Preparation of a 1,8-Anthracene-linked Manganese(IV) Porphyrin Dimer and Its Reduction with H_2O_2. The O_2 Evolution Stage by the Reduction of the $Mn(IV)_2$ Complex Is Not a Rate-determining Step in the Catalytic Disproportionation of H_2O_2

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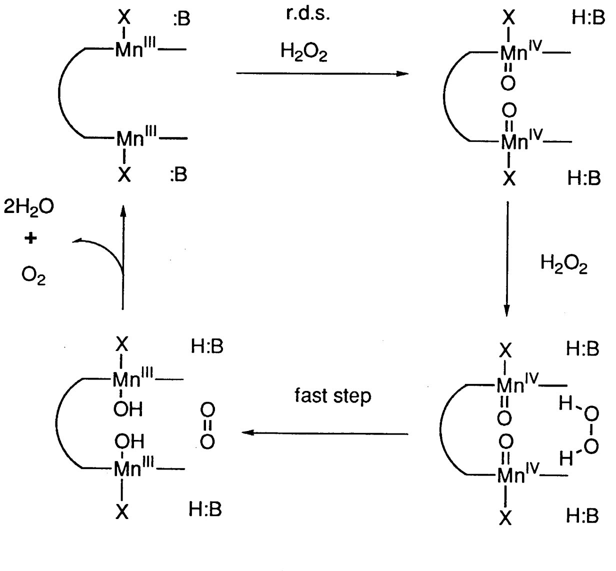
The reduction rate of 1,8-anthracene-linked Mn(IV) porphyrin dimer with H_2O_2 was photometrically determined. This process is 6.5 times faster than that of the overall O_2-evolution rate in the catalytic disproportionation of H_2O_2 with the Mn(III) porphyrin dimer and the formation of the corresponding $Mn(IV)_2$ complex is the rate-determining step in this catalytic reaction.

We have exhibited that Mn(III) porphyrin dimers having a short Mn-Mn separation excellently catalyzed the disproportionation of H_2O_2 in the presence of an appropriate nitrogen base.[1] This system is considered to be a good functional model of manganese catalases, which contain two manganese ions in their active sites.[2]

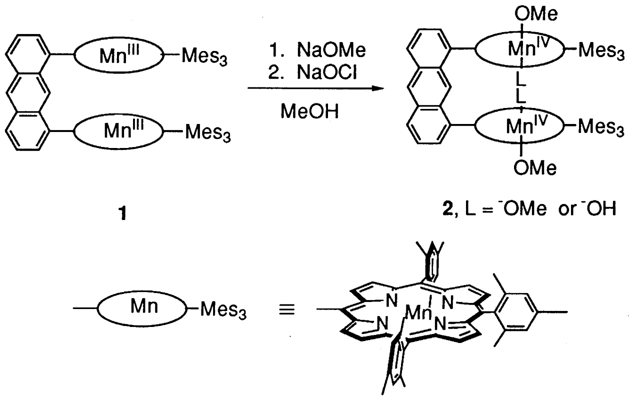
$$2H_2O_2 \xrightarrow{\text{Mn catalyst}} O_2 + 2H_2O$$

From mechanistic study including kinetic and isotope labeling experiments,[1a] this model reaction could proceed through the formation of the corresponding $Mn(IV)_2$ complex as an intermediate by the homolytic O-O bond cleavage of the Mn-O-O-H. The resultant $Mn(IV)_2$ complex would react with the second H_2O_2 molecule much faster than the Mn(III) porphyrin dimer (Scheme 1). To confirm this catalytic cycle, we separately prepared a Mn(IV) porphyrin dimer and compared its reduction rate by H_2O_2 with the O_2-evolution rate in the Mn^{III} dimer-H_2O_2 system.

In this experiment, we used the dimanganese(III) complex of 1,8-bis[5-(10,15,20-trimesityl)porphrinyl]anthracene (**1**),[3] that did not form the corresponding μ-oxo dimer in inter- and intramolecular modes.[4] The $Mn(III)_2$ complex was converted to the corresponding $Mn(IV)_2$ **2** by hypochlorite oxidation (Scheme 2).[5] A methanolic solution of **1** was mixed with NaOMe. To the filtrate of the solution, aqueous NaOCl was added at -10°C. The resultant brown precipitate was filtered to give the corresponding $Mn(IV)_2$ complex **2**.[6] This complex showed characteristic electronic absorption at $\lambda_{max} = 423$ nm (Soret) in CH_2Cl_2 at -65°C. In its esr spectrum in CH_2Cl_2 at 4 K, a strong and broad band at $g = 4.4$ proved the absence of any electronic coupling between the two Mn ions by the formation of a μ-oxo complex. The IR spectrum supported the presence of Mn-O bond $\nu(\text{Mn–O}) = 558\ \text{cm}^{-1}$.



Scheme 1.



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2, L = ⁻OMe or ⁻OH

Scheme 2.

The reduction rate of the $Mn(IV)_2$ complex **2** with $H_2O_2$was determined from the time-course of its UV-vis spectral change in CH_3CN at the temperature range from -40 to -20°C (Figure 1). In the kinetic analysis, we assume that each manganese ion in the dimer independently reacts with H_2O_2. Its rate is expressed as equation 1, where $[Mn^{III}P]$ and $[Mn^{IV}P]$ are the concentrations of the Mn(III) and Mn(IV) porphyrin monomer residues, respectively.

$$\frac{d[Mn^{III}P]}{dt} = k_3[Mn^{IV}P]^2[H_2O_2] \tag{1}$$

$$k_3 t = R$$

$$R = \frac{1}{A}\cdot\frac{2[Mn^{III}P]}{[Mn^{IV}P]_0([Mn^{IV}P]_0-2[Mn^{III}P])} + \frac{1}{B^2}\ln\left\{\frac{[H_2O_2]_0([Mn^{IV}P]_0-2[Mn^{III}P])}{([H_2O_2]_0-[Mn^{III}P])[Mn^{IV}P]_0}\right\}$$

$$A = 2[H_2O_2]_0+[Mn^{IV}P]_0$$

$$B = 2[H_2O_2]_0-[Mn^{IV}P]_0 \tag{2}$$

The rate constant k_3 is estimated from equation 2 by the direct calculation of the right term (R), where $[Mn^{IV}P]_0$ and $[H_2O_2]_0$ are the initial concentrations of the Mn(IV) porphyrin residue and H_2O_2, respectively. The spectral change and the plot according to equation 2 at -40°C was shown in Figure 1. Absorption at 422 nm that corresponds to the Soret band of the Mn(IV) complex was decreased according to the increase of the absorption at 468 nm (the Mn(III) complex). Good linear correlation according to equation 2 was obtained and the rate constant k_3 was determined by the time-course of the absorption change at 468 nm to be 2.61×10^5 mol^{-2} dm^6 s^{-1} at -40°C. The Arrhenius plot of this reaction (T = -20 to -40°C) gave the activation parameters, $E_a = 8.9$ kcal mol^{-1} and $A = 4.3 \times 10^{13}$ mol^{-2} dm^6 s^{-1}. Thus, one can estimate the reduction rate (1.3×10^{-2} mol dm^{-3} s^{-1}) of the Mn(IV) porphyrin dimer **2** with H_2O_2 under the conditions applied to the measurement of its catalase activity ($[Mn^{III}{}_2P] = 1.25 \times 10^{-4}$ mol dm^{-3}, $[H_2O_2] = 6.4 \times 10^{-2}$ mol dm^{-3}, T = 10°C). On the other hand, the O_2 evolution rate of the catalytic H_2O_2 disproportionation with **1** was 2.0×10^{-3} mol dm^{-3} s^{-1} under the same conditions in the presence of 4-dimethylaminopyridine, which gave the highest O_2-evolution rate among nitrogen bases ever examined in the catalase-modeling reaction.[1d] Thus, the reduction rate of the $Mn(IV)_2$ complex was 6.5 times higher than the overall disproportionation reaction of H_2O_2 with the corresponding $Mn(III)_2$ catalyst. Furthermore, since the applied MeO^- ion as an axial ligand of the $Mn(IV)_2$ complex is more electron-donating than most nitrogen bases, the applied Mn(IV) complex **2** would less active in the reduction by H_2O_2 than the corresponding Mn(IV)-nitrogen base complex, which is assumed as an intermedeate in the catalytic reaction. Thus, the reduction rate of the Mn(IV)-nitrogen base complex is expected to be larger than that of the present alkoxy complex,. These results support that the rate-determining step in the catalase reaction is the formation of Mn(IV) dimer in Scheme 1 as we predicted in our previous work.[1a]

Conclusively, we synthesized the Mn(IV) porphyrin dimer in a short Mn-Mn separation. The complex reacted with H_2O_2 to give the corresponding $Mn(III)_2$ complex. From its reduction rate constants and the activation parameters, it was compared with the O_2 evolution rate in the relating catalytic disproportionation with the $Mn(III)_2$ complex. These results support that the rate-determining step in its catalytic cycle is the formation of the $Mn(IV)_2$ complex.

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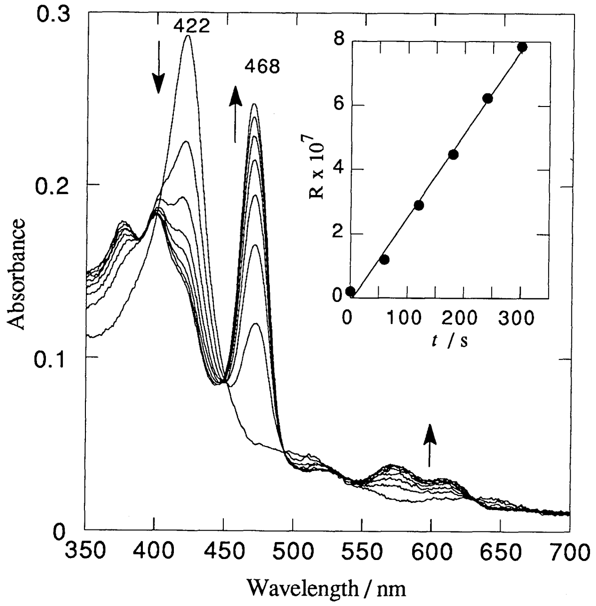

Figure 1. The time-course of the reduction of the $Mn(IV)_2$ porphyrin dimer **2** with H_2O_2 at -40°C. Inset is the plot according to equation 2.

References and Notes

1 (a) Y. Naruta and K. Maruyama, *J. Am. Chem. Soc.*, **113**, 3593 (1991). (b) Y. Naruta, M. Sasayama, and K. Maruyama, *Chem. Lett.*, **1992**, 1267. (c) Y. Naruta and M. Sasayama, *J. Chem. Soc., Chem. Commun.*, in press. (d) Y. Naruta and M. Sasayama, *Chem. Lett.*, in press.

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3 Satisfactory elemental analysis was obtained for **1**; UV-vis (CH_2Cl_2) λ_{max}= 621, 586, 479, 376 nm; Found: *m/z* 1608.602. Calcd. for $C_{108}H_{90}N_8Mn_2$: M, 1608.605.

4 The Mn-Mn separation in **2** was estimated to be 7.4 Å by means of MM+ calculation in HyperChem package.

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6 Since the $Mn(IV)_2$ complex was unstable at room temperature, its satisfactory elemental analysis could not be obtained. All spectroscopic data, however, support the Mn(IV) dimer structure. At -80°C, **2** as microcrystals was stable for several hours. At -20°C in CH_3CN, the extent of its decomposition to the $Mn(III)_2$ was negligibly small within the time range of the kinetic measurement.