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OXIDATION OF ASCORBIC ACID CATALYZED BY *N,N'*-ETHYLENEBIS(SALICYLIDENEAMINATO)COBALT(II)

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N,N'-Ethylenebis(salicylideneaminato)cobalt(II) catalyzed the autoxidation of ascorbic acid in methanol. The kinetic evidence of a transient-oxygen complex with ascorbic acid was obtained by the measurements of the oxygen consumption in this catalytic oxidation.

N,N'-Etylenebis(salicylideneaminato)cobalt(II), [Co(salen)], which is a model of oxygen carriers in biological systems, catalyzes an autoxidation of organic substrate. The autoxidation of indol, for example, is reported to be promoted via the formation of the oxygen complex with indol.1) However, there are few kinetic studies and the evidence of the transient-O_2 complex with substrate is not sufficient. Although the autoxidation of ascorbic acid (H_2A) to dehydroascorbic acid (A) is slow, metal ions catalyze this reaction.2) We have previously reported3) that $[Cu(trans\text{-}[14]dieneN_4)]^{2+}$, which is not reduced by ascorbic acid, catalyzes the autoxidation of ascorbic acid and that the intermediate $[H_2ACu(II)O_2]$ complex should be formed. In this letter, we report the kinetic evidence upon a transient-O_2 complex with ascorbic acid $[H_2ACo(salen)O_2]$.

[Co(salen)] was prepared by the method described elsewhere4) and recrystallized from benzene. L-ascorbic acid and methanol were used of garanteed grade without further purification. The oxidation of ascorbic acid was carried out in methanol using a closed oxygen-circulating system. The reaction was initiated by the addition of 1 cm^3 of [Co(salen)] solution to 25 cm^3 of ascorbic acid solution saturated with oxygen under an atmospheric pressure with vigorous stirring. The amount of oxygen absorbed during the course of the reaction was followed by the use of a gas buret.

The absorption spectrum of [Co(salen)] in methanol has the maximum at 390 nm, which is in accord with that of $[\{Co(salen)\}_2O_2]$ in methanol, but is different from that of a planar [Co(salen)] in dichloromethane (λ_{max} 408 nm and 347 nm) or in methanol under a nitrogen atmosphere (λ_{max} 400 nm and 340 nm). A methanol solution containing $[\{Co(salen)\}_2O_2]$ and ascorbic acid under a nitrogen atmosphere has the absorption maxima at 403 and 348 nm, which are characteristic of those of the planar [Co(salen)], and was stable for at least one day. This suggests the following reaction occurs:

$$[\{Co(salen)\}_2O_2] + H_2A \longrightarrow 2[Co(salen)] + A + H_2O_2 \qquad (1)$$

Although the autoxidation of ascorbic acid in methanol was very slow, the rate of the oxidation increased in the presence of [Co(salen)] (Fig. 1). At the beginning of the reaction the solution showed the reddish yellow color which turned yellow in a few minutes. This color change was ascribed to a side reaction. The rate constants of the catalysis, therefore, were determined by the initial rate method. The amount of oxygen uptake at the end of the reaction was equimolar to the initial amount of ascorbic acid (O_2:H_2A = 1.1±0.2 from five runs).

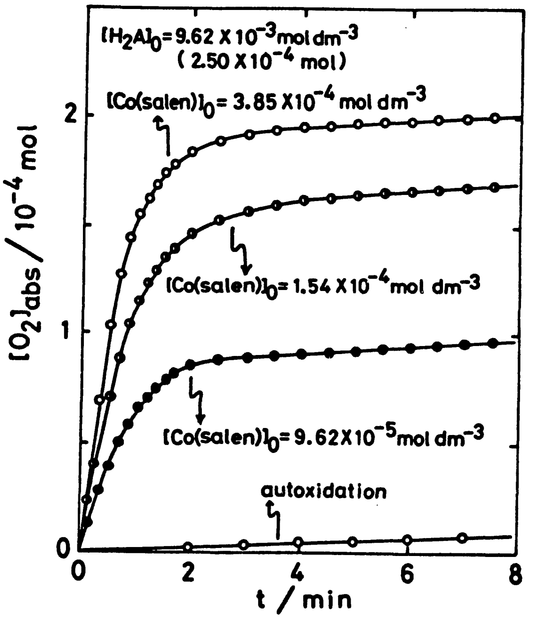

Fig. 1. Oxidation of ascorbic acid catalyzed by [Co(salen)] in methanol at 12.5 °C.

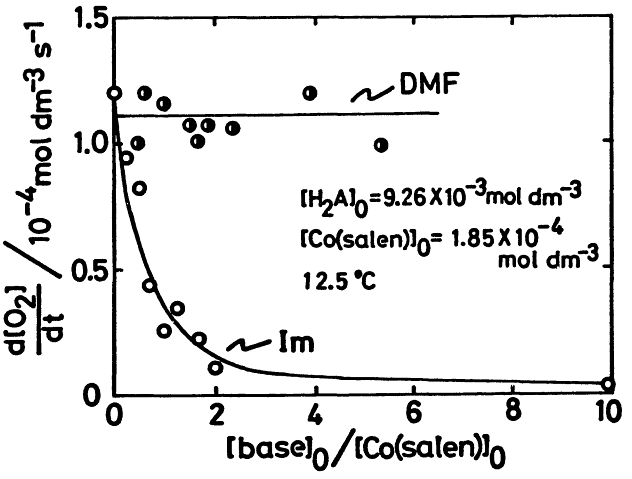

Fig. 2. Influence of bases on the rate of oxidation of ascorbic acid.

Imidazol (Im) inhibited the [Co(salen)]-catalyzed oxidation of ascorbic acid (Fig. 2), which is probably due to the formation of a cobalt-oxygen complex with imidazol. On the other hand, *N*,*N*-dimethylformamide (DMF) did not inhibit this reaction. This may be attributed to that the coordination of DMF to [Co(salen)] is much slower than that of ascorbic acid or imidazol. In fact the formation of $[\{(DMF)Co(salen)\}_2O_2]$ dimer in DMF is slow.5) From these results the coordination of ascorbic acid to cobalt may be necessary to the catalysis by [Co(salen)].

The initial rate was proportional to the initial concentrations of [Co(salen)] (5.49×10^{-5} mol dm^{-3} to 3.85×10^{-4} mol dm^{-3}). On the other hand no linear dependency of the initial concentrations of ascorbic acid on the initial rate was observed (Fig. 3).

The formation of the dimer $[\{Co(salen)\}_2O_2]$ is expected to be much slower than that of an O_2-monomer with ascorbic acid $[H_2ACo(salen)O_2]$. If the following catalytic reactions occur after the reaction (1),6)

$$[Co(salen)] + O_2 \underset{}{\overset{K_1}{\rightleftharpoons}} [Co(salen)O_2] \qquad (2)$$

$$[\mathrm{Co(salen)O_2}] + \mathrm{H_2A} \underset{}{\overset{K_2}{\rightleftharpoons}} [\mathrm{H_2ACo(salen)O_2}] \tag{3}$$

$$[\mathrm{H_2ACo(salen)O_2}] \xrightarrow{k} [\mathrm{Co(salen)}] + \mathrm{H_2A^{\dot{+}}} + \mathrm{O_2^{\dot{-}}} \tag{4}$$

Eq. (5) is derived.

$$\frac{d[\mathrm{O_2}]}{dt} = \frac{kK[\mathrm{H_2A}]_0[\mathrm{O_2}]_0}{1+K[\mathrm{H_2A}]_0[\mathrm{O_2}]_0} \cdot [\mathrm{Co(salen)}]_0 \tag{5}$$

where $K = K_1K_2$ and $[\mathrm{H_2A}]_0$, $[\mathrm{O_2}]_0$, and $[\mathrm{Co(salen)}]_0$ are the initial concentrations of $\mathrm{H_2A}$, $\mathrm{O_2}$, and [Co(salen)], respectively. Inverting Eq. (5) leads to

$$\left(\frac{d[\mathrm{O_2}]}{dt}\right)^{-1} \cdot [\mathrm{Co(salen)}]_0 = \frac{1}{k} + \frac{1}{kK[\mathrm{O_2}]_0} \cdot \frac{1}{[\mathrm{H_2A}]_0} \tag{6}$$

The plots of the left-hand side of Eq. (6) *vs.* $[\mathrm{H_2A}]_0^{-1}$ gave a linear relation (Fig. 4) and the rate constant of the intramolecular electron transfer, k, and the equilibrium constant, K, were determined from the intercept and the slope of this straight line, respectively. The kinetic parameters thus obtained at various temperatures are given in Table.

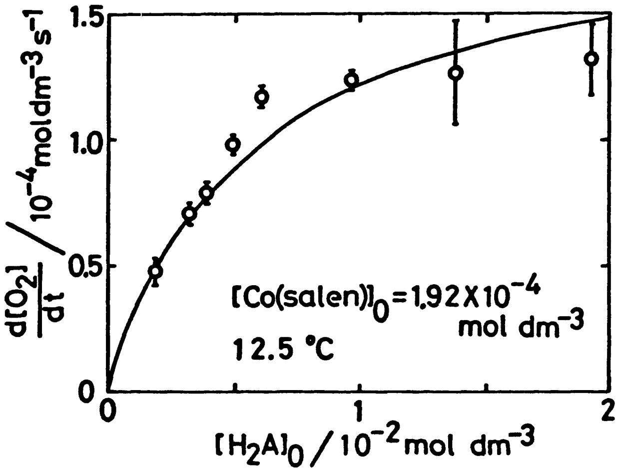

Fig. 3. The dependency of $[\mathrm{H_2A}]_0$ on the rate of oxidation of ascorbic acid.

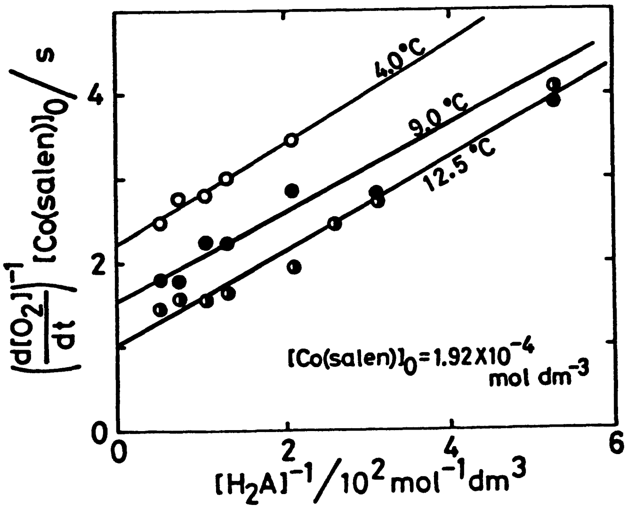

Fig. 4. The plots of $(d[\mathrm{O_2}]/dt)^{-1} \times [\mathrm{Co(salen)}]_0$ *vs.* $[\mathrm{H_2A}]_0^{-1}$.

Table

Temp	k^a	K^b
°C	s^{-1}	10^4 mol^{-2} dm^6
4.0	0.45 ± 0.01	3.9 ± 0.5
9.0	0.67 ± 0.09	3.1 ± 0.7
12.5	1.0 ± 0.1	1.8 ± 0.3

[a] $\Delta H^{\ddagger} = 58 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger} = -41 \pm 4$ J K^{-1} mol^{-1}.

[b] $\Delta H° = -59 \pm 4$ kJ mol^{-1}, $\Delta S° = -130 \pm 5$ J K^{-1} mol^{-1}.

Ascorbic acid is a π-donor and oxygen a π-acceptor, so the π-donor-π-acceptor couple can stabilize the complex $[H_2ACo(salen)O_2]$;the large values of K are thus explained. The presence of $[H_2ACo(salen)O_2]$ is also supported by the values of $\Delta H°$ and $\Delta S°$, which are characteristic of the 1:1 cobalt-oxygen complexes.[8)]

The negative activation entropy (-41 J K^{-1} mol^{-1}) suggestes that the solvation increases, since $[H_2ACoO_2]$ or $[H_2ACo^+O_2^-]$ is converted into $[H_2A^+CoO_2^-]$.[9)]

In this work it is found that the transient-O_2 complex with ascorbic acid forms in the [Co(salen)]-catalyzed oxidation of ascorbic acid. We are currently investigating in detail this electron transfer mechanism.

References and Notes

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6) The dismutation of ascorbic acid radicals and the reaction of $O_2^{\cdot -}$ with ascorbic acid are very fast[7)] and the reaction (2) may be also fast. The sixth coordination site of $[Co(salen)O_2]$ would be occupied by methanol.
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