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The Autoxidation of Ascorbic Acid[1]

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The availability of ascorbic acid (vitamin C) is seriously diminished through destruction by autoxidation. Although a considerable amount of research has been carried out on this autoxidation, the literature is full of contradictions on practically every phase of the problem. This situation is caused by the failure until recently to control the many factors which influence the reaction, as pointed out by Barron, De Meio and Klemperer[2a] and also by Schümmer.[2b] This investigation attempts to clear up some of the contradictions in the literature and to increase our knowledge of the methods of inhibiting the oxidation of vitamin C.

Experimental

The ascorbic acid, obtained from Merck and Co., was shown to be over 99.8% pure, with a melting point of 188–190°. The water was purified by distilling twice from an all glass apparatus.

The *p*H readings were made with a Beckman *p*H meter. For *p*H values above 9.00 the special type E glass electrode was used, corrections being made at the very high *p*H values. The water was freed from oxygen by bubbling nitrogen through it. One-tenth of one gram of ascorbic acid in 150 cc. of solution was used for each run.

Since the oxidation of ascorbic acid results in a considerable change in the *p*H which in turn has a large effect on the rate of reaction, it was necessary to buffer the solutions. The ascorbic acid solutions were placed in 300-cc. flasks of the type described by Filson and Walton.[3] These were fastened in a shaking apparatus[4] and connected with water-jacketed gas burets. The nitrogen was evacuated from the flask and buret, and pure oxygen was introduced. The course of the reaction was followed by observing the decrease in the volume of oxygen at various time intervals. During this period the flask was shaken. The rate of shaking was approximately 1000 vibrations per minute, one vibration of the reaction flask being a rotation about a vertical axis through an angle of 70° and back. This rate of shaking was sufficient to keep the solution saturated with oxygen during the most rapid runs. Insufficient shaking is partly responsible for the many contradictory results found in the literature on this problem. The reaction was run at 25°.

The results are reported in terms of the half-life or quarter-life of the reaction. These values were obtained directly by noting the time necessary for one-half or one-quarter, respectively, of the total volume of oxygen to be absorbed.

(1) Original manuscript received May 20, 1942.

(2) (a) Barron, De Meio and Klemperer, *J. Biol. Chem.*, **112**, 625 (1936). (b) Schümmer, *Biochem. Z.*, **304**, 1 (1940).

(3) Filson and Walton, *J. Phys. Chem.*, **36**, 740 (1932).

(4) Walton, *Z. physik. Chem.*, **47**, 185 (1904).

Results and Discussion

(1) Effect of the *p*H on the Rate of the Reaction. (a) In the Absence of Copper.—Although the rate of reaction is extremely great at high *p*H values (quarter-life = 5 sec. at *p*H 13.0; 36 sec. at *p*H 10.6) it falls off rapidly as the acid range is approached (quarter-life = 5.5 min. at *p*H 9.1; 340 min. at *p*H 8.0). At lower *p*H values, oxidation proceeded at a very slow rate. Even at *p*H 3.6, the lowest *p*H value at which the reaction was studied, some oxidation was observed. In most runs at *p*H values below 8.0 no oxidation would occur for fifteen to twenty minutes, but then very slow absorption of oxygen would start. Such an induction period has been characterized by Milas[5] as typical of autoxidation reactions.

(b) In the Presence of Copper.—The increase in the rate of oxidation with the increase in the concentration of the copper is very pronounced (Tables I and II). At both concentrations of

TABLE I

THE EFFECT OF *p*H ON THE COPPER CATALYZED REACTION

Concn. of copper, 1 part/million (1.57×10^{-5} mole/liter)

Buffer	*p*H	Half-life, seconds	95% life, seconds	Ratio of 95% life to half-life
	3.00	3000	..	..
PO_4^{---}	6.05	132	625	4.73
	6.20	118	560	4.73
	7.20	87	337	3.88
	8.10	370	891	2.40
BO_3^{---}	9.05	648	854	1.32
	9.95	236	427	1.81
	11.15	24	77	3.20
BO_3^{---}	8.00	664	900	1.36

TABLE II

THE EFFECT OF *p*H ON THE COPPER CATALYZED REACTION

Concn. of copper, 1 part/10 million (1.57×10^{-6} mole/liter)

Buffer	*p*H	Half-life, seconds	95% life, seconds	Ratio of 95% life to half-life
PO_4^{---}	4.2	1839	5212	2.84
	6.0	447	1950	4.37
	6.65	336	1177	3.50
	7.01	354	1140	3.22
	7.16	376	1185	3.15
	7.30	402	1250	3.11
	7.50	483	1388	2.87
	7.80	678	1820	2.69
	11.90	13	51	3.92
PO_4^{---}	7.5	570		..
BO_3^{---}	7.5	564		.

(5) Milas, *Chem. Rev.*, **10**, 295 (1932).

copper a minimum rate of oxidation occurs between *p*H 8 and 10 and a maximum rate between 6 and 8. No attempt was made to determine these values more exactly, since it was observed in agreement with Schümmer[2] that the maximum and minimum values are dependent upon the conditions of the experiment. For example, it was necessary to use at least two different buffers to cover the *p*H range which was studied. The results obtained at a given *p*H are affected by interchanging the buffers as shown in Table I where a borate buffer is substituted for a phosphate buffer at *p*H 8.0. However, in the presence of a smaller quantity of copper (Table II) no difference was observed when the same buffers were interchanged at *p*H 7.5. Furthermore, the conclusions which may be drawn from this study are dependent upon the manner in which the data are compared. Table I shows that although at *p*H 8.1 the half-life is smaller than at *p*H 9.05, the reverse is true for the 95% life.

(2) **The Auto-catalysis and the Order of the Reaction.**—The ratio of the 95% life to the half-life (Tables I and II) gives a measure of the degree of the acceleration of the reaction. Such an acceleration has been reported by Dekker and Dickinson[6] who claimed that it was caused by the accumulation of hydrogen peroxide during the reaction. If this were a simple first order reaction (pseudo-unimolecular), as one might expect, since the concentration of oxygen is kept constant by rapid shaking, the ratio of the 95% life to the half-life should be approximately 4.25. In the runs made below *p*H 7 and above *p*H 11 it can be shown, by plotting the log of the concentration of ascorbic acid against the time, that only the first part of the reaction is first order. At *p*H 12 in the presence of one part of copper in ten million parts of solution, the entire reaction is first order. At *p*H values between 7 and 11, even the first half of the reaction is not first order. A ratio of 95% life to half-life which is greater than 4.25 indicates a falling off in the first order reaction rate, while a ratio lower than 4.25 indicates an acceleration. Table I shows that a maximum acceleration occurs at a *p*H value of about 9. At a *p*H of 9.05 it takes only about one-third as long for the second half of the sample to be oxidized as it does for the first half. Table II shows that a similar acceleration occurs in the presence of a smaller quantity of copper.

(6) Dekker and Dickinson, THIS JOURNAL, **62**, 2165 (1940).

By oxidizing a sample of ascorbic acid in the presence of a previously oxidized solution, a marked increase in the rate of reaction was observed (half-life, 141 sec. *vs.* 648 sec. for the control). The reaction is, therefore, auto-catalytic.

An attempt was made to find the substance responsible for this auto-catalysis. The substances which are known to be products of the autoxidation of ascorbic acid under the conditions of this experiment are sodium oxalate, sodium *l*-threonate, hydrogen peroxide, and possibly a small amount of dehydroascorbic acid. When an equivalent weight of sodium oxalate was added to a control run, the reaction was speeded up (half-life, 372 sec.) but not to as great an extent as when a previously oxidized solution was used as a catalyst. Therefore, sodium oxalate is probably involved in the auto-catalysis but some other substance is also contributing to this effect. Krishnamurthy and Giri,[7] who studied this reaction under different experimental conditions, report that oxalic acid is a good inhibitor for the reaction.

Since sodium *l*-threonate was not available, it was thought advisable to determine whether the COOH group in general might possess the catalytic property. To test this point sodium acetate was added. No catalysis resulted (half-life, 649 sec.).

Hydrogen peroxide cannot account for the auto-catalysis because upon addition of ascorbic acid to a previously oxidized solution, the hydrogen peroxide is immediately used up. This was indicated by a failure to obtain a test for hydrogen peroxide and by a decrease in the volume of oxygen absorbed by an amount equivalent to the quantity of hydrogen peroxide previously present in the solution. Separate experiments confirmed the report of Hand and Greisen[8] that, in the presence of copper, ascorbic acid reacts readily with two moles of hydrogen peroxide.

Dehydroascorbic acid is the main product of the autoxidation in highly acid solutions. However, the amount of this product falls off as the *p*H is increased until in slightly alkaline solutions very little if any is formed.[1] Thus, if this compound were the catalyst, it seems unlikely that maximum catalysis would occur at *p*H 9.0 (Table I). The activity of dehydroascorbic acid was tested as follows. Ten equivalents of sodium citrate were

(7) Krishnamurthy and Giri, *J. Ind. Chem. Soc.*, **18**, 201 (1941).
(8) Hand and Greisen, THIS JOURNAL, **64**, 358 (1942).

added to the normal solution. Since hydrogen peroxide, which is formed during the autoxidation of ascorbic acid, is responsible for any oxidation of dehydroascorbic acid which may occur, the addition of sodium citrate, a substance which is readily oxidized by peroxides formed during the autoxidation of other substances (induced oxidation), should result in the formation of practically one equivalent of dehydroascorbic acid. Upon the addition of sodium citrate the reaction was inhibited (half-life, 1351 sec.) and no autocatalysis was observed. Some product formed upon oxidation of the dehydroascorbic acid by hydrogen peroxide must account for the catalysis.

In the reaction between hydrogen peroxide and dehydroascorbic acid, it is evident that the splitting of the bond between the two keto groups and the addition of hydrogen peroxide would result in a monoester of oxalic acid and *l*-threonic acid. This ester may be the active catalyst. Its saponification in the slightly alkaline solution would account for the observation that the catalytic activity of a previously oxidized solution falls off upon standing. The half-life varied from 141 to 220 to 330 seconds when the previously oxidized solutions stood for 10, 35 and 90 minutes, respectively. This assumption is supported by the fact that upon acidification of a previously oxidized solution its catalytic activity does not fall off upon standing. In order to prove that the intermediate ester is responsible for the autocatalysis of the reaction, an attempt was made to prepare the ester. An aqueous solution of ascorbic acid, buffered to *p*H 6.8, was oxidized by oxygen and hydrogen peroxide in the presence of copper. Upon extraction with ether a small amount of a colorless, non-crystallizing sirup was obtained. Its catalytic activity was only slightly greater than that of oxalic acid (half-life, 353 sec.) and cannot account for the activity of the freshly oxidized solution. The hypothetical ester should react with two equivalents of alkali upon neutralizing and a third upon saponifying. The prepared sirup reacted with one equivalent upon titrating, one equivalent upon shaking at room temperature, and a third equivalent upon refluxing for thirty-six hours. If it is assumed that during the isolation of the ester the other COOH group of the oxalic acid esterified with the β-OH group of the threonic acid to form a six-membered ring, the above experimental facts could be accounted for.

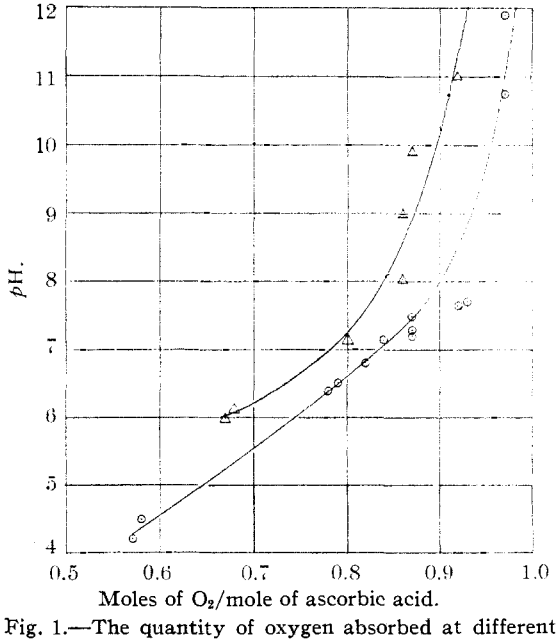

Fig. 1.—The quantity of oxygen absorbed at different *p*H values: concn. of ascorbic acid, 0.0038 mole/liter; △, concn. of copper, 1 part/million; ○, concn. of copper, 1 part/10 million.

It is fully appreciated that the experimental evidence supporting the claim that the intermediate mono-ester of oxalic acid and *l*-threonic acid is responsible for the auto-catalysis is inconclusive. However, such an assumption does explain all the experimental observations.

(3) **The Quantity of Hydrogen Peroxide Formed at Different *p*H Values.**—A colorimetric determination of the concentration of hydrogen peroxide which is among the products of the reaction at different *p*H values was carried out. For this purpose the reaction between hydrogen peroxide and titanium sulfate was used. Small amounts of hydrogen peroxide were found among the products in both acid and alkaline solutions and in the presence and in the absence of copper. No correlation could be made between the amount of peroxide found and the change in the rate of autoxidation with *p*H or the change in the volume of oxygen absorbed with *p*H.

(4) **The Quantity of Oxygen Absorbed per Mole of Ascorbic Acid.**—Reported values for the ratio of moles of oxygen absorbed to moles of ascorbic acid oxidized include 0.25, 0.50, 1.0, 1.5, and intermediate values. The data obtained by Hand and Greisen,[8] however, have cleared up the problem. The data in Fig. 1, which were obtained before the paper by Hand and Greisen appeared, confirm the work of these investigators.

The number of moles of oxygen absorbed in the presence of one part of copper per ten million of solution increases continuously from 0.57 to 0.97 in going from *p*H 4.2 to 11.9. In the presence of one part of copper per million of solution the ratio increases from 0.67 to 0.92 in going from *p*H 6.0 to 11.0. These results show that the volume of oxygen absorbed falls off upon increasing the concentration of copper. Below *p*H 4.5 the oxygen absorbed in excess of one-half mole is accounted for by the hydrogen peroxide present. Above *p*H 4.5 this is not true. At *p*H 11.9 only 0.05 mole of the 0.97 mole of oxygen absorbed is present as hydrogen peroxide.

In the absence of copper the number of moles of oxygen absorbed per mole of ascorbic acid is practically constant between *p*H values of 9 and 13, 0.93 ± 0.03 mole being absorbed.

The explanation for the increase in the volume of oxygen absorbed as the *p*H is increased will be discussed later.

Hand and Greisen[8] studied the effect of *p*H on the volume of oxygen absorbed in order to see whether the autoxidation of ascorbic acid could be used as an analytical method for dissolved oxygen. They concluded that the method would be impractical. In the present investigation it was observed that when an excess of sodium citrate is added to the solution of ascorbic acid, exactly one mole of oxygen is absorbed at any *p*H. The use of these two reagents may be the basis of a method of analyzing for dissolved oxygen.

(5) **Inhibition of the Reaction.**—Investigations on the inhibition of the autoxidation of ascorbic acid have resulted in numerous contradictions. No attempt[9] has been made to compare, under the same experimental conditions, the inhibiting effect of the many substances which have been studied. Compounds shown to have an appreciable inhibiting effect in the present investigation are listed in Table III. The following compounds were slightly effective in decreasing order: tyrosine, sarcosine, pyridine, quinoline, nicotinic acid, ammonium chloride, creatine and taurine. Starch, aniline, potassium acid tartrate, sodium benzoate, ethyl amine, methyl amine, urea, *d*-glucose, sodium chloride, dioxane and ethyl alcohol were ineffective. Most of these compounds have been reported to be definite inhibitors. If the quarter-lives are compared, 0.001 *M* uric acid is the most effective; but if the half-lives are compared, 0.0001 *M* cystine is the most effective. This anomaly is explained by the fact that as the reaction proceeds the inhibiting power of the cystine increases while that of uric acid decreases. A similar decrease in effectiveness was observed for pyridine and quinoline.

(9) A recent paper, Krishnamurthy and Giri, *J. Ind. Chem. Soc.*, **18**, 192 (1941), which was abstracted in April, 1942, reports a comprehensive study of many inhibitors.

TABLE III

EFFECT OF VARIOUS COMPOUNDS ON THE RATE OF AUTOXIDATION OF ASCORBIC ACID IN THE PRESENCE OF COPPER

Concn. of ascorbic acid, 0.0038 molar (0.1 g. in 150 cc.). Concn. of copper, 1 part/2 million (7.9×10^{-6} molar). All solutions were buffered to *p*H 7.25 with a phosphate buffer.

Solution	Quarter-life, min.	Half-life, min.
Control	0.9	2.2
0.001 *M* Cystine	41.2	160.2
.0005 *M* Cystine	66.5	270.0 (approx.)
10^{-4} *M* Cystine	97.8	900.0 (approx.)
10^{-5} *M* Cystine	74.4	351.0
10^{-6} *M* Cystine	1.3	3.1
10^{-7} *M* Cystine	1.0	2.4
0.001 *M* Uric acid	463.0	845.0 (approx.)
.0001 *M* Uric acid	193.0	352.0
.01 *M* *l*-Aspartic acid	67.6	165.0
.001 *M* *l*-Aspartic acid	4.3	9.8
.0001 *M* *l*-Aspartic acid	1.3	3.0
.01 *M* Asparagine	47.2	122.9
.01 *M* *d*-Glutamic acid	25.4	58.7
.5 g. Gelatine	32.8	64.3
.25 g. Gelatine	19.2	34.6
.01 *M* Sodium citrate	13.4	31.1
.001 *M* Sodium citrate	5.9	13.1
.01 *M* Glycine	13.0	30.3
.01 *dl*-Alanine	8.8	20.9
.001 *M* *dl*-Alanine	1.7	3.9
.01 *M* *l*-Cysteine[a]	4.8	14.4

[a] Cysteine was also autoxidized. The values are calculated from the total volume of oxygen absorbed in oxidizing both the ascorbic acid and the cysteine.

With the exception of sodium citrate, all of the substances which were appreciably effective contain one or more amino groups and one or more acid groups. In general an increase in the number of acid groups or the number of amino groups increases the inhibiting effect.

When the solution was shaken with oxygen, the half-life of the oxidation in the presence of cystine was 410 times as large as the half-life of the control. When the solution was not shaken, the ratio of the half-life of the cystine-inhibited reaction to the half-life of the control was four (twenty hours to five hours). It is evident that the inhibitors are not as effective for solutions which are allowed to stand exposed to oxygen.

It is probable that there is no inhibitor known today which can prevent the complete oxidation of aqueous solutions of vitamin C which are allowed to stand exposed to sufficient oxygen for several days. The only practical method of preserving aqueous solutions of the vitamin for long periods is to exclude oxygen.

To determine the mechanism by which the inhibitors function, the most effective inhibitors in the presence of copper were added to solutions of *p*H 10 in the absence of copper. Since no significant effect was observed, it was concluded that the inhibitors must function by combining with the catalytic copper. Schümmer[2] has observed that the best inhibition that can be obtained is complete nullification of the catalytic effect of the copper.

The ability of copper ions to form stable coördination complexes is well known. Diehl[10] gives many examples of such complexes and states that the dissociation of the inner complexes of copper is so slight that their solutions show practically none of the reactions of copper ions. However, the dissociation is definite and can be measured.

All of the inhibitors for the autoxidation of ascorbic acid can form coördination complexes with copper ions. Very stable complexes are formed when copper is linked to two acid groups and to two coördinating groups. The most effective inhibitors contain at least one acid group and one coördinating group and, thus, can form especially stable complexes. The ineffective substances either have no tendency to form coördination complexes or form easily dissociated complexes. These facts give considerable support to the claim that the function of the inhibitor is to tie up the catalytic copper ions by forming coördination complexes with them.

Compounds with several acid groups or several coördinating groups or both (uric acid, aspartic acid, etc.) are more effective, since with a greater concentration of such groups the dissociation of the complex is repressed. The increase in the effectiveness of cystine upon decreasing its concentration from 0.001 to 0.0001 *M* (Table III) and the increase in its effectiveness with time can be explained in this way. If the probability of the formation of a nine-membered ring in "inner coördination complexes" is accepted (see Diehl's review article[10] for examples), one cystine molecule can tie up one copper ion with the formation of a very stable "inner complex." This complex, however, would form more slowly than the less stable complex (less effective inhibitor) which involves linkage of the copper to two of the cystine molecules. In the more concentrated solutions of cystine the latter type of complex would form to a much greater extent than the mono-cystine complex. Upon standing, however, more of the stable complex would form, increasing the effectiveness of the inhibitor. When the concentration of cystine is decreased, the probability of two cystine molecules contacting a copper ion before the mono-cystine complex is formed would be decreased. A more effective inhibition would result.

(6) **Mechanism of the Reaction.**—Some facts brought forth by this investigation may help to clear up the mechanism of the autoxidation of ascorbic acid.

Small traces of hydrogen peroxide can be found among the products of the reaction in acid or alkaline solutions both in the presence and in the absence of copper. The fact that one equivalent of hydrogen peroxide is formed intermediately was established in the following two ways: (1) When ascorbic acid is oxidized in highly alkaline solution in the presence of an activated nitrogenous charcoal, which is extremely active in decomposing hydrogen peroxide, the quantity of oxygen absorbed decreases from the normal value of practically 1.0 mole to exactly 0.5 mole. (Oxidation was complete in fifteen seconds.) Steinman and Dawson[11] obtained similar results using catalase to decompose the hydrogen peroxide. (2) When an excess of sodium citrate was added to highly acid solutions of ascorbic acid, the quantity of oxygen absorbed increased from 0.5 mole to 1.0 mole. The tendency for sodium citrate to be oxidized through induced oxidation has been discussed. Each hydrogen peroxide molecule, which normally decomposes or oxidizes an ascorbic acid molecule, oxidizes a sodium citrate molecule, thus accounting for the doubled quantity of oxygen which is absorbed.

The disappearance of most of the hydrogen peroxide during the reaction can be explained in the following manner. In solutions of *p*H less than 4.5 all of the hydrogen peroxide with the exception of that which is found among the products either oxidizes ascorbic acid or is decom-

(10) Diehl, *Chem. Rev.*, **21**, 39 (1937).

(11) Steinman and Dawson, THIS JOURNAL, **64**, 1212 (1942).

posed. Both of these reactions have been reported to take place readily with freshly formed hydrogen peroxide in the presence of copper.[8,12] Although there is no oxidation of dehydroascorbic acid by hydrogen peroxide at *p*H values less than 4.5, this oxidation does occur at *p*H values greater than 4.5, the extent of the reaction increasing as the *p*H is increased until in moderately alkaline solutions practically all of the hydrogen peroxide is involved in this reaction. Hand and Greisen[8] presented the above explanation to account for their observation of the increase in the volume of oxygen absorbed with an increase in *p*H. This mechanism also explains the fact that ascorbic acid can be recovered quantitatively from oxidized solutions of the vitamin when the *p*H is less than 4.5 but that the percentage recovery falls off as the *p*H is increased until in alkaline solution it is zero.[1]

The recovery of ascorbic acid by reduction of its oxidized solutions is not only dependent upon the extent of oxidation of the dehydroascorbic acid but also upon an irreversible non-oxidative change in the dehydroascorbic acid which apparently involves a splitting of the lactone ring[13] and the formation of diketogulonic acid.

The reaction of hydrogen peroxide with the dehydroascorbic acid involves the splitting of the bond between the two keto groups and the addition of two hydroxy groups to form a mono-ester of oxalic acid and *l*-threonic acid. In alkaline solutions the ester is saponified forming the known products, sodium oxalate and sodium *l*-threonate.

Oxygen does not oxidize dehydroascorbic acid at a measurable rate, since under most conditions the autoxidation of ascorbic acid goes to a definite completion before one mole of oxygen is absorbed.

The authors wish to call attention to a paper on "The Kinetics of the Reaction between Ascorbic Acid and Oxygen in the Presence of Copper Ion," by Silverblatt, Robinson and King, THIS JOURNAL, **65**, 137 (1943). The manuscript of the prseent paper was received about one year before the publication of the paper by King, *et al.*, but its publication was disapproved until recently by the Censor.—J. H. W. (6/1/43).

(12) von Kliss and Lederer, *Rec. trav. chim.*, **46**, 453 (1927).

(13) Borsook, Davenport, Jeffreys and Warner, *J. Biol. Chem.*, **117**, 237 (1937).

Summary

1. In the absence of copper very slow autoxidation of ascorbic acid occurs below *p*H 8.0; but as the *p*H is increased above this value, the rate of reaction increases until in highly alkaline solutions it is extremely large. In the presence of copper the reaction takes place readily in both acid and alkaline solutions. A minimum rate of oxidation occurs between *p*H 8 and 10 and a maximum rate between 6 and 8, the exact values being dependent upon the experimental conditions.

2. A marked auto-catalysis of the reaction is observed in the presence of copper. Evidence is given to support the claim that a mono-ester of oxalic acid and *l*-threonic acid is the active catalytic product.

3. The order of the reaction is dependent upon the *p*H of the solution.

4. A determination of the concentration of hydrogen peroxide which is among the products of the reaction at different *p*H values was carried out. No correlation could be made between the results and the change in the rate of reaction with *p*H or the change in the volume of oxygen absorbed with *p*H.

5. The volume of oxygen absorbed in the presence of one part of copper per ten million of solution varied from approximately 0.5 mole in highly acid solutions to approximately 1.0 mole in highly alkaline solutions. Increasing the concentration of the copper decreased the volume of oxygen absorbed.

6. The inhibiting effects of a considerable number of substances were determined. Those substances which contain one or more acid groups and one or more coördinating groups (cystine, uric acid, aspartic acid, glutamic acid) were the most effective inhibitors. None of these compounds inhibited the reaction in the absence of copper.

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