Synthesis of the High-valent Mn Porphyrin Species by Peroxy Acid Oxidation of Mn^{III} Dimers. Characterization of the Mn^{IV}_2 Species and Evidence of the Mn^{V}-Mn^{III} Intermediate

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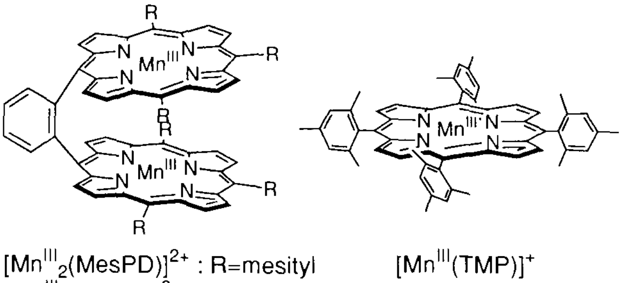
The Mn^{IV} porphyrin dimers were synthesized and characterized by UV-vis, ESI-MS, etc. Epoxidation of olefins indicated the transient formation of the $Mn^{V}(=O)$ species, which were transformed into the Mn^{IV} species by the intramolecular comproportionation between Mn^{V}-Mn^{III} moieties.

High-valent Mn complexes have attracted much interest both as an active oxidant in catalytic oxidation of a wide variety of organic substances and a possible intermediate in water oxidation or H_2O_2 dismutation.[1-5] Since Mn porphyrins can take the corresponding high-valent oxidation states with a reasonable stability, its $Mn^{IV}(=O)$,[2] Mn^{IV}-O-Mn^{IV} dimer[3] and $Mn^{IV}(MeO)_2$[4] complexes have been characterized spectroscopically and crystallographically, and their reactivities have been intensively examined so far. $Mn^{V}(=O)$ porphyrin is also suggested to be a highly reactive, transient intermediate that is immediately reduced to $Mn^{IV}(=O)$ complex or oxidizes olefins in high efficiency.

In our previous work,[6] we found that Mn porphyrin dimers of such rigidly linked, co-facial structures catalyze four-electron oxidation of water to evolve molecular oxygen under anodic oxidation conditions. We also reported the extremely high catalase activity of this kind of complexes.[7] In both examples, high-valent Mn porphyrin dimers were considered to be essential intermediates in these O_2 evolution reactions. To further study, the chemical synthesis of high-valent Mn porphyrin dimers has been attempted by the oxidation of Mn^{III} species with *m*-chloroperbenzoic acid (mCPBA). The direct observation of high-valent species has succeeded by ESI-MS. The reaction of these Mn porphyrin dimers and mCPBA in the presence of an olefin resulted in the formation of the Mn^{IV}_2 dimers with efficient olefin epoxidation. The result indicates that a rapid and intramolecular comproportionation in the $Mn^{V}Mn^{III}$ dimer leads to the more stable Mn^{IV}_2 dimer.



$[Mn^{III}_2(MesPD)]^{2+}$: R=mesityl $[Mn^{III}(TMP)]^{+}$
$[Mn^{III}_2(tBuPD)]^{2+}$: R=4-*t* butylphenyl

To the Mn^{III} porphyrin dimer, $Mn^{III}_2(MesPD)Cl_2$, in CH_2Cl_2 was successively added pyridine (100 equiv. to each Mn ion), Me_4NOH (1.3 equiv. in MeOH), and mCPBA (1.1 equiv.) at −45°C.[8] During the next several minutes, the UV-vis spectral change showed the formation of a new species **1** (λ_{max} = 402 and 520 nm), which was stable for hours at temperature ranging from −78 to −20°C. The features of this spectrum were similar to those reported for $Mn^{IV}(=O)$ porphyrin monomers.[3] By iodometric titration with $[Bu_4N]I$, the oxidation state of this species was confirmed to be the Mn^{IV}_2 state.

The solution of **1** was directly analyzed by ESI-MS technique.[9] The spectrum showed $[Mn^{IV}_2L(MeO)_3(MeOH)]^+$ (**L** = porphyrin ligand) (*m*/*z* = 1633) as a main $[M+1]^{+1}$ species and other Mn^{IV}_2 species (peaks C, D and E in Figure 1, **a**), with

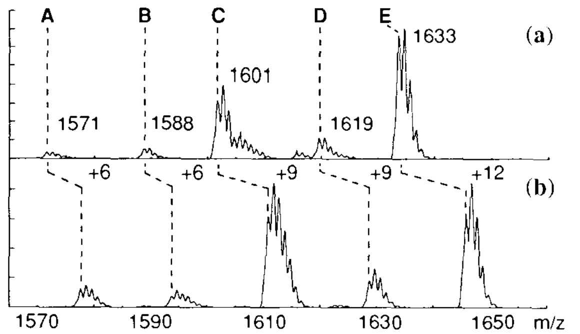


Figure 1. ESI-MS peaks of $[Mn^{IV}_2(MesPD)X_4]$. The mass number of a base peak in each cluster peaks is shown. Solvent: (**a**) 1.8% v/v CH_3OH-CH_2Cl_2, (**b**) 1.8% v/v CD_3OD-CH_2Cl_2.
A: $[Mn^{III}_2(MeO)(MeOH)]^+$, B: $[Mn^{IV}Mn^{III}(OH)(MeO)(MeOH)]^+$, C: $[Mn^{IV}_2(MeO)_3]^+$, D: $[Mn^{IV}_2(OH)(MeO)_2(MeOH)]^+$, E: $[Mn^{IV}_2(MeO)_3(MeOH)]^+$.

comparatively weak peaks arising from the thermal reduction to the Mn^{III} species during the analysis. These assignments were confirmed by isotope shift with CD_3OD in place of MeOH (Figure 1, **b**). The pure sample of $[Mn^{IV}_2L(MesPD)(MeO)_4]$, which was synthesized and isolated according to the known method,[10] showed the same mass peaks that are assignable to $[Mn^{IV}_2L(MeO)_3(MeOH)]^+$ and its fragmented or partially reduced species. From these results, we proposed that **1** was a mixture of $[Mn^{IV}_2LX_4]$ (X = MeO^- or OH^-). It was supposed that highly basic $Mn^{V}(=O)$ species formed at first by mCPBA oxidation, and succeeding single-electron reduction and protonation could give Mn^{IV} species. This is the first obvious detection of high-valent Mn porphyrin dimers by mass spectrometry.[11]

Epoxidation of cyclooctene with stoichiometric amounts of the Mn porphyrin dimer and mCPBA was used as a probe for the transient formation of the $Mn^{V}(=O)$ species and to clarify the formation pathway of Mn^{IV}_2. $Mn(MesPD)Cl_2$ or $Mn(tBuPD)Cl_2$ in CH_2Cl_2 was oxidized by mCPBA (1.1 equiv. to each Mn ion) at −78°C in the presence of 1-methylimidazole (20 equiv.), Me_4NOH (1.3 equiv. in MeOH), and cyclooctene (75 equiv.). The reaction was quenched after 5 min by the addition of excess amount of $[Bu_4N]I$, and the reaction mixture was analyzed by

GC.[12] The olefin oxidation with $Mn(MesPD)Cl_2$ gave the epoxide in 41% yield (based on the amount of mCPBA). Without any Mn porphyrin complex, epoxide yield by the direct oxidation with mCPBA was negligibly small (< 1%) under these conditions. Interestingly, the Mn complex was recovered at the Mn^{IV}_2 state on visible spectrum after the completion of the epoxidation reaction (Figure 2, **a**). These results demonstrate

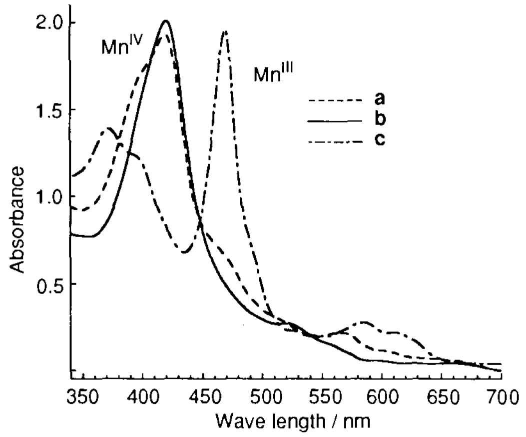
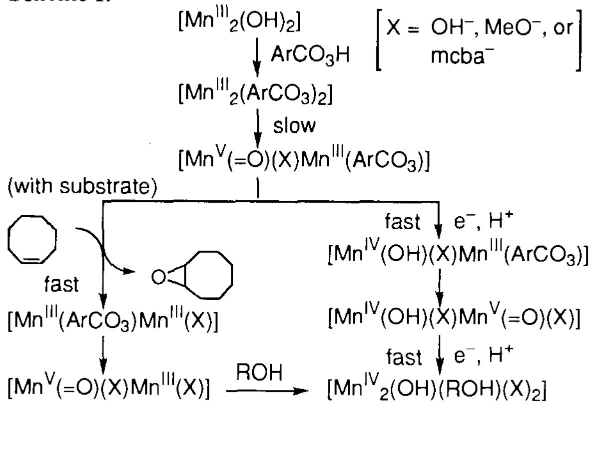


Figure 2. UV-vis spectra (at −70°C) of the reaction mixture in the cyclooctene epoxidation after the completion of the reaction. The concentration of Mn complexes is about 1.5×10^{-5} M in CH_2Cl_2. **a)** $[Mn^{IV}_2(MesPD)X_4]$, **b)** $[Mn^{IV}_2(tBuPD)X_4]$, **c)** $[Mn^{III}_2(MesPD)Cl_2]$.

that the Mn^V species has caused the epoxidation of an olefin and only one $Mn^V(=O)$ in the dimer was effective for the epoxidation. Another equivalent of the oxidant was consumed for the conversion of the Mn^{III}_2 to the Mn^{IV}_2. This is a unique feature of the reaction using Mn porphyrin dimer, because a Mn porphyrin monomer gives the epoxide in 85-90% yield with simultaneous recovery of the Mn^{III} under the same reaction conditions.[2] In the reaction of $Mn(tBuPD)Cl_2$, cyclooctene oxide formed in 49% yield with concomitant formation of the corresponding Mn^{IV}_2 complex (Figure 2, **b**). Thus, the efficiency of epoxidation with $Mn(tBuPD)Cl_2$ is almost 100% based on the effective oxidation equivalent. From the spectral features, the final stage of this reaction seemed to be a mixture of several kinds of Mn^{IV} dimers bearing different axial ligands. Besides, these Mn^{IV} dimers were inactive toward cyclooctene epoxidation, which indicates they were not $Mn^{IV}(=O)$ species,

Scheme 1.



but $[Mn^{IV}_2X_4]$ (X=MeO^-, HO^-, or $mCBA^-$). Consistently, only small amount of epoxide (1.4% yield) was detected in the cyclooctene oxidation with the use of $[Mn^{IV}_2(MesPD)(MeO)_4]$ which was separately synthesized and confirmed its structure.[10]

A possible mechanism for the reaction of Mn porphyrin dimers and mCPBA in the presence of cyclooctene is shown in Scheme 1. The initially formed $Mn^V(=O)$ could react with cyclooctene to give the epoxide and the resultant Mn^VMn^{III} porphyrin dimers would rapidly transform into the Mn^{IV}_2 porphyrin dimers by an intramolecular electron transfer with the incorporation of H_2O or MeOH, presumably because of some proximity effect.[13] This assumption is partly supported by the fact that intermolecular electron transfer between Mn^V and Mn^{III}TMP monomers is slower than olefin epoxidation by $Mn^V(=O)$ species.

In summary, we detected Mn^{IV} porphyrin dimers by ESI-MS technique, and demonstrated a unique $2e^-$ oxidation system via Mn^V oxidation state. The formation of porphyrin dimers with the Mn^{IV} oxidation state in a reasonable stability at the very proximal positions is useful for the construction of a functional model of Mn cluster in photosynthetic water oxidation, which also involves the corresponding Mn^{IV} state at the O_2 evolution stage.[14] Further mechanistic study of this reaction is now under way.

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References and Notes

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8 Pyridine or 1-methylimidazole can coordinate to the Mn ions only at the external site of the dimer. These nitrogenbases are used in order to stabilize high-valent Mn ions.

9 Perkin-Elmer SCIEX API-300 was used. The cooled solution in a dry ice-acetone bath was directly introduced to the ionization port by applying N_2 gas pressure.

10 UV-vis absorptions: $\lambda_{max}(CH_2Cl_2, -70°C)$ 417, 517, 560, 620, and 657 nm; ESR (CH_2Cl_2, 4 K) g = 4.35, 2.0 ; Anal. Found: C, 74.10; H, 5.91; N, 6.77%. Calcd for $C_{104}H_{104}N_8O_7Mn_2$ $[Mn^{IV}_2(MesPD)(MeO)_4 \cdot 3H_2O]$: C, 74.02; H, 6.04; N, 6.64%. $[Mn^{IV}_2(MesPD)(MeO)_4]$ was prepared by the treatment of $[Mn^{III}_2(MesPD)(MeO)_2]$ with NaOCl in cold MeOH in a similar way with the corresponding monomer.[4]

11 The ESI-MS spectrum of porphyrin monomer $[Mn^{IV}(TMP)(MeO)_2]$ showed a similar ionization to give $[Mn^{IV}L(MeO)]^+$ (m/z = 866) as a main peak accompanied by relatively weak peaks for $[Mn^{IV}L(OH)]^+$ (m/z = 852) and $[Mn^{III}L]^+$ (m/z = 835).

12 Other oxidation products (alcohols or ketones) were not detected. Longer reaction period did not give any change in the epoxide yield nor UV-vis spectra.

13 Such a possibility of the comproportionation between Mn^V and Mn^{III} has been suggested for Mn porphyrin monomers at high pH conditions; P. N. Balasubramanian, E. S. Schmidt, and T. C. Bruice, *J. Am. Chem. Soc.*, **109**, 7865 (1987).

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