Dioxygen-activated reductive epoxidation of cyclohexene using Mn(III) porphyrin as catalyst and hexylviologen as electron mediator

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Abstract

In a monooxygenation reaction of cyclohexene in an air-equilibrated dichloromethane suspension containing 5,10,15,20-tetraphenylporphyrinatomanganese(III) chloride (Mn(III)(tpp)Cl) as a catalyst, insoluble zinc powder as a reductant, and benzoic anhydride as a cleaving reagent of dioxygen double-bond, a large amount of cyclohexene oxide was produced by adding an axial ligand for Mn(tpp)Cl such as Cl^- ion, Br^- ion, and 1-methylimidazole (1-MeIm) besides an electron mediator such as hexylviologen (HV^{2+}). The role of the ligand and the mediator has been investigated in detail by cyclic voltammetry. The Cl^- and Br^- ions promoted this epoxidation probably by assisting the oxygen transfer from Mn(V)-oxo complex, that is an intermediate in this reaction cycle, to cyclohexene, and HV^{2+} functioned as the mediator of electron transfer from zinc to Mn(II)(tpp)–dioxygen adduct, enhancing the production of epoxide. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many attempts have been carried out using Mn(III) and Fe(III) porphyrins as model complexes in order to elucidate the activity of a monooxygenase such as cytochrome P-450. Its enzyme catalyzes the addition reaction of one atomic oxygen to substrate such as alkane in vivo by activating dioxygen molecule reduc-

tively. Many model systems were roughly divided into two systems; one contained an oxygen donor such as iodosylbenzene [1–9] and hydrogen peroxide [10–19], and the other contained an activated dioxygen molecule by a metal porphyrin which was reduced chemically with a reducing reagent such as H_2/Pt [20–23] and zinc powder [24–28], or electrochemically on an electrode [28–38]. In both systems, an active high-valent oxo-metalloporphyrin complex was produced as an important intermediate,

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and the amount of the produced oxide increased by the addition of nitrogen base such as 1-methylimidazole(1-MeIm) coordinating to the metalloporphyrin. Battioni et al. [11] reported that imidazole assisted the production of Mn(V)-oxo complex and the transfer of atomic oxygen from Mn(V)-oxo complex to substrate in the system of Mn porphyrin-imidazole-H_2O_2-cyclooctene. However, Creager and Murray [32] reported that in the electrochemical activation of dioxygen using Mn porphyrin, 1-MeIm prevented the coordination of dioxygen to Mn(II) porphyrin.

In this paper, in the dioxygen-activated reductive epoxidation of cyclohexene using Mn porphyrin as the catalyst in dichloromethane, we have investigated the role of the axial ligand and the electron mediator by cyclic voltammetry. Especially, the effect of Cl^- and Br^- ions as the axial ligands and HV^{2+} ion as the electron mediator [24,26,28], about which little is known, was studied.

2. Experimental

5,10,15,20-Tetraphenylporphyrinatomanganese(III)chloride (Mn(III)(tpp)Cl) was synthesized and purified by literature methods [39,40]. Dichloromethane and cyclohexene were distilled after dehydration by calcium hydride and molecular sieves (3A), respectively. 1-Methylimidazole (1-MeIm) was distilled under reduced pressure in an N_2 atmosphere after dehydration by molecular sieves (3A). They were stored over molecular sieves (3A). Benzoic anhydride ($(C_6H_5CO)_2O$) was recrystallized from the mixed solvent of ethanol–water (1:4 by volume) after removal of the contained acid by washing with aqueous sodium hydrogencarbonate. Hexylviologen bromide was synthesized by refluxing 4,4'-bipyridyl with hexylbromide in acetonitrile. Hexylviologen perchlorate (HV-$(ClO_4)_2$) and tetrabutylammonium perchlorate (Bu_4NClO_4) were obtained as precipitate by mixing the aqueous solutions of corresponding

bromide with concentrated perchloric acid, and they were recrystallized from ethanol and the mixed solvent of ethyl acetate–hexane (1:4 by volume), respectively. $(C_6H_5CO)_2O$, HV(ClO$_4)_2$, and Bu_4NClO_4 were used after drying in vacuo at room temperature.

The epoxidation reaction was carried out as follows. An air-equilibrated dichloromethane suspension containing soluble Mn(III)(tpp)Cl, insoluble zinc powder, soluble $(C_6H_5CO)_2O$, soluble HV(ClO$_4)_2$, and soluble cyclohexene was stirred at a constant rate with a magnetic stirrer at 30°C during 12 h. The quantitative analysis and the identification for the oxidation product of cyclohexene were performed by a Shimadzu GC-8A Gas Chromatograph with a silicon DC 550 column. The amount of consumed zinc powder was estimated from the amount of unreacted zinc powder determined by EDTA titration [28]. Cyclic voltammetry was performed using a glassy carbon disk (3 mm diameter) as the working electrode, a Pt coil as the counter electrode, and Ag/0.1 M AgNO$_3$ (1 M = 1 mol dm^{-3}) in acetonitrile solution as the reference electrode at 25°C. Potential control was carried out using a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator. Cyclic voltammograms were recorded on a Rikadenki RW-21 X-Y recorder. Half-wave potentials ($E_{1/2}$) were estimated as the average of cathodic and anodic peak potentials. The electrode potential and the half-wave potential were described on the basis of the half-wave potential of ferrocene/ferrocenium ion (Fc$^+$/Fc).

3. Results and discussion

3.1. Effect of hexylviologen on the epoxidation of cyclohexene

Though no oxidation product of cyclohexene was obtained in an air-equilibrated dichloromethane suspension containing 1×10^{-4} M Mn(III)(tpp)Cl, 7.3×10^{-2} M zinc powder, 4.2

$\times 10^{-2}$ M benzoic anhydride, and 0.47 M cyclohexene (abb. to Mn(III)(tpp)Cl + Zn + O_2 + $(C_6H_5CO)_2O$ + cyclohexene system hereafter), cyclohexene oxide(epoxide) was obtained as a single oxidation product by adding a large amount of 1-MeIm into this system. Fig. 1a shows the effect of the concentration of 1-MeIm, [1-MeIm], on the amount of the produced epoxide. When either zinc powder as a reductant, dioxygen as an oxygen source, or Mn(tpp)Cl as a catalyst was not contained, no oxidation product was obtained. The result suggests that this epoxidation was due to the reductive activation of dioxygen by Mn porphyrin catalyst.

By adding 1×10^{-4} M hexylviologen (HV^{2+}) into this system, the epoxide was obtained even in the absence of 1-MeIm, see the region I in Fig. 1b. ($HV(ClO_4)_2$ was used as the source of HV^{2+} ions). However, when a small amount of 1-MeIm was added in this system containing HV^{2+}, the epoxide was not produced and zinc was hardly consumed, see the region II in Fig. 1b. Moreover, a larger amount of epoxide was obtained by adding 1-MeIm further, see the region III in Fig. 1b. The epoxidation profile for [1-MeIm] was distinguished by naming the regions I–IV in Fig. 1 to clarify the effect of [1-MeIm] on the amount of the produced epoxide.

The maximum turnover number of Mn(tpp)Cl reached 40 in the absence of HV^{2+} and 110 in the presence of HV^{2+} in the system with 1-MeIm corresponding to the region III in Fig. 1a and b. The turnover number of HV^{2+} and Mn(tpp)Cl was 30 in the system without 1-MeIm but with HV^{2+} corresponding to the region I in Fig. 1b. These results suggest that HV^{2+} as well as Mn(tpp)Cl acted as catalysts in this epoxidation system. The Zn-utilizing efficiency, which was estimated on the assumption that 1 mol of epoxide is obtained from 1 mol of the consumed zinc, exhibited the maximum value of 40% at 8×10^{-2} M 1-MeIm in the system with HV^{2+}. The maximum value of 36% was obtained at 8×10^{-2} M 1-MeIm in the system without HV^{2+} though the amount of the produced epoxide was less than that in the system with HV^{2+}.

The amount of the produced epoxide and the Zn-utilizing efficiency decreased above 0.1 M 1-MeIm because of bleaching of porphyrin (region IV in Fig. 1). No decomposition of porphyrin ring occurred when either zinc powder, benzoic anhydride, dioxygen, or 1-MeIm was not contained, but further investigation was not carried out.

3.2. Effect of Br^- ions on the epoxidation of cyclohexene

Though no oxidation product of cyclohexene was obtained at 5×10^{-3} M 1-MeIm in (Mn(III)(tpp)Cl + Zn + O_2 + $(C_6H_5CO)_2O$ + cyclohexene) system containing 1×10^{-4} M
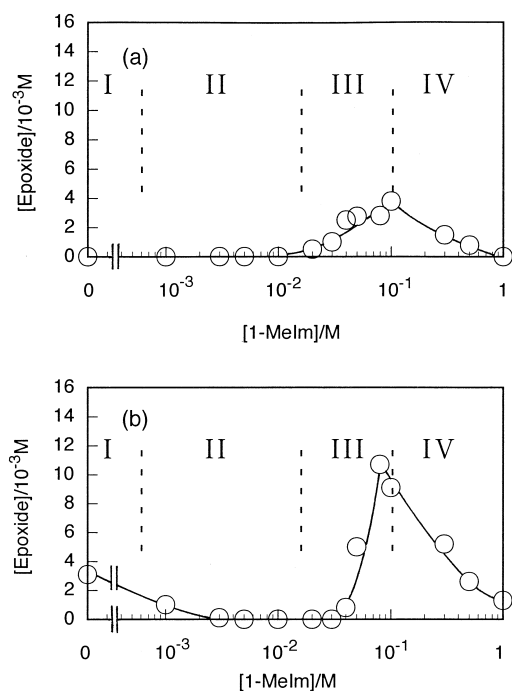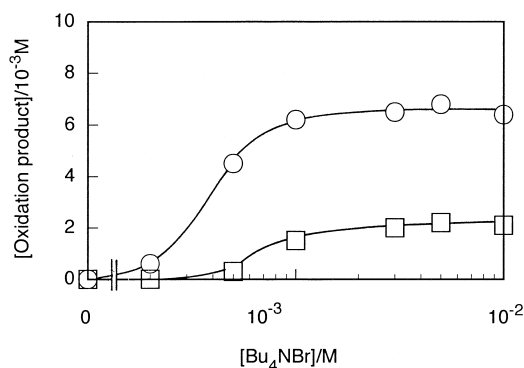

Fig. 1. Effect of the addition of 1-MeIm on the amount of the produced epoxide in the absence of $HV(ClO_4)_2$ (a) and at 1×10^{-4} M $HV(ClO_4)_2$ (b) in an air-equilibrated dichloromethane suspension containing 1×10^{-4} M Mn(tpp)Cl, 7.3×10^{-2} M Zn powder, 4.2×10^{-2} M benzoic anhydride, and 0.47 M cyclohexene at 30°C (reaction time: 12 h). The region numbers I–IV were named to distinguish clearly the addition effect of 1-MeIm.

Fig. 2. Effect of the addition of Bu_4NBr on the amount of the oxidation products (epoxide ($\bigcirc$) and 2-cyclohexene-1-one ($\square$)) in an air-equilibrated dichloromethane suspension containing 1×10^{-4} M Mn(tpp)Cl, 1×10^{-4} M HV(ClO$_4$)$_2$, 5×10^{-3} M 1-MeIm, 7.3×10^{-2} M Zn powder, 4.2×10^{-2} M benzoic anhydride, and 0.47 M cyclohexene at 30°C (reaction time: 12 h).

HV^{2+} (see the region II in Fig. 1b), the oxidation product was obtained by adding Br^- ions into the system with the Zn-utilizing efficiency of about 40%, where Bu_4NBr was used as the source of Br^- ion. On the other hand, when the Br^- ions were added in the system with a small amount of 1-MeIm but without HV^{2+} corresponding to the regions I and II in Fig. 1a, the oxidation product was slightly obtained. Fig. 2 shows the dependence of the amount of the oxidation product on the concentration of Br^- ions, $[Br^-]$, in the system containing (1×10^{-4} M HV^{2+} + 5×10^{-3} M 1-MeIm). Epoxide and 2-cyclohexene-1-one were obtained with molar ratio ($[$epoxide$]/[$2-cyclohexene-1-one$]$) of about 3 by the addition of Br^- ions. Since these amount decreased hardly by adding 3,5-di-*tert*-butyl-*p*-hydroxyltoluene as a radical inhibitor, it is found that no radical reaction but still the catalytic reaction by Mn(tpp)Cl limited this epoxidation. The amount of the produced epoxide by adding 1×10^{-3} M Br^- ion was comparable to that by adding 5×10^{-2} M 1-MeIm (see Fig. 1b). We infer from these results that the Cl^- counter ions in Mn(tpp)Cl and the added Br^- ions as well as the 1-MeIm played an important role as an axial ligand of Mn porphyrin in this catalytic system.

3.3. Effect of 1-MeIm and Br^- ions on the redox potential of Mn(III / II)(tpp)

The reduction (Eq. (1)) of $[$Mn(III)(tpp)$]^+$ to Mn(II)(tpp) was first step in the epoxidation cycle activating molecular dioxygen reductively by Mn porphyrin catalyst [22–26,29–32]. Thus, we have investigated the role of an axial ligand such as 1-MeIm and Br^- ion for the reaction (1).
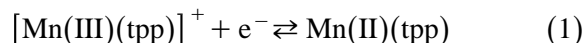
$$[\text{Mn(III)(tpp)}]^+ + e^- \rightleftarrows \text{Mn(II)(tpp)} \qquad (1)$$

Fig. 3 shows the dependence of the half-wave potential($E_{1/2}$) of Mn(III/II)(tpp) couple on [1-MeIm] and [Br^-] in an N_2-purged dichloromethane solution containing 5×10^{-4} M Mn(III)(tpp)Cl. The $E_{1/2}$ value of Mn(III/II)-(tpp) couple increased linearly with increasing [1-MeIm] by the slope of about 44 mV/log[1-MeIm] below 2.5×10^{-3} M 1-MeIm, and decreased linearly by the slope of about 69 mV/log[1-MeIm] above it. While, the $E_{1/2}$ was the constant value of -0.78 V in spite of the addition of Br^- ions. This suggests that Br^- ions in contrast to 1-MeIm did not quite take part in the reduction (Eq. (1)).
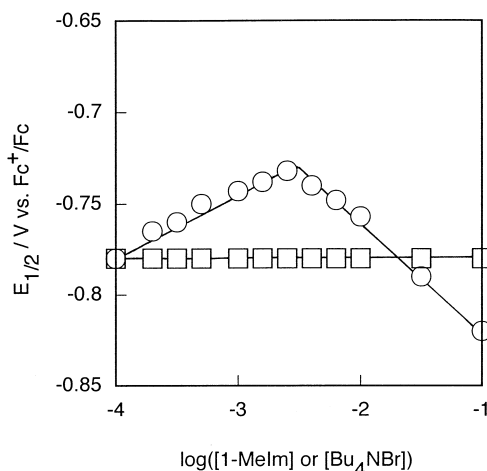

Fig. 3. Relation between half-wave potential ($E_{1/2}$) of Mn(III/II)(tpp) couple and concentration of 1-MeIm ($\bigcirc$) or Bu_4NBr ($\square$) in an N_2-purged dichloromethane solution containing 5×10^{-4} M Mn(tpp)Cl and 0.1 M Bu_4NClO_4 as a supporting electrolyte at 25°C. Scan rate: 100 mV s^{-1}, working electrode: glassy carbon disk with 0.07 cm^2 area.

It was reported that one or two ligands coordinated to $[Mn(III)(tpp)]^+$ and no or one ligand coordinated to $Mn(II)(tpp)$, depending on the solvent and the ligand [41,42]. Since the counter Cl^- ion can coordinate relatively strong to the central manganese ion in $[Mn(III)(tpp)]^+$ by the assistance of an electrostatic interaction in non-bonding solvent such as dichloromethane with small dielectric constant, its manganese ion may not exist in the porphyrin plane, but lie to the coordinating side of the Cl^- ion. This implies that the coordination of 1-MeIm onto the opposite axial position of the Cl^- ion was relatively difficult. This idea is supported by the experimental evidence that the absorption at Soret band of $Mn(III)(tpp)Cl$ decreased only by adding a large amount of 1-MeIm. That is, the ligand-exchange reaction (2) for $Mn(III)(tpp)Cl$ occurred only at higher [1-MeIm].

$$Mn(III)(tpp)Cl + 2(1\text{-MeIm})$$
$$\rightarrow [Mn(III)(tpp) \cdot (1\text{-MeIm})_2]^+ + Cl^- \qquad (2)$$
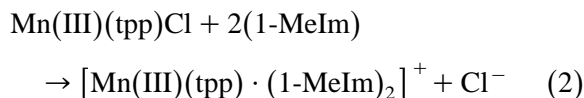
By contrast, the absorption at Soret band of $Mn(II)(tpp)$ increased starting from the addition of a small amount of 1-MeIm, where $Mn(II)(tpp)$ was produced by the reduction of $Mn(III)(tpp)Cl$ with tetrabutylammonium borohydride in an N_2-purged dichloromethane solution. That is, the coordination reaction (3) of 1-MeIm to $Mn(II)(tpp)$ was easy.

$$Mn(II)(tpp) + 1\text{-MeIm}$$
$$\rightarrow Mn(II)(tpp) \cdot 1\text{-MeIm} \qquad (3)$$
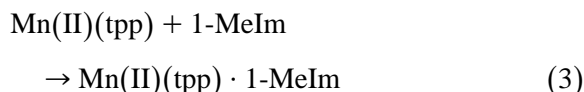
Therefore, since a ligand-exchange from the Cl^- ion to 1-MeIm occurred only by the reduction of $Mn(III)(tpp)Cl$ below 2.5×10^{-3} M 1-MeIm as indicated by Eq. (4), the $E_{1/2}$ increased linearly with increasing [1-MeIm] by the slope close to the value of 59 mV/log[1-MeIm] predicted by the Nernst's equation at 25°C.

$$Mn(III)(tpp)Cl + 1\text{-MeIm} + e^-$$
$$\rightleftarrows Mn(II)(tpp) \cdot 1\text{-MeIm} + Cl^- \qquad (4)$$
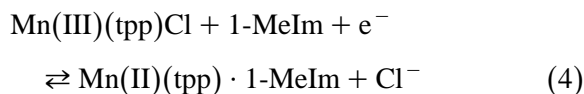
On the other hand, above 2.5×10^{-3} M 1-MeIm, the Cl^- ion was first displaced by two 1-MeIm molecules as indicated by the reaction (2), and $[Mn(III)(tpp) \cdot (1\text{-MeIm})_2]^+$ were formed. Then one 1-MeIm molecule was released by the reduction (Eq. (5)) of $[Mn(III)(tpp) \cdot (1\text{-MeIm})_2]^+$.

$$[Mn(III)(tpp) \cdot (1\text{-MeIm})_2]^+ + e^-$$
$$\rightleftarrows Mn(II)(tpp) \cdot 1\text{-MeIm} + 1\text{-MeIm} \qquad (5)$$
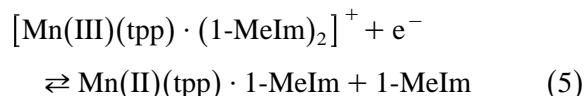
This is supported by the decrease of $E_{1/2}$ with the slope close to the Nernst's slope.

The $E_{1/2}$ of the redox reaction of HV^{2+} indicated by Eq. (6) was the constant value of -0.77 V regardless of [1-MeIm] and $[Br^-]$.

$$HV^{2+} + e^- \rightleftarrows HV^+ \qquad (6)$$

It is predicted from these results that whether or not the electron transfer from HV^+ to $[Mn(III)(tpp)]^+$ occurred depended on [1-MeIm] since the $E_{1/2}$ of $Mn(III/II)(tpp)$ couple was larger below about 1×10^{-2} M 1-MeIm than that of HV^{2+}/HV^+ couple but smaller above about 3×10^{-2} M 1-MeIm.

In Sections 3.4 and 3.5, we have examined by cyclic voltammetry how the redox properties of $Mn(tpp)Cl$ were influenced by HV^{2+} and benzoic anhydride containing in our catalytic system, and assigned their redox reactions to the elementary reactions in our epoxidation system by the assistance of previously reported reaction mechanism in literature [22–24,29–32].

3.4. Role of hexylviologen on the redox reaction of Mn porphyrin in (Mn(III)(tpp)Cl + O₂) system

Fig. 4a shows the cyclic voltammograms of $Mn(III)(tpp)Cl$ (solid line), HV^{2+} (broken line), and $(Mn(III)(tpp)Cl + HV^{2+})$ (dotted line) at the sweep-rate of 100 mV s^{-1} in an N_2-purged dichloromethane solution. The $E_{1/2}$ values of $Mn(III/II)(tpp)$ and HV^{2+}/HV^+ redox couples were -0.79 and -0.77 V, respectively. The potential difference between cathodic and an-
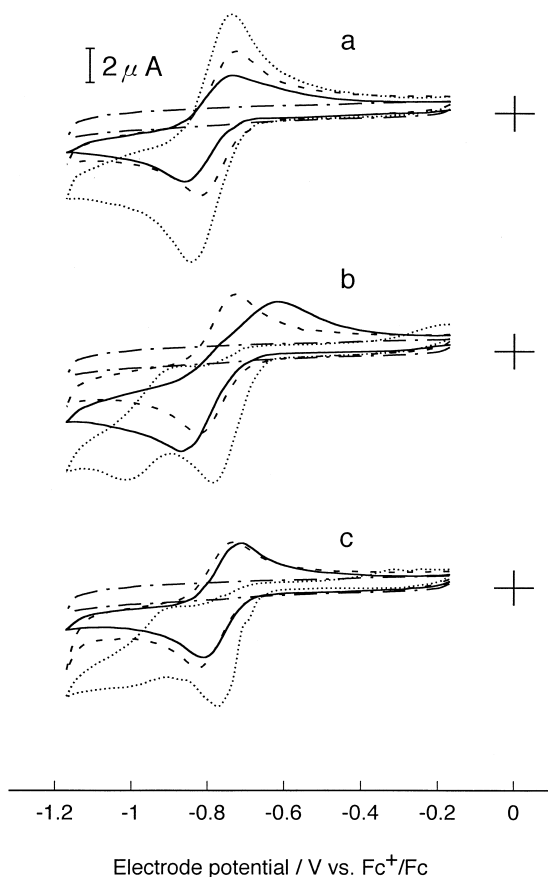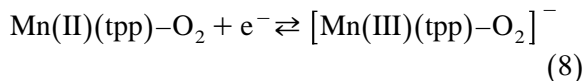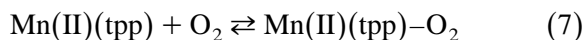
Fig. 4. Cyclic voltammograms of 5×10^{-4} M Mn(tpp)Cl (solid line), 5×10^{-4} M HV(ClO$_4$)$_2$ (broken line), and (5×10^{-4} M Mn(tpp)Cl + 5×10^{-4} M HV(ClO$_4$)$_2$) (dotted line) in an N$_2$-purged dichloromethane solution (a) and in an O$_2$-saturated solution (b), and in an O$_2$-saturated solution at 1×10^{-2} M 1-MeIm (c) containing 0.1 M Bu$_4$NClO$_4$ as a supporting electrolyte at 25°C. (— - —) lines indicated cyclic voltammograms for the blank solutions. Scan rate: 100 mV s^{-1}, working electrode: glassy carbon disk with 0.07 cm^2 area.

odic peaks was 130 mV for the former and 80 mV for the latter. This indicates that the redox property of HV^{2+} was more reversible than that of Mn(tpp)Cl. The cyclic voltammogram of (Mn(III)(tpp)Cl + HV^{2+}) indicated the simple sum of those of Mn(III)(tpp)Cl and HV^{2+}. This implies that HV^{2+} did not act as the mediator of the electron transfer (Eq. (1)) for Mn(III/II)(tpp) couple under the N$_2$-purged condition because both the redox potentials were near.

In the cyclic voltammogram of Mn(III)(tpp)Cl under an O$_2$-saturated condition in the absence

of 1-MeIm (solid line in Fig. 4b), the large difference between anodic and cathodic peak potentials was observed, and the cathodic peak current (i_{pc}) was larger than that under the N$_2$-purged condition (solid line in Fig. 4a). This suggests that both the coordination (Eq. (7)) of dioxygen to Mn(II)(tpp) and the reduction (Eq. (8)) of the Mn(II)(tpp)–O$_2$ adduct occurred successively after the reduction (Eq. (1)).
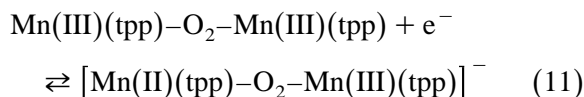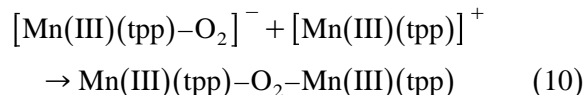
$$Mn(II)(tpp) + O_2 \rightleftarrows Mn(II)(tpp)\text{–}O_2 \qquad (7)$$

$$Mn(II)(tpp)\text{–}O_2 + e^- \rightleftarrows \left[Mn(III)(tpp)\text{–}O_2\right]^- \qquad (8)$$

In the cyclic voltammogram of HV^{2+} under the O$_2$-saturated condition (broken line in Fig. 4b), the $E_{1/2}$ and i_{pc} values were approximately the same as those under the N$_2$-purged condition (broken line in Fig. 4a). By contrast, the cyclic voltammogram of (Mn(III)(tpp)Cl + HV^{2+}) in the O$_2$-saturated solution (dotted line in Fig. 4b) differed quite from that in the N$_2$-purged solution (dotted line in Fig. 4a). No anodic peaks of HV$^+$ and Mn(II)(tpp) were observed, and a new redox pair appeared around -1.0 V. An intermolecular electron transfer (Eq. (9)) from HV$^+$ to Mn(II)(tpp)–O$_2$ adduct may occur.

$$Mn(II)(tpp)\text{–}O_2 + HV^+$$
$$\rightarrow \left[Mn(III)(tpp)\text{–}O_2\right]^- + HV^{2+} \qquad (9)$$
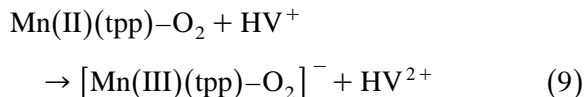
Creager and Murray [32] reported that the reduction (Eq. (8)) occurred at more positive potential by about 0.23 V than the reduction (Eq. (1)) for Mn(III)(tpp)(benzoate) with benzoate ion as a counter ion in dichloromethane. This supports that the HV^{2+} acted as the mediator for the electron transfer (Eq. (8)) although it did not act as the mediator for electron transfer (Eq. (1)). The concentration of [Mn(III)(tpp)]$^+$ in the vicinity of the working electrode around -0.75 V under the O$_2$-saturated condition may be smaller than its concentration under the N$_2$-purged condition, because the i_{pc} value under the former condition was smaller than that un-

der the latter condition. We believe that this decrease and the redox pair around -1.0 V were ascribed to a dimmer formation (Eq. (10)) from $[Mn(III)(tpp)-O_2]^-$ and $[Mn(III)(tpp)]^+$ and the redox reaction (11) of its dimmer, respectively [43].

$$[Mn(III)(tpp)-O_2]^- + [Mn(III)(tpp)]^+$$
$$\rightarrow Mn(III)(tpp)-O_2-Mn(III)(tpp) \qquad (10)$$

$$Mn(III)(tpp)-O_2-Mn(III)(tpp) + e^-$$
$$\rightleftarrows [Mn(II)(tpp)-O_2-Mn(III)(tpp)]^- \qquad (11)$$

By the addition of 1×10^{-2} M 1-MeIm, the cyclic voltammogram of Mn(III)(tpp)Cl in an O_2-saturated solution (solid line in Fig. 4c) resembled that in the N_2-purged solution (solid line in Fig. 4a). This result implies that the coordination (Eq. (7)) of dioxygen to Mn(II)(tpp) was depressed because of the axial coordination of 1-MeIm to Mn(II)(tpp). By adding HV^{2+} further, however, the voltammogram (dotted line in Fig. 4c) resembled that in the absence of 1-MeIm (dotted line in Fig. 4b). Even in the absence of HV^{2+}, such redox profiles appeared by reducing the sweep-rate below 10 mV s^{-1} independent of [1-MeIm] (not illustrated). That is, even at higher [1-MeIm], the Mn(II)(tpp)-O_2 adduct was slowly formed after the formation of Mn(II)(tpp), the reactions (8) (or (9)) and (10) proceeded successively and rapidly, thus the electrode reaction (11) occurred.

3.5. Role of benzoic anhydride on the redox reaction of Mn porphyrin in (Mn(III)(tpp)Cl + O_2) system

Fig. 5a shows the dependence of the cyclic voltammogram of Mn(III)(tpp)Cl on [1-MeIm] in an O_2-saturated dichloromethane containing benzoic anhydride. The i_{pc} value for Mn(III)-(tpp)Cl increased remarkably by adding benzoic anhydride. This indicates that the formation (Eq. (12)) of Mn(V)-oxo complex ([Mn(V)-(tpp)=O]$^+$), that is presumed as an intermediate in Mn porphyrin catalytic system, by cleaving
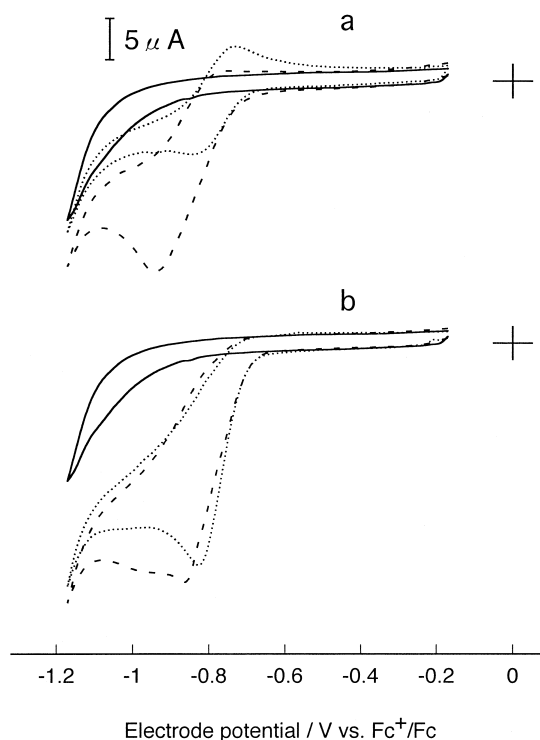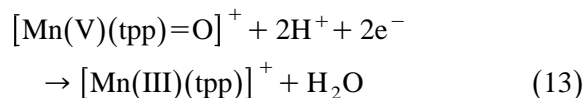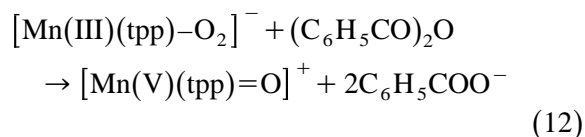

Fig. 5. Effect of the addition of 1-MeIm on cyclic voltammograms of 5×10^{-4} M Mn(tpp)Cl (a) and (5×10^{-4} M Mn(tpp)Cl + 5×10^{-4} M HV(ClO$_4$)$_2$) (b) in an O_2-saturated dichloromethane solution containing 4×10^{-2} M benzoic anhydride and 0.1 M Bu$_4$NClO$_4$ as a supporting electrolyte at 25°C. Solid lines indicated a cyclic voltammogram for an O_2-saturated blank solution containing 4×10^{-2} M benzoic anhydride and 0.1 M Bu$_4$NClO$_4$. Scan rate: 100 mV s^{-1}, working electrode: glassy carbon disk with 0.07 cm^2 area. Concentration of 1-MeIm: 0 M (broken line), 1×10^{-2} M (dotted line).

dioxygen double-bond was caused by benzoic anhydride and the reduction (Eq. (13)) of $[Mn(V)(tpp)=O]^+$ occurred successively on the working electrode though the proton source was unknown.

$$[Mn(III)(tpp)-O_2]^- + (C_6H_5CO)_2O$$
$$\rightarrow [Mn(V)(tpp)=O]^+ + 2C_6H_5COO^- \qquad (12)$$

$$[Mn(V)(tpp)=O]^+ + 2H^+ + 2e^-$$
$$\rightarrow [Mn(III)(tpp)]^+ + H_2O \qquad (13)$$

Since the coordination reaction (3) of dioxygen to Mn(II)(tpp) was depressed at higher [1-

MeIm], a quasi-reversible wave of Mn(III/II)(tpp) couple appeared. But, at slow sweep-rate below 5 mV s^{-1}, an irreversible cathodic wave of the reaction (13) appeared even at higher [1-MeIm] (not illustrated) because the relatively large amount of Mn(II)(tpp)–O$_2$ adduct was slowly formed during the slow sweep and the faster reactions (8) and (12) occurred in sequence. That is, the reduction rate in this system was mainly determined by the rate of the O$_2$ addition (Eq. (7)) to Mn(II)(tpp).

When HV^{2+} was added in this system (Fig. 5b), the i_{pc} value indicated a large value independent of the sweep-rate because the slightly produced Mn(II)(tpp)–O$_2$ adduct at higher [1-MeIm] was reduced efficiently by the remarkably fast electron mediation (Eq. (9)) with HV^{2+}, and the reactions (12) and (13) occurred subsequently.

4. Summary

A small amount of halogen ions acted favorably in this catalytic system though the $E_{1/2}$ value of Mn(III/II)(tpp) couple was not quite influenced by adding Br$^-$ ions see Figs. 2 and 3. Thus, we infer that the coordination of Cl$^-$ or Br$^-$ anion to the manganese ion in [Mn(V)-(tpp)=O]$^+$ cation was easy compared with that of 1-MeIm because of an additive electrostatic interaction, and this promoted the oxygen transfer (Eq. (14)) from [Mn(V)(tpp)=O]$^+$ to cyclohexene. However, since the reaction (14) competed with the consuming reaction (13) of Mn(V)-oxo complex by zinc powder as a reductant, the Zn-utilizing efficiency was about 40%.

$$[Mn(V)(tpp)=O]^+ + \text{cyclohexene}$$

$$\rightarrow [Mn(III)(tpp)]^+ + \text{epoxide} \qquad (14)$$
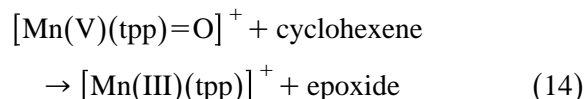
On the other hand, since 1-MeIm probably coordinated to [Mn(V)(tpp)=O)]$^+$ only at higher [1-MeIm], a large amount of 1-MeIm may be necessary for the reaction (14). However, since the reduction (Eq. (1)) from [Mn(III)(tpp)]$^+$ to

Mn(II)(tpp) became difficult by adding a large amount of 1-MeIm (see Fig. 3), it is predicted that the epoxide is not obtained at higher [1-MeIm]. Nevertheless, the epoxide was produced at higher [1-MeIm] (see the region III in Fig. 1a). This is reasonably explained by assuming that the addition of a large amount of 1-MeIm not only proceeds the reaction (14) but also leads the increase of the reducing power of zinc (by a complex formation between Zn^{2+} ions and 1-MeIm) proceeding the direct reduction (Eq. (1)) of [Mn(III)(tpp)]$^+$ to Mn(II)(tpp) with zinc. Further, since HV^{2+} mediated the electron transfer (Eq. (9)) from zinc to Mn(II)(tpp)–O$_2$ adduct in the region III of Fig. 1b, a larger amount of epoxide was produced compared with in the absence of HV^{2+} in the region III of Fig. 1a.

In conclusion, (i) the hexylviologen acted effectively as the mediator of electron transfer from zinc powder to Mn(II)(tpp)–O$_2$ adduct, (ii) since the halogen ion can coordinate easily to the manganese ion in [Mn(V)(tpp)=O]$^+$ cation due to an additive electrostatic interaction, the oxygen transfer (Eq. (14)) proceeded by the assistance of its coordinate bond. Thus, when HV^{2+} was added in the catalytic system
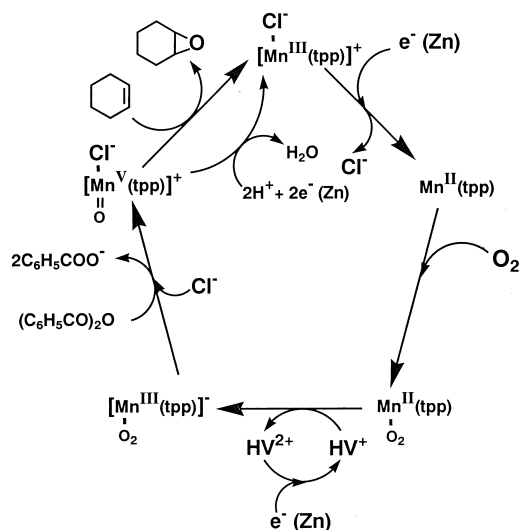
Scheme 1. Catalytic epoxidation cycle of cyclohexene using Mn(tpp)Cl as catalyst in the absence of 1-MeIm.

using the Mn porphyrin catalyst with the Cl^- counter ion, the dioxygen-activated reductive epoxidation of cyclohexene occurred even in the absence of 1-MeIm. The catalytic epoxidation cycle proposed by this study is summarized in Scheme 1. The decrease of the epoxide production with increasing [1-MeIm] in the regions I and II of Fig. 1b may be explained from the factor that the coordination of 1-MeIm to Mn(II)(tpp) depressed the formation of the Mn(II)(tpp)–O_2 adduct. Further, the epoxide was obtained by adding a large amount of 1-MeIm in the region III of Fig. 1a and b because the reducing power of Zn may become strong by a complex formation between Zn^{2+} and 1-MeIm.

Acknowledgements

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