter the nature of the complex formed. Runs made with concentration of oxalic acid from 0.1 *N* to 0.05 *N* both showed the equimolecular relationship.

In order to determine the effect of the hydrogen ion, a run was made in which sodium oxalate was substituted for oxalic acid. This run gave results in exact accordance with those of the oxalic acid. The speed of reaction was greater, however, due to the fact that the presence of free acid suppresses the formation of *ferric acid*,[2,7] the intermediate both in the decomposition of the hydrogen peroxide and in the oxidation reactions.

The conclusion that a definite, stable complex was formed is further substantiated by freezing point measurements which, for varying quantities of ferric chloride in the presence of constant concentrations of oxalic acid and hydrogen peroxide, showed a slight break in the freezing point–composition curve, at the point where the molecular concentration of the oxalic acid equaled that of the ferric chloride. This freezing point–composition curve is given in Fig. 2, which represents concentrations of ferric chloride varying from zero to 12 millimoles per 100 cc.

The data for this curve are given in Table II.

Freezing point measurements with ferric chloride and oxalic acid in the absence of hydrogen peroxide showed no break in the freezing point curve; consequently the complex formed is not a simple compound of ferric chloride and oxalic acid.

TABLE II

FREEZING POINT–COMPOSITION DATA FOR SOLUTIONS CONTAINING 50 CC. OF 3% HYDROGEN PEROXIDE, 5 MILLIMOLES OF OXALIC ACID AND VARYING QUANTITIES OF FERRIC CHLORIDE, PER 100 CC. OF SOLUTION

$FeCl_3$ present in 100 cc. soln., mmls.	Freezing point	$FeCl_3$ present in 100 cc. soln., mmls.	Freezing point
0	−0.944	5.50	−1.287
1.00	−1.030	6.00	−1.320
2.00	−1.107	7.00	−1.372
3.00	−1.157	8.00	−1.422
4.00	−1.212	9.00	−1.447
4.50	−1.232	10.00	−1.482
5.00	−1.262	12.00	−1.532

Formic Acid.—Since formic acid is one of the intermediates formed in the oxidation of some of the more complex acids a study of its oxidation was undertaken. The data obtained were of value only in that they showed that formic acid was much more readily attacked by hydrogen peroxide in the presence of ferric chloride than in the presence of copper salts, and that the presence of carbon dioxide in the solution played an important role in determining the rate of the oxidation, markedly decreasing the rate when ferric chloride was used as the catalyst. The end products were carbon dioxide and water.

Other Oxidations.—Other reactions studied were the oxidation of succinic acid and its α-hydroxy derivatives, malic, tartaric and lactic acids. It was observed that the introduction of the hydroxy groups made the acids more readily oxidizable and, except for the case in which ferric chloride was used as the catalyst, decreased the ability of the acid

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

to inhibit the decomposition of the hydrogen peroxide. It was further noted in the case of malic and lactic acids, both of which contain the structure —$CH_2CHOHCOOH$, that the concentration of the catalyst within the limits studied (0.005 *M* to 0.02 *M*) had very little effect either on the oxidation itself or on the rate of decomposition of the hydrogen peroxide.

The oxidations of glycerine and of ethylene glycol were also studied. In the case of these polyhydric alcohols, the acidity, due to formic acid as an intermediate, increased to a maximum. After the alcohol was almost gone, the acidity began to fall rapidly. In an earlier part of this paper attention was called to the fact that formic acid alone is readily oxidized. As a consequence one could expect that any formic acid formed as an intermediate would rapidly disappear. As such is not the case, it must be concluded that the presence of a hydroxyl group attached to a primary carbon atom exerts a protective action over formic acid in the presence of hydrogen peroxide and any of the catalysts studied. That is,

TABLE III

THE OXIDATION OF VARIOUS ORGANIC COMPOUNDS BY HYDROGEN PEROXIDE IN THE PRESENCE OF CERTAIN CATALYSTS AT A TEMPERATURE OF 25°

		Time in hours			
Catalyst used	Compound studied	For $^1/_2$ decomp. of H_2O_2	For $^1/_2$ oxidation of acid	For acidity to reach maximum	Ref. numbers for variation of acidity (see notes below)
1.00 mml. $FeCl_3$	Succinic acid	7	..	...	1
	Malic acid	22	43	...	2
	Lactic acid	8	..	10	3
	Tartaric acid	20	12	...	2
	Ethylene glycol	4	..	3	3
	Glycerine	$2^1/_2$	..	10	3
1.00 mml. $CuCl_2$	Malic acid	120	..	...	1
	Lactic acid	700	..	...	4
	Tartaric acid	220	..	80	3
	Tartaric acid (reduced pressure)	$1^1/_2$	3	...	2
	Ethylene glycol	500	..	550	3
	Glycerine	420	..	600	3
1.00 mml. $CuSO_4$	Succinic acid	350	..	180	3
	Malic acid	80	1000	...	2
	Lactic acid	200	..	150	3
	Tartaric acid	4	10	...	2
	Tartaric acid (reduced pressure)	12	..	4	3
	Ethylene glycol	300	..	300	3
	Glycerine	170	..	250	3

Notes: (1) falls very slowly with the loss of less than 50% of the acid during the life of the hydrogen peroxide; (2) falls smoothly and regularly; (3) rises to maximum and then falls smoothly; (4) shows initial sudden drop followed by gradual rise until hydrogen peroxide is exhausted.

the rate of oxidation of formic acid is much slower than in the absence of the alcohol. This protective action is apparently strictly a property of the primary carbinol, as no such marked effect was noted in the cases of tartaric and malic acids.

A general summary of these reactions is given in Table III. It is evident that, aside from the brief generalizations just outlined, it is impossible to express the relative oxidizability of these compounds quantitatively. This is due to the general complexity of the system, in which different parts of the molecule are undergoing simultaneous oxidation at different rates, accompanied in most cases by the formation of a number of oxidation intermediates. At the same time the catalytic decomposition of the hydrogen peroxide is also going on. A number of varying factors, moreover, all have marked effects on the reaction. The increase in hydrogen ion concentration tends in all cases to inhibit both the decomposition of the hydrogen peroxide and any simultaneous reaction of oxidation. The carbon dioxide content, on the other hand, while having a marked effect, is less regular. When the carbon dioxide was removed by suction during the oxidation of tartaric acid, it was found that when copper sulfate was used as the catalyst the rate was decreased to one-third of the original value, while in the case of copper chloride it was increased over 100 times. It is the number of such variable factors, impossible to control completely and most difficult to interpret accurately, that makes it almost impossible to reach a quantitative expression for the relationships between structure and facility of oxidation.

Summary

1. Oxalic acid combines with the ferric ion in the presence of hydrogen peroxide to form a stable complex in which there is one mole of ferric ion for each mole of oxalate.

2. The introduction of hydroxy groups into the succinic acid molecule, giving malic and tartaric acids, increases the rate of its oxidation by hydrogen peroxide in the presence of catalysts and tends in general to decrease its ability to inhibit the decomposition of the hydrogen peroxide by the catalysts studied.

3. The carbon dioxide content of the reacting solution has a marked effect on the nature of the reaction.

4. An increase in acidity tends to decrease both the rate of decomposition of the peroxide and the rate of oxidation of the acid.

5. In the presence of the lactic acid structure, $-CH_2CHOHCOOH$, when copper salts are used to catalyze oxidation with hydrogen peroxide, the concentration of the catalyst, within the limits studied, has little effect either on the oxidation itself or on the rate of decomposition of the hydrogen peroxide.

6. The presence of a primary alcohol group exerts a protective action over formic acid in the presence of hydrogen peroxide and any of the catalysts studied, making the rate of oxidation of such an acid as formic or acetic, much slower than in the absence of the alcohol.

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THE PREPARATION OF BORIC ACID ANHYDRIDE AND ITS EFFICIENCY AS A DRYING AGENT

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Boric acid anhydride has been used by Schlesinger in the preparation of pure, dry formic acid[1] and also in the preparation of dry ether.[2] Since this substance is so efficient as a drying agent, it was of interest to determine the conditions which yield a product of maximum drying efficiency.

Preparation of Boric Acid Anhydride.—Fifty grams of pure boric acid crystals were placed in a 100-cc. platinum dish and heated over a Méker burner to a temperature of about 600°, a process attended by considerable frothing and the evolution of water vapor. The dish containing the clear, viscous liquid was then placed in an electrically heated muffle furnace and different samples were dehydrated at various temperatures for about an hour. At the end of this time, the dish was removed and the contents poured on a marble slab, where it immediately hardened to a clear glass. Although the boric acid melts at 577° a temperature of 800° is necessary for sufficient fluidity to permit easy pouring. Samples of the anhydride were dehydrated at 800, 900 and 1000°.

The glassy boric anhydride is extremely hard and is best ground in a ball mill using flint pebbles. After grinding for three days a powder was obtained that passed through a 100-mesh sieve, 90% of it passing through a 160-mesh sieve. To help eliminate this prolonged grinding a sample of the anhydride was prepared at 900° and the molten glass poured into purified carbon tetrachloride that had been chilled to 0°. This yielded material in the shape of small pellets which could be much more easily ground after evaporation of the carbon tetrachloride. Some of this preparation was used in the following tests.

In view of the fact that it has been stated that boric acid anhydride vaporizes at a red heat,[3,4] it should be possible to take advantage of this property for the preparation of this substance in a finely divided form and thus avoid the use of the ball mill. Preliminary experiments with this method were unsatisfactory. To effect volatilization in a current of dry air, a temperature of 1000° was necessary. The experiments were not continued because of the small yield and the fact to be shown later that boric acid prepared at high temperatures is not a satisfactory drying agent.

[1] Schlesinger and Martin, THIS JOURNAL, **36**, 1589 (1914).

[2] Communication from Professor Schlesinger.

[3] Ebelmen, *Ann. chim. phys.*, **22**, 211 (1848).

[4] Tiede and Birnbräuer, *Z. anorg. Chem.*, **87**, 129 (1914).