[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 766]

Oxidation of Ascorbic Acid by Oxygen with Cupric Ion as Catalyst

BY ALBERT O. DEKKER AND ROSCOE G. DICKINSON

By means of the Warburg respirometer Barron and co-workers[1] have investigated the rate of the reaction of ascorbic acid with oxygen in the presence and in the absence of cupric ion. They found that in the absence of cupric salts the oxidation of ascorbic acid proceeds at an immeasurably slow rate in acid solutions. The addition of small amounts of cupric chloride was found to increase the rate of oxidation tremendously. Their study of the effects of hydrogen cyanide and carbon monoxide on the rate of oxidation in solutions containing small amounts of cupric chloride indicated that cuprous ion was produced in the reaction and then rapidly oxidized to cupric copper by oxygen. On the basis of these experiments it was postulated that cupric ion oxidizes the ascorbic acid to dehydroascorbic acid, the cuprous ion thus formed being assumed to react rapidly with oxygen, regenerating the cupric ion and forming hydrogen peroxide. The peroxide was assumed to decompose rapidly in accord with the observation that one-half mole of oxygen was absorbed for every mole of ascorbic acid oxidized. In some experiments the rate was found to be proportional to the partial pressure of oxygen above the solution. In further experiments made to determine the effect of the concentrations of cupric copper and hydrogen ion on the rate the results were inconclusive for it appears that no attempt was made to determine whether or not the concentration of oxygen was here, too, important in establishing the net rate of the reaction.

In a study of the effect of various acids on the rate of the copper-catalyzed oxidation of ascorbic acid[2] considerably larger amounts of oxygen were found to be consumed than were expected on the basis of the above assumptions. This was attributed to an accumulation of hydrogen peroxide due to slow (rather than fast) decomposition of the peroxide assumed to be formed during the reaction, and to corroborate this assumption the presence of hydrogen peroxide was demonstrated by means of qualitative tests.

The experiments described in the present paper were carried out for the purpose of obtaining more specific information concerning the nature of the copper-catalyzed oxidation of ascorbic acid. All of the experiments reported here were carried out under such conditions that steps involving oxygen as a reactant were not rate determining. Furthermore, in order to avoid the possibility of cupric ion complexing with buffers no buffers were used, but instead the hydrogen-ion concentration was maintained at an effectively constant value throughout the course of the reaction by the addition of a comparatively large amount of acid at the start.

Materials

Cupric Perchlorate.—A good grade of basic cupric carbonate was added in slight excess to an aqueous solution of pure perchloric acid. The solution was shaken and heated until no more gas evolved. It was then cooled, filtered, and diluted with the proper amount of distilled water. The solution was standardized iodimetrically with standard sodium thiosulfate.

Indophenol.—The salt was prepared according to the directions of Bessey and King[3] by coupling 2,6-dichloroquinone chloroimide with phenol in the presence of sodium hydroxide. In stability in aqueous solution the purified product was superior to a purchased sample. The salt was extracted with boiling water, filtered, cooled, and diluted to the desired concentration. The solution was standardized by means of weighed ascorbic acid. It was found necessary to prepare a fresh solution of the indophenol about every three days.

Ascorbic Acid.—Iodine titrations showed that each of the samples used contained more than 99.5% ascorbic acid on the assumption that the reduction of the iodine was all due to ascorbic acid. Consequently the material was used without further treatment. The ascorbic acid solutions were made up by weighing out the solid and dissolving it in ordinary distilled water immediately before each experiment. There was always a slow oxidation of the ascorbic acid in these solutions. This slow decomposition was followed by means of titrations with indophenol, and it was thus possible to calculate the ascorbic acid concentration in the stock solution at any time. The slow oxidation was expected to be unimportant in the reaction mixtures since in these the hydrogen-ion concentration was always large and indeed it was not detectable in the blank experiments in which cupric ion was omitted.

Hydrogen Peroxide.—Two samples were used. One was a 30% solution containing no preservative. The other was a U. S. P. grade containing a small quantity of acetanilide. Each was diluted to approximately the proper con-

(1) Barron, Demeio and Klemperer, *J. Biol. Chem.*, **112**, 624 (1936).

(2) Lyman, Schultze and King, *ibid.*, **118**, 757 (1937).

(3) Bessey and King, *ibid.*, **103**, 687 (1933).

centration and standardized by titrating with potassium permanganate. The two solutions gave identical results in rate experiments which were duplicates in all other respects.

The other solutions used in the experiments were prepared by dissolving the pure substances in distilled water. Where standardizations were required they were carried out by conventional methods.

Experimental Procedure

Portions of the proper stock solutions were pipetted into a flask which was then placed in the thermostat for half an hour. The ascorbic acid solution was also kept at the temperature of the thermostat. At an observed time a portion of the ascorbic acid solution was added to the flask, the contents were mixed well, and the flask was replaced in the thermostat. At suitable intervals portions of the reacting mixture were withdrawn, metaphosphoric acid was added to quench the reaction, and the samples were titrated with indophenol to determine the concentration of ascorbic acid, end-point corrections being made with solutions to which no ascorbic acid had been added. Analyses by this method carried out on mixtures containing known amounts of ascorbic acid and cupric perchlorate showed that cupric ion does not interfere in the analysis. It was also found that although indophenol rapidly oxidizes cuprous ion, the addition of the large excess of metaphosphoric acid used completely inhibited this oxidation.

Although the reaction by which oxidation is stopped when metaphosphoric acid is added is not known, it is presumed that the acid stops the reaction by forming a complex with the cupric ion and also by increasing the hydrogen-ion concentration.

Blank rate experiments in which only cupric ion was omitted always showed a negligible decay of ascorbic acid.

Results of the Rate Measurements

Preliminary experiments showed that although the rates of oxidation at constant cupric ion concentration were equal in nitric and perchloric acids of the same concentration, the rates in hydrochloric acid were about fifty or a hundred times faster. Since nitrate ion and perchlorate ion do not show a tendency to form complexes to the extent that chloride ion does, it was decided to consider that hydrochloric acid exerts a specific effect; the remaining experiments were performed in perchloric acid solutions. It may be noted that the experiments in hydrochloric acid solution gave specific rate constants which were only about 25 to 75% greater than that calculated by us from the one experiment of Barron which was carried out in hydrochloric acid solution.

In Table I are given the detailed results of representative experiments concerning the dependence of the rate of the reaction upon the concentrations of cupric perchlorate, ascorbic acid, and perchloric acid. All experiments were made at 24.89 ± 0.02°. The concentrations are expressed in formula weights per liter of solution and time is expressed in minutes. The values of the specific reaction rate k given in the last column were calculated on the assumption that the rate is directly proportional to the concentrations of cupric ion and ascorbic acid and inversely proportional to the square of the hydrogen ion concentration. That is

$$-\frac{d(H_2A)}{dt} = \frac{k(Cu^{++})(H_2A)}{(H^+)^2} \qquad (1)$$

and

$$k = 2.30\,\frac{(H^+)^2}{(Cu^{++})t}\log_{10}\frac{(H_2A)_0}{(H_2A)} \qquad (2)$$

where $(H_2A)_0$ is the initial concentration of ascorbic acid and (H_2A) its concentration at the time t. The hydrogen ion concentration (H^+) and the cupric ion concentration (Cu^{++}) were assumed constant during the reaction.

TABLE I

SPECIFIC RATE CONSTANTS FOR THE COPPER-CATALYZED OXIDATION OF ASCORBIC ACID

Experiment 1

$(Cu(ClO_4)_2) = 5.03 \times 10^{-4}$ f.
$(HClO_4) = 0.01060$ f.
$(H_2A)_0 = 2.92 \times 10^{-4}$ f.

t, min.	$(H_2A) \times 10^4$	$k \times 10^4$
0	2.92	..
25.8	2.15	26.3
43.8	1.64	29.4
68.7	1.09	32.0
89.2	0.750	34.0
104.0	.572	34.9
122.0	.421	35.4
145.4	.276	36.2
163.1	.186	37.6

Experiment 2

$(Cu(ClO_4)_2) = 1.01 \times 10^{-4}$
$(HClO_4) = 0.01060$
$(H_2A)_0 = 2.83 \times 10^{-4}$
$(NaClO_4) = 0.00121$

t, min.	$(H_2A) \times 10^4$	$k \times 10^4$
0	2.83	..
62.4	2.39	30.3
124.6	1.98	31.8
181.7	1.65	33.0
241.4	1.34	34.5
304.8	1.04	36.4
368.4	0.790	38.4
430.8	.589	40.4

Experiment 3

$(Cu(ClO_4)_2) = 5.03 \times 10^{-4}$
$(HClO_4) = 0.01060$
$(H_2A)_0 = 1.46 \times 10^{-4}$

t, min.	$(H_2A) \times 10^4$	$k \times 10^4$
0	1.46	..
17.2	1.15	31.0
33.5	0.884	33.4
49.7	.655	36.0
66.1	.485	37.2
82.1	.328	40.6
102.1	.223	41.0

Experiment 4

$(Cu(ClO_4)_2) = 1.01 \times 10^{-4}$
$(HClO_4) = 0.01060$
$(H_2A)_0 = 76.2 \times 10^{-4}$

t, min.	$(H_2A) \times 10^4$	$k \times 10^4$
0	76.2	..
22.5	72.2	27.3
55.4	65.3	31.1
89.6	58.6	32.7
126.4	52.0	33.6

Experiment 5

$(Cu(ClO_4)_2) = 5.29 \times 10^{-4}$
$(HClO_4) = 0.00558$
$(H_2A)_0 = 1.47 \times 10^{-4}$
$(NaClO_4) = 0.00558$

t, min.	$(H_2A) \times 10^4$	$k \times 10^4$
0	1.47	..
19.5	0.661	24.1
29.1	.392	26.7
42.7	.152	31.3

TABLE II

SPECIFIC RATE CONSTANTS FOR THE COPPER-CATALYZED OXIDATION OF ASCORBIC ACID

	$(HClO_4)$, f.	$(NaClO_4)$, f.	$(Cu(ClO_4)_2)$, f.	$(H_2A) \times 10^4$, f.	t, min.	$(H_2A)/(H_2A)_0$	$k \times 10^4$
Series 1	0.0211	0	5.03×10^{-4}	3.51	30.0	0.875	39.4
	.0161	0.0050	5.03×10^{-4}	3.50	30.0	.793	39.8
	.0111	.0100	5.03×10^{-4}	3.49	31.0	.623	37.3
Series 2	.0582		2.52×10^{-4}	2.84	609.4	.718	73.0
	.0482	.0100	2.52×10^{-4}	2.82	431.3	.725	70.4
	.0382	.0200	2.52×10^{-4}	2.81	257.1	.715	75.5
	.0182	.0400	2.52×10^{-4}	2.80	54.3	.747	70.6
	.0582		112.0×10^{-4}	2.84	33.6	.466	68.8

TABLE III

THE EFFECT OF HYDROGEN PEROXIDE ON THE RATE OF THE COPPER-CATALYZED OXIDATION OF ASCORBIC ACID

Expt.	$(HClO_4)$, f.	$(Cu(ClO_4)_2)$, f.	$(H_2A) \times 10^4$, f.	$(H_2O_2)_0 \times 10^4$, f.	t, min.	$(H_2A)/(H_2A)_0$	k	k'
1	0.01056	1.01×10^{-4}	2.84	0.166	60.0	0.840	32.2×10^{-4}	
2	.01056	1.01×10^{-4}	2.83	.332	60.0	.821	36.3	
3	.01056	1.01×10^{-4}	2.82	.392	69.0	.792	37.1	
4	.01056	1.01×10^{-4}	2.82	.453	55.7	.817	40.1	
5	.01056	1.01×10^{-4}	2.80	.664	60.0	.790	43.2	
6	.01056	1.01×10^{-4}	5.46	.166	60.0	.872	25.2	
7	.01056	1.01×10^{-4}	5.50	.332	60.0	.861	27.5	
8	.01056	5.03×10^{-4}	2.81	.166	60.0	.396	34.3	
9	.01056	5.03×10^{-4}	2.82	.332	60.0	.379	35.8	
10	.01056	5.03×10^{-4}	5.58	.166	60.0	.477	27.3	
11	.01056	1.01×10^{-4}	3.44	1.23	64.0	.754	48.6	6.8
12	.01056	1.01×10^{-4}	3.42	2.46	62.2	.673	70.2	7.4
13	.01056	1.01×10^{-4}	3.41	4.92	62.0	.532	112.4	7.6
14	.01056	1.01×10^{-4}	3.40	7.38	62.0	.440	146.2	7.1
15	.01056	1.01×10^{-4}	6.76	4.92	62.0	.677	69.6	7.4
16	.01056	5.03×10^{-4}	3.45	1.23	62.0	.293	43.9	7.2
17	.01056	5.03×10^{-4}	3.46	2.46	62.0	.198	57.9	7.2

Although there is a considerable drift in the rate constants with time, it is to be noted that the initial rate constants agree fairly well with one another in spite of the facts that: experiments 2 and 4 differ from expts. 1 and 3 by fivefold in cupric ion concentration; expts. 3 and 4 differ by about fiftyfold in ascorbic acid concentration; expts. 1 and 5 differ by twofold in hydrogen ion concentration.

It should be noted that it was found to be necessary to bubble oxygen continuously through the solution during expt. 4 in order to prevent slowing down of the reaction due to depletion of dissolved oxygen as a result of the large amount of ascorbic acid present. In other experiments in which smaller amounts of ascorbic acid were used, bubbling air or oxygen through the solutions had no effect upon the rate.

Further experiments were performed in which the hydrogen ion concentration was changed by the addition of varying amounts of a standard solution of sodium hydroxide. In Table II are summarized the results of these experiments. The two series were performed using two different samples of perchloric acid. It is to be noted that within each series k is essentially a constant but that k is different for each series in spite of the fact that they overlap in hydrogen ion concentration. Moreover, independent experiments upon the effect of added electrolytes show that this large difference in rate is not to be attributed to ionic strength effect. Since reactions catalyzed by cupric ion are often promoted by iron salts,[4,5,6] experiments were carried out in which the acid of Series 1 was used and varying amounts of a ferric sulfate solution were added to the reaction mixture. It was found that the effect upon the rate was such that the presence of about 10^{-5} mole per liter of ferric ion in the reaction mixtures of Series 2 could account for the higher rates observed in this latter series. Rough colorimetric analysis of the two perchloric acid solutions by means of potassium ferrocyanide showed that the sample used in Series 2 contained ferric ion in approximately such quantity that the reaction mixtures prepared from it contained about 10^{-5} mole

(4) Price, *Z. physik. Chem.*, **27**, 474 (1898).
(5) Brode, *ibid.*, **37**, 257 (1901).
(6) Schilow and Buligen, *Chem.-Ztg.*, **37**, 512 (1913).

TABLE IV

EFFECT OF ADDED ELECTROLYTES UPON THE RATE

$(HClO_4) = 0.01056$ f. $(Cu(ClO_4)_2) = 2.52 \times 10^{-4}$ f. $(H_2A)_0 = 2.80 \times 10^{-4}$ f. to 2.90×10^{-4} f.

Expt.	Added salt	Concn. of added salt, f.	Initial ionic strength	t, min.	$(H_2A)/(H_2A)_0$	$k \times 10^4$
1a			0.0116	51.1	0.737	26.5
b			.0116	51.1	.740	26.1
c			.0116	51.3	.729	27.2
d			.0116	51.1	.730	27.3
e			.0116	51.0	.733	26.9
2	$NaClO_4$	0.054	.067	51.3	.749	24.9
3	$NaClO_4$	.058	.070	51.2	.765	23.2
4	$NaClO_4$	.161	.173	51.3	.754	24.3
5	$NaClO_4$	.323	.334	51.3	.754	24.3
6	$NaNO_3$	.155	.167	51.2	.799	19.5
7	$NaNO_3$	.930	.942	51.2	.822	16.9
8	KNO_3 Sample (1)	.0707	.083	50.1	.791	20.7
9	KNO_3 Sample (1)	.424	.436	51.2	.815	17.7
10	KNO_3 Sample (2)	.135	.147	51.0	.692	31.9
11	KNO_3 Sample (2)	.270	.282	51.0	.603	43.9
12	$Ba(NO_3)_2$	.0124	.049	51.3	.765	23.1
13	$Ba(NO_3)_2$	.0824	.259	51.0	.794	20.0
14	$Ba(NO_3)_2$	.462	1.40	51.2	.771	22.5

of ferric iron per liter. The iron in the perchloric acid used in Series 1 was evidently much less since it could not be detected by the method used. It thus appears probable that the discrepancies in Series 1 and 2 may be ascribed to impurities and that the rate of the reaction is inversely proportional to the second power of the hydrogen ion concentration.

In view of the fair agreement of the initial rates in the experiments in Table I it seems reasonable to assume that the differential equation (1) for the rate is essentially correct and that one of the products of the reaction is responsible for the drift of the rate constants with time. Since other investigators[2] have demonstrated that hydrogen peroxide is present in such solutions as these and since we also were able to show by means of the titanium sulfate test that hydrogen peroxide accumulated in our solutions during the reaction, it was decided to determine whether the addition of peroxide would cause an increase in the initial rate. Experiments 1 to 5 in Table III were carried out for this purpose. $(H_2O_2)_0$ represents the initial concentration of hydrogen peroxide. Plotting each k obtained in these five experiments against the corresponding $(H_2O_2)_0$ gives a straight line. Rough colorimetric analysis made with the use of titanium sulfate indicated that the reaction mixture described in expt. 2 in Table I contained (after most of the ascorbic acid had been consumed) about 10^{-5} to 10^{-4} mole of hydrogen peroxide per liter. This suggests that the hydrogen peroxide formed by the reaction is responsible for the trend in the rate constants calculated from equation (1). The situation is further complicated by the possibility that the cupric ion can catalyze the decomposition of the hydrogen peroxide.[7] Additional experiments were carried out in order to obtain more information concerning the manner in which the hydrogen peroxide concentration appears in the differential equation for the rate. The data for these experiments are shown in Table III. Experiments 6 to 10 represent a continuation of the first five experiments with the exception that the cupric ion and ascorbic acid concentrations have been altered. It is interesting to note that increasing the ascorbic acid concentration decreases the effect of the hydrogen peroxide upon k. This fact is also shown by the results of expts. 11 to 17 in which higher concentrations of peroxide were used. The constants k' were calculated from the equation

$$-\frac{d(H_2A)}{dt} = 30 \times 10^{-4}\frac{(H_2A)(Cu^{++})}{(H^+)^2} + k'(Cu^{++})^{0.79}(H_2O_2) \quad (3)$$

which is equation (1) with $k = 30 \times 10^{-4}$ and with an added empirical term $k'(Cu^{++})^{0.79}(H_2O_2)$. It should be mentioned that at the hydrogen ion concentrations employed in these experiments the rate of oxidation of ascorbic acid by hydrogen peroxide alone was found to be negligible.

(7) Von Kiss and Lederer, *Rec. trav. chim.*, **46**, 453 (1927).

To obtain additional information concerning the mechanism of the reaction, experiments were carried out in which the ionic strength was varied. The data are summarized in Table IV. The lack of quantitative agreement with any Debye-Hückel limiting slope may be attributed in part to the relatively high ionic strengths employed and in part to the previously mentioned increase of the reaction rate by very small amounts of iron salts. That is, the deviations may be a result of impurities in the salts used. The fact that two different samples of potassium nitrate differ as to the direction of the effect is in accord with this explanation. Furthermore, by means of potassium ferrocyanide spot tests iron was detected in Sample 2 but not in Sample 1. It appears then that there is at most a small negative salt effect.

Discussion

If we restrict ourselves at first to the main reaction, omitting consideration of the effect of the hydrogen peroxide produced, we have the problem of presenting a probable mechanism which would yield a dependence of the rate upon the first powers of the cupric ion and ascorbic acid concentrations and the inverse square of the hydrogen ion concentration. In addition, the mechanism postulated must provide a means for maintaining the cupric ion concentration essentially constant during the course of the reaction. Schemes fulfilling these requisites may be formulated on the assumptions that a CuA, present at low concentration, decomposes to give cuprous ion and intermediate products; that the cuprous ion is immediately reoxidized to cupric (with the incidental production of peroxide); and that the intermediate products yield dehydroascorbic acid. The present experiments seem to afford no way of deciding whether the CuA is to be regarded simply as un-ionized cupric ascorbate formed in a rapidly established equilibrium or as a "critical complex" formed transiently from Cu^{++} and $A^{=}$. The following is a scheme based on the first supposition

$$Cu^{++} + H_2A \rightleftharpoons CuA + 2H^+ \quad (4)$$

$$CuA \longrightarrow Cu^+ + \text{Intermediate products} \quad (5)$$

$$\text{Intermediate products} \longrightarrow \text{Dehydroascorbic acid} \quad (6)$$

$$Cu^+ + H^+ + {}^1/_2O_2 \longrightarrow Cu^{++} + {}^1/_2H_2O_2 \quad (7)$$

If (4) is substantially at equilibrium and (5) is rate-determining, it is readily shown that the reaction rate, in dilute aqueous solution at 25°, should be given by

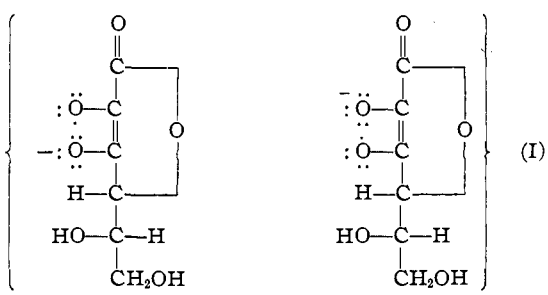
$$\frac{-d(H_2A)}{dt} = k_5K_4\frac{(Cu^{++})(H_2A)}{(H^+)^2}\,10^{-\sqrt{\mu}} \quad (8)$$

where μ is the ionic strength of the solution. An expression of the same form but with a different significance to the constant is obtained if instead of (4) one writes

$$Cu^{++} + A^{=} \longrightarrow CuA$$

and regards the CuA as a critical complex[8] decomposing according to (5). An expression formally equivalent to (8) may also be derived on the assumption that the un-ionized ascorbic acid forms an unstable copper complex containing two hydroxyl ions; this, however, seems less probable. These various possibilities have in common oxidation of the ascorbic acid in two stages.

Reasonable suggestions also can be made with reference to the constitution of the intermediate compound formed by the decomposition of the copper compound. Since it is necessary to remove two electrons from ascorbic acid to form dehydroascorbic acid, the product of the oxidation, and since the rate-determining step involves the first power only of the cupric ion concentration, it follows that the initial product of the decomposition or rearrangement of the copper compound must be a compound capable of reacting with an additional cupric ion or some other oxidizing agent such as oxygen to give dehydroascorbic acid. It is reasonable to suppose that the first product of the decomposition of the copper salt of ascorbic acid is an ion with the resonating structure

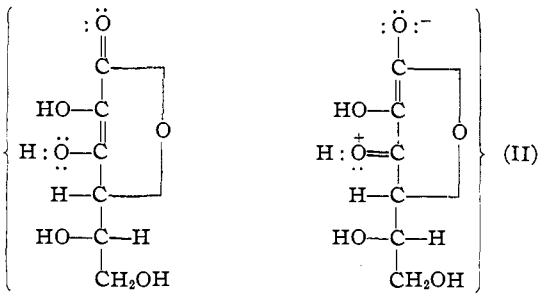


(I)

This ion would be expected to possess less stability in the acid solutions used than in basic solution, for the presence of a hydrogen atom on one of the oxygens involved in the resonance would destroy the equivalence of the two structures and decrease the resonance energy. Furthermore, the resonance (II) responsible for the acidic character

(8) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925); *Chem. Rev.*, **5**, 231 (1928); Bjerrum, *Z. physik. Chem.*, **108**, 82 (1924); **118**, 251 (1925).

of ascorbic acid competes with the semiquinone-type resonance shown above and thus decreases the stability of the intermediate.



(II)

A few rate experiments were performed with the object of determining whether the presence of oxygen was necessary in order for the reaction to take place. To this end experiments were carried out in evacuated Thunberg tubes. In experiments for which the time was long, equilibria seemed to be attained for which the experimentally determined equilibrium constants varied about two-fold and were within the limits calculated for the reaction

$$2Cu^{++} + H_2A \rightleftharpoons 2Cu^{+} + D + 2H^{+} \qquad (9)$$

where D represents dehydroascorbic acid. The limits for the value of the constant for the above equilibrium were calculated using the result of the work of Borsook, *el. al.*,[9] and of Ball[10] upon the oxidation-reduction potential of the system of which ascorbic acid is the reductant, and the measurements of Fenwick[11] of the cuprous ion–cupric ion potential. In additional experiments similar to those in which equilibria were obtained but using shorter times it was possible to determine the rate of oxidation of ascorbic acid in the absence of oxygen. It was noted that the rates of oxidation of the ascorbic acid were between one-fiftieth and one-seventy-fifth of the rates calculated from the expression for the rate of oxidation in air and the expression for the rate of the reverse reaction, the specific rate of the reverse reaction being calculated from the equilibrium constant for (10) and the value 30×10^{-4} for k in (1). This might indicate that in the rate experiments in the presence of air the oxygen was involved along with intermediate (I) in the series of steps with high specific rates indicated by equation (8) while in the absence of air cupric ion is involved, the rate with cupric ion being assumed slow. Denoting the intermediate (I) by B^-, the equations for the above reactions might be written:

$$B^- + Cu^{++} \longrightarrow D + Cu^{+} \qquad (6')$$
$$B^- + O_2 + H^{+} \longrightarrow D + HO_2 \qquad (6'')$$

Perhydroxyl, HO_2, is thermodynamically unstable in acid solution with respect to the decomposition[12]

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (10)$$

Equation (7) should probably be written similarly

$$Cu^{+} + O_2 + H^{+} \longrightarrow Cu^{++} + HO_2 \qquad (7')$$
$$2HO_2 \longrightarrow H_2O_2 + O_2$$

Little can be said concerning the mechanism of the effect of hydrogen peroxide upon the rate. The guess might be made that since the ascorbic acid concentration does not appear in the second term on the right in equation (3), the supposed reaction between the cupric ion and hydrogen peroxide is slow and a product of this reaction, possibly a complex $CuH_2O_2^{++}$, reacts rapidly with the ascorbate ion to produce the intermediate B^- which is rapidly oxidized to dehydroascorbic acid. Furthermore, since hydrogen peroxide accumulates in the solution, the mechanism must provide for the regeneration of hydrogen peroxide. The following reactions can account for the observations

$$Cu^{++} + H_2O_2 \longrightarrow CuH_2O_2^{++} \qquad (11)$$
$$CuH_2O_2^{++} + A^- \longrightarrow Cu^{+} + H_2O_2 + B^- \qquad (12)$$

The fact that the cupric ion concentration in (3) appears to a power slightly less than one might be attributed to a decomposition of peroxide catalyzed by cupric ion.[7]

The aid supplied by Professor Henry Borsook through the loan of apparatus and through helpful discussions is gratefully acknowledged.

Summary

The catalytic effect of cupric ion on the oxidation of ascorbic acid by oxygen has been studied. It was found that the initial rates were substantially directly proportional to the concentrations of cupric ion and ascorbic acid and inversely proportional to the square of the hydrogen ion concentration. In the initial stages the reaction mechanism is assumed to consist in the slow oxidation by cupric ion of the ascorbate ion to an ion with a semiquinone-like structure, followed by the immediate oxidation by oxygen of this semiqui-

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

(10) Ball, *ibid.*, **118**, 219 (1937).

(11) Fenwick, THIS JOURNAL, **48**, 860 (1926).

(12) Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, N. Y., 1938, *p.* 41.

none-like ion to dehydroascorbic acid. The cupric ion concentration is maintained constant through oxidation by oxygen of the cuprous ion formed. An observed increase in the specific reaction rate during the course of the reaction is attributed to the accumulation of hydrogen peroxide formed through the oxidation of cuprous ion by oxygen.

A marked increase of the rate of the reaction upon the addition of ferric ion was observed.

PASADENA, CALIFORNIA RECEIVED APRIL 22, 1940

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA

Mixed Potentials at the Dropping Mercury Electrode

BY I. M. KOLTHOFF AND C. S. MILLER[1]

When an electrode is placed in a solution and the system is not in oxidation–reduction equilibrium, the electrode potential measured by classical methods may be called a *mixed potential.* The dropping mercury electrode is ideally suitable for the measurement of such mixed potentials, as the electrode is renewed with each drop of mercury formed. When dealing with a depolarized electrode there is no net electrode reaction when the electrode is placed in the solution. This is no longer true when the electrode adopts a mixed potential. When such an electrode is placed in the solution, a cathodic and an anodic reaction occur, both yielding the same current. Although no current flows through the cell when the mixed potential is measured in the classical way, actually a cathodic reaction yielding a cathodic (positive) current and an anodic reaction yielding an anodic (negative) current occur, the positive and negative currents being of equal magnitude. Hence, under these conditions, the total current as indicated by the null point instrument is equal to zero.

Mixed potentials, as measured with the dropping mercury electrode, are of theoretical and practical interest as will be shown in this paper. In order to make clear the concept of mixed potentials at the dropping electrode we will consider a case which, for the sake of simplicity, is slightly idealized. In the experimental part mixed potentials and current–voltage curves actually measured will be given and interpreted. For the sake of simplicity we also neglect the very small effect of the charging or condenser current.[2] In Fig. 1 current ABC represents the current voltage curve obtained with the dropping electrode in an alkaline solution saturated with air. The cathodic (positive) current of oxygen starts at a potential A, and the diffusion current, BC, is attained at a potential of the dropping electrode corresponding to D. The anodic current AQ corresponds to the reaction $Hg + 2OH^- \longrightarrow Hg(OH)_2 + 2e$, and need not further be considered. In the same diagram (Fig. 1) we have represented the current voltage curve obtained in an air-free solution of an anion which depolarizes the dropping electrode at fairly negative potentials (in the diagram at E). Let EFG represent such a current voltage curve, say of dilute sulfide solution in alkaline medium. The anodic diffusion current FG is reached at a potential, H, of the d. e. We will now consider the current voltage curve when the mercury drops in the alkaline sulfide solution which is saturated with air. In Fig. 1 the diffusion current of sulfide is greater than that of oxygen. Coming from positive potentials we start with the anodic current IG of the hydroxyl ions, and at potentials more negative than G the diffusion current of sulfide is measured. When we have reached point G the potential has become equal to A, and at more negative po-

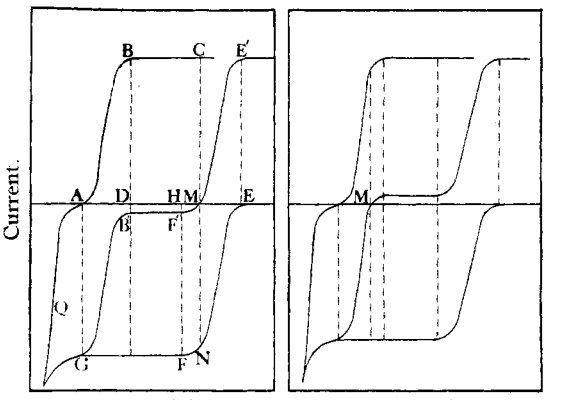


Fig. 1. Fig. 2.

(1) From the experimental work in a thesis submitted by C. S. Miller to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the doctor's degree (1940).

(2) Compare I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).