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VALENCE CHANGE OF COPPER IN CATALYTIC OXIDATION OF L-ASCORBIC ACID BY MOLECULAR OXYGEN

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The copper(II) chloride-catalyzed oxidation of L-ascorbic acid (AA) by O_2 was found to involve both the anaerobic oxidation of AA by copper(II) chloride and the reoxidation steps of copper(I) chloride by O_2 in the catalytic cycle, by comparing the rate of copper(II)-catalyzed oxidation of AA by O_2 (R_{AIIO}) with those of anaerobic oxidation of AA by copper(II) (R_{AII}) and oxidation of copper(I) by O_2 (R_{IO}).

In spite of a number of kinetic studies on copper(II)-catalyzed oxidation of L-ascorbic acid (AA) by O_2, the role of copper ion or complexes in the catalytic cycle is not completely elucidated yet. Khan and Martell[1], Ogata and coworkers[2], and Jameson and Blackburn[3] assumed the formation of ternary complexes among AA, Cu(II) and O_2 to explain the observed kinetic data. Hanaki[4] found the retardation effect of halides, cyanide, thiocyanate and 1,10-phenanthroline on the rate of Cu(II)-catalyzed oxidation of AA and suggested the participation of Cu(I) oxidation in the catalytic cycle.

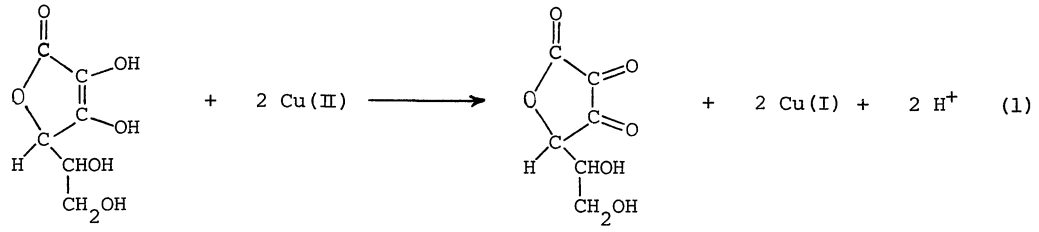
In the present study, with the intension of examining the ease of the interconversion between Cu(II) and Cu(I) states, the rate of reduction of copper(II) chloride to copper(I) by AA (R_{AII}) and the rate of oxidation of copper(I) chloride to copper(II) by O_2 (R_{IO}) were measured separately and compared with the rate of copper(II) chloride-catalyzed oxidation of AA by O_2 (R_{AIIO}).

The rate of O_2 consumption by AA or Cu(I) were determined by using a Clark type O_2-electrode. All the reactions were carried out at 30.0±0.1°C in a 0.1 M acetate buffer solution(pH 4.25) containing 1.0 M of KCl, which was added to increase the solubility of copper(I) chloride.

Copper(II) chloride-catalyzed oxidation of AA by O_2 The time course of the copper(II) chloride-catalyzed oxidation of AA by O_2 followed a first-order kinetics with respect to O_2 concentration up to 60 % conversions at the initial concentrations of 10 mM of AA, 1.1 mM of O_2 and 1,2,4 and 8 mM of Cu(II). The logarithmic plots of the concentrations of the remaining O_2 vs. the reaction time give first-order rate constants, k_{AIIO}. The initial rates (R_{AIIO}) of the AA oxidation can be obtained from the k_{AIIO} mutiplied by the initial concentration of O_2(1.1 mM) and were plotted against Cu(II) concentration, as shown in Fig. 1. The values of R_{AIIO} show a 1.7th order dependence on the initial concentration of Cu(II).

Anaerobic oxidation of AA by copper(II) chloride Addition of Cu(II) to AA

solutions in the absence of O_2 caused the decrease in the absorbance of ascorbate anion at 263 nm according to the following reaction,



Ascorbic acid (AA) Dehydroascorbic acid (DAA)

as shown in Fig. 2. The reaction is very rapid and completed within 1 min after mixing Cu(II) with AA. The quantitative formation of Cu(I) species was confirmed colorimetrically (Fig. 2) by bathocuproine sulfonate (BCS) method[5].

The rates of the anaerobic oxidation of AA were determined by a stopped-flow spectrophotometer(Union Giken, Model RA-401). At the initial concentrations of 0.29 to 0.33 mM of AA and 1 to 4 mM of Cu(II), the decay of the absorbance at 263 nm followed a first-order kinetics with the half-life times of 4 to 0.6 msec. The pseudo first-order rate constants (k_{AII}) calculated from the half-life times were $(1.1\pm0.2)\times10^4$, $(3.6\pm0.6)\times10^4$, and $(8.1\pm2.3)\times10^4$ min^{-1} at 1,2 and 4 mM of Cu(II), respectively. The presence of O_2 in the AA solution showed no effect on k_{AII}, indicating that the anaerobic oxidation of AA by Cu(II) is much faster than the Cu(II)-catalyzed oxidation of AA by O_2. From the kinetics described above, one can calculate the initial rates of the anaerobic oxidation of AA (R_{AII}) for the initial concentration of 10 mM of AA at each Cu(II) concentration. As the values of R_{AII} in Fig. 1 are ca. 10^5 times the R_{AIIO}, the copper species should exist in Cu(I) state during the oxidation of AA by O_2. In fact, the addition of 10 mM of AA to the O_2-saturated copper(II) solution(4mM) immediately depleted the blue color of the copper(II) ion.

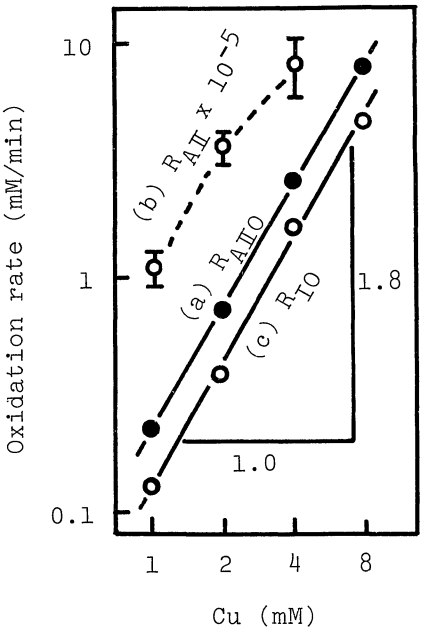


Fig.1 Comparison of the rates of (a) Cu(II)-catalyzed oxidation of AA by O_2 (R_{AIIO}) with those of (b) anaerobic oxidation of AA by Cu(II) (R_{AII}) and (c) oxidation of Cu(I) by O_2 (R_{IO}). 30.0°C, pH=4.25(0.1 M acetate buffer), KCl=1.0 M, AA=10 mM for (a) and (b), O_2=1.1 mM for (a) and (c).

Oxidation of copper(I) chloride to copper(II) by O_2 Copper(I) chloride, generated by the reduction of copper(II) according to Eq.(1), can be re-oxidized to Cu(II) by O_2. The rates of the oxidation of Cu(I) by O_2 were measured separately in the absence of AA. The time course of O_2 consumption by Cu(I) follow the rate equation(2),

$$R_{IO} = k_{IO}[Cu(I)]^2[O_2] \qquad (2)$$

up to 50 % conversion of O_2. In the determination of k_{IO}, the concentrations of Cu(I) were calculated from the stoichiometric relationship as follows,

$$2\ Cu(I) + O_2 + 2H^+ = 2\ Cu(II) + H_2O_2 \qquad (3)$$

for the initial stage of the oxidation. The values of k_{IO} thus obtained were essentially constant, $(8.4\pm1.6) \times 10^4\ M^{-2}min^{-1}$, over the range of the initial concentrations from 1 to 8 mM of Cu(I) and from 0.24 to 1.1 mM of O_2. The initial rates (R_{IO}) at 1.1 mM of O_2, calculated from Eq.(2), are about one-half(40~60 %) the overall oxidation rates (R_{AIIO}), as shown in Fig. 1.

The simplest redox mechanism which includes only Eqs. (1) and (3), therefore, accounts for the half of R_{AIIO}. A possible reaction for another half will be Cu(I) oxidation accelerated by AA. In fact, addition of 10 mM of AA raised R_{IO} from 1.65± 0.05 to 2.62±0.08 mM/min, which is very close to R_{AIIO}(2.59±0.06 mM/min). In Fig.3, the rates of oxidation of copper(I) chloride (4 mM) by O_2 in the presence of various amounts of AA (R_{AIO}) are compared with R_{AIIO}. On plotting R_{AIIO} in Fig. 3, the concentrations of AA are corrected for the anaerobic oxidation by Cu(II)(4 mM) as follows:

$$[AA] = [AA]_{added} - [Cu(II)]_{added} / 2$$

As illustrated in Fig. 3, R_{AIIO} agree well with R_{AIO} over the whole range of AA concentrations. Since oxalic and malonic acids (10 mM) also raised R_{IO}(1.65 mM/min) to 45 and 2.8 mM/min, respectively, the acceleration effect of AA on R_{IO} is due to complex formation with Cu(I).

All the kinetic data available are consistent with the minimal mechanism shown in Scheme 1 (possible decomposition reactions of the oxidation products, for instances, H_2O_2 to H_2O and DAA to diketogulonic acid, are not included).

The rates of the reactions in steps 1, 2 and 4 correspond to R_{AII}, R_{IO} and $(R_{AIO}-R_{IO})$, respectively. In step 1, Cu(II) is rapidly reduced to Cu(I), which is in turn re-oxidized to Cu(II) by the reactions in steps 2 and 4. Thus, the catalyst oscillates between the Cu(II)

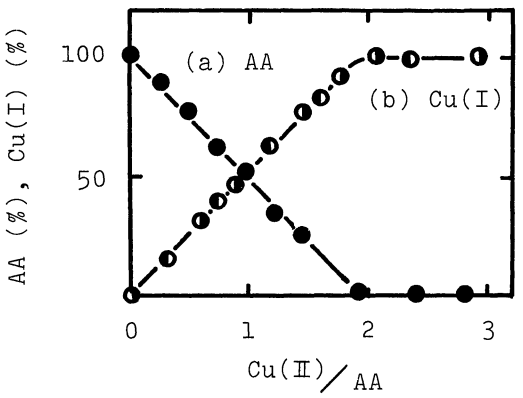


Fig.2 Anaerobic titration of AA with copper(II) chloride. (a) Decrease of AA determined from the absorbances at 263 nm. (b) Formation of copper(I) species determined by BCS method[5]. BCS(0.24 mM) was added to AA solution (0.035 mM) before(●) or after(◐) addition of Cu(II) to AA solution .

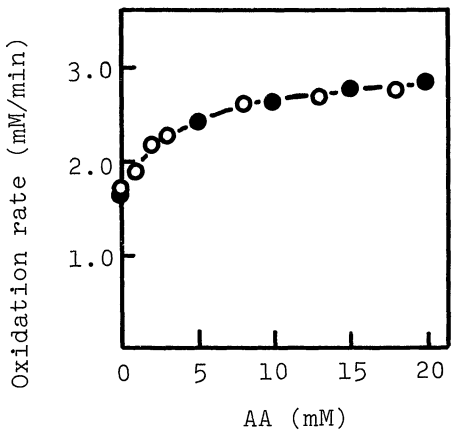
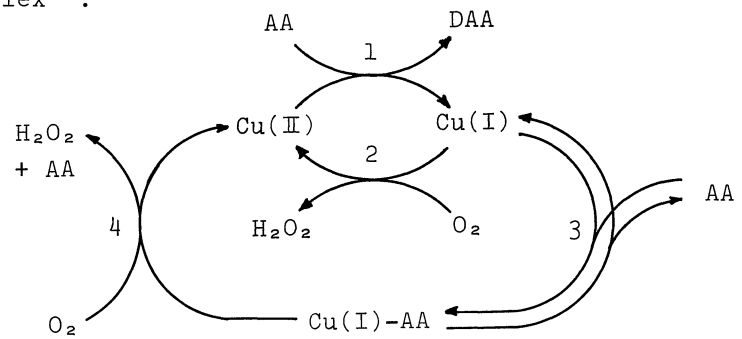


Fig.3 Comparison of the rates of Cu(II)-catalyzed oxidation of AA by O_2 (○) with those of oxidation of copper(I) chloride by O_2 in the presence of AA (●).

and Cu(I) forms in the usual catalytic cycle and molecular oxygen reacts with the Cu(I) forms, not with the Cu(II) form. Since R_{AII} is much greater than R_{IO} (or R_{AIO}) under the present reaction conditions, the rate-determining steps for O_2 consumption should be steps 2 and 4, accounting for the first-order dependence on O_2 concentration.

According to this mechanism, it is expected that chelating agents which complex with either Cu(II) or Cu(I) will inhibit the catalytic oxidation of AA. In Table 1, the effects of EDTA and BCS (typical masking agents for Cu(II) and Cu(I), respectively) on the R_{AIIO}, R_{AII}, and R_{IO} were summarized. Though both chelating agents inhibited the catalytic oxidation of AA by O_2, the role of these inhibitors are quite different from each other. As is shown in Table 1, EDTA suppresses the anaerobic oxidation of AA by Cu(II) , while BCS inhibits the oxidation of Cu(I) by O_2 with the formation of an orange BCS-Cu(I) complex[5].

A zero-order dependence of R_{AIIO} on O_2 concentration observed in Cu(II)-EDTA catalyzed oxidation of AA[1] can be explained straightfowardly by the proposed mechanism. Thus the formation of Cu(II)-EDTA complex may decrease the rate of the anaerobic oxidation (R_{AII}) to an extent much less than R_{IO} (or R_{AIO}), resulting in a zero-order kinetics with step 1 as the rate-determining step. Most of the discrepancies in the reaction kinetics reported previously (especially with respect to O_2 dependence[1)2)3)]) are attributable to the change of the rate-determining step, depending on the reaction conditions (pH, kind of buffer solution used and additives).



Scheme 1

Table 1 Effects of Chelating Agents on R_{AIIO}, R_{AII}, and R_{IO}

Additive (10mM)	Oxidation rates (mM/min) R_{AIIO}	R_{AII}	R_{IO}
None	2.59	8×10^5	1.65
EDTA	0.011	0.012	29
BCS	0	1×10^6	0

Reaction conditions are the same as shown in Fig. 1.

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References and Note

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6) The formation of H_2O_2 was confirmed by titanium sulfate method (H. Erlenmeyer, Helv. Chim. Acta., 47, 792(1964)). The yields of H_2O_2 were more than 40% in both the catalytic oxidation of AA by O_2 and the oxidation of copper(I) chloride by O_2.

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