The Catalytic Effects of Copper Complexes on the Oxidation of l-Ascorbic Acid

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In the preceding paper,[1] the catalytic effects of metal ions on the oxidation of *l*-ascorbic acid were examined, and copper(II) was found to be the most active among them. The present study has been carried out in order to determine the relationship between the catalytic acitivity of various kinds of copper(II) complexes and the stability of the complexes. Though the discussions have often been made qualitatively with regard to the relationship between the catalytic activity of metal complexes and their stability, no quantitative relationship has been reported. The catalytic activity of copper(II) decreases more or less in the presence of the chelating agent, which forms a stable complex with copper(II). Since the decrease in the catalytic activity changes depending on the kinds of chelating agents and on the mole ratios of copper to the chelating agents, the stability constants of copper complexes can be calculated by measuring the rate constant with the solutions of the same composition as the copper(II) complexes. The results obtained by this method will be compared with those obtained by the polarographic method, etc. As for the relationship between k and the stability constant, K_S, k will be found to be inversely proportional to the $\log(1+K_S\cdot[Y]^n)$, in which [Y] means the concentration of the dissociated chelating agent.

Experimental

Apparatus and Reagents.—The same apparatus and reagents were used as in the preceding paper except for the following. For the measurement of the polarogram, a Yanagimoto polarograph, Model PR-2, was used. Each chelating agent was prepared as $n\times10^{-4}$ M solution by taking the mole ratio, n, of the chelating agent to copper into consideration.

Procedure.—Take a definite amount of metal ions or an additional chelating agent in a test-tube fitted with a glass-stopper, adjust the pH to either 4.3 or 6.0 with an acetate buffer, and dilute to 90 ml. with water. Take an aliquot volume of an *l*-ascorbic acid solution in another test-tube. Stopper the test-tubes, place in the thermostat held at 25±0.1°C, and treat in a manner similar to that described in the preceding paper.

Results and Discussion

The Relation between the Amount of Copper(II) and k.—The rate constant, k, for the oxidation of *l*-ascorbic acid was measured in

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[1] I. Onishi and T. Hara, This Bulletin, 37, 1314 (1964).

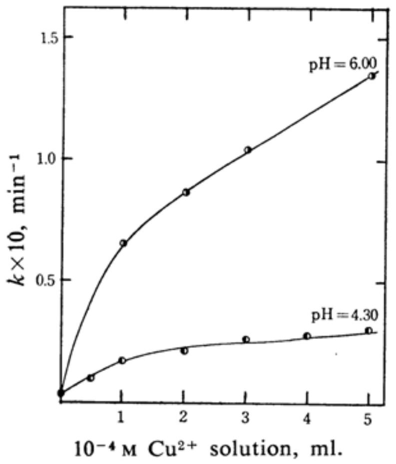

Fig. 1. Relations between the amount of Cu^{2+} and k.

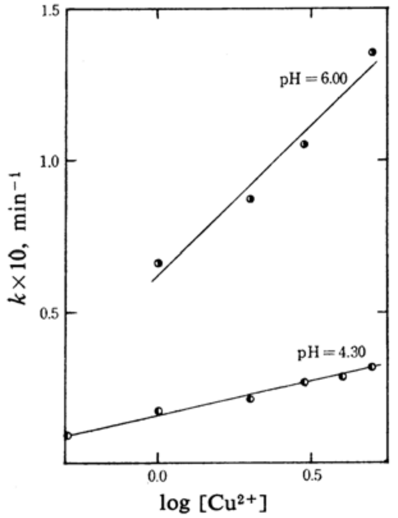

Fig. 2. Relations between log [Cu^{2+}] and k.

the presence of various amounts of copper(II) and with an accuracy of within 5%. The results obtained are shown in Fig. 1. By taking the logarithm of the copper concentration in Fig. 1, Fig. 2 is obtained. As can be seen from Fig. 2, there are two straight lines, and the relations between the amount of copper(II) and k are generally given by Eq. 1;

$$k=a \log [Cu^{2+}]+b \tag{1}$$

Since a and b are constant under the limited conditions and since their numerical values may easily be estimated from Fig. 2, Eq. 1 is replaced by Eq. 2 or 3 respectively:

$$\text{at pH}=4.3 \quad k_{4.3}=0.023 \log [Cu^{2+}]+0.0155 \tag{2}$$

$$\text{at pH}=6.0 \quad k_{6.0}=0.100 \log [Cu^{2+}]+0.064 \tag{3}$$

By measuring the value of $k_{4.3}$ or $k_{6.0}$ and by substituting them into Eq. 2 or 3, log[Cu^{2+}] is easily found.

The Effects of Chelating Agents on *k*.—The rate constant for the oxidation of *l*-ascorbic acid was measured in the presence of various kinds of chelating agents, which were added to copper(II) in the same ratios as with copper complexes. The results obtained are shown in Table I. It is apparent from Table I that the values of k vary with the chelating agents, but no definite relation exists between the stability constant and k. The relation between k and the mole ratio of EDTA to copper(II) is

TABLE I. THE RATE CONSTANTS IN THE PRESENCE OF VARIOUS KINDS OF CHELATING AGENTS ([Cu^{2+}] : 5×10^{-6} M/l., 25±0.1°C)

Chelating agent	mole ratio	$k\times10$, min^{-1} pH =4.30	pH =6.00
—*	—	0.031	0.031
Cu alone	—	0.313	1.360
Citric acid	1	0.302	1.270
NTA**	1	0.131	0.134
EDTA***	1	0.077	0.403
1, 10-Phenanthroline	2	0.200	0.524
Oxine	2	0.228	0.400
α, α'-Dipyridyl	2	0.054	0.420
Oxalic acid	2	0.259	1.350
Glycine	2	0.298	1.320
Ethylenediamine	2	0.292	1.370

* Blank
** Nitrilotriacetic acid
*** Ethylenediaminetetraacetic acid

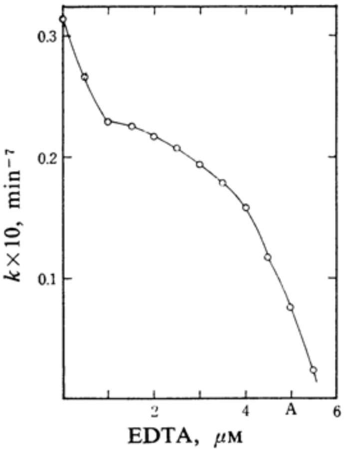

Fig. 3. Relation between k and the mole ratio of EDTA to Cu^{2+}.
Cu^{2+} : 5 μM, A : equivalence point

shown in Fig. 3. As can be seen from Fig. 3, the value of k decreases with an increase in the mole ratio of EDTA to copper(II). Therefore, the catalytic activity of the copper-EDTA system is considered to be due to the free copper ion alone. This was later confirmed by the agreement between the experimental and the theoretical results.

The Estimation of the Stability Constant.—The stability constants of copper(II) complexes are calculated on the basis of the assumption that the catalytic activity of copper(II) complexes are due to the free copper ions which have been liberated from the copper(II) complexes at equilibrium.

If Cu is made to react with n mol. of dissociated chelating agents, Y, to form CuY_n, the formation reaction is expressed by Eq. 4. (Here, the charges on the ions are omitted for the sake of simplicity.)

$$Cu + nY \rightleftharpoons CuY_n \tag{4}$$

$$K = [CuY_n]/[Cu]\,[Y]^n \tag{5}$$

If the initial concentration of Cu, $[Cu]_0$, is known,

$$[CuY_n] = [Cu]_0 - [Cu] \tag{6}$$

Similarly, Eq. 7 is derived:

$$[Y]_t = [Y]_0 - n[Cu\,Y_n] = n[Cu] \tag{7}$$

where $[Y]_0$: initial concentration of chelating agent,

$[Y]_t$: total concentration of unbound chelating agent at equilibrium.

[Y] is calculated from $[Y]_t$ by the following process. The dissociation of the chelating agent, H_mY, is given by Eq. 8:

$$\begin{aligned}
&H_mY \rightleftharpoons H^+ + H_{m-1}Y\\
&\qquad K_{d_1} = [H^+]\,[H_{m-1}Y]/[H_mY]\\
&H_{m-1}Y \rightleftharpoons H^+ + H_{m-2}Y\\
&\qquad K_{d_2} = [H^+]\,[H_{m-2}Y]/[H_{m-1}Y]\\
&\qquad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \qquad (8)\\
&H_2Y \rightleftharpoons H^+ + HY\\
&\qquad K_{d_{m-1}} = [H^+]\,[HY]/[H_2Y]\\
&HY \rightleftharpoons H^+ + Y \quad K_{d_m} = [H^+]\,[Y]/[HY]
\end{aligned}$$

$[Y]_t$ is also given by Eq. 9:

$$[Y]_t = [H_mY] + [H_{m-1}Y] + \cdots\cdots + [HY] + [Y] \tag{9}$$

The terms, $[H_mY] \sim [HY]$ in Eq. 9 are given by rewriting Eq. 8;

$$\begin{aligned}
&[HY] = [H^+]\,[Y]/K_{d_m}\\
&[H_2Y] = [H^+]^2[Y]/K_{d_m}\cdot K_{d_{m-1}} \qquad (10)\\
&[H_mY] = [H^+]^m[Y]/K_{d_m}\cdot K_{d_{m-1}}\cdots\\
&\qquad \cdot K_{d_2}\cdot K_{d_1}
\end{aligned}$$

By substituting Eq. 10 into Eq. 9, Eqs. 11 and 12 are obtained:

$$[Y]_t = \frac{[H^+]^m[Y]}{K_{d_1}\cdot K_{d_2}\cdot\cdots\cdot K_{d_m}} + \frac{[H^+]^{m-1}[Y]}{K_{d_2}\cdot K_{d_3}\cdot\cdots\cdot K_{d_m}} + \cdots \frac{[H^+]\,[Y]}{K_{d_m}} + [Y] \tag{11}$$

$$[Y] = [Y]_t \Big/ \left(\frac{[H^+]^m}{K_{d_1}\cdots K_{d_m}} + \cdots + \frac{[H^+]}{K_{d_m}} + 1 \right) \tag{12}$$

If k is measured in the presence of a copper-complex, log[Cu] is found by Eq. 2 or 3, followed by the calculation of $[CuY_n]$ and $[Y]_t$ by Eqs. 6 and 7. [Y] is also calculated by Eq. 12, and the stability constant is finally calculated by Eq. 5. The results obtained by this method are shown in Table II, along with those obtained by the polarographic method, etc. The results agree well with those obtained by other methods.

TABLE II. THE STABILITY CONSTANTS OF COPPER COMPLEXES CALCULATED FROM k (pH=4.3, 25±0.1°C, ionic strength=0.2)

Chelating agent	lok k_s from		
	rate constant	polarographic method*	literature
EDTA	15.2	15.1	18.80[2]
NTA	12.1	13.8	12.96[3]
1, 10-Phenanthroline	12.9	—	12.45[4]
α, α'-Dipyridyl	14.1	12.3	—
Oxine	25.4	—	26.22[5]
Oxalic acid	10.4	—	10.3[6]

* Calculated from the shifts of half-wave potentials.

Correlation among k, K_s and Y.—Figure 4 is obtained by plotting k against $\log(1+K_s\cdot[Y]^n)$. As can be seen from Fig. 4, k is inversely proportional to $\log(1+K_s[Y]^n)$. This relationship may also be derived theoretically. Eq. 5 is expressed by Eq. 13:

$$K_s = ([Cu]_0 - [Cu])/[Cu]\,[Y]^n \tag{13}$$

By rewriting Eq. 13,

$$[Cu] = [Cu]_0/(1+K_s[Y]^n) \tag{14}$$

By taking a logarithm and combining it with Eq. 1,

$$k = a\,\log[Cu]_0 - a\log(1+K_s[Y]^n) + b \tag{15}$$

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[2] G. Schwarzenbach et al., *Helv. Chim. Acta*, **37**, 937 (1954).

[3] G. Schwarzenbach et al., ibid., **38**, 1144 (1955).

[4] F. P. Dwyer and R. Nyholm, *J. Proc. Roy. Soc., New South Wales*, **80**, 28 (1946).

[5] W. D. Johnston and H. Freiser, *J. Am. Chem. Soc.*, **74**, 5239 (1952).

[6] L. Meites, ibid., **72**, 184 (1950).

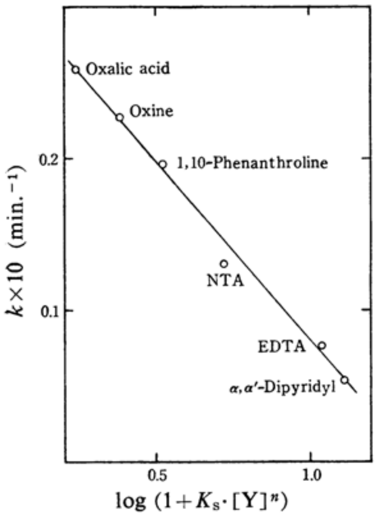

Fig. 4. Relation between k and log $(1+K_S[Y]^n)$ (pH=4.3, ionic strength=0.2, 25±0.1°C)

Since the first term on the right-hand side is thought to be a constant, Eq. 16 is glven:

$$k=-a\log(1+K_s[Y]^n)+b' \tag{16}$$

According to Fig. 4, the value of k for a given copper-complex at a definite pH can be estimated by the use of the values for K_s and Y. It is expected that Eq. 16 generally holds for the various kinds of reactions which proceed as of the first order.

Summary

The stability constants of various kinds of copper complexes have been estimated on the basis of the decrease in the catalytic activity of copper(II) in the presence of chelating agents. The rate constant, k, has been found to be inversely proportional to log $(1+K_s[Y]^n)$.

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