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Electrocatalytic Epoxidation of Cyclohexene by Manganese(III) Porphyrin Using Electron Mediator

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For an electrocatalytic oxidation of cyclohexene in an air-equilibrated acetonitrile solution containing (5,10,15,20-tetraphenylporphyrinato)manganese(III) as a catalyst, benzoic anhydride as an acylating reagent and 1-methylimidazole as a ligand to Mn porphyrin, the addition of the compounds such as Methylene Blue, Safranine-T, and viologens promotes the production of cyclohexene oxide. The result implies that these compounds act effectively as mediators for the electron transfer from electrode to Mn porphyrin because they have more negative reduction potential than Mn porphyrin. The faradaic efficiency reaches about 100% by the use of benzylviologen under an optimum condition. But, in the presence of methylene blue, the maximum faradaic efficiency gives low values of about 30%. On the other hand, cyclohexene oxide is also produced by the use of zinc powder as a reductant, but the utilization efficiency of zinc gives relatively low values of 30—40% regardless of the kind of the mediator. This result is ascribed to the irreversible reduction of the mediator and the direct reaction of oxomanganese complex, which is an intermediate in this epoxidation reaction, with zinc powder.

Because of elucidating the mechanism of the catalytic activation of cytochrome P-450, many attempts have been carried out by the use of Mn and Fe porphyrins as model complexes,[1—5] and the mechanism of the hydroxidation of alkane has been proposed. However, in the systems that molecular dioxygen is used as an oxygen source, the utilization efficiency of the reductant is usually low because of the direct reaction between the excessive reductant and a oxometalloporphyrin complex, which is an intermediate of this catalytic cycle. Tabushi et al.[6] reported a small value of 0.057 as the ratio of the reaction rate between oxoiron complex and cyclohexene to that between oxoiron complex and the reductant in the system of Fe(III)porphyrin–O_2–[H_2–Pt/poly(1-vinyl-2-pyrrolidone)]–benzoic anhydride–cyclohexene–1-methylimidazole (1-MeIm). Battioni et al.[7] reported a value of 50% as the utilization efficiency of zinc for the production of cyclohexene oxide in the system of (5,10,15,20-tetraphenylporphyrinato)manganese(III) chloride(Mn^{III}(tpp)Cl)–O_2–Zn–acetic acid–cyclohexene–1-MeIm. On the other hand, the epoxidation reaction of olefin by using electrochemically reduced metalloporphyrin has been investigated too.[8—10] Creager et al.[8] reported the faradaic efficiency of 56% for the production of cyclooctene oxide in the system of Mn(tpp)Cl–O_2–benzoic anhydride–cyclooctene–1-MeIm. It was reported that the deviation from 100% for the faradaic efficiency was due to the electrochemical reduction of the oxo high-valent manganese complex.

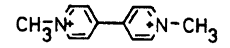
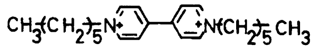
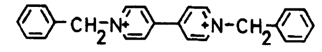
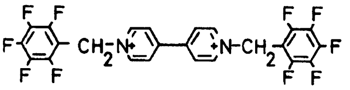
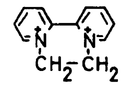
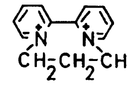
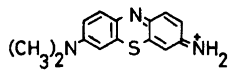
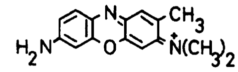
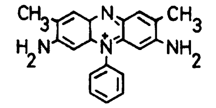
We reported previously that the epoxidation of cyclohexene easily occurred by the addition of the benzylviologen as the electron mediator into the system of Mn porphyrin–O_2–Zn–benzoic anhydride–1-MeIm.[11] In this study, we have confirmed the effectiveness of the various mediators, and further, by the electrocatalytic epoxidation, the role of the electron mediator has been investigated in detail.

Experimental

Synthesis and purification of (5,10,15,20-tetraphenylporphyrinato)manganese(III) chloride (Mn^{III}(tpp)Cl), (5,10,15,20-tetraphenylporphyrinato)manganese(III) perchlorate ($Mn^{III}(tpp)ClO_4$), zinc powder, cyclohexene, 1-methylimidazole (1-MeIm), benzoic anhydride, and acetonitrile were described in previous paper.[11] Methylviologen dibromide ($MVBr_2$), hexylviologen dibromide ($HVBr_2$), benzylviologen dibromide ($BVBr_2$), and [(pentafluorophenyl)methyl] viologen dibromide ($FBVBr_2$) were prepared by refluxing 4,4′-bipyridyl with methyl bromide, hexyl bromide, benzyl bromide, and (pentafluorophenyl)methyl bromide in toluene of acetonitrile, respectively. 6,7-Dihydrodipyrido[1,2-*a*:2,1-*c*] pyrazinium dibromide ($DQBr_2$) and 7,8-dihydro-6*H*-dipyrido[1,2-*a*:2,1-*c*][1,4]diazepinium dibromide ($PDQBr_2$) were synthesized by the literature method.[12] The perchlorates of the above bromides were precipitated by the addition of concentrated perchloric acid into saturated aqueous solutions of the bromides. The perchlorates of Methylene Blue (MB), Brilliant Cresyl Blue (BCB), and Safranine-T (S-T) were also precipitated by the addition of sodium perchlorate aqueous solution into saturated aqueous solutions of these commercial reagents (MB and S-T: Nacarai, BCB: Chroma). All electron mediators were recrystallized and dried in vacuo. The structural formulas and reduction potentials (in acetonitrile) of the electron mediators are shown in Table 1.

The epoxidation reaction by the use of zinc powder as the reductant was carried out as follows. The air-equilibrated acetonitrile solution containing $Mn(tpp)ClO_4$, zinc powder, benzoic anhydride, 1-MeIm, electron mediator and cyclohexene was stirred at a constant rate with a magnetic stirrer at 30 °C. After 6 h, the acetonitrile solution was filtered through a sintered-glass filter. The amount of zinc powder consumed during the epoxidation reaction was estimated by quantitative analysis (EDTA titration[13]) of unreacted zinc powder on the filter. The electrocatalytic epoxidation reac-

Table 1. Structural Formulas and Half-Wave Potentials of Reduction[a] ($E_{1/2}$/V vs. Fc^+/Fc) of Electron Mediators in Acetonitrile at Room Temperature

Electron mediator	Structural formula	$E_{1/2}$
MV^{2+}		−0.85
HV^{2+}		−0.85
BV^{2+}		−0.76
FBV^{2+}		−0.68
DQ^{2+}		−0.78
PDQ^{2+}		−0.97
MB		−0.75
BCB		−0.61
S-T		−1.14[b]

a) Concentration of mediator: 1×10^{-3} M, Scan rate: 100 mV s^{-1}. b) Irreversible cathodic peak value.

Table 2. Amount of Produced Epoxide ($Q/10^{-3}$ M) and Utilization Efficiency of Zinc (E/%) in the Presence of Various Electron Mediators[a]

In the presence of Mn por.			In the absence of Mn por.	
Electron mediator	Q	E	Q	E
MV^{2+}	14.3	36	0.9	6
HV^{2+}	9.2	34	0.6	9
BV^{2+}	9.8	35	0.8	5
FBV^{2+}	2.8	29	0.6	5
DQ^{2+}	5.2	43	1.8	8
PDQ^{2+}	1.3	25	0.2	8
MB	10.5	30	n.d.[b]	—
BCB	8.8	31	n.d.	—
S-T	7.9	38	n.d.	—

a) Concentration of reactants in acetonitrile: 1.2×10^{-4} M Mn(tpp)ClO$_4$, 7.3×10^{-2} M Zn, 4.2×10^{-2} M benzoic anhydride, 5.9×10^{-3} M 1-MeIm, 0.47 M cyclohexene, 5×10^{-4} M mediator. reaction temperature: 30 °C, reaction time: 6 h. b) n.d.: not detected.

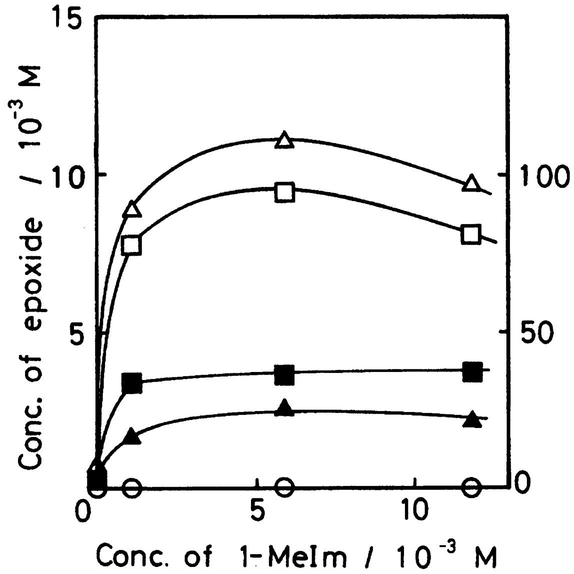


Fig. 1. Effect of BV^{2+} and MB on the amount of the produced epoxide (○,□,△) and the utilization efficiency of zinc (■,▲) in air-equilibrated acetonitrile solution containing 1.2×10^{-4} M Mn(tpp)ClO$_4$, 7.3×10^{-2} M zinc powder, 4.2×10^{-2} M benzoic anhydride and 0.47 M cyclohexene at 30 °C (reaction time: 6 h). Concentration of mediators: in the absence (○), 5.7×10^{-4} M BV^{2+} (□,■), 6.5×10^{-4} M MB (△,▲).

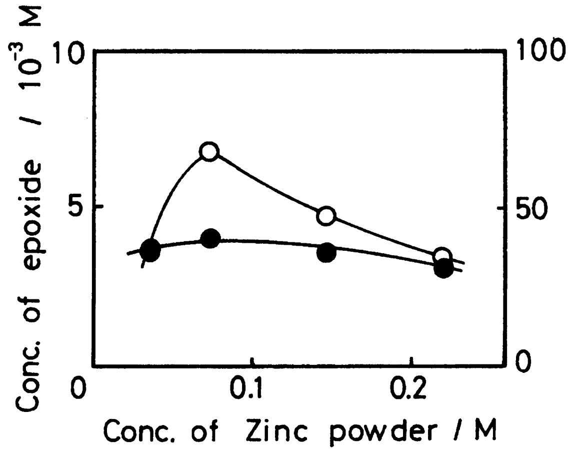


Fig. 2. Effect of the amount of zinc powder on the concentration of the produced epoxide (○) and the utilization efficiency of zinc (●) in air-equilibrated acetonitrile solution containing 6.2×10^{-4} M Mn(tpp)ClO$_4$, 4.2×10^{-2} M benzoic anhydride, 5.9×10^{-3} M 1-MeIm and 0.47 M cyclohexene at 30 °C (reaction time: 6 h).

tion was carried out by the use of H-type cell, in which cathodic and anodic chambers were separated by a fine-porosity sintered-glass filter. The air-equilibrated acetonitrile solution (20 cm^3) containing Mn(tpp)ClO$_4$, 0.04 M benzoic anhydride, 0.2 M cyclohexene, 1×10^{-3} M 1-MeIm, 0.1 M tetraethylammonium perchlorate (Et$_4$NClO$_4$), and benzylviologen (or Methylene Blue) was placed in the cathodic chamber, and the acetonitrile solution (20 cm^3) containing only 0.1 M Et$_4$NClO$_4$ was placed in the anodic chamber. A Pt net (13 cm^2), a Pt coil and Ag/0.1 M AgNO$_3$ (1 M=1 mol dm^{-3}) in acetonitrile were employed as a working elec-

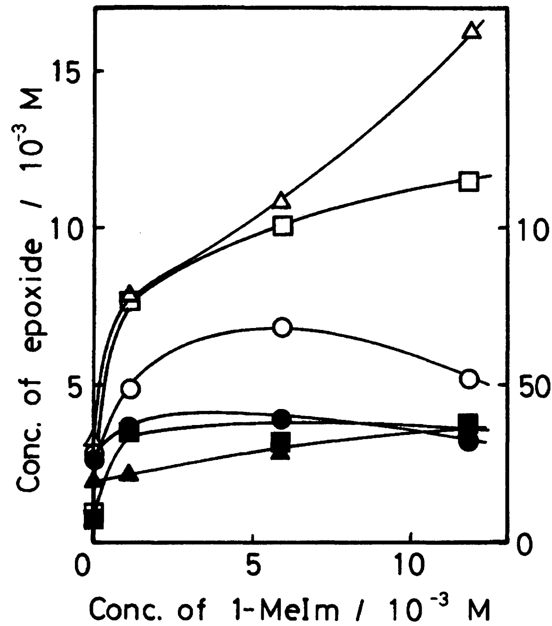


Fig. 3. Effect of BV^{2+} and MB on the amount of the produced epoxide (○,□,△) and the utilization efficiency of zinc (●,■,▲) in air-equilibrated acetonitrile solution containing 6.2×10^{-4} M Mn(tpp)ClO$_4$, 7.3×10^{-2} M zinc powder, 4.2×10^{-2} M benzoic anhydride and 0.47 M cyclohexene at 30 °C (reaction time: 6 h). Concentration of mediators: in the absence (●,○), 5.7×10^{-4} M BV^{2+} (□,■), 6.5×10^{-4} M MB (△,▲).

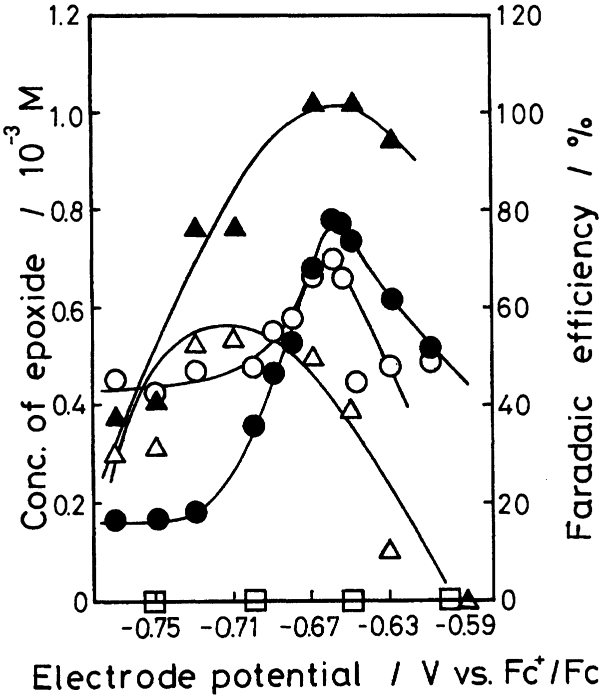


Fig. 4. Effect of the electrode potential on the amount of the produced epoxide (○,□,△) and the faradaic efficiency (●,▲) in air-equilibrated acetonitrile solution containing 1×10^{-3} M BV^{2+}, 4×10^{-2} M benzoic anhydride, 1×10^{-3} M 1-MeIm, 0.1 M Et$_4$NClO$_4$ and 0.2 M cyclohexene at room temperature (reaction time: 2 h). Concentration of Mn(tpp)ClO$_4$: in the absence (□), 2×10^{-5} M (△,▲), 5×10^{-4} M (○,●).

trode, a counter electrode and a reference electrode, respectively. Potential control was obtained by using a Hokuto Denko HA-301 potentiostat, the quantity of passed electricity was measured by using a Hokuto Denko HF-201 Coulomb meter. The electrolysis was carried out for 2 h at room temperature at a constant agitation rate with a magnetic stirrer. The quantitative analysis and the identification of the oxidation products were performed by Shimadzu GC-8A or a Yanako G2800 gas chromatography on a silicone DC 550 columm. Cyclic voltammetry was performed in an N$_2$-purged acetonitrile solution by using a Pt wire, a Pt coil and Ag/0.1 M AgNO$_3$ in acetonitrile, which were employed as a working electrode, a counter electrode and a reference electrode, respectively. Potential control was carried out by using a Hokuto Denko HA-301 potensiostat and Hokuto Denko HB-104 function generator. Cyclic voltammograms were recorded on a Rikadenki RW-21 X-Y recorder. Half-wave potentials were mesured as the average of cathodic and anodic peak potentials. The electrode potential and the half-wave ones were described on the basis of the half-wave potential of ferrocence/ferrocenium ion (Fc$^+$/Fc).

Results and Discussion

Effect of the Various Electron Mediators on the Epoxidation of Cyclohexene. At relatively low concentration (1.25×10^{-4} M) of Mn^{III}(tpp)ClO$_4$, no oxidation product of cyclohexene is obtained after the reaction for 6 h in the air-equilibrated acetonitrile solution containing zinc powder (7.2×10^{-2} M), benzoic anhydride (4.2×10^{-2} M), 1-MeIm (0—1.18×10^{-2} M), and cyclohexene (0.47 M). However, by the addition of the compound such as MB or BV^{2+} that has more negative reduction potential than Mn(tpp)ClO$_4$ (−0.66 V, in acetonitrile solution containing 1.2×10^{-2} M 1-MeIm), cyclohexene oxide (abb. to epoxide hereafter) is obtained as the only oxidation product of cyclohexene. The compounds that have various reduction potentials as shown in Table 1 are used as the electron mediator in this work. The results are shown in Table 2. Epoxide was produced particularly a large quantity by the addition of MV^{2+}, BV^{2+} or MB. Anyhow, it is found that these mediators act effectively for the electron transfer from zinc powder to Mn porphyrin. Further, no oxidation product is obtained in an N$_2$-purged condition or in the absence of zinc powder. This indicates that the production of epoxide is attributable to the reductive activation of molecular dioxygen. The turnover numbers of Mn porphyrin (mole ratio of [epoxide] to [Mn porphyrin]) and the mediator (mole ratio of [epoxide] to [mediator]) are 11—119 and 3—29, respectively. The utilization efficiencies of zinc, which are estimated on the assumption that one mole of the epoxide is obtained from one mole of the consumed zinc, are also listed in Fig. 1 and Table 2. The efficiency gives relatively low values of 30—40% regardless of the kind of

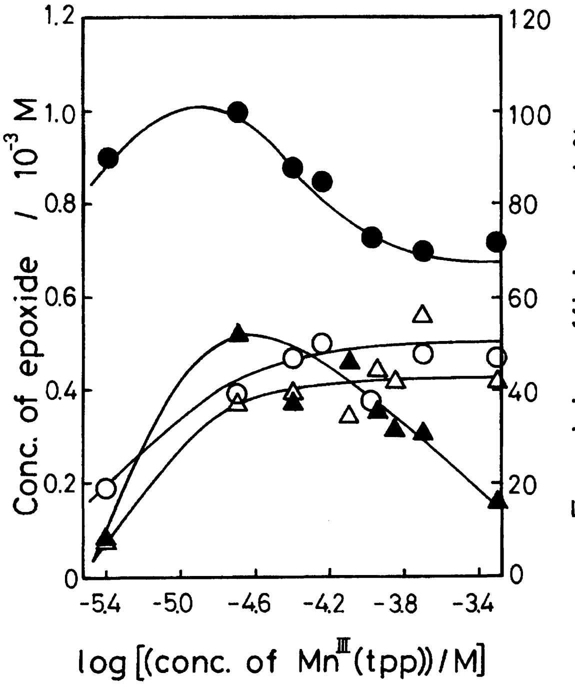


Fig. 5. Effect of the concentration of Mn(tpp)ClO$_4$ on the amount of the produced epoxide (○,△) and the faradaic efficiency (●,▲) in air-equilibrated acetonitrile solution containing 1×10^{-3} M BV^{2+}, 4×10^{-2} M benzoic anhydride, 1×10^{-3} M 1-MeIm, 0.1 M Et$_4$NClO$_4$ and 0.2 M cyclohexene at room temperature (reaction time: 2 h). Electrode potential: −0.65 V (○,●), −0.75 V (△,▲).

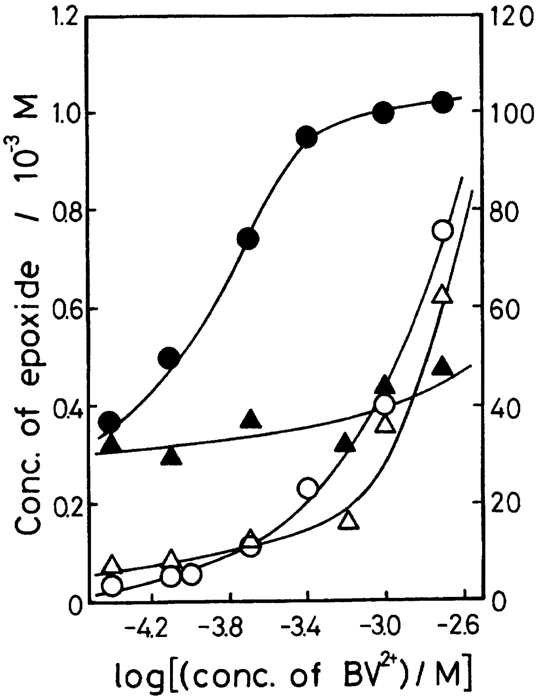


Fig. 6. Effect of the concentration of BV^{2+} on the amount of the produced epoxide (○,△) and the faradaic efficiency (●,▲) in air-equilibrated acetonitrile solution containing 2×10^{-5} M Mn(tpp)ClO$_4$, 4×10^{-2} M benzoic anhydride, 1×10^{-3} M 1-MeIm, 0.1 M Et$_4$NClO$_4$, and 0.2 M cyclohexene at room temperature (reaction time: 2 h). Electrode potential: −0.65 V (○,●), −0.75 V (△,▲).

the mediator.

Even in the absence of Mn porphyrin, when viologens are used, epoxide as main product and 2-cyclohexen-1-ol as by-product are obtained, but the utilization efficiency of zinc is low. No oxidation product is obtained in the absence of benzoic anhydride. On the other hand, when MB, S-T, and BCB are used, no oxidation product of cyclohexene is detected in the absence of Mn porphyrin, and the amount of the consumed zinc powder is very small. A characteristic blue color of MV$^{+\bullet}$and BV$^{+\bullet}$radical cations produced reductively by zinc powder readily changes to colorless in acetonitrile owing to the air-oxidation, while colorless species produced by one electron reduction of MB and BCB are not easily air-oxidized compared with viologen radical cations. It is assumed that the superoxide ion, which may be produced by the reaction of molecular dioxygen with viologen radical cations, and benzoic anhydride are responsible for the epoxidation reaction.[10] At relatively high concentration of 6.2×10^{-4} M Mn(tpp)ClO$_4$, the epoxide is produced even in the absence of the mediator, and the utilization efficiency of zinc gives 30—40%. The results are shown in Fig. 2. The amount of epoxide has a maximum at 7.3×10^{-2} M zinc powder, but the efficiency is nearly constant. The amount of the produced epoxide increases appreciably by the further addition of the mediator as shown in Fig. 3. But, the utilization efficiency of zinc changes hardly. In order to discuss this epoxidation reaction in more detail, the electrocatalytic epoxidation is further carried out.

Electrocatalytic Epoxidation Using BV^{2+} as the Electron Mediator. In the presence of 1×10^{-3} M BV^{2+}, the dependence of the amount of the produced epoxide and the faradaic efficiency on the electrode potential are shown in Fig. 4. No epoxide is produced in the absence of Mn porphyrin or BV^{2+} under these conditions. Also, the epoxide is obtained as the only oxidation product of cyclohexene at more negative potential than −0.61 V. When 1×10^{-3} M BV^{2+} acetonitrile solution is electrochemically reduced by the use of a working electrode (Pt) of wide area (13 cm^2), the characteristic blue color of BV$^{+\bullet}$radical cation is observed below the electrode potential of about −0.60 V that is the fairly positive potential compared with the half-wave potential of reduction of BV^{2+} (−0.76 V). Therefore, the epoxidation reaction proceeds at lower electrode potential than −0.61 V because of the electron transfer from BV$^{+\bullet}$ to Mn^{III}(tpp). It is particularly noteworthy that the faradaic efficiency of epoxidation reaches about 100% at the concentration of 2×10^{-5} M Mn^{III}(tpp)ClO$_4$ and the electrode potential of −0.65 V.

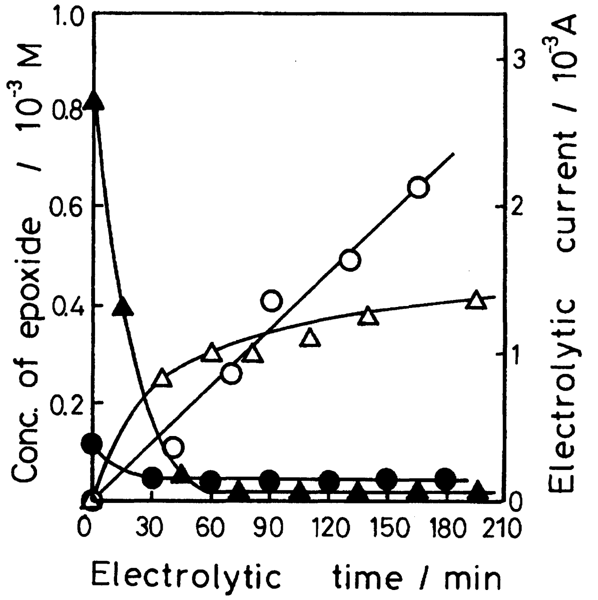


Fig. 7. Effect of the electrolytic time on the amount of the produced epoxide (○,△) and the electrolytic current (●,▲) in air-equilibrated acetonitrile solution containing 4×10^{-5} M $Mn(tpp)ClO_4$, 1×10^{-3} M BV^{2+}, 4×10^{-2} M benzoic anhydride, 1×10^{-3} M 1-MeIm, 0.1 M Et_4NClO_4, and 0.2 M cyclohexene at room temperature. Electrode potential: −0.65 V (○,●), −0.75 V (△,▲).

However, the faradaic efficiency decreases with lowering the electrode potential or increasing the concentration of $Mn^{III}(tpp)$.

The dependence of the amount of the produced epoxide and the faradaic efficiency on the concentration of Mn porphyrin at electrode pontentials of −0.65 V and −0.75 V are shown in Fig. 5. The amount of epoxide is nearly constant above 2×10^{-5} M Mn porphyrin at both potentials. The faradaic efficiency is higher at −0.65 V than −0.75 V, and decreases with increasing the concentration of Mn porphyrin at both potentials. The results imply that the direct reduction of oxomanganese complex by the electrode occurs appreciably.

The dependence of the amount of the produced epoxide and the faradaic efficiency on the concentration of BV^{2+} at electrode potentials of −0.65 and −0.75 V are shown in Fig. 6. The amount of epoxide is approximately same at both potentials, and increases with increasing the concentration of BV^{2+}. The faradaic efficiency increases with increasing the concentration of BV^{2+}, and reaches about 100% above the concentration at 4×10^{-4} M BV^{2+} at −0.65 V. However, at −0.75 V, the faradaic efficiency gives low values of 30—50%.

The time-dependence of the amount of the produced epoxide and the electrolytic current in the electrocatalytic epoxidation at constant electrode potentials of −0.65 and −0.75 V are shown in Fig. 7. At −0.65 V, the amount of epoxide linearly increases with the electrolytic time, and the electrolytic current is nearly constant. This indicates that BV^{2+} sufficiently functions as the electron mediator. At −0.75 V, the epoxide is produced more than at −0.65 V in the initial electrolysis, but the amount of epoxide does not so increase with the electrolytic time. Further, the large electrolytic current flows in the initial electrolysis, but the current suddenly decreases with promoting the electrolysis. When the acetonitrile solution containing only BV^{2+} is electrochemically reduced at −0.65 V for 2 h, the absorption spectra of the solution shows two peaks around 400 and 600 nm which are assigned to $BV^{+\bullet}$ radical cation. On the other hand, in the case of the electrolysis at −0.75 V, a new absorption peak around 470 nm appears with the elapse of the electrolytic time, and the peaks of $BV^{+\bullet}$ disappear completely after 2 h. The species produced in this way, does not revert to BV^{2+} even when air is bubbled into that solution, and, in addition, shows in the cyclic voltammogram only one reversible wave whose half-wave potential is −1.31 V. The result indicates that benzylviologen decomposes because of the additional reduction of $BV^{+\bullet}$ at lower electrode potential. Therefore, the faradaic efficiency of the epoxide production is small at −0.75 V.

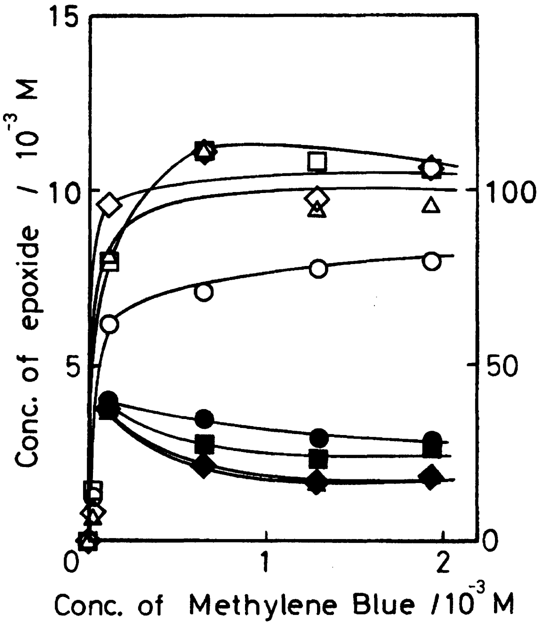


Fig. 8. Effect of the concentrations of MB and zinc on the amount of the produced epoxide (○,□,△,◇) and the utilization efficiency of zinc (●,■,▲,◆) in air-equilibrated acetonitrile solution containing 1.2×10^{-4} M $Mn(tpp)ClO_4$, 5.9×10^{-3} M 1-MeIm, 4.2×10^{-2} M benzoic anhydride, and 0.47 M cyclohexene at 30 °C (reaction time: 6 h). Concentration of zinc powder: 3.6×10^{-2} M (○,●), 7.3×10^{-2} M (□,■), 1.5×10^{-1} M (△,▲), 2.2×10^{-1} M (◇,◆).

Epoxidation of Cyclohexene Using MB as the Electron Mediator. The dependence of the amount of the produced epoxide and the utilization efficiency of zinc on the concentration of MB are shown in Fig. 8,

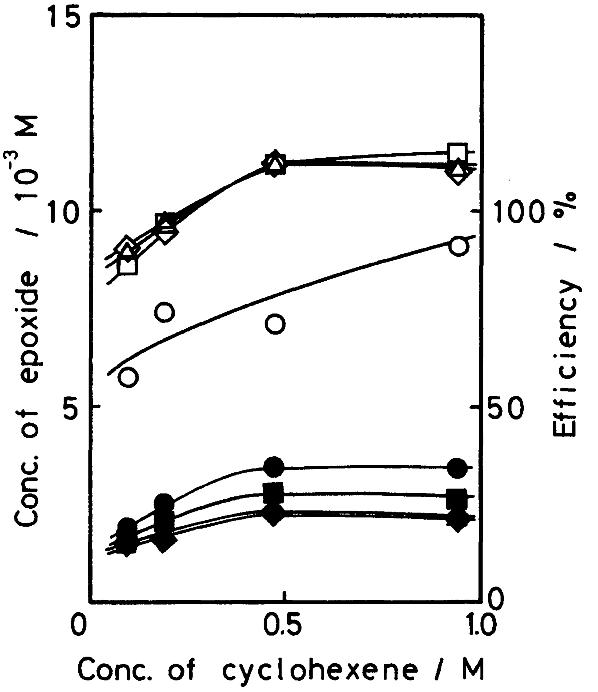


Fig. 9. Effect of the concentrations of cyclohexene and zinc on the amount of the produced epoxide (○,□,△,◇) and the utilization efficiency of zinc (●,■,▲,◆) in air-equilibrated acetonitrile solution containing 1.2×10^{-4} M Mn(tpp)ClO$_4$, 5.9×10^{-3} M 1-MeIm, 6.5×10^{-4} M MB, and 4.2×10^{-2} M benzoic anhydride at 30 °C (reaction time: 6 h). Concentration of zinc powder: 3.6×10^{-2} M (○,●), 7.3×10^{-2} M (□,■), 1.5×10^{-1} M (△,▲), 2.2×10^{-1} M (◇,◆).

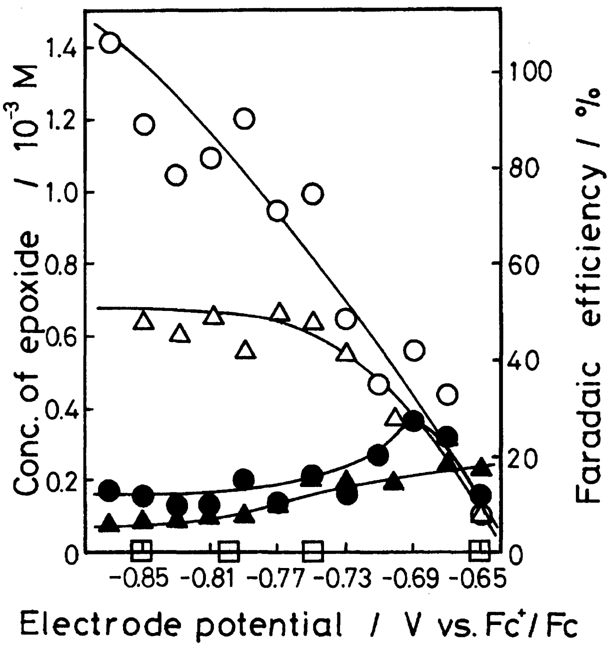


Fig. 10. Effect of the electrode potential on the amount of the produced epoxide (□,○,△) and the faradaic efficiency (●,▲) in air-equilibrated acetonitrile solution containing 1×10^{-3} M MB, 4×10^{-2} M benzoic anhydride, 1×10^{-3} M 1-MeIm, 0.1 M Et$_4$NClO$_4$, and 0.2 M cyclohexene at room temperature (reaction time: 2 h). Concentration of Mn(tpp)ClO$_4$: In the absence (□), 2×10^{-4} M (△,▲), 5×10^{-4} M (○,●).

when zinc powder is used as the reductant. The amount of epoxide is nearly constant above 1×10^{-4} M MB. On the other hand, the efficiency decreases with increasing the concentration of MB or zinc powder. That may be due to the increase of the air-oxidation of reduced MB or the direct reduction of oxomanganese complex with zinc powder. Figure 9 shows the dependence of the amount of epoxide and the efficiency on the concentration of cyclohexene. Both quantities increase until the concentration of cyclohexene reaches 0.47 M, and approximately saturate above 0.47 M. The results suggest that the oxomanganese complex competitively reacts with zinc powder and cyclohexene. In order to discuss in detail, the effect of the electrode potential on the faradaic efficiency is investigated below.

The dependence of the amount of the produced epoxide and the faradaic efficiency on the electrode potential are shown in Fig. 10. The epoxide is obtained as the only product by using MB as the electron mediator and at the lower electrode potential than −0.65 V. The amount of epoxide monotonously increases with decreasing the electrode potential, and the maximum faradaic efficiency is about 30%. The potential-profile is particularly different from in the case of BV^{2+}, and the efficiency is low. Also, the decrease of the faradaic efficiency is observed with lowering the electrode potential and increasing the concentration of MB. From the dependence of the amount of the produced epoxide on the electrolytic time and the measurement of the absorption spectra of MB before and after the electrolysis, it is found that MB sufficiently operates as the electron mediator during the electrocatalytic epoxidation. In addition, the electron transfer from the reduced MB to Mn porphyrin may be slower than that from BV$^{+\bullet}$ to Mn porphyrin because the onset potential for the epoxide production is more negative in the system containing MB than BV^{2+} in spite of the same redox potential of the two electron mediators (Figs. 4 and 10). This may be responsible for the lower faradaic efficiency of the electrolytic epoxidation.

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