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CATALYTIC ACTIVITY OF BINUCLEAR MANGANESE(III) COMPLEXES FOR THE DECOMPOSITION OF HYDROGENPEROXIDE

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Some alkoxo-bridged binuclear manganese(III) complexes showed high catalytic activity for the decomposition of hydrogenperoxide compared with mononuclear manganese(III) complexes.

In the photosynthetic process, water molecules are decomposed to give O_2 and $2H^+$ by a manganese enzyme. According to Sauer,1) the reaction proceeds in four steps. In the last step of water splitting reaction($S_4 \longrightarrow S_0$, cf. Fig. 6 in ref. 1), the decomposition of O_2^{2-} is assumed to proceed through the formation of a $Mn_2^{III}-O_2^{2-}$ complex followed by the two electron transfer from O_2^{2-} to two manganese ions. Thus, it is desirable to study the catalytic function of binuclear manganese complexes for the decomposition of hydrogenperoxide.

The catalytic activities specific for binuclear copper(II) complexes for the oxidation reactions of catechol, ascorbic acid, etc., by molecular oxygen were already shown in our previous papers.3-5) According to our preliminary results, it was also shown that2) some planar binuclear copper(II) complexes show high catalytic activity for the decomposition of hydrogenperoxide compared with planar mononuclear copper(II) complexes. In this report, we report the catalytic activity of some alkoxo-bridged binuclear manganese(III) complexes for the decomposition of H_2O_2, comparing with that of mononuclear complexes with similar coordination environment. This result will provide a basic idea for the elucidation of the function of the manganese enzyme.

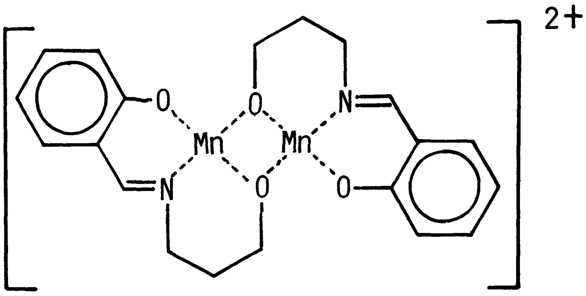

Fig. 1 Chemical structure of a $[Mn_2(salpa)_2]^{2+}$ complex

The binuclear manganese(III) complexes, $[Mn_2(salpa)_2]^{2+}$(cf. Fig. 1) were obtained according to the literature method.6) To evaluate the catalytic activity of these complexes, the residual H_2O_2 in the reaction mixture(in dmf, 18°C) of manganese(III) complex($[Mn^{3+}]=1\times10^{-4}$ mol dm^{-3}) and H_2O_2(1×10^{-3} mol dm^{-3}) was determined by the Fe^{2+}-NH_4NCS

method,7) the results being plotted against time in Fig. 2.

The mononuclear complexes, [Mn(salen)NCS] and [Mn(amben)NCS] show little catalytic activity for the decomposition of H_2O_2(H_2(salen) and H_2(amben) denote N,N'-disalicylideneethylenediamine and N,N'-bis(o-aminobenzylidene)ethylenediamine, respectively), whereas the binuclear manganese(III) complexes, $[Mn_2(salpa)_2]Cl_2$ and $[Mn_2(salpa)_2](AcO)_2$, show high catalytic activity, as shown in Fig. 2. A similar result was obtained when copper(II) complexes were used instead of manganese(III) complexes.2) Those results are explainable on assuming that the decomposition of H_2O_2 is catalyzed by binuclear manganese(III) complexes via the formation of an "intermediate" complex as depicted in Fig. 3, as already assumed for the redox reaction catalyzed by binuclear copper(II) complexes.2,3)

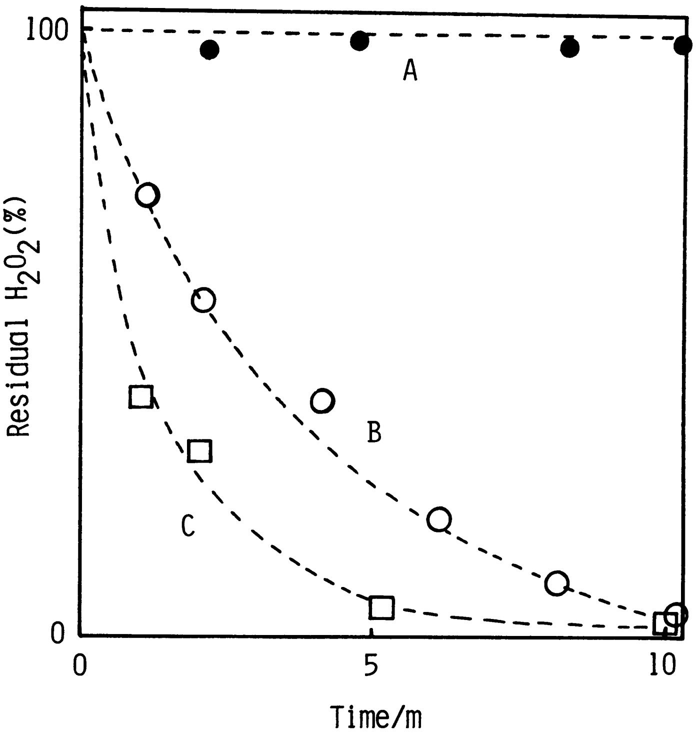

Fig. 2 Time course of H_2O_2 decomposition at the presence of Mn(III) complexes, (A) [Mn(salen)NCS], (B) $[Mn_2(salpa)_2]Cl_2$ and (C) $[Mn_2(salpa)_2](AcO)_2$

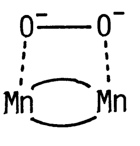

Fig. 3 Assumed intermediate complex between O_2^{2-} and a binuclear manganese(III) complex

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