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Catalytic Electron-Transfer Oxygenation of Substrates with Water as an Oxygen Source Using Manganese Porphyrins

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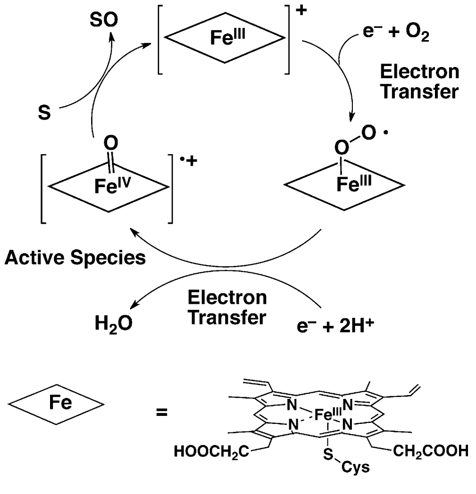
Abstract: Manganese(V)–oxo–porphyrins are produced by the electron-transfer oxidation of manganese–porphyrins with tris(2,2′-bipyridine)ruthenium(III) ($[Ru(bpy)_3]^{3+}$; 2 equiv) in acetonitrile (CH_3CN) containing water. The rate constants of the electron-transfer oxidation of manganese–porphyrins have been determined and evaluated in light of the Marcus theory of electron transfer. Addition of $[Ru(bpy)_3]^{3+}$ to a solution of olefins (styrene and cyclohexene) in CH_3CN containing water in the presence of a catalytic amount of manganese–porphyrins afforded epoxides, diols, and aldehydes efficiently. Epoxides were converted to the corresponding diols by hydrolysis, and were further oxidized to the corresponding aldehydes. The turnover numbers vary significantly depending on the type of manganese–porphyrin used owing to the difference in their oxidation potentials and the steric bulkiness of the ligand. Ethylbenzene was also oxidized to 1-phenylethanol using manganese–porphyrins as electron-transfer catalysts. The oxygen source in the substrate oxygenation was confirmed to be water by using ^{18}O-labeled water. The rate constant of the reaction of the manganese(V)–oxo species with cyclohexene was determined directly under single-turnover conditions by monitoring the increase in absorbance attributable to the manganese(III) species produced in the reaction with cyclohexene. It has been shown that the rate-determining step in the catalytic electron-transfer oxygenation of cyclohexene is electron transfer from $[Ru(bpy)_3]^{3+}$ to the manganese–porphyrins.

Keywords: electron transfer · homogeneous catalysis · manganese · oxygenation · porphyrinoids

Introduction

Cytochrome P450 enzymes catalyze a number of important metabolic oxidation reactions by dioxygen.[1,2] The remarkable catalytic reactivity results from an oxoiron(IV)–porphyrin π-radical cation (compound I), which has been suggested to be the ultimate oxidant in these enzymatic systems.[1,2] The reaction mechanism to produce compound I in the cytochrome P450 enzymes involves two distinct electron-transfer processes to activate dioxygen (Scheme 1).[1–3] An oxoiron(IV)–porphyrin π-radical cation (compound I) derived from horseradish peroxidase (HRP) has been produced by reaction with H_2O_2.[4] In addition, the use of synthetic model systems has provided valuable mechanistic insights into the molecular catalytic mechanism of P450.[5–11] Groves et al.[9,10] were the first to report cytochrome P450 type activity in a model system using iron–tetraphenylporphyrin–chloride $[(tpp)Fe^{III}(Cl)]$ (tpp^{2-} = tetraphenylporphyrin dianion) and iodosylbenzene (PhIO) as an oxidant, which can oxidize the Fe^{III}–porphyrin directly to produce $[(tpp)Fe^{IV}(O)]^{\bullet+}$ in a so-called “shunt” pathway. Groves et al.[11] also prepared and characterized synthetic oxoiron(IV)–porphyrin π-radical cation complexes and the oxygen-transfer reactions with these reactive intermediates was monitored successfully. High-valent metal–oxo–porphyrins are now generally produced by oxygen-atom transfer from active oxygen species



Scheme 1.

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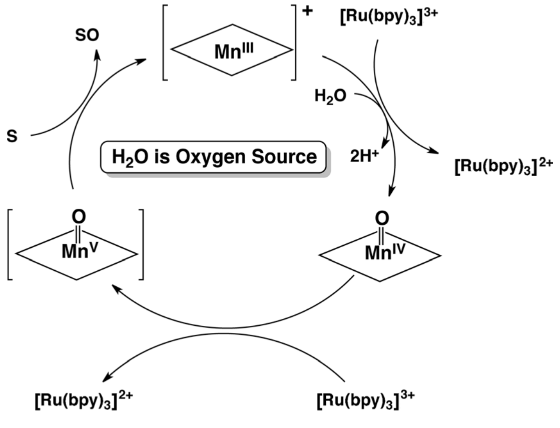
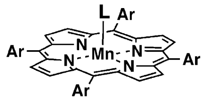
such as iodosylbenzene, hydroperoxide, *m*-chloroperoxybenzoic acid (*m*CPBA), and oxone (HSO_5^-).[5–8]

Among high-valent metal–oxo species, $Mn^V(O)$ species have merited special attention because they are postulated as important intermediates in the conversion of water to dioxygen during water oxidation in photosynthesis.[12,13] The active species in the oxygenation of substrates with manganese–porphyrins (P) are generally believed to be $[(P)Mn^V(O)]$.[14,15] The $[(P)Mn^V(O)]$ intermediate has been isolated and characterized and the oxygenation of substrates by $[(P)Mn^V(O)]$ has been studied extensively.[16–21] The $[(P)Mn^V(O)]$ and $[(P)Mn^{IV}(O)]$ species have also been produced by the photoexcitation of the $(P)Mn^{III}$–perchlorate and –chlorate complexes, respectively.[22] The high reactivity of the $[(P)Mn^V(O)]$ species has been demonstrated by determining the rate constant of the oxo transfer from $[(P)Mn^V(O)]$ to a substrate with use of laser flash photolysis measurements; the representative rate constant for the reaction of $[(tpfpp)Mn^V(O)]$ (tpfpp: 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin) with *cis*-stilbene is $6.1\times10^5\,\text{M}^{-1}\,\text{s}^{-1}$.[22] Because $[(P)Mn^{IV}(O)]$ and $[(P)Mn^V(O)]$ are the one-electron and two-electron oxidized species of $(P)Mn^{III}$, respectively, they can be formed by the electron-transfer oxidation of $(P)Mn^{III}$ with appropriate one-electron oxidants.[23] However, the kinetics and mechanism of formation of $[(P)Mn^{IV}(O)]$ and $[(P)Mn^V(O)]$ by the electron-transfer oxidation of $(P)Mn^{III}$ or the catalytic electron-transfer oxygenation of substrates, in which water rather than oxygen is used as an oxygen source, have yet to be reported.

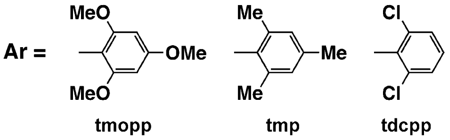
We report herein the catalytic electron-transfer oxygenation of alkanes and olefins using a one-electron oxidant, $[Ru(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine), rather than active oxygen species and manganese–porphyrins as the catalyst in the presence of water, which acts as an oxygen source as shown in Scheme 2. The electron-transfer oxidation of $(P)Mn^{III}$ to $[(P)Mn^{IV}(O)]$ and $[(P)Mn^V(O)]$ has also been examined and the electron-transfer kinetics were analyzed to determine the reorganization energy of the electron transfer in light of the Marcus theory of electron transfer.[24,25] Following this, a detailed kinetic study was performed on the oxygenation of cyclohexene with $[(P)Mn^V(O)]$ (single-turnover conditions) as well as the kinetics of the overall catalytic reactions, which provides valuable insight into the catalytic mechanism for the electron-transfer oxygenation of substrates using water as an oxygen source. Manganese–porphyrins employed as catalysts in this study are $[(tmp)Mn^{III}]^+$ (tmp^{2-} = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin dianion), $[(tdcpp)Mn^{III}]^+$ ($tdcpp^{2-}$ = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin dianion), $[(tmopp)Mn^{III}]^+$ ($tmopp^{2-}$ = 5,10,15,20-tetrakis(2,4,6-trimethoxyphenyl)porphyrin dianion), and $[(dtmpd)Mn^{III}{}_2]^{2+}$ ($dtmpd^{4-}$ = di(trimesitylporphyrin)dibenzofuran tetraanion).

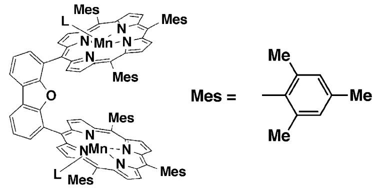


Scheme 2.



$[(P)Mn^{III}]^+$ (P: Porphyrin)





$[(dtmpd)Mn_2]^{2+}$

Experimental Section

General: ^{1}H NMR spectra were measured on a JEOL JNM-AL300 NMR spectrometer. GC analyses were performed on a Shimadzu GC-17A equipped with a DB-5MS column (Agilent Technologies, 30 m) and a mass spectrograph (Shimadzu QP-5050) as a detector. Fast-atom-bombardment mass spectra (FAB-MS) were obtained on a JEOL JMS-DX300 mass spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer.

Materials: Acetonitrile (CH_3CN) used as solvent was purified and dried by a standard procedure.[26] A small amount of H_2O (6.5 mM) was added to CH_3CN to study oxidation of manganese–porphyrins in the presence of H_2O. $[Ru(bpy)_3](PF_6)_3$ as an oxidant was prepared according to the literature method.[27] $MnCl_2{\cdot}4H_2O$ and $Mn(OAc)_2{\cdot}4H_2O$ were purchased from Wako Pure Chemical Ind. Ltd., Japan. Porphyrins tmp and tdcpp were purchased from Tokyo Kasei Organic Chemicals. Porphyrins tmopp and dtmp were prepared according to the literature method.[28–31] $[(tmp)Mn^{III}(H_2O)_2](PF_6)$ was prepared by adding $MnCl_2{\cdot}4H_2O$ to the porphyrin, followed by heating under reflux conditions for 24 h in DMSO. The solid $[(tmp)Mn(H_2O)_2(Cl)]$ obtained was dissolved in CH_2Cl_2, and $AgPF_6$ (1 equiv) was added. The reaction mixture was filtered to remove AgCl (1 equiv) according to the literature method.[32] $[(tmp)Mn^{III}(OH)]$ was prepared by adding $Mn(OAc)_2$ to the porphyrin, followed by heating under reflux conditions for 24 h in DMSO according to the literature method.[33] $[(dtmpd)Mn_2]Cl_2$ has been synthesized and characterized according to the literature (see the Supporting Information, Figures S1–S3).[31a,34] All ethylbenzene and olefins (styrene, cyclohexene) used in this study were purchased from Tokyo Kasei Organic Chemicals. CH_3CN and toluene used as a solvent were purified and dried by using the standard procedure.[33] Purification of water (18.2 MΩcm) was performed with a Milli-Q system (Millipore; Milli-Q Jr). [D$_3$]Acetonitrile, deuterium oxide, and [D]chloroform were obtained from EURI SO-TOP, CEA, France. $H_2{}^{18}O$ (95 %) was purchased from Wako Pure Chemical Ind. Ltd., Japan. TLC Alufolien Kieselgel and flash column chromatography were performed with Art. 5554 DC-60 F_{254} (Merck) and Fujisilica BW300, respectively.

Spectral measurements: The formation of [(tmp)Mn^{IV}(O)] and [(tmp)Mn^{V}(O)]$^+$ was examined from the change in the UV/Vis spectrum of a solution of [(tmp)Mn^{III}]$^+$ in CH_3CN in the presence of [Ru(bpy)$_3$]-(PF$_6$)$_3$ and H_2O by using a Hewlett Packard 8453 diode array spectrophotometer with a quartz cuvette (path length = 10 mm) at various temperatures (233–298 K).

Kinetic measurements: All kinetic measurements were performed on a UNISOKU RSP-601 stopped-flow spectrophotometer with an MOS-type high-selective photodiode array at various temperatures (233–298 K) using a Unisoku thermostated cell holder designed for low-temperature experiments. In a typical reaction, a solution of each porphyrin in CH_3CN containing a substrate was transferred to the spectrophotometric cell with a glass syringe. Rates of the oxidation reactions catalyzed by [(tmp)Mn^{III}]$^+$ in CH_3CN/H_2O (9:1 v/v) at 298 K were monitored by following an increase in absorbance at $\lambda = 450$ nm attributable to [Ru(bpy)$_3$]$^{2+}$. The rate constants of oxidation reactions of substrates catalyzed by the porphyrins were determined by pseudo-first-order plots in which concentrations of substrates were maintained at more than a tenfold excess amount of the porphyrins.

Electrochemical measurements: Electrochemical measurements were performed on a BAS 100 W electrochemical analyzer in CH_3CN containing H_2O (6.5 mM) and Bu_4NPF_6 (TBAPF$_6$: 0.10 M) as a supporting electrolyte at 298 K. Differential pulse voltammetry measurements were also performed on a BAS 50 W electrochemical analyzer in CH_3CN containing H_2O (6.5 mM) and TBAPF$_6$ (0.10 M) as a supporting electrolyte at 298 K (10 mV s^{-1}). A conventional three-electrode cell was used with a platinum working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode. The Pt working electrode (BAS) was routinely polished with a BAS polishing alumina suspension and was rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/AgNO$_3$ (0.01 M) reference electrode. All potentials (vs. Ag/Ag$^+$) were converted to values versus SCE by adding 0.29 V.[35] All electrochemical measurements were carried out under an atmospheric pressure of Ar.

EPR measurements: The EPR spectra of high-valent manganese–oxo–porphyrins produced by adding [Ru(bpy)$_3$](PF$_6$)$_3$ (2 equiv) to a deaerated solution of each porphyrin in CH_3CN were recorded on a JEOL X-band spectrometer (JES-RE1XE) with a quartz EPR tube (4.5 mm i.d.). The EPR spectra were measured under nonsaturating microwave-power conditions. The magnitude of modulation was chosen to optimize the resolution and the signal-to-noise (*S*/*N*) ratio of the observed spectra. The *g* values were calibrated with an Mn^{2+} marker.

General procedure for catalytic oxygenation reactions: In a typical reaction, a solution of 4.0×10^{-3} M [Ru(bpy)$_3$](PF$_6$)$_3$ in CD_3CN (0.50 mL) was delivered by syringe pump to a solution of manganese–porphyrin (2.0×10^{-5} M) and substrate (2.0×10^{-3} M) in CH_3CN/H_2O (9:1 v/v; 0.50 mL) . The solution was stirred for 15 min. The products were identified by comparison of their GC retention times, GC/MS spectra, and ^{1}H NMR spectra with those of authentic compounds.

Results and Discussion

Formation of high-valent manganese–oxo porphyrins: The cyclic voltammogram and differential pulse voltammogram of [(tmp)Mn^{III}(Cl)] in CH_3CN exhibits two reversible waves consisting of the first one-electron oxidation at E_{ox1} versus SCE at 1.02 V and the second one-electron oxidation at E_{ox2} versus SCE at 1.22 V as shown in Figure 1a.[36] When [(tmp)Mn^{III}(Cl)] is replaced by [(tmp)Mn^{III}(H$_2$O)$_2$](PF$_6$), two reversible waves merge into a single wave, which corresponds to the two-electron oxidation of [(tmp)Mn^{III}(H$_2$O)$_2$]-(PF$_6$) as shown in Figure 1b.[37] Because the one-electron reduction potential of [Ru(bpy)$_3$]$^{3+}$ (E_{red} versus SCE = 1.24 V) is more positive than the second oxidation potential of [(tmp)Mn^{III}(Cl)] (E_{ox} versus SCE = 1.22 V), not only the one-electron oxidation but also the two-electron oxidation of [(tmp)Mn^{III}(Cl)] is thermodynamically feasible.

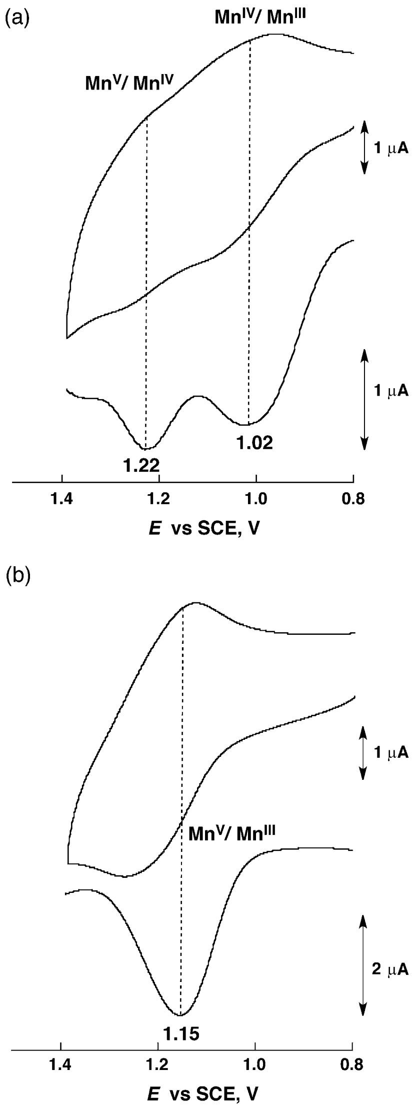


Figure 1. Cyclic voltammograms and differential pulse voltammograms (DPV) of a) [(tmp)Mn^{III}(Cl)] (5.0×10^{-4} M) and b) [(tmp)Mn^{III}(H$_2$O)$_2$] (5.0×10^{-4} M) in CH_3CN containing H_2O (6.5 mM) and TBAPF$_6$ (0.10 M) at 298 K; scan rate 100 mV s^{-1}.

Figure 2 shows the spectral change upon the electron-transfer oxidation of [(tmp)Mn^{III}(Cl)] with one equivalent of [Ru(bpy)$_3$]$^{3+}$ in CH_3CN at 233 K. A new absorption band appears at 411 nm accompanied by the disappearance of the absorption band at 477 nm attributed to [(tmp)Mn^{III}(Cl)]. The appearance of the new absorption band supports that reported for [(tmp)Mn^{IV}(O)] as shown in Figure S1 in the

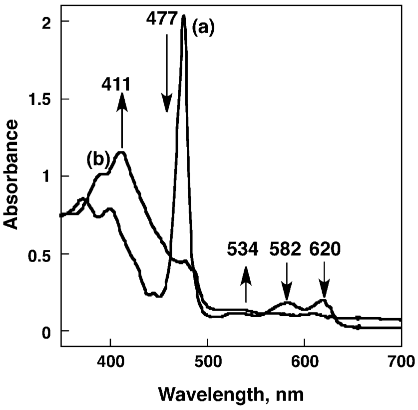


Figure 2. UV/Vis spectra of a) [(tmp)Mn^{III}(Cl)] and b) [(tmp)Mn^{IV}(O)] formed in the electron-transfer oxidation of [(tmp)Mn^{III}(Cl)] (1.6×10^{-5} M) by [Ru(bpy)$_3$]$^{3+}$ (1.6×10^{-5} M) in CH_3CN containing H_2O (6.5 mM) at 233 K.

Supporting Information, which is prepared by the reaction of [(tmp)Mn^{III}(Cl)] with *m*CPBA. The EPR spectrum of the resulting solution of the one-electron oxidation of [(tmp)Mn^{III}(Cl)] in CH_3CN with [Ru(bpy)$_3$]$^{3+}$ (1 equiv) is shown in Figure S2 (see the Supporting Information). The observed broad EPR signal at $g=4$ agrees with that of [(tmp)Mn^{IV}(O)].[38] Thus, the electron-transfer oxidation of [(tmp)Mn^{III}(Cl)] occurs at the metal center rather than at the porphyrin ligand to produce [(tmp)Mn^{IV}(O)]. The addition of two equivalents of [Ru(bpy)$_3$]$^{3+}$ to a solution of [(tmp)Mn^{III}(Cl)] in CH_3CN results in the disappearance of the Soret band at 477 nm attributable to [(tmp)Mn^{III}(Cl)] and the appearance of the absorption bands at 389 and 650 nm in Figure 3. In Figure S2b (see the Supporting Information), no EPR signal attributable to the further oxidation of [(tmp)Mn^{IV}(O)] was observed; the only bands appearing in the EPR spectrum are those attributable to [Ru(bpy)$_3$]$^{3+}$ in the two-electron oxidation of [(tmp)Mn^{III}(Cl)] in CH_3CN with two equivalents of [Ru(bpy)$_3$]$^{3+}$. Thus, [(tmp)Mn^{V}(O)]$^+$ may be formed by the one-electron oxidation of [(tmp)Mn^{IV}(O)].[39]

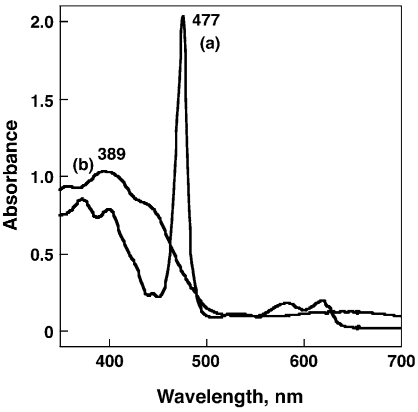


Figure 3. UV/Vis spectra of a) [(tmp)Mn^{III}(Cl)] and b) [(tmp)Mn^{V}(O)] formed in the electron-transfer oxidation of [(tmp)Mn^{III}(Cl)] (1.6×10^{-5} M) by [Ru(bpy)$_3$]$^{3+}$ (3.2×10^{-5} M) in CH_3CN containing H_2O (6.5 mM) at 233 K.

When [(tmp)Mn^{III}(Cl)] is replaced by [(tmp)Mn^{III}(H_2O)$_2$](PF$_6$),[40] the electron-transfer oxidation of [(tmp)Mn^{III}(H_2O)$_2$]$^+$ with one equivalent of [Ru(bpy)$_3$]$^{3+}$ results in a two-electron oxidation to leave a half equivalent of [(tmp)Mn^{III}(H_2O)$_2$]$^+$. As shown in Figure 4, a new absorption band appears at 443 nm, but the Soret band at 472 nm attributable to [(tmp)Mn^{III}(H_2O)$_2$]$^+$ still remains with half intensity (Figure 4b). The addition of a further equivalent of [Ru(bpy)$_3$]$^{3+}$ (total two equivalents) results in complete disappearance of the Soret band at 472 nm accompanied by a further increase in absorbance at 443 nm (Figure 4c). This indicates that a two-electron transfer of [(tmp)Mn^{III}(H_2O)$_2$]$^+$ occurs directly without formation of the one-electron oxidized species.

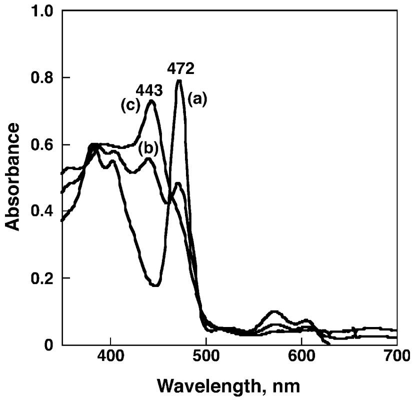


Figure 4. UV/Vis spectra of a) [(tmp)Mn^{III}(H_2O)$_2$](PF$_6$) (1.2×10^{-5} M) and b), c) of [(tmp)Mn^{V}(O)]$^+$ formed in the electron-transfer oxidation of [(tmp)Mn^{III}(H_2O)$_2$](PF$_6$) in the presence of b) 1.2×10^{-5} and c) 2.4×10^{-5} M [Ru(bpy)$_3$]$^{3+}$ in CH_3CN containing H_2O (6.5 mM) at 233 K.

Such two-electron oxidation of [(tmp)Mn^{III}(H_2O)$_2$]$^+$ with [Ru(bpy)$_3$]$^{3+}$ is consistent with the observation of the two-electron oxidation wave in the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of [(tmp)Mn^{III}(H_2O)$_2$]$^+$ shown in Figure 1b. In contrast with the case of [(tmp)Mn^{III}(Cl)], no EPR signal attributable to [(tmp)Mn^{IV}(O)] was observed in the solution of the electron-transfer oxidation of [(tmp)Mn^{III}(Cl)] with one equivalent of [Ru(bpy)$_3$]$^{3+}$ in CH_3CN (see Figure S3 in the Supporting Information). Thus, the two-electron oxidation of [(tmp)Mn^{III}(H_2O)$_2$]$^+$ occurs even with one equivalent of [Ru(bpy)$_3$]$^{3+}$ to produce the EPR-silent species, [(tmp)Mn^{V}(O)]$^+$, when a half equivalent of [(tmp)Mn^{III}(H_2O)$_2$]$^+$ remains unreacted. The absorption band at 445 nm attributable to [(tmp)Mn^{V}(O)]$^+$ agrees with the Soret band at 450 nm due to [(tmpyp)Mn^{V}(O)]$^+$ produced by the laser flash photolysis of [(tmpyp)Mn^{III}]$^+$ perchlorate (tmpyp^{2-} = tetra-*N*-(methylpyridyl)porphyrinato dianion).[22]

Electron-transfer dynamics of the formation of high-valent manganese–oxo–porphyrins: The electron-transfer dynamics of formation of high-valent manganese–oxo–porphyrins was examined by stopped-flow measurements at 233 K. When more than two equivalents of $[Ru(bpy)_3]^{3+}$ are employed for the oxidation of $[(tmp)Mn^{III}(Cl)]$, the rapid increase in absorbance at 450 nm attributable to the formation of $[Ru(bpy)_3]^{2+}$ is followed by a slower further increase in $[Ru(bpy)_3]^{3+}$. Figure 5 shows the time profile for the initial one-electron oxidation of $[(tmp)Mn^{III}(Cl)]$ to produce $[(tmp)Mn^{IV}(O)]$. The rate of increase in absorbance at 450 nm obeys pseudo-first-order kinetics. The observed pseudo-first-order rate constant (k_{obs}) increases linearly with increasing concentration of $[Ru(bpy)_3]^{3+}$ (Figure 5b). The second slower step in Figure 6a corresponds to the further oxidation of $[(tmp)Mn^{IV}(O)]$ to $[(tmp)Mn^{V}(O)]^+$. The rate constant (k_{et}) of the first and second electron-transfer steps are determined from the slopes of the linear plots of k_{obs} versus $[Ru(bpy)_3{}^{3+}]$ in Figures 5b and 6b, respectively. The k_{et} values thus determined are listed in Table 1. Those of the first electron-transfer step from $[(tmp)Mn^{III}(OH)]$ to $[Fe(bpy)_3]^{3+}$, $[Fe(5\text{-}Clphen)_3]^{3+}$, $[Ru(bpy)_3]^{3+}$, and $[Fe(5\text{-}NO_2phen)]$ were also determined under the pseudo-first-order conditions using large excess amounts of oxidants.

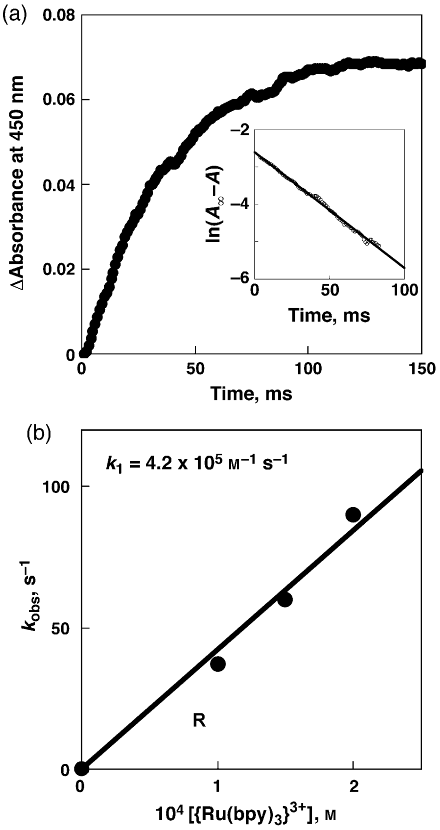


Figure 5. a) Time profile of the formation of $[Ru(bpy)_3]^{2+}$ for the first oxidation step monitored by absorbance at $\lambda = 450$ nm ($\varepsilon = 13800\,\text{M}^{-1}\text{cm}^{-1}$) in the electron-transfer oxidation of $[(tmp)Mn^{III}(Cl)]$ (5.0×10^{-6} M) with $[Ru(bpy)_3]^{3+}$ (2.0×10^{-4} M) in CH_3CN containing H_2O (6.5 mM) at 233 K. Inset: First-order plots. b) Plot of k_{obs} versus $[Ru(bpy)_3{}^{3+}]$ for the first oxidation step of $[(tmp)Mn^{III}(Cl)]$ (5.0×10^{-6} M) with $[Ru(bpy)_3]^{3+}$ in CH_3CN containing H_2O (6.5 mM) at 233 K.

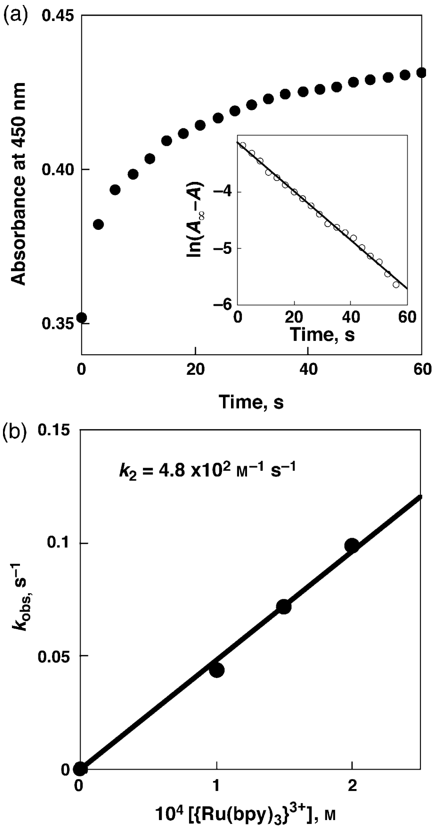


Figure 6. a) Time profile of formation of $[Ru(bpy)_3]^{2+}$ for the second oxidation step monitored by absorbance at $\lambda = 450$ nm ($\varepsilon = 13800\,\text{M}^{-1}\text{cm}^{-1}$) in the electron-transfer oxidation of $[(tmp)Mn^{III}(Cl)]$ (5.0×10^{-6} M) by $[Ru(bpy)_3]^{3+}$ (2.0×10^{-4} M) in CH_3CN containing H_2O (6.5 mM) at 233 K. Inset: First-order plots. b) Plot of k_{obs} versus $[Ru(bpy)_3{}^{3+}]$ for the second oxidation step of $[(tmp)Mn^{III}(Cl)]$ (5.0×10^{-6} M) with $[Ru(bpy)_3]^{3+}$ in CH_3CN containing H_2O (6.5 mM) at 233 K.

Table 1. Rate constants (k_{et}) and free-energy changes (ΔG_{et}) of the electron transfer in the oxidation of $[(tmp)Mn^{III}(OH)]$ in CH_3CN containing H_2O (6.5 mM) at 233 K.

Porphyrin	Oxidant	ΔG_{et} [eV]	k_{et} [$\text{M}^{-1}\text{s}^{-1}$]
$[(tmp)Mn^{III}(Cl)]$ (1st)	$[Ru(bpy)_3]^{3+}$	−0.22	4.2×10^5
$[(tmp)Mn^{III}(Cl)]$ (2nd)	$[Ru(bpy)_3]^{3+}$	−0.02	4.8×10^2
$[(tmp)Mn^{III}(H_2O)_2](PF_6)$	$[Ru(bpy)_3]^{3+}$	−0.09	3.0×10^5
$[(dtmpd)Mn^{III}{}_2(Cl)_2]$ (1st)	$[Ru(bpy)_3]^{3+}$	−0.31	2.0×10^5
$[(dtmpd)Mn^{III}{}_2(Cl)_2]$ (2nd)	$[Ru(bpy)_3]^{3+}$	−0.13	2.3×10^2
$[(tmp)Mn^{III}(OH)]$	$[Fe(5\text{-}NO_2phen)_3]^{3+}$	−0.19	1.3×10^7
$[(tmp)Mn^{III}(OH)]$	$[Ru(bpy)_3]^{3+}$	−0.16	1.0×10^7
$[(tmp)Mn^{III}(OH)]$	$[Fe(5\text{-}Cl\text{-}phen)_3]^{3+}$	−0.09	1.9×10^6
$[(tmp)Mn^{III}(OH)]$	$[Fe(bpy)_3]^{3+}$	0.02	1.3×10^5
$[(tmp)Mn^{III}(OH)]$	$[Ru(bpy)_3]^{3+}$	−0.02	8.5×10^4

The four-electron oxidation of a manganese–porphyrin dimer $[(dtmp)Mn^{III}{}_2(Cl)_2]$ with $[Ru(bpy)_3]^{3+}$ also proceeds by means of two-step electron-transfer processes (Figures S4a and S5a in the Supporting Information). In each step, a two-electron oxidation of the dimer occurs simultaneously at the two Mn^{III} centers. The k_{et} values are determined from the slopes of the linear plots of k_{obs} versus concentration of

$[Ru(bpy)_3]^{3+}$ (Figures S4b and S5b in the Supporting Information, respectively). The k_{et} values thus determined are also listed in Table 1.

In contrast with the cases of $[(tmp)Mn^{III}(Cl)]$ and $[(dtmp)Mn^{III}_2(Cl)_2]$, the two-electron oxidation of $[(tmp)Mn^{III}(H_2O)_2]^+$ with a large excess amount of $[Ru(bpy)_3]^{3+}$ occurs by a single step as shown in Figure 7a, in which the disappearance of absorbance at 472 nm attributable to $[(tmp)Mn^{III}(H_2O)_2]^+$ coincides with the appearance of absorbance at 450 nm attributable to two equivalents of $[Ru(bpy)_3]^{2+}$. Both the decay of $[(tmp)Mn^{III}(H_2O)_2]^+$ and the formation of $[Ru(bpy)_3]^{2+}$ obey pseudo-first-order kinetics with the same pseudo-first-order rate constant (k_{obs}). The k_{et} value was determined from the slope of the linear plot of k_{obs} versus the concentration of $[Ru(bpy)_3]^{3+}$ (Figure 7b).

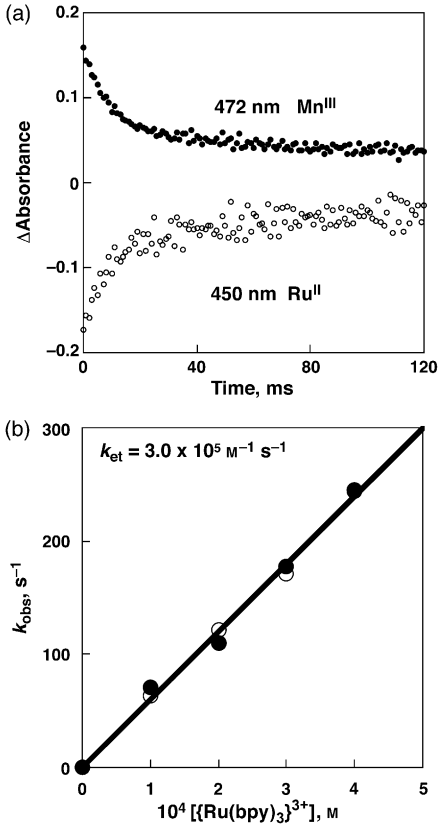


Figure 7. a) Time profile of the formation of $[Ru(bpy)_3]^{2+}$ and $[(tmp)Mn^{III}(H_2O)_2](PF_6)$ for one-step oxidation monitored by absorbance at $\lambda = 450$ and 472 nm in the electron-transfer oxidation of $[(tmp)Mn^{III}(H_2O)_2](PF_6)$ (8.0×10^{-6} M) by $[Ru(bpy)_3]^{3+}$ (1.0×10^{-4} M) in CH_3CN containing H_2O (6.5 mM) at 233 K. b) Plot of k_{obs} versus $[Ru(bpy)_3]^{3+}$ for the one-step oxidation of $[(tmp)Mn^{III}(H_2O)_2](PF_6)$ (5.0×10^{-6} M) with $[Ru(bpy)_3]^{3+}$ in CH_3CN containing H_2O (6.5 mM) at 233 K. The k_{obs} values were determined from the decay of absorbance at 472 nm (●) and the rise of absorbance at 450 nm (○).

Driving-force dependence of the electron transfer: The dependence of the $\log k_{et}$ of the electron-transfer reactions of manganese–porphyrins with one-electron oxidants (Table 1) on the free-energy change of electron transfer (ΔG^0_{et}) is shown in Figure 8, in which the $\log k_{et}$ value increases with increasing driving force of electron transfer ($-\Delta G_{et}$). Such driving-force dependence of $\log k_{et}$ can be fitted well using the Marcus theory of adiabatic outer-sphere electron transfer [Eq. (1)], in which Z is the collision frequency taken as 1×10^{11} M^{-1}s^{-1} and λ is the reorganization energy of the electron transfer.[24]

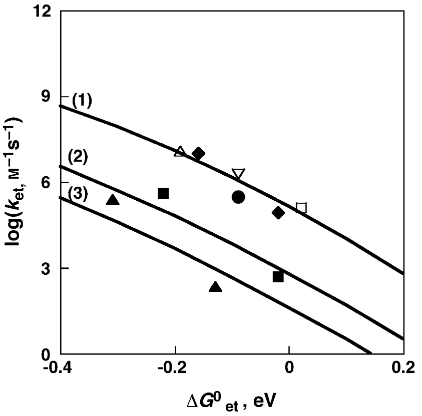


Figure 8. Dependence of $\log(k_{et}$, M^{-1}s$^{-1})$ on ΔG^0_{et} for the electron-transfer oxidation of $[(tmp)Mn^{III}(OH)]$ with various oxidants: △ $[Fe(5\text{-}NO_2phen)_3](PF_6)_3$ (△), $[Ru(bpy)_3](PF_6)_3$ (◆), $[Fe(5\text{-}Cl\text{-}phen)_3](PF_6)_3$ (▽), $[Fe(bpy)_3](PF_6)_3$ (□) and of $[(tmp)Mn^{III}(H_2O)_2]^+$ (●), $[(tmp)Mn^{III}(Cl)]$ (■), and $[(dtmpd)Mn^{III}_2(Cl)_2]$ (▲) with $[Ru(bpy)_3]^{3+}$ in CH_3CN containing H_2O (6.5 mM). The solid line represents the fits to Equation (1) with (1) $\lambda = 24$ kcal mol^{-1}, (2) $\lambda = 35$ kcal mol^{-1}, and (3) $\lambda = 40$ kcal mol^{-1}.

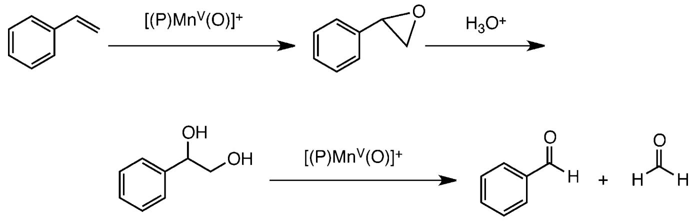
$$k_{et} = Z\exp[-(\lambda/4)(1+\Delta G_{et}/\lambda)^2/RT] \tag{1}$$

The best-fit value of λ in Figure 8a, which includes both electron transfer from $[(tmp)Mn^{III}(OH)]$ and $[(tmp)Mn^{IV}(O)]$ to one-electron oxidants, is determined to be 24 kcal mol^{-1}. The larger λ value (35 kcal mol^{-1}) is obtained for the first and second electron transfer from $[(tmp)Mn^{III}(Cl)]$ to $[Ru(bpy)_3]^{3+}$ (Figure 8b). The larger λ value may result from the reorganization of the Cl ligand associated with the electron transfer.[25] Thus, the two-electron oxidation of $[(tmp)Mn^{III}(Cl)]$ may afford $[(tmp)Mn^{V}(O)(Cl)]$, which is different from $[(tmp)Mn^{V}(O)]^+$ produced by the two-electron oxidation of $[(tmp)Mn^{III}(H_2O)_2]^+$.[41,42] The different absorption spectra between $[(tmp)Mn^{V}(O)(Cl)]$ (Figure 3) and $[(tmp)Mn^{V}(O)]^+$ (Figure 4) result from the binding of Cl^- in the former case.

The k_{et} value of electron transfer from $[(tmp)Mn^{III}(H_2O)_2]^+$ to $[Ru(bpy)_3]^{3+}$ (filled circle in Figure 8), determined as one half of the observed rate constant of the two-electron oxidation of $[(tmp)Mn^{III}(H_2O)_2]^+$ with $[Ru(bpy)_3{}^{3+}$, is significantly smaller than the k_{et} value of electron transfer from $[(tmp)Mn^{IV}(O)]$ to $[Ru(bpy)_3]^{3+}$ (diamond in Figure 8) determined as the second electron transfer from

$[(tmp)Mn^{III}(OH)]$ to $[Ru(bpy)_3]^{3+}$. This is consistent with the fact that the two-electron oxidation of $[(tmp)Mn^{III}(H_2O)_2]^+$ with $[Ru(bpy)_3]^{3+}$ occurs by means of a single step: the rate-determining electron transfer from $[(tmp)Mn^{III}(H_2O)_2]^+$ to $[Ru(bpy)_3]^{3+}$ to produce $[(tmp)Mn^{IV}(O)]$, followed by rapid electron transfer from $[(tmp)Mn^{IV}(O)]$ to $[Ru(bpy)_3]^{3+}$.

Catalytic oxygenation by electron transfer: Because a high-valent metal–oxo species ($[(tmp)Mn^V(O)]^+$) is produced by the electron-transfer oxidation with $[Ru(bpy)_3]^{3+}$, the catalytic oxygenation of substrates by electron transfer with $[Ru(bpy)_3]^{3+}$ in the presence of water was examined using manganese–porphyrins as catalysts (see below). Addition of $[Ru(bpy)_3]^{3+}$ to a solution of olefins (styrene, cyclohexene) in CH_3CN containing water in the presence of a catalytic amount of manganese–porphyrins afforded epoxides, diols, and aldehydes. Epoxides were converted to the corresponding diols by hydrolysis, and the diols were further oxidized to the corresponding aldehydes, which are four-electron oxidized products of olefins (Scheme 3). These products were detected by ^1H NMR spectroscopy (see the Experimental Section).



Scheme 3.

Table 2. Turnover numbers (TONs) in the oxygenation of cyclohexene (5.0×10^{-3} M) with $[Ru(bpy)_3]^{3+}$ (1.0×10^{-2} M) catalyzed by solutions of various manganese–porphyrins in CD_3CN/D_2O (9:1 v/v) at 298 K.

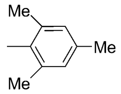
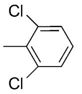
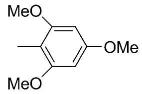
Catalyst	Ar	TON	
		Cyclohexene	Styrene
$[(tmp)Mn^{III}(Cl)]$		130	20
$[(tmp)Mn^{III}(H_2O)_2](PF_6)$		170	65
$[(tdcpp)Mn^{III}(Cl)]$		160	70
$[(tdcpp)Mn^{III}(H_2O)_2](PF_6)$		210	85
$[(tmopp)Mn^{III}(Cl)]$		80	trace
$[(tmopp)Mn^{III}(H_2O)_2](PF_6)$		110	35
$[(dtmp)Mn^{III}_2(Cl)_2]$		20	trace
$[(dtmp)Mn^{III}_2(H_2O)_2](PF_6)_2$		80	20

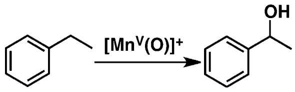
Table 3. Redox potentials of various manganese–chloride–porphyrins $[(P)Mn(Cl)]$ in CH_3CN containing H_2O (6.5 mM) at 298 K.

	tmopp	tmp	tdcpp
E_{ox1} vs. SCE [V][a]	0.95	1.02	1.20
E_{ox2} vs. SCE [V][a]	1.11	1.20	1.48

[a] $TBAPF_6$: 0.10 M.

It was confirmed that no oxygenated product was obtained in the absence of a manganese–porphyrin under otherwise the same experimental conditions. When $[Ru(bpy)_3]^{3+}$ was replaced by $[Fe(bpy)_3]^{3+}$, no oxygenated product was obtained in the presence of $[(tmp)Mn^{III}(OH)]$. This indicates that the formation of $[(tmp)Mn^V(O)]^+$ is essential for the oxygenation of olefins. The turnover numbers (TONs) were calculated on the basis of the amount of catalysts and the results are summarized in Table 2. TONs vary significantly depending on the type of manganese–porphyrins owing to the difference in their oxidation potentials (Table 3) and the steric bulkiness of the porphyrin ligand. When $[(tmp)Mn^{III}(H_2O)_2](PF_6)$ was used as the catalyst, oxygenation of cyclohexene occurred more efficiently than that of styrene probably because of the stronger steric repulsion of styrene against the bulky tmp ligand of $[(tmp)Mn^V(O)]^+$ compared with that of cyclohexene. Such preference of cyclohexene for styrene in the catalytic oxygenation has also been observed under photocatalytic oxygenation of olefins using porphyrins.[43] In the case of the tdcpp ligand, the oxygenation of cyclohexene and styrene is more reactive than that with the tmp ligand (Table 2) because the tdcpp ligand is less sterically hindered than the tmp ligand and exhibits higher redox potentials (Table 3).[44] In the case of $[(dtmpd)Mn_2(Cl)_2]$, the TON values are significantly smaller than those of the corresponding monomer, $[(tmp)Mn(Cl)]$, because the $Mn^V(O)$ species derived from $[(dtmpd)Mn_2(Cl)_2]$ may be produced inside the diporphyrin cavity to prevent the interaction with substrates.

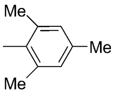
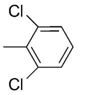
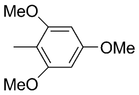
Alkane hydroxylation by catalytic electron-transfer reactions: Hydroxylation of alkane (ethylbenzene) also occurs by the manganese–porphyrin-catalyzed electron-transfer oxidation with $[Ru(bpy)_3]^{3+}$. Addition of $[Ru(bpy)_3]^{3+}$ to a solution of alkane (ethylbenzene) in CH_3CN containing water in the presence of a catalytic amount of manganese–porphyrins resulted in the formation of alcohols (Scheme 4).[45]



Scheme 4.

The oxygenated products were detected by ^1H NMR spectroscopy (see the Experimental Section). TONs were determined and the results are given in Table 4. Ethylbenzene is also oxidized to 1-phenylethanol using $[(tmp)Mn^{III}(H_2O)_2](PF_6)$, $[(tdcpp)Mn^{III}(H_2O)_2](PF_6)$, and $[(tmopp)Mn^{III}(H_2O)_2](PF_6)$. These TONs also vary significantly depending on the type of manganese–porphyrins as a result of their different oxidation potentials (Table 3).

Table 4. Turnover numbers (TONs) in the oxygenation of ethylbenzene (5.0×10^{-3} M) with $[Ru(bpy)_3]^{3+}$ (1.0×10^{-2} M), catalyzed by solutions of various manganese–porphyrins in CD_3CN/D_2O (9:1 v/v) at 298 K.

Catalyst	Ar	TON
$[(tmp)Mn^{III}(H_2O)_2](PF_6)$		15
$[(tdcpp)Mn^{III}(Cl)]$		70
$[(tdcpp)Mn^{III}(H_2O)_2](PF_6)$		30
$[(tmopp)Mn^{III}(H_2O)_2](PF_6)$		0

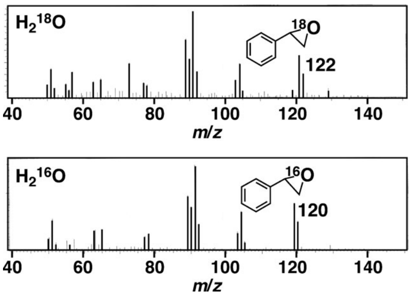


Figure 9. Mass spectra of styrene oxide produced by styrene (1.0×10^{-2} M) with $[Ru(bpy)_3]^{3+}$ (4.0×10^{-2} M) catalyzed by a solution of $[(tmp)Mn^{III}(OH)]$ (5.0×10^{-7} M) in CH_3CN/H_2O (9:1 v/v) at 298 K. Using a) $H_2{}^{18}O$ and b) $H_2{}^{16}O$ as an oxygen source.

^{18}O-labeling experiments: The oxygen source in the manganese–porphyrin-catalyzed electron-transfer oxygenation of substrates with $[Ru(bpy)_3]^{3+}$ was examined by ^{18}O-labeling experiments using $[(tmp)Mn^{III}(OH)]$ as a catalyst. The epoxidation of styrene and the hydroxylation of ethylbenzene with $[Ru(bpy)_3]^{3+}$ in the presence of 95% ^{18}O-labeled water containing a catalytic amount of manganese–porphyrin afforded the corresponding epoxide and alcohol with 90% incorporation of ^{18}O in the oxygenated products as shown in Figure 9 and Figure S6 (see the Supporting Information), respectively. Thus, the oxygen source in the oxygenated products in the manganese–porphyrin-catalyzed electron-transfer oxygenation of substrates with $[Ru(bpy)_3]^{3+}$ has been confirmed to be water in the mixed solvent (CH_3CN/H_2O).

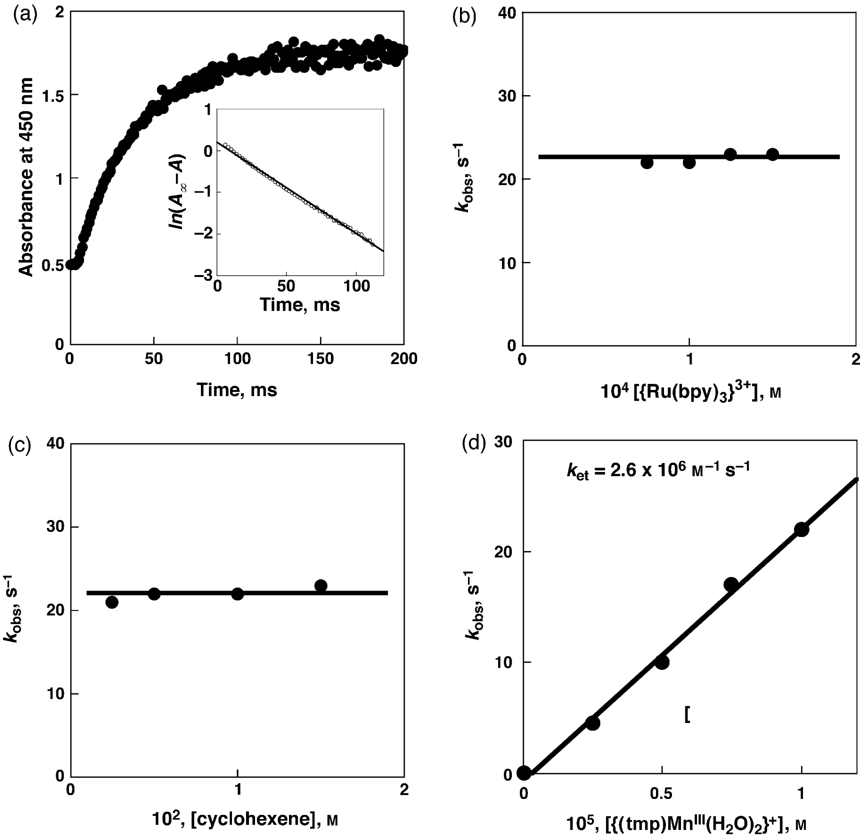


Figure 10. a) Time profile of the formation of $[Ru(bpy)_3]^{2+}$ monitored by absorbance at $\lambda = 450$ nm ($\varepsilon = 13800\ M^{-1}cm^{-1}$) in the electron-transfer oxidation of $[Ru(bpy)_3]^{3+}$ (1.0×10^{-4} M), catalyzed by $[(tmp)Mn^{III}(H_2O)_2]^+$ (1.0×10^{-5} M), with substrate (cyclohexene; 5×10^{-3} M) in CH_3CN/H_2O (9:1 v/v) at 298 K. Inset: First-order plot. b) Plot of k_{obs} versus $[Ru(bpy)_3{}^{3+}]$ in the presence of 1.0×10^{-5} M $[(tmp)Mn^{III}(H_2O)_2]^+$ and 5.0×10^{-3} M cyclohexene in $CH_3CN{:}H_2O$ (9:1 v/v) at 298 K. c) Plot of k_{obs} versus [cyclohexene] in the presence of 1.0×10^{-5} M $[(tmp)Mn^{III}(H_2O)_2]^+$ and 1.0×10^{-4} M $[Ru(bpy)_3]^{3+}$ in CH_3CN/H_2O (9:1 v/v) at 298 K. d) Plot of k_{obs} versus $[(tmp)Mn^{III}(H_2O)_2]^+$ in the presence of 1.0×10^{-4} M $[Ru(bpy)_3]^{3+}$ and 5.0×10^{-3} M cyclohexene in CH_3CN/H_2O (9:1 v/v) at 298 K.

Catalytic electron-transfer mechanism: The rate of formation of $[Ru(bpy)_3]^{2+}$ in the $[(tmp)Mn^{III}(H_2O)_2](PF_6)$-catalyzed oxygenation of cyclohexene with $[Ru(bpy)_3]^{3+}$ in the presence of 5.5 M H_2O in CH_3CN was monitored by an increase in the absorption band at 450 nm attributable to $[Ru(bpy)_3]^{2+}$ (Figure 10a). The rate obeyed first-order kinetics (inset of Figure 10a). The observed first-order rate constant remained constant with the change in concentration of $[Ru(bpy)_3]^{3+}$ (Figure 10b) and cyclohexene (Figure 10c). In contrast, the observed first-order rate constant increased linearly with an increase in concentration of the catalyst, $[(tmp)Mn^{III}(H_2O)_2](PF_6)$ (Figure 10d). Thus, the rate of formation of $[Ru(bpy)_3]^{2+}$ in the $[(tmp)Mn^{III}(H_2O)_2]$-catalyzed oxygenation of cyclohexene with $[Ru(bpy)_3]^{3+}$ is given by Equation (2).

$$d[[Ru(bpy)_3]^{2+}]/dt = k_{et}[[(tmp)Mn^{III}]^{+}][[Ru(bpy)_3]^{3+}] \qquad (2)$$

Because the rate is independent of the cyclohexene concentration, the reaction of $[(tmp)Mn^{V}(O)]^{+}$ with cyclohexene is faster than the electron-transfer step to generate $[Ru(bpy)_3]^{2+}$, which is the rate-determining step.

To confirm this point, the rate constant of the reactions of $[(tmp)Mn^{V}(O)]^{+}$ with cyclohexene was determined directly under stoichiometric (noncatalytic) reaction conditions by monitoring an increase in the absorption band at 470 nm attributable to $[(tmp)Mn^{III}]^{+}$, which was produced by the oxygenation of cyclohexene with $[(tmp)Mn^{V}(O)]^{+}$, in the presence of various concentrations of cyclohexene in CH_3CN/H_2O (9:1 v/v) at 298 K. The rate obeyed pseudo-first-order kinetics (Figure 11a) and the observed first-order rate constant (k_{obs}) increased linearly with increasing cyclohexene concentration (Figure 11b). From the slope of the linear plot of k_{obs} versus cyclohexene concentration in Figure 11b the second-order rate constant (k_{ox}) of the reaction of $[(tmp)Mn^{V}(O)]^{+}$ with cyclohexene in CH_3CN/H_2O (9:1 v/v) at 298 K was determined to be $1.6\times10^{5}\,M^{-1}s^{-1}$.

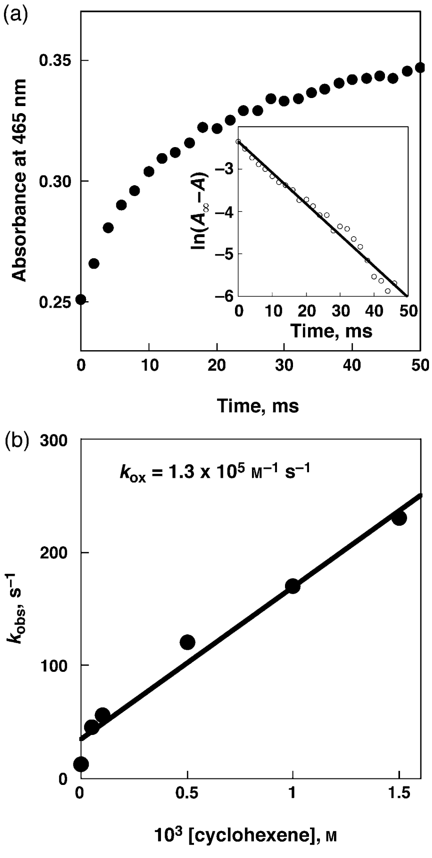


Figure 11. a) Time profile of the formation of $[(tmp)Mn^{III}]^{+}$ monitored by absorbance at $\lambda = 465$ nm in the oxidation of cyclohexene ($5.0\times10^{-3}\,M$), in the presence of $[(tmp)Mn^{V}(O)]^{+}$ in CH_3CN/H_2O (9:1 v/v) at 298 K. Inset: First-order plot. b) Plot of k_{ox} versus [cyclohexene] in the presence of $5.0\times10^{-6}\,M$ $[(tmp)Mn^{III}(H_2O)_2]^{+}$ and $1.0\times10^{-5}\,M$ $[Ru(bpy)_3]^{3+}$.

The rate constant of the electron transfer from $[(tmp)Mn(H_2O)_2]^{+}$ to $[Ru(bpy)_3]^{3+}$ under the same conditions as those employed for the catalytic oxygenation of cyclohexene with $[Ru(bpy)_3]^{3+}$ (Figure 10d) was determined from the time profile of the electron transfer under stoichiometric conditions (Figure 12). The rate obeyed second-order kinetics and the second-order rate constant of the electron transfer (k_{et}) was determined to be $2.4\times10^{6}\,M^{-1}s^{-1}$ in CH_3CN/H_2O (9:1 v/v) at 298 K. This k_{et} value is much larger than the value ($3.0\times10^{5}\,M^{-1}s^{-1}$) determined in CH_3CN at 233 K. More importantly, the k_{et} value determined directly under stoichiometric conditions agrees well with the value ($2.6\times10^{6}\,M^{-1}s^{-1}$) determined under catalytic conditions (Figure 10d). Thus, it was confirmed that electron transfer from $[(tmp)Mn(H_2O)_2]^{+}$ to $[Ru(bpy)_3]^{3+}$ was indeed the rate-determining step in the catalytic oxygenation of cyclohexene with $[Ru(bpy)_3]^{3+}$, when the first-order rate constant of the reaction of $[(tmp)Mn^{V}(O)]^{+}$ with $1.0\times10^{-3}\,M$ cyclohexene ($1300\,s^{-1}$) is significantly larger that the value of formation of $[(tmp)Mn^{V}(O)]$ with $1.0\times10^{-4}\,M$ ($260\,s^{-1}$).

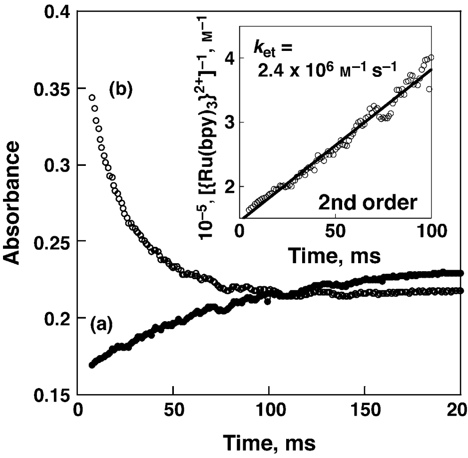
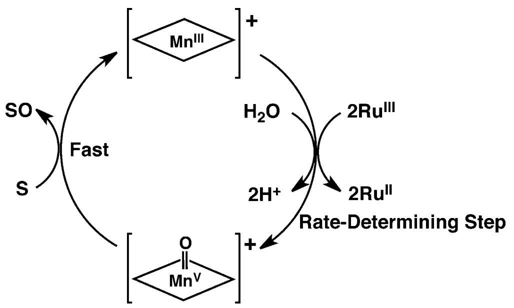


Figure 12. Time profile of a) the formation of $[Ru(bpy)_3]^{2+}$ and b) the decay of $[(tmp)Mn^{III}(H_2O)_2]^{+}$ for oxidation monitored by absorbance $\lambda =$ 450 and 465 nm in the electron-transfer oxidation of $[(tmp)Mn^{III}(H_2O)_2]^{+}$ ($5.0\times10^{-6}\,M$) by $[Ru(bpy)_3]^{3+}$ ($1.0\times10^{-5}\,M$) in CH_3CN/H_2O (9:1 v/v). Inset: Second-order plot.

Based on the above results, the catalytic mechanism of the manganese–porphyrin-catalyzed oxygenation of substrates (S: alkanes and olefins) with $[Ru(bpy)_3]^{3+}$ is summarized as shown in Scheme 5. The electron transfer from $[Ru(bpy)_3]^{3+}$ to $[(P)Mn^{III}(H_2O)_2]$ generates $[(P)Mn^{V}(O)]^{+}$, which can oxygenate a substrate (S) to yield SO in the presence of H_2O to regenerate $[(P)Mn^{III}(OH)]$. The presence of H_2O is essential to accelerate the oxygenation of S with $[(P)Mn^{V}(O)]^{+}$. In this context, it is interesting to note that the high reactivity of $[(P)Mn^{V}(O)]^{+}$ with a large rate constant ($6.5\times10^{5}\,M^{-1}s^{-1}$) has been reported using a water-soluble manganese–porphyrin, tetra-*N*-(methylpyridyl)-porphyrinato)manganese(III) $[(tmpyp)Mn^{III}]$, in the reaction of $[(tmpyp)Mn^{V}(O)]^{+}$ with a water-soluble olefin (carbama-



Scheme 5.

zepine) in an aqueous solution.[16] Water can certainly accelerate the one-electron oxidation of the substrate owing to the strong solvation and hydrogen bonding to the substrate radical cation.[46] In the case of HRP compound I, the reactions with *N*,*N*-dimethylanilines and thioanisoles have been reported to proceed through initial electron transfer from the substrates to the oxoiron(IV)–porphyrin π-radical cation.[47] The *N*-demethylation of *N*,*N*-dimethylaniline by a synthetic oxoiron(IV)–porphyrin π-radical cation also proceeds by electron transfer.[47] Such electron-transfer processes are enhanced in polar solvents, whereas hydrogen- or oxygen-atom transfer reactions are known to be rather insensitive to the polarity of solvents.[48] However, the role of water to accelerate the oxygenation of S with $[(P)Mn^V(O)]^+$ has yet to be further clarified.

The direct determination of the rate constants of manganese(V)–oxo species with substrates has also been made by Zhang and Newcomb,[49] who reported the rate constant of manganese(V)–oxo species with substrates by using laser flash photolysis. A large rate constant $(6.1\times10^5\,\mathrm{M^{-1}s^{-1}})$[49] was determined for the reaction of $[(F_{20}tpp)Mn^V(O)]^+$ (F_{20}tpp=tetrakis(pentafluorophenyl)porphyrinato dianion) with *cis*-stilbene in the absence of water in CH_3CN. This value is larger than the k_{ox} values in Figure 11d.

Conclusion

The present study has demonstrated that the electron-transfer oxidation of $(P)Mn^{III}$ with $[Ru(bpy)_3]^{3+}$ in the presence of H_2O affords $[(P)Mn^{IV}(O)]$ and $[(P)Mn^V(O)]$ and the electron-transfer rate constants were thoroughly analyzed in light of the Marcus theory of electron transfer. The $[(P)Mn^V(O)]$ oxygenates substrates to reproduce $(P)Mn^{III}$ when catalytic electron-transfer oxygenation of substrates occurs efficiently with $[Ru(bpy)_3]^{3+}$ as a one-electron oxidant, H_2O as an oxygen source, and $(P)Mn^{III}$ as a catalyst. The rate-determining step in the catalytic oxygenation of cyclohexene is proved to be the electron-transfer oxidation of $(P)Mn^{III}$ to produce $[(P)Mn^V(O)]$, followed by rapid oxygenation of substrates by $[(P)Mn^V(O)]$. Thus, the present study provides a rational way to design catalytic electron-transfer oxygenation of substrates using H_2O as an oxygen source.

Acknowledgements

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