

Catalytic epoxidation of cyclohexene by covalently linked manganese porphyrin–viologen complex

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Received 24 June 1997; accepted 26 September 1997

Abstract

When a viologen-linked Mn(III)porphyrin complex with a short methylene-chain, in which a viologen is covalently linked by the methylene-chain into one phenyl group of 5,10,15,20-tetraphenylporphyrinatomanganese(III)chloride (Mn(III)(tpp)Cl), was used as a catalyst for a monooxygenation of cyclohexene in an air-equilibrated acetonitrile solution containing insoluble zinc powder as a reductant, more cyclohexene oxide was obtained as a single product than when Mn(tpp)Cl was used as a catalyst. Benzoic acid as a cleaving reagent of the dioxygen double-bond and 1-methylimidazole as a ligand to Mn porphyrin were further contained in the reaction mixture. This result implies that the viologen moiety in the viologen-linked Mn(III)porphyrin acted effectively as a mediator for electron transfer from zinc powder to the Mn(III)porphyrin moiety in the epoxidation cycle activating molecular dioxygen reductively. Though Mn(tpp)Cl was remarkably demetallated by H⁺ ion from benzoic acid during the epoxidation reaction in the mixed system of Mn(III)(tpp)Cl and viologen, the demetallation of the viologen-linked Mn porphyrin with the short methylene-chain was partly prevented because the reduction of a Mn(II)porphyrin-dioxygen adduct was easily caused by fast intramolecular electron-transfer between the two moieties of the viologen and the Mn porphyrin, proceeding the epoxidation cycle smoothly. © 1998 Elsevier Science B.V.

Keywords: Manganese porphyrin; Epoxidation; Cytochrome P-450 model reaction; Intramolecular electron-transfer

1. Introduction

Many attempts have been carried out on the reductive activation of molecular dioxygen by a Mn(III)porphyrin or an Fe(III)porphyrin as the catalyst in order to elucidate the mechanism of the catalytic activation of cytochrome P-450 [1–38]. It is expected from their clarified reac-

tion mechanisms that the amount of the monooxygenation product such as epoxide increased by accelerating the reduction of the metal porphyrin. Tabushi et al. [33], Karasevich et al. [36] and Suzuki et al. [28] reported that colloidal Pt and the various mediators such as viologen were allowed to increase the oxidation rate, because these acted effectively as the electron-mediator from the reductant to the metal porphyrin in the several systems, for example,

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Fe(III)porphyrin-O₂-H₂-benzoic anhydride-cyclohexene-1-methylimidazole (1-MeIm) [33], Fe(III)porphyrin-O₂-Zn(Hg)-acetic anhydride-hydrocarbon [36] and Mn(III)porphyrin-O₂-Zn-benzoic anhydride-cyclohexene-1-MeIm [28].

In this paper, in order to improve the catalytic ability of Mn porphyrin, we have investigated the epoxidation of cyclohexene using covalently linked Mn(III)porphyrin–viologen complexes, which have a viologen moiety as electron mediator, since their complexes were not used so far for catalytic epoxidation of olefin. A proton was added in our catalytic system since it is used to cleave the double-bond of dioxygen molecule *in vivo*. We wish to show how the length of the methylene-group linked between the viologen moiety and the Mn porphyrin moiety influences the epoxidation reaction. Furthermore, to clarify the role of the electron-mediator for the epoxidation reaction, the amount of the produced epoxide was measured in the mixed catalytic system of Mn porphyrin and mediator as a function of the redox potential of the mediator.

2. Experimental

5,10,15,20-tetraphenylporphyrinat manganese(III)chloride (Mn(III)(tpp)Cl) was synthesized and purified by literature methods [39,40]. Covalently linked manganese porphyrin–viologen complex (MnPC_xMV), where *x* indicates the number of the methylene-group, as shown in Fig. 1 was synthesized and purified by literature methods [40–42] (ex. anal. found for MnPC₂MV(C₅₇H₄₃N₆OMnClBr₂) (M.W.: 1076.3): C, 63.66; H, 4.05; N, 7.88%. Calcd.: C, 63.55; H, 3.90; N, 7.80%). Acetonitrile 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 N₂ atmosphere after dehydration by molecular sieves (3A). They were stored over molecular sieves (3A) in brown bottles, respectively. Benzoic

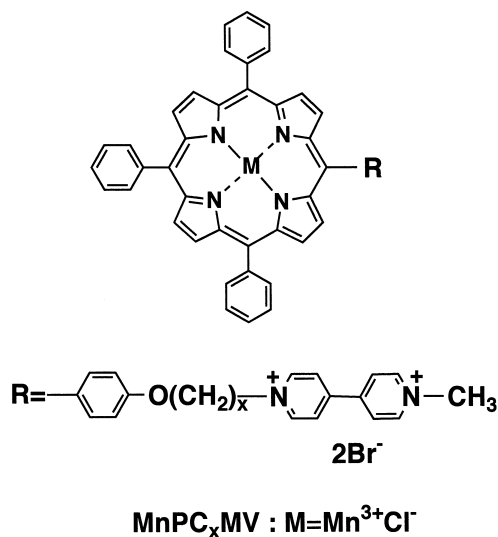


Fig. 1. Structure and abbreviation of covalently linked manganese(III)porphyrin–viologen.

acid was recrystallized from ethanol–water (1:4 by volume), benzoic anhydride was recrystallized from ethanol–water (1:4 by volume) after removal of the contained acid by washing with aqueous sodium hydrogencarbonate and they were dried *in vacuo* at room temperature. Synthesis and purification of the electron mediators, methylviologen (MV²⁺), hexylviologen (HV²⁺), benzylviologen (BV²⁺), 6,7-dihydrodipyrido[1,2-a:2,1-c]pyrazinium (DQ²⁺), 7,8-dihydro-6H-dipyrido[1,2-a:2,1-c][1,4]diazepinium (PDQ²⁺), methylene blue (MB), brilliant crezol blue (BCB) and safranin-T (S-T), were described in a previous paper [28].

The epoxidation reaction was carried out as follows. The air-equilibrated acetonitrile suspension containing soluble Mn porphyrin, insoluble zinc powder, soluble benzoic acid, soluble electron mediator, and soluble cyclohexene was stirred at a constant rate with a magnetic stirrer at 30°C. The quantitative analysis and identification of the oxidation product of cyclohexene were performed by a Shimadzu GC-8A gas chromatograph with a silicon DC 550 column. After a reaction time, the acetonitrile suspension was filtered through a sintered-glass filter, the unreacted zinc powder on the filter was dis-

solved by hydrochloric acid and the amount was determined by EDTA titration for the estimation of the zinc-utilizing-efficiency. The concentration of Mn porphyrin was estimated from the peak absorbance of Mn(III)porphyrin at 477 nm by a JASCO Ubest-30 UV/VIS spectrophotometer. Cyclic voltammetry was performed in acetonitrile using a glassy carbon disk as the working electrode, a Pt coil as the counter electrode and Ag/0.1 M AgNO₃ (1 M = 1 mol dm⁻³) in acetonitrile solution as the reference electrode at 25°C. Tetrabutylammonium perchlorate (Bu₄NClO₄) was used as the supporting electrolyte. Potential control was carried out by 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 measured 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

According to the reaction of an air-equilibrated acetonitrile suspension containing 1×10^{-4} M Mn(tp)Cl, 5×10^{-3} M 1-MeIm, 7.3×10^{-2} M zinc powder, 2×10^{-2} M benzoic acid and 0.47 M cyclohexene for 3 h at 30°C, about 1×10^{-3} M cyclohexene oxide (epoxide) was obtained as the single oxidation product of cyclohexene. Since the turnover number of Mn(tp)Cl was about 10, it was found that Mn(tp)Cl acted as catalyst. Further, when 1×10^{-4} M MnPC₂MV or the mixture of 1×10^{-4} M Mn(tp)Cl and 1×10^{-4} M MV²⁺ (Mn(tp)Cl + MV²⁺) was used as the catalyst, the amount of the produced epoxide remarkably increased and the turnover number reached about 40 for 3 h. The time-dependence of the amount of the produced epoxide is shown in Fig. 2. This suggests that the viologen and the viologen moiety in MnPC₂MV acted as the mediator for

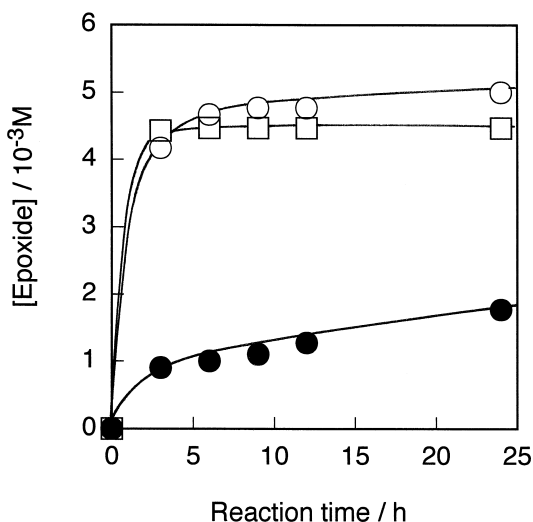


Fig. 2. Time-dependence of the amount of produced epoxide in air-equilibrated acetonitrile suspension containing 1×10^{-4} M Mn porphyrin, 5×10^{-3} M 1-MeIm, 7.3×10^{-2} M zinc powder, 2×10^{-2} M benzoic acid and 0.47 M cyclohexene at 30°C. Catalyst: Mn(tp)Cl (●), MnPC₂MV (○) and Mn(tp)Cl + 1×10^{-4} M MV²⁺ (□).

the electron transfer from zinc powder to Mn porphyrin [28]. Though the amount of produced epoxide saturated above the reaction time of 3 h, the extra epoxide was produced by adding benzoic acid to this reaction mixture. No oxidation product was obtained when either of molecular dioxygen, zinc powder or benzoic acid was lacking. The zinc-utilizing-efficiency could not be determined when benzoic acid was used as a proton source to cleave the dioxygen double-bond because zinc ions (dissolved by ionization of zinc due to the reduction of viologen, Mn(tp)Cl and proton) precipitated as white zinc hydroxide (Zn(OH)₂) on the surface of zinc powder. Hence, the zinc-utilizing-efficiency was determined when benzoic anhydride was used as the cleaving reagent [28]. When Mn(tp)Cl + MV²⁺ and MnPC₂MV were used as the catalyst, the zinc-utilizing-efficiency (assumed that one mole of epoxide is ideally obtained by consuming one mole of zinc) were 44 and 40%, respectively. (Reaction conditions were as follows: 1×10^{-4} M Mn(tp)Cl + 1×10^{-4} M MV²⁺ or 1×10^{-4} M MnPC₂MV,

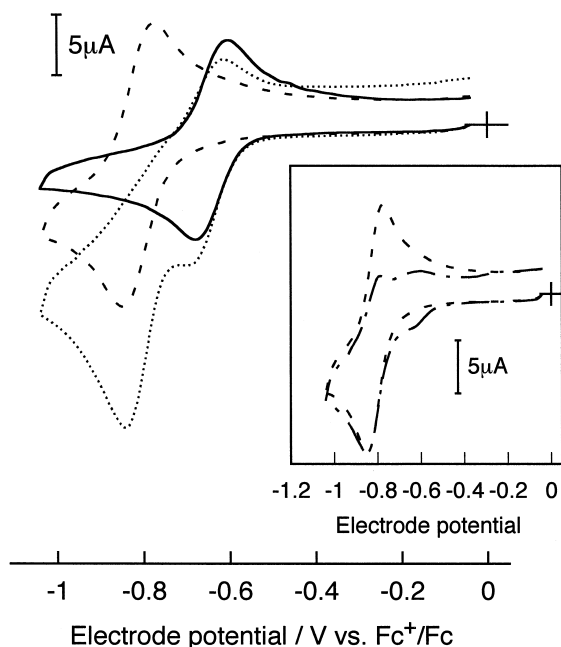
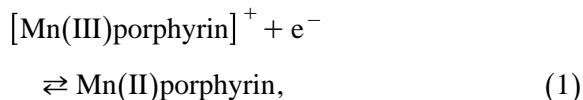


Fig. 3. Cyclic voltammograms of 5×10^{-4} M Mn(tp)Cl (—), 5×10^{-4} M MV^{2+} (---) and 5×10^{-4} M Mn(tp)Cl + 5×10^{-4} M MV^{2+} (· · ·) in N_2 -purged acetonitrile solution containing 0.1 M Bu_4NClO_4 and 1×10^{-2} M 1-MeIm. Scan rate: 100 mV s^{-1} , working electrode: glassy carbon disk with 0.07 cm^2 area. The inset indicates the cyclic voltammograms of 7×10^{-5} M Mn(tp)Cl + 5×10^{-4} M MV^{2+} (---) and 5×10^{-4} M MV^{2+} (· · ·).

7.3×10^{-2} M zinc powder, 4.2×10^{-2} M benzoic anhydride and 0.47 M cyclohexene, reaction temperature: 30°C , reaction time: 12 h. Under this condition, the epoxide was hardly produced and zinc was hardly consumed in the absence of viologen.)

Cyclic voltammetry was carried out for Mn(tp)Cl, MV^{2+} and Mn(tp)Cl + MV^{2+} in the N_2 -purged acetonitrile solution in order to clarify the role of the mediator for this epoxidation cycle. As shown in Fig. 3, Mn(tp)Cl and MV^{2+} showed half-wave potentials ($E_{1/2}$) of -0.64 V (Mn(III/II)(tp)) and -0.81 V (MV^{2+}/MV^+), respectively. Since the difference of cathodic and anodic peak-potentials of the redox wave was 100 mV for Mn(III/II)(tp) and 70 mV for MV^{2+}/MV^+ , the redox property of viologen was more reversible than that of Mn(III/II)porphyrin. Further, the diffusion

coefficients of MV^{2+} and Mn(III)(tp)Cl estimated from the dependence of their cathodic peak currents on scan rate of electrode potential were 7.3×10^{-6} and $2.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. For the equimolar mixed solution of Mn(tp)Cl + MV^{2+} , the reversible redox wave at -0.64 V of Mn(III/II)(tp) and the cathodic peak at -0.85 V assigned to the reduction of MV^{2+} were obtained, but the anodic peak assigned to the oxidation of MV^+ was hardly obtained. Even for the mixed solution of 5×10^{-4} M MV^{2+} and 7×10^{-5} M Mn(tp)Cl containing lower concentration of Mn(tp)Cl, the anodic peak of MV^+ became small compared to for the solution containing only 5×10^{-4} M MV^{2+} as shown in the insertion of Fig. 3. These imply that MV^+ was easily consumed by the intermolecular electron-transfer from MV^+ to Mn(III)(tp)Cl because of the faster electron-transfer and the faster diffusion of MV^+ . That is to say, methyl viologen can become the mediator for one-electron reduction,



of Mn(III)(tp)Cl, which is the first step of this epoxidation cycle [33–38].

Fig. 4 shows the cyclic voltammograms of MnPC_2MV and MnPC_6MV in the N_2 -purged acetonitrile solution. MnPC_6MV as well as MnPC_xMV s of $x = 4, 8, 10$ showed two cathodic peaks around -0.7 and -0.8 V and the shape of the voltammograms was similar to that for Mn(tp)Cl + MV^{2+} mixed solution even though the cathodic peak current around -0.8 V was small somewhat. Therefore the peaks around -0.7 and -0.8 V were assigned to the reduction waves of Mn(III)porphyrin and viologen moieties, respectively. In MnPC_2MV molecule, the redox potentials of Mn(III)(tp)Cl and viologen moieties became so closely probably because of the large electronic interaction between two moieties linked by short methylene-chain and eventually only one broad cathodic peak was observed around -0.75 V. The

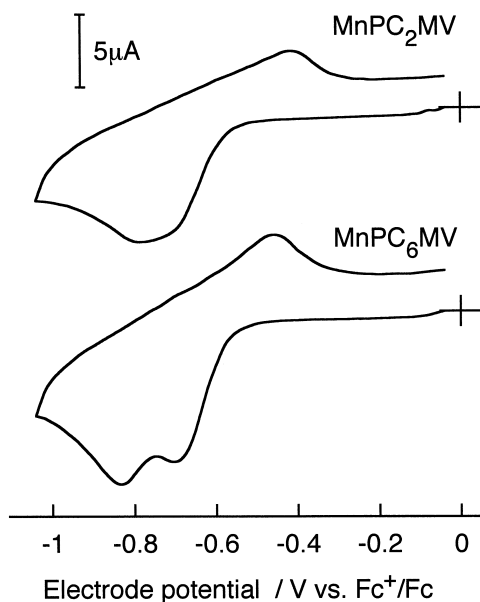
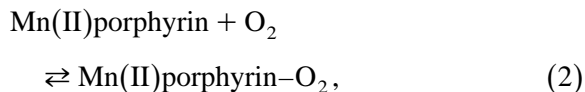


Fig. 4. Cyclic voltammograms of 5×10^{-4} M MnPC_xMV in N_2 -purged acetonitrile solution containing 0.1 M Bu_4NClO_4 and 1×10^{-2} M 1-MeIm. Scan rate: 100 mV s^{-1} , working electrode: glassy carbon disk with 0.07 cm^2 area.

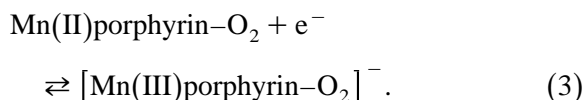
oxidation wave of the Mn(II)porphyrin appeared for all MnPC_xMV s, but the oxidation wave of the reduced form of the viologen moiety did not appear. This implies that the intramolecular electron transfer (Eq. (1)) from the viologen moiety to the Mn porphyrin moiety occurred.

The epoxidation reaction did not occur when neither molecular dioxygen nor benzoic acid is contained in this epoxidation system. Therefore, we have investigated the influence of molecular dioxygen and benzoic acid on the redox properties of $\text{Mn}(\text{tpp})\text{Cl}$ and MnPC_xMV and assigned their redox reactions to the redox reactions in our epoxidation reaction by the assistance of previously reported reaction mechanism in literature [33–38]. As shown in Fig. 5(a), $\text{Mn}(\text{tpp})\text{Cl}$ and MV^{2+} showed a pair of redox wave in the O_2 -saturated solution as well as in the N_2 -purged solution in the absence of benzoic acid. However, in the case of $\text{Mn}(\text{tpp})\text{Cl} + \text{MV}^{2+}$ and MnPC_4MV in the O_2 -saturated solution as shown in Fig. 5(c), the anodic peak of Mn(II)porphyrin disappeared contrary to the

cyclic voltammograms in the N_2 -purged solution (see Figs. 3 and 4). This suggests that Mn(II)porphyrin formed the adduct with molecular dioxygen,

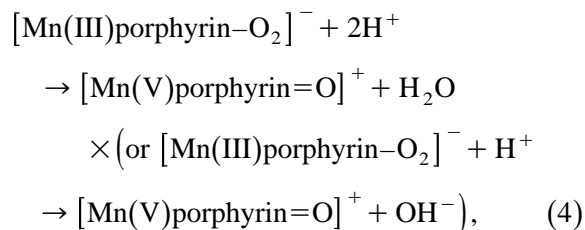


and that its adduct was reduced further,



Creager et al. [38] reported that, for $\text{Mn(III)(tpp)(benzoate)}$ with benzoate ion as counter ion, the electron-transfer reaction in Eq. (3) occurred at the more positive potential by about 0.23 V than the electron-transfer reaction in Eq. (1) in dichloromethane. That is, MV^{2+} and the viologen moiety in MnPC_4MV can become the electron-mediator for the reduction in Eq. (3) of the Mn(II)porphyrin-dioxygen adduct as well as for reduction in Eq. (1) of Mn(III)porphyrin.

In a blank cyclic voltammogram of the O_2 -saturated system containing solely benzoic acid (Fig. 5b and d), the cathodic current flowed below about -0.8 V, where the reduction of molecular dioxygen was promoted by proton from benzoic acid [43]. However, in the case of $\text{Mn}(\text{tpp})\text{Cl} + \text{benzoic acid}$ (Fig. 5b), the relatively large cathodic current flowed below about -0.6 V. This potential corresponded to the reduction potential of Mn(III)(tpp)Cl and the cathodic current around -0.75 V reached about four-fold in comparison with that of $\text{Mn}(\text{tpp})\text{Cl}$ (Fig. 5a). This suggests that the proton promoted both the production of Mn(V)-oxo intermediate by the cleavage,



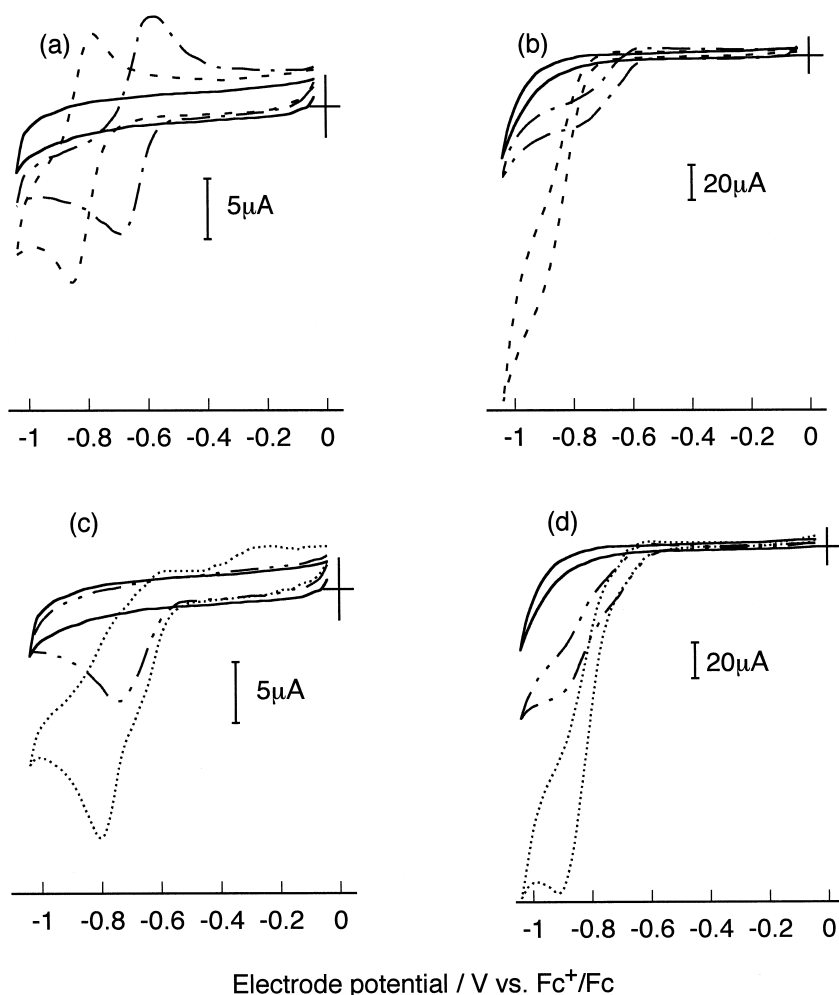
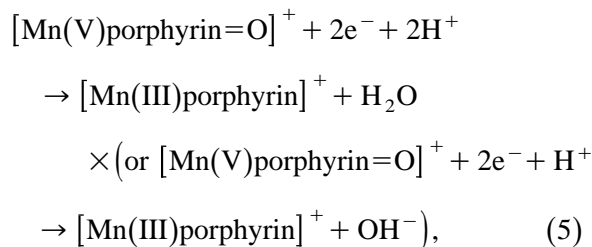


Fig. 5. Cyclic voltammograms of 5×10^{-4} M Mn(tp)Cl (— — —), 5×10^{-4} M MnPC₄MV (— · — · —), 5×10^{-4} M MV²⁺ (— · — · —) and 5×10^{-4} M Mn(tp)Cl + 5×10^{-4} M MV²⁺ (· · · · ·) in the absence of benzoic acid (a and c) and with 0.02 M benzoic acid (b and d) in O₂-saturated acetonitrile solution containing 0.1 M Bu₄NClO₄ and 1×10^{-2} M 1-MeIm. Solid line indicates CV for the O₂-saturated solution containing 0.1 M Bu₄NClO₄ (a and c) and 0.02 M benzoic acid + 0.1 M Bu₄NClO₄ (b and d). Scan rate: 100 mV s^{-1} , working electrode: glassy carbon disk with 0.07 cm^2 area.

of the dioxygen double-bond and the regeneration of [Mn(III)porphyrin]⁺ by its reduction,



which occurred successively after reduction (Eq. (3)) of the Mn(II)(tp)-dioxygen adduct.

The Mn(V)-oxo compound in Eq. (5) is a very important intermediate in the epoxidation cycle [33–38], that is, when its intermediate is produced in the solution containing cyclohexene, the epoxide is produced. Further, as Gutierrez-Garnados et al. [24] reported by use of the rotating disk electrode that the molecular dioxygen did four electrons reduction in acetonitrile

containing Mn(tpp)Cl and benzoic anhydride, the three reductions, Eqs. (1), (3) and (5), which the total electron-transfer number is four may occur in the O₂-saturated solution containing Mn(tpp)Cl and benzoic acid.

In the cyclic voltammogram of MV²⁺ with 0.02 M benzoic acid (Fig. 5b), the anodic peak for MV⁺ disappeared and the cathodic current around -0.85 V reached about five-fold in comparison with that in the absence of benzoic

acid (Fig. 5a). The reduction of dioxygen proceeded easily when both MV⁺ and benzoic acid existed [44]. On the other hand, the cathodic current of the Mn(III)(tpp)Cl + MV²⁺ + benzoic acid system (Fig. 5d) flowed from more positive potential than that of the MV²⁺ + benzoic acid system (Fig. 5b) and the cathodic current around -0.9 V reached about four-fold compared to the Mn(III)(tpp)Cl + benzoic acid system (Fig. 5b). In MnPC₄MV in the presence of benzoic

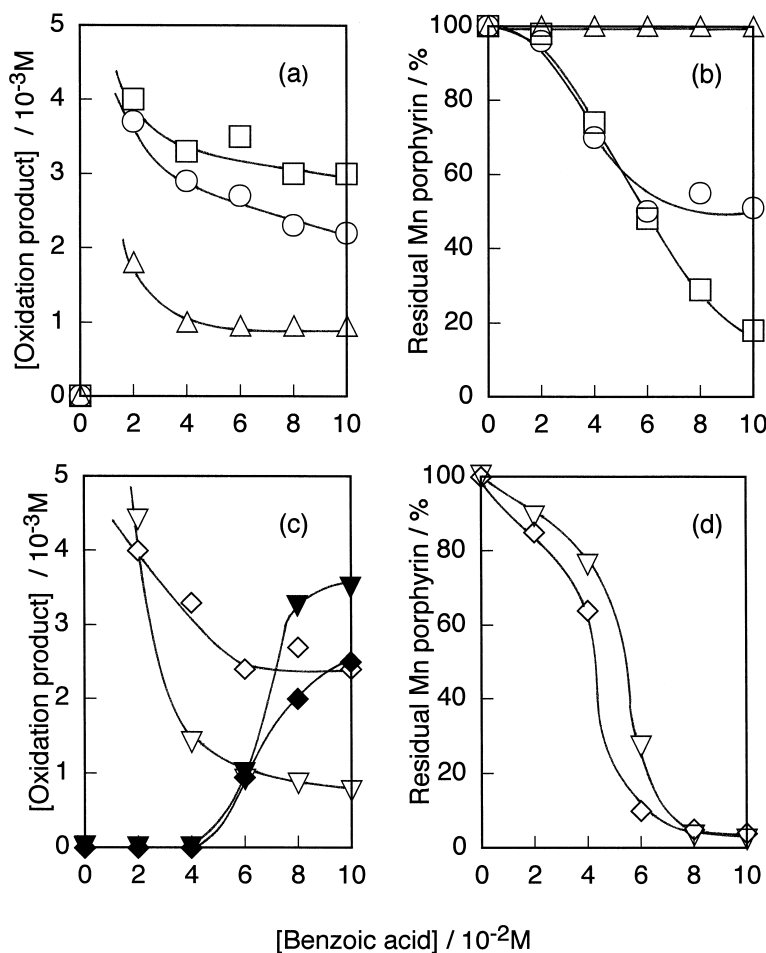


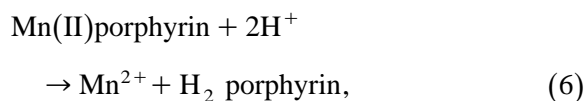
Fig. 6. Effect of the addition of benzoic acid on the amount of the oxidation products (a and c) and on the residual Mn porphyrin (b and d) in air-equilibrated acetonitrile suspension containing 1×10^{-4} M Mn porphyrin, 5×10^{-3} M 1-Melm, 7.3×10^{-2} M zinc powder and 0.47 M cyclohexene at 30°C (reaction time: 12 h). The epoxide was obtained as the single oxidation product of cyclohexene using Mn(tpp)Cl, MnPC₂MV and MnPC₄MV below 0.1 M benzoic acid, but both epoxide and 1-ol were obtained using MnPC₆MV and Mn(tpp)Cl + MV²⁺ above 0.06 M benzoic acid. (a) Mn(tpp)Cl (Δ : epoxide), MnPC₂MV (\circ : epoxide) and MnPC₄MV (\square : epoxide). (b) Mn(tpp)Cl (Δ), MnPC₂MV (\circ) and MnPC₄MV (\square). (c) MnPC₆MV (\diamond : epoxide, \blacklozenge : 1-ol) and Mn(tpp)Cl + MV²⁺ (∇ : epoxide, \blacktriangledown : 1-ol). (d) MnPC₆MV (\diamond) and Mn(tpp)Cl + MV²⁺ (∇).

acid (Fig. 5d), the cathodic current at -0.75 V reached about four-fold in comparison with that in the absence of benzoic acid (Fig. 5c). These suggest that the reaction cycle of Eqs. (1)–(5) proceeded more smoothly in the Mn porphyrin + viologen + benzoic acid + O_2 system since the electron mediator such as MV^{2+} and viologen moiety in $MnPC_4MV$ promoted the electron-transfer reactions Eqs. (1) and (3). Eventually, these cyclic voltammetric results indicate that the epoxidation of olefine by the reductive activation of molecular dioxygen using Mn porphyrin catalyst can be promoted by the electron mediator such as methyl viologen and viologen moiety in $MnPC_xMV$.

It was investigated how the number of methylene chain linking two moieties of Mn porphyrin and viologen influenced the epoxidation reaction. Fig. 6(a) and (c) show the dependence of the amount of the oxidation product on the concentration of benzoic acid, [benzoic acid], in systems using $Mn(tpp)Cl$, $MnPC_xMV$ ($x = 2, 4, 6$), and $Mn(tpp)Cl + MV^{2+}$ as the catalyst. Because Mn(III)porphyrin partially disappeared and metal free porphyrin appeared by an exchange between Mn^{2+} ion in the reductively produced Mn(II)porphyrin and H^+ ion from benzoic acid, the molar ratio of Mn(III)porphyrin remaining after 12 h reaction to an initial Mn(III)porphyrin (residual Mn porphyrin) was also shown in Fig. 6(b) and (d). When $Mn(tpp)Cl$, $MnPC_2MV$ and $MnPC_4MV$ were used as the catalyst, the epoxide was the single oxidation product below 0.1 M of [benzoic acid] and the amount of the produced epoxide decreased with increasing [benzoic acid] as shown in Fig. 6(a). Since hydrogen which can not reduce the viologen or the Mn porphyrin without a catalyst such as Pt abundantly evolved from zinc powder with increasing [benzoic acid], the amount of the produced epoxide decreased. Further, the elimination of Mn^{2+} ion from Mn porphyrin for all Mn porphyrin–viologen systems was promoted with increasing [benzoic acid] as shown in Fig. 6(b) and (d). However, when $Mn(tpp)Cl$ was used as the catalyst, the

elimination was not observed though the amount of epoxide reduced by half compared with when viologen-linked Mn porphyrin was used. When $MnPC_6MV$ or $Mn(tpp)Cl + MV^{2+}$ was used as the catalyst, the amount of the produced epoxide decreased with increasing [benzoic acid] and the oxidation product changed from epoxide to the mixture of epoxide and 2-cyclohexene-1-ol (1-ol) as shown in Fig. 6(c). The similar results were also obtained by use of $MnPC_8MV$ and $MnPC_{10}MV$ (not illustrated). The ratio of 1-ol in the oxidation mixture increased with increasing [benzoic acid]. Even in the absence of Mn porphyrin, 1-ol (main product) and epoxide (by-product) were produced because the viologen acted as a catalyst of the oxidation. Further, as shown in Fig. 6(b) and (d), the residual Mn porphyrin remarkably decreased with increasing [benzoic acid] when $MnPC_6MV$ and $Mn(tpp)Cl + MV^{2+}$ were used compared with when $MnPC_2MV$ and $MnPC_4MV$ were used. Therefore, the reduction of molecular dioxygen by the reduced viologen moiety in H_2PC_xMV (produced by the elimination of Mn^{2+} ion) or by MV^+ in the mixed system was responsible for the production of 1-ol at higher [benzoic acid].

Eqs. (2)–(4) may compete with the elimination,



of Mn^{2+} ion from Mn(II)porphyrin by H^+ ion.

This elimination can be inhibited by accelerating the electron-transfer reaction in Eq. (3). In this epoxidation using viologen-linked $MnPC_xMV$, as the methylene-chain-length in $MnPC_xMV$ becomes short, the ratio of residual Mn porphyrin became large as shown in Fig. 6(b) and (d). That is to say, since the intramolecular electron-transfer reaction, Eq. (3), was enhanced with shorting the methylene-chain-length, the reaction in Eq. (6) was partially prevented. The fast intramolecular electron-transfer of electron acceptor-linked porphyrin with a short spacer was reported for a viologen-

linked Zn porphyrin [45–47] and a Flavin-linked Mn porphyrin [48].

In the system without mediator, the elimination of Mn^{2+} ion was hardly observed though the amount of produced epoxide was much less than that in the mediation system as shown in Fig. 6(a). This implies that since the reactions in Eqs. (2)–(4) occurred successively and immediately in the vicinity of zinc powder after the reduction (Eq. (1)) of Mn(III)(tpp)Cl caused by colliding with its zinc powder having strong reducing power, the elimination reaction, Eq. (6), was prevented. However, in the system containing the viologen, the reductions, Eqs. (1) and (3), of Mn porphyrin by the reduced viologen occurred preferentially rather than the direct reduction by zinc because of faster diffusion of MV^{2+} for the $\text{Mn(tpp)Cl} + \text{MV}^{2+}$ system and faster reduction of viologen moiety for the MnPC_xMV system. This caused the elimination reaction in Eq. (6). On the other hand, since the important Mn(V) porphyrin-oxo intermediate produced in the vicinity of zinc powder was easily reduced by its zinc (Eq. (5)), the amount of the produced epoxide considerably decreased. If we can construct a mediation system such that its intermediate keeps away from zinc powder and the demetallation of Mn porphyrin does not occur, a greater amount of produced epoxide and higher zinc-utilizing-efficiency would be expected.

The electron-transfer reaction should be governed by the reducing power of the electron mediator. The dependence of the amount of the oxidation product on the redox potential ($E_{1/2}$) of the electron mediator in $\text{Mn(tpp)Cl} + \text{mediator}$ systems is shown in Fig. 7. At relatively low concentration (1.0×10^{-2} M) of benzoic acid, the epoxide was obtained as the single oxidation product of cyclohexene independent of the $E_{1/2}$ value. The results indicate that the electron-transfer reactions, Eqs. (1) and (3), proceeded smoothly, preventing the demetallation of Mn(tpp)Cl . The amount of produced epoxide exhibited a maximum value by using MV^{2+} and HV^{2+} with the redox potential of

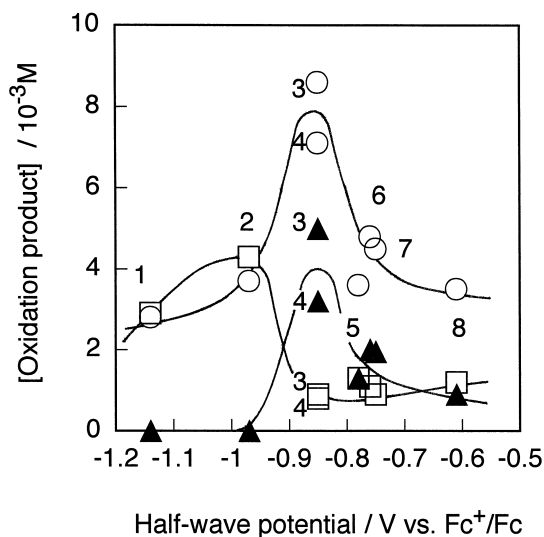


Fig. 7. Relation between the half-wave potential of electron mediator and the amount of the oxidation products in air-equilibrated acetonitrile suspension containing 1×10^{-4} M Mn(tpp)Cl , 5×10^{-3} M 1-MeIm, 1×10^{-4} M mediator, 7.3×10^{-2} M zinc powder and 0.47 M cyclohexene at 30°C (reaction time: 24 h). The epoxide (O) was obtained as the single oxidation product of cyclohexene with 1×10^{-2} M benzoic acid, but the epoxide (□) and 1-ol (▲) were obtained with 6×10^{-2} M benzoic acid. Electron mediator: (1) S-T, (2) PDQ^{2+} , (3) HV^{2+} , (4) MV^{2+} , (5) DQ^{2+} , (6) BV^{2+} , (7) MB and (8) BCB.

–0.85 V. At a relatively high concentration (6×10^{-2} M) of benzoic acid, the epoxide was obtained as the single oxidation product only when the mediator with an $E_{1/2}$ value below –0.9 V was used. However, both epoxide and 1-ol were obtained using the mediator with an $E_{1/2}$ value above –0.9 V and H_2tpp appeared by the demetallation of Mn porphyrin. This indicates that the electron-transfer reaction, Eq. (3), preferentially proceeded only when the mediator has strong reducing power, depressing the elimination reaction, Eq. (6). In contrast, in the system containing the electron mediator which has a more positive $E_{1/2}$ than –0.9 V, the elimination reaction, Eq. (6), preferentially proceeded rather than the electron-transfer reaction, Eq. (3). Then, the oxidation of cyclohexene was caused by the electron-mediator remaining in the system.

In conclusion, when MnPC_xMV is used as the catalyst, zinc powder as the reductant, ben-

zoic acid as the cleaving reagent of dioxygen double-bond and molecular dioxygen as the oxygen atom source, cyclohexene oxide and 2-cyclohexene-1-ol were obtained as the oxidation products of cyclohexene, in which the viologen moiety in MnPC_xMV and $\text{H}_2\text{PC}_x\text{MV}$ formed by the demetallation of MnPC_xMV acted as the electron mediator and/or the oxidation catalyst. In the system containing MnPC_2MV with a short methylene-chain, particularly, the elimination of Mn^{2+} ion from Mn(II)porphyrin by H^+ ion from benzoic acid was partly prevented because of the fast intramolecular electron-transfer from viologen moiety to O_2 adduct of Mn(II)porphyrin moiety and eventually the epoxide was obtained as single oxidation product of cyclohexene since the viologen moiety acted effectively as the electron mediator. Furthermore, in the mixed catalytic system of Mn(tpp)Cl and mediator, the epoxide was more preferentially produced when the mediator had a lower redox potential, because the intermolecular electron-transfer from the reduced form of the mediator to the Mn porphyrin occurred rapidly.

Acknowledgements

We thank Dr. Kazuhiko Murata (Nippon Shokubai Co., Japan) for his helpful suggestion and discussion.

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