Kinetics and Mechanism of the Copper Catalysed Autoxidation of Ascorbic Acid

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Based on a discussion of earlier investigations of the copper catalysed reaction between oxygen and ascorbic acid the following mechanism is suggested

The corresponding kinetic expression is derived, certain justified approximations being introduced. It is shown that there is complete agreement between the integrated velocity expression and the course of the reaction as determined by experiment. From the kinetic expression the steady state distribution of copper in the two oxidation states is calculated for the conditions of a special experiment, and the values calculated are compared with the result of a spectrophotometric determination of cupric ion as a function of time in an identical experiment. The values of the velocity constants for the single steps are derived from the experiments, and a discussion proves them to be reasonable. It is therefore evident that the above mechanism is correct.

The most remarkable feature in the chemistry of ascorbic acid is its reaction with oxygen, strongly and specifically catalysed by copper ions. In view of the physiological importance of ascorbic acid it is understandable that most of the available investigations of the kinetics of this reaction have been carried out in solution near the physiological pH region. However, the protolytic properties of ascorbic acid, and the ability of copper ions to form complexes with various components of buffered solutions, introduce unnecessary complications, the result being that none of the earlier investigators have been able to provide experimental material from which an established mechanism can be derived. In the present investigation an attempt is made to overcome these difficulties by a choice of conditions much more convenient from the point of

view of physical chemistry. In this way it proves possible to remove the uncertainty completely, and thence to derive a mechanism.

In previous investigations it is almost universally maintained that the autoxidation of ascorbic acid in the presence of copper ion is a transference catalysis:

(H_2A = ascorbic acid; A = dehydro ascorbic acid).

The most careful investigations of the kinetics of this reaction are due to Barron, de Meio and Klemperer¹, Weissberger and LuValle² and Lyman *et al.*³ Barron *et al.*¹ found in 1936 that the rate of the uncatalysed reaction is negligible at $\text{pH} < 7.6$. In alkaline solution ascorbic acid reacts with one molecule of oxygen, even without a catalyst, forming oxalic acid and L-treonic acid. This reaction is, as opposed to the catalytic reaction in neutral or acid solution, irreversible and uninhibited by cyanide ion. At pH values lower than 6.6, in the presence of copper, one molecule of ascorbic acid reacts with one atom of oxygen only, forming dehydro ascorbic acid as by the oxidations with iodine or 2,6-dichlorophenoleindophenole. Accordingly the ascorbic acid is recovered quantitatively by reduction with hydrogen sulphide. The velocity of the reaction, according to Barron *et al.*, increases with increasing copper concentration, but less than corresponding to a simple proportionality law. The rate decreases with increasing acidity, but is still measurable in 0.1 *M* hydrochloric acid. The rate increases with oxygen concentration, but less than according to proportionality. These are the facts on which Barron *et al.* based the undetailed transference mechanism. They are all confirmed by the present investigation.

Weissenberger and LuValle² suggest that the rate determining step in the copper catalysed autoxidation of ascorbic acid is

the semiquinone (HA) and the cuprous ion formed both reacting further with oxygen. All steps except this one are considered fast. This is hardly in accordance with an experimental finding by the same authors: that the velocity is proportional to the oxygen concentration. The complex relationship between velocity and copper concentration is, according to Weissberger and LuValle, associated with the ability of copper to form complexes with buffer components.

Ball⁴ has determined the redox potential of the reaction

to be 0.390 volt. This potential has been verified by various investigators. Fenwick⁵ has determined the potential for the reaction

to be 0.167 volt. These figures mean that the equilibrium

in acid solution is displaced to the left hand side. The solutions used in the present investigation was 1.000 *M* in chloride ion throughout. Therefore the formation of dichloro cuprous ion was significant for the distribution of copper on the two oxidation states:

The dissociation constant of the dichloro cuprous ion is estimated by Latimer⁶ as 2.9×10^{-6} and by Bjerrum⁷ as about 3.0×10^{-6} . These values combined with the redox potential for the free cuprous ion gives about 0.487 volt for the reaction

Handbook of Physics and Chemistry (1947) p. 1418, quotes 0.455 volt. The writer has been unable to trace the origin of this value, but has confirmed it by his own measurements. Cupric ion is thus almost completely reduced by ascorbic acid in acid chloride solution.

Lyman *et al.*³ have shown that the velocity of the copper catalysed autoxidation in 0.1 *N* sulphuric acid solution is vanishingly small, but quite measurable in 0.1 *M* hydrochloric acid solution, where the rate as a function of the hydrochloric acid concentration has a minimum. In the present investigation it was found that the velocity of the reaction is zero in 0.1 *M* perchloric acid and conveniently measurable in a solution which is 0.1 *M* in hydrochloric acid and 0.9 *M* in sodium chloride.

The first two steps in the mechanism suggested by Weissberger and LuValle were

These steps are essentially uninfluenced by chloride ions, so apparently they are not sole rate-determining. Chloride ion will trap the cuprous ion formed by (+2) and therefore prevent or at least grossly inhibit the reaction

The third step in the Weissberger and LuValle mechanism is

which we shall accept. The fourth step suggested is

which seems very unlikely as the concentrations of copper and oxygen are comparable. There is no obvious reason to assume that A^- should prefer to react with oxygen when HA^- prefers the cupric ion. The fourth step is rather

In a preceding paper it was suggested that the oxygen molecule is reduced stepwise by four cuprous ions, the final product being water. Therefore a solution in which oxidation of cuprous ion is going on must contain partly reduced oxygen molecules such as H_2O , H_2O_2 and HO . Experiments in which cuprous ion was oxidised in the presence of oxalic acid, formic acid or pyrogallol showed that these organic compounds are not subject to "induced oxidation",

the organic compounds being present quantitatively after the experiments, and the rate of oxidation of cuprous ion being unimpaired by their presence. It is therefore suggested that the following reactions are insignificant:

We shall also neglect

etc. as the ascorbic acid derivatives are rare in the reacting solutions compared with the cuprous ions with which the oxygen derivatives are supposed to react fast. Also the possibility that the complexes CuHA^+ and CuA^+ have a significant lifetime is disregarded. It is well known that copper complexes with polyalcohols and similar compounds do not exist in acid solution.

As a result of the introductory discussion, the following mechanism is suggested:

The overall velocity of this reaction will be a function of the concentrations of ascorbic acid, hydrogen ion, copper ion and oxygen. It is also influenced by temperature and chloride ion concentration, but these two factors were kept constant, their variation not being necessary to solve the problem set, to establish a mechanism of the reaction. In the individual runs all factors except the ascorbic acid concentration (and of course the concentration of dehydro ascorbic acid) were constant. It is our task to calculate what kind of function of time the ascorbic acid concentration should be in an experiment were the above mechanism right. The method used is that of steady state calculations, *i.e.*, writing down of equations assuming the rates of appearance and disappearance of the intermediate molecular species to be equal. From these equations the concentrations of the intermediates are then eliminated.

The system of equations would have been linear in the ascorbic acid concentration, c , had each step involved formation and disappearance of not more than one intermediate. Whenever two intermediates appear on the same side of an element of the sequence the degree of the kinetic expression is raised by one. As both the ascorbic acid derivatives (except dehydro ascorbic acid) and the two oxidation steps of copper are intermediates in the reaction-kinetic sense of the word, this occurs three times: in the reactions (+ 2), (− 2) and (+ 4). Therefore our expression will be strictly one of the fourth degree in c . Obviously certain approximations are necessary to solve the system of equations.

One simplification is justified by the following: When an ascorbic acid ion (HA^-) is formed it may either react with a cupric ion, (+2), or it may recombine with a hydrogen ion, (-1). Hydrogen ions are much more abundant than cupric ions, so the probability of (-1) is therefore likely to be much higher than that of (+2). The final result of the present investigation is that only few of the encounters between cupric ion and ascorbic acid ion lead to reaction according to (+2), so (-1) is definitely the fate of the great majority of ascorbic acid ions. Therefore the concentration of ascorbic acid ion (HA^-) can be calculated simply by using the mass action law on the dissociation according to (1). This simplification reduces the degree of our system of equations to three.

A great simplification is introduced by the experimental finding that the velocity of the reaction is uninfluenced by the concentration of dehydro ascorbic acid, *i. e.*, the velocity of (-4) is almost zero. This is only true when the system investigated contains chloride ions to trap the cuprous ions formed by (+2) and by (+4). Otherwise (-4) is so dominating that the overall rate of the reaction is negligible.

It is an important assumption that the state of the cuprous chloride system is the same as in the solutions used in a previous investigation⁸ of the cuprous ion autoxidation.

We are now able to write down the equations necessary to derive the overall kinetics according to the mechanism suggested:

where the dots denote differentiation with respect to time.

s is the rate of disappearance of ascorbic acid, $-\frac{dc}{dt}$, and two cuprous ions are oxidised in each cycle of the reaction. We thus have three equations with five unknowns. The distribution of copper on two oxidation states gives a fourth equation:

where complex formation between copper and chloride is disregarded, and (Cu) is the total copper concentration. The remaining equation is

as found in the preceding investigation⁸.

Elimination of $[\text{HA}]$ and $[\text{A}^-]$ from the first three equations gives:

$$s = \frac{k_2 k_3 k_4 [\text{HA}^-][\text{Cu}^{++}]^2}{k_3 k_4 [\text{Cu}^{++}] + k_{-2} k_4 [\text{Cu}^+][\text{Cu}^{++}] + k_{-2} k_{-3} [\text{Cu}^+][\text{H}^+]}$$

$$\text{or } \frac{1}{s} = \frac{1}{k_2 [\text{HA}^-][\text{Cu}^{++}]} + \frac{k_{-2} [\text{Cu}^+]}{k_2 k_3 [\text{HA}^-][\text{Cu}^{++}]} + \frac{k_{-2} k_{-3} [\text{H}^+][\text{Cu}^+]}{k_2 k_3 k_4 [\text{HA}^-][\text{Cu}^{++}]^2} \quad (\text{VI})$$

In the preceding paper it was found that the velocity of the oxidation of cuprous ion at 25° C in a medium which is 1.000 *M* in chloride ion and at least 0.1 *M* in hydrogen ion is

$$s' = \frac{61.8 \cdot pO_2 \cdot [Cu^+][H^+]}{0.863 + [H^+]}$$

where pO_2 is the partial pressure of oxygen in a gas phase with which the solution is in equilibrium. The velocity with which ascorbic acid is oxidised is, according to the mechanism suggested, equal to the velocity of oxidation of two cuprous ions:

$$s = \frac{30.9 pO_2 [Cu^+][H^+]}{0.863 + [H^+]} = H [Cu^+] \quad (VII)$$

where H is a known function of experimental conditions.

Introduction of K_s , the acid dissociation constant of ascorbic acid, gives

$$[HA^-] = \frac{[H_2A]}{[H^+]} K_s = \frac{c}{[H^+]} K_s$$

We further define:

$$[Cu^+] = \alpha (Cu) \text{ and } [Cu^{++}] = (1-\alpha) (Cu) \quad (VIII)$$

We can therefore rewrite (VI):

$$\frac{1}{s} = \frac{1}{H\alpha (Cu)} \frac{[H^+]}{K_s k_2 \cdot c(1-\alpha) (Cu)} + \frac{k_{-2}[H^+] \alpha (Cu)}{K_s k_2 k_3 c(1-\alpha) (Cu)} + \frac{k_{-2} k_{-3} [H^+]^2 \alpha (Cu)}{K_s k_2 k_3 k_4 c(1-\alpha)^2 (Cu)^2}$$

Introducing simpler symbols for constants and concentrations not changed in individual experiments gives:

$$\frac{1}{s} = \frac{H}{L c (1-\alpha)} \left\{ 1 + \frac{(Cu)}{M} \alpha + \frac{1}{N} \frac{\alpha}{1-\alpha} \right\} \quad (IX)$$

where $L = \frac{K_s k_2}{[H^+]}$, $M = \frac{k_3}{k_{-2}}$ and $N = \frac{k_3 k_4}{k_{-2} k_{-3} [H^+]}$.

(IX) is an equation between c and α . (VII) and (VIII) define a simple relationship between s and α . From this is seen that were the second term in the bracket of equation (IX) vanishingly small compared with the other terms, the velocity of the reaction would be proportional to (Cu) . Without this term (IX) is a second degree equation. As it turns out that the velocity of the reaction is nearly, but not quite, proportional to (Cu) it proves useful to solve (IX) as a quadratic equation, i. e., without considering the variation of the term in question:

$$\begin{aligned} \frac{L c}{H} \left(\frac{1-\alpha}{\alpha} \right)^2 - \frac{1-\alpha}{\alpha} - \left\{ \frac{(Cu) (1-\alpha)}{M} + \frac{1}{N} \right\} &= 0 \\ \frac{1-\alpha}{\alpha} &= \frac{1 + \sqrt{1 + \frac{4L c}{H} \left(\frac{(Cu) (1-\alpha)}{M} + \frac{1}{N} \right)}}{2 \frac{L c}{H}} \\ \frac{1}{\alpha} &= 1 + \frac{H}{2L c} (1 + \sqrt{1 + R c}) \end{aligned} \quad (X)$$

where
$$R = \frac{4L}{H} \left(\frac{(\text{Cu}) (1-\alpha)}{M} + \frac{1}{N} \right) \quad (\text{XI})$$

Introduction of $\frac{1}{s} = -\frac{dt}{dc} = \frac{1}{H\alpha(\text{Cu})}$ gives

$$\frac{1}{s} = \frac{1}{H(\text{Cu})} + \frac{1}{2L(\text{Cu})} \left(\frac{1}{c} + \frac{1}{c} \sqrt{1 + Rc} \right)$$

or

$$t = \int_c^{c_0} \left[\frac{1}{H(\text{Cu})} + \frac{1}{2L(\text{Cu})} \left(\frac{1}{c} + \frac{1}{c} \sqrt{1 + Rc} \right) \right] dc$$

c_0 being the initial concentration of ascorbic acid. Considering R constant we have

$$t = \frac{c_0 - c}{H(\text{Cu})} + \frac{1}{2L(\text{Cu})} \left[\ln c + 2 \sqrt{1 + Rc} - 2 \coth^{-1} \sqrt{1 + Rc} \right] \frac{c_0}{c}$$

which is not changed when $\ln x = \ln Rc$ is substituted for $\ln c$, so we have:

$$t = \frac{c_0 - c}{H(\text{Cu})} + \frac{1}{2L(\text{Cu})} \left[\ln x + 2 \sqrt{1 + x} - 2 \coth^{-1} \sqrt{1 + x} \right] \frac{c_0}{c} \quad (\text{XII})$$

As H is known from the preceding investigation we can calculate the zero order term, and so define:

$$t' = t - \frac{c_0 - c}{H(\text{Cu})}$$

The ascorbic acid used in the present investigation was a synthetic product from Hoffmann-La Roche. The experimental set up was the same as in the previous paper. As the absolute rate of the reaction is low compared with the rate of dissolution of oxygen, the reacting solution was nearly saturated with oxygen at the partial pressure of the oxygen-nitrogen mixture blown through the solution. The course of the reaction was followed by extraction of 1.000 ml samples from the solutions in the reaction vessel at suitable intervals by means of a Krogh syringe. The samples were transferred to a small titration vessel in which they were diluted to about 4 ml by the washing of the syringe with oxygenfree water, and they were stirred and de-oxygenated by a fast stream of carbon dioxide during the titration. The titrations were performed with 0.1 $N I_2$ solution with starch as an indicator. The burette was a 100 μ l calibrated Rehberg micro burette.

The nature of the course of the reaction is shown on Fig. 1. It is seen that "the order of the reaction" is between zero and one. It is further seen that the velocity falls off as the acidity is increased. The velocity increases with oxygen concentration, but less than according to a proportionality law. The velocity is most sensitive to change of oxygen concentration at the lower acidity.

In chemical kinetics it is usual to investigate a first order reaction by plotting $\ln c$ against t , the proof of the first order character being that the plot is a straight line. In the present case (see XII) a plot of the function

$$y = \ln x + 2 \sqrt{1 + x} - 2 \coth^{-1} \sqrt{1 + x}$$

Fig. 1. Ordinate: Concentration of ascorbic acid. Abscissa: Time. It is seen that the rate is higher at the lower hydrogen ion concentration. Further that the rate is more sensitive to change of oxygen concentration at the lower hydrogen ion concentration.

against t' should be linear. Furthermore, when the conditions of experiment are changed, the variation of the reciprocal slopes from plots corresponding to individual experiments should vary in agreement with the coefficient $1/2L(\text{Cu})$, i. e., the slopes should be proportional to the concentration of copper and to the reciprocal hydrogen ion concentration, but should be independent of the oxygen concentration. The problem is therefore to investigate whether it is possible to assign such values to R , defined by (XI), that these conditions are fulfilled. We reintroduce the original meanings of the symbols L , M and N into R and have:

$$\ln x = \ln c + \ln \frac{4K_3k_2}{[H^+]H} \left\{ \frac{k_{-2}k_{-3}}{k_3k_4} [H^+] + \frac{k_{-2}}{k_3} (\text{Cu}) (1-\alpha) \right\}$$

Further introducing

$$H = F pO_2; F = \frac{30.9 [H^+]}{0.863 + [H^+]}$$

we have:

$$\ln x = \ln c + \ln \frac{4K_3k_2k_{-2}k_{-3}}{k_3k_4} - \ln F - \ln pO_2 + \ln \left\{ 1 + \frac{k_4(\text{Cu})}{k_{-3}[H^+]} \right\} (1-\alpha) \quad (\text{XIII})$$

The second term on the left hand side is a constant, common to all experiments, the third and fourth terms are known functions of the experimental conditions. The fifth term is regarded a constant; that was one of the assumptions necessary to solve the mathematical problem. From the definition of t' it is seen that $t - t'$ is the time the reaction from c_0 to c would have taken, had all the copper been in the cuprous state. Therefore, $1-\alpha = \frac{dt'}{dt}$ or, as long as the order of the reaction is regarded zero, $1-\alpha = \frac{t'}{t}$. The procedure

has been to use the value t'/t from the initial part of individual runs to calculate $1-\alpha$, and to use this value for the whole run. This is an approximation, but special calculations have shown that the value of y as a function of $\ln x$ is not

Table 1. Experimental conditions and results for 21 experiments. β is the slope of the (y, t') plots. The last column confirms that these slopes are proportional to the total copper concentration, inversely proportional to the hydrogen ion concentration and independent of the oxygen concentration.

$[H^+]$	$c_0 \cdot 10^3$	$(Cu) \cdot 10^4$	pO_2	$-\beta$	$-\beta \cdot \frac{[H^+]}{(Cu)}$
0.1	5	2	1.00	0.187	93.5
0.1	5	2	0.660	0.174	87.0
0.1	5	2	0.208	0.175	87.5
0.1	5	2	0.104	0.170	85.0
0.1	5	1	1.00	0.092	92.0
0.1	5	3	1.00	0.265	88.3
0.1	5	5	1.00	0.435	87.0
0.1	5	1	0.208	0.090	90.0
0.2	5	2	1.00	0.084	84.0
0.2	5	2	0.447	0.0821	82.1
0.2	5	2	0.208	0.0853	85.3
0.2	5	2	0.116	0.0862	86.2
0.2	10	1	1.00	0.0453	90.6
0.2	10	1	0.537	0.0450	90.0
0.2	10	1	0.208	0.0430	86.0
0.3	5	2	1.00	0.0597	85.5
0.3	5	2	0.0208	0.0605	90.7
0.3	5	2	0.117	0.0590	88.5
0.4	5	2	1.00	0.0443	88.6
0.4	5	2	0.208	0.0430	86.0
0.4	5	2	0.105	0.0470	94.0

seriously sensitive to the variations of $1-\alpha$ during an experiment, so the credibility of the investigation is not influenced.

The method was to determine a set of values of $\ln R$ which gave oxygen independent slopes for the last three runs in Table 1. Afterwards these values were slightly adjusted to give proper copper concentration dependence of the slopes of the four experiments with hydrogen ion concentration 0.1 M and oxygen pressure of 1.00 atmosphere. As independent checks (apart from the linearity of the y, t' plots), consistency was found in the determination of the term $k_4(Cu)(1-\alpha)/k_3[H^+]$ from the four experiments mentioned, and universal agreement between theory and experiment as far as dependences on concentrations of hydrogen ion and copper ion of the y, t' slopes are concerned, as demonstrated in Table 1. A further decisive test is reported at the end of the present paper.

The equation for determination of $\ln x$ derived was:

$$\ln x = \ln 10^3 c + 0.72 - \ln F - \ln pO_2 + \ln \left\{ 1 + 330 \frac{(Cu)}{[H^+]} (1-\alpha) \right\} \quad (XIV)$$

Table 2 gives the details of the calculation of an experiment, and the linearity of the corresponding y, t' plot is demonstrated on Fig. 2.

Table 2. Details of the first experiment in Table 1. By introduction of the values for concentrations it is found that $H = 3.21$, and by application of the value $(1-a) = 0.78$ further that $\ln x = \ln c \cdot 10^3 - 0.04$ (XIV).

t	$10^3 \cdot c$	$(c_0 - c) \cdot 10^3$	$\frac{c_0 - c}{H \text{ (Cu)}}$	t'	$\ln c \cdot 10^3$	$\ln x$	y	$1-a$
0	4.91	—	—		1.59	1.55	5.42	
3.5	4.46	0.45	0.70	2.80	1.50	1.46	5.12	0.80
6	4.06	0.85	1.32	4.68	1.40	1.36	4.77	0.78
9	3.64	1.77	1.98	7.02	1.29	1.25	4.43	0.78
12	3.13	1.78	2.77	9.23	1.14	1.10	3.98	0.77
15	2.74	2.17	3.38	11.62	1.01	0.97	3.60	
18	2.35	2.56	3.99	14.01	0.85	0.81	3.15	
21	2.01	2.90	4.52	16.48	0.70	0.66	2.74	
24	1.67	3.24	5.05	18.95	0.51	0.47	2.22	
27	1.36	3.55	5.53	21.47	0.30	0.26	1.68	
30	1.14	3.77	5.87	24.13	0.13	0.09	1.25	
33	0.90	4.01	6.25	26.75	-0.10	-0.14	0.77	
36	0.74	4.17	6.50	29.50	-0.30	-0.34	0.26	
39	0.58	4.33	6.74	32.26	-0.54	-0.58	-0.26	
42	0.40	4.44	6.92	35.08	-0.75	-0.79	-0.71	
45	0.35	4.56	7.10	37.90	-1.05	-1.09	-1.38	

From (XIII) and (XIV) we derive the following equations:

$$\frac{4K_s \cdot k_2 \cdot k_{-2} \cdot k_{-3}}{k_3 \cdot k_4} = 10^3 \cdot e^{0.72} = 2.05 \cdot 10^3$$

$$\frac{k_4}{k_{-3}} = 330 \quad (\text{XV})$$

Table 1 shows:

$$-\beta \frac{[H^+]}{(\text{Cu})} = 2 \cdot K_s \cdot k_2 = 88$$

Fig. 2. Demonstration of the linearity of y as a function of t' (see text and Table 2).

The first dissociation constant for ascorbic acid, K_s , is about $6.2 \cdot 10^{-5}$, so we have

$$k_2 \sim 7 \cdot 10^5 \text{ liter mole}^{-1} \text{ min}^{-1} \text{ or } k_2 \sim 10^4 \text{ liter mole}^{-1} \text{ sec}^{-1} \quad (\text{XVI})$$

and

$$\frac{k_{-2}}{k_3} \sim 4 \cdot 10^3.$$

(XVI) shows that (+2) is slow compared with (—1) (probable value 10^{11}), so no error was introduced by the simplified calculation of the ascorbic acid ion concentration.

According to a principle pointed out by Christiansen⁹ (—2) should be fast. The direct reaction

is probably impossible. To determine the proportion between the genuine constants for (—2) and (+3) we must (the medium being 1 *M* in sodium chloride) divide the value from (XVI) by the mass action constant for the reaction

which is given as $3 \cdot 10^{-6}$,

$$\frac{k_{-2}}{k_3} = \frac{4 \cdot 10^3}{3 \cdot 10^{-6}} \sim 1.3 \cdot 10^9$$

The assumption of low energy of activation for (—2) is justified. It is therefore understandable that the reactions

and

can hardly compete with

in chloride free medium.

As (+3) is slow (—3) should be fast, which means that HA is a weak acid. The independence of velocity on dehydro ascorbic acid concentration shows that (—4) is slow, so (+4) should also be fast. Therefore k_{-5}/k_4 should not be far from unity. The value 330 is in fair agreement with the difference expected for electrostatic reasons, as an ion with one negative charge should encounter a double charged positive ion more frequently than a single charged ion, other conditions being equal.

The mathematical problem of the present investigation was solved by derivation of the distribution of copper on the two oxidation states. The absorption of cupric ion at 800 *mμ* is just sufficient to allow a reasonable estimate at concentrations around 10^{-4} when 10 cm cells are used in a Beckman DU spectrophotometer. It must however be emphasised that the determination is rather coarse as the extinctions measured are from about 0.06 downwards.

Table 3. *D* means the extinction of the reacting solution at 800 mμ in 10 cm cells. The value for a corresponding solution without ascorbic acid was 0.076.

<i>t</i>	H ₂ A	pO ₂	<i>α</i> calc.	<i>D</i>	<i>α</i> obs.
0	4.93	1.00			
5	4.25	1.00			
10	3.45	1.00			
13	3.03	0.80	0.25	0.058	0.24
16	2.71	0.59	0.27	0.055	0.28
19	2.41	0.49	0.30	0.054	0.29
22	2.14	0.35	0.32	0.051	0.33
25	1.93	0.25	0.36	0.047	0.38
28	1.76	0.17	0.41	0.042	0.45
31	1.66	0.12	0.46	0.037	0.52
34	1.58	0.08	0.52	0.032	0.58
37	1.50	0.04	0.61	0.027	0.64
40	1.45	0.02	0.74	0.021	0.72
43	1.42	0.01	0.78	0.017	0.78

An experiment was performed as follows: 25 ml of a solution of ascorbic acid ($\text{Co} = 5 \cdot 10^{-3}$, $\text{Cu} = 2 \cdot 10^{-4}$, $[\text{H}^+] = 0.1$) was placed in the reaction vessel, and oxygen was bubbled through for 10 minutes. Then the solution was quickly transferred to the absorption cell which was filled up into the neck so that there was no gas phase when the glass stopper was inserted. The extinction at 25° C was measured every third minute. From the extinctions the concentrations of cupric copper was determined, and α computed. In a similar kinetic run the bubbling through of oxygen was discontinued after 10 minutes, and the solution was left in the reaction vessel so that dissolved oxygen was allowed to react with the ascorbic acid. The course of the reaction was followed in the usual way (see the experimental section). Stirring of the solution by extraction of samples was carefully avoided.

Introduction of the numerical values for concentrations and constants into (X) gives:

$$\frac{1}{\alpha} = 1 + 3.67 \cdot \frac{\text{pO}_2}{c \cdot 10^3} \left\{ 1 + \sqrt{1 + 0.64 \cdot \frac{c \cdot 10^3}{\text{pO}_2} [1 + 0.66(1 - \alpha)]} \right\}$$

c was determined by experiment, pO_2 was calculated from stoichiometry.

Hence

α could be calculated by iteration. Table 3 demonstrates the accordance between

α calculated in this way and determined by spectrophotometry.

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Received October 13, 1954.