Oxidation of Sulfides with Electrocatalytic P-450 Model System

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Controlled potential electrolysis (CPE) of *meso*-tetraphenylporphyrinatomanganese (III) chloride (1 mM, 1a) at −0.4 V (*vs.* saturated calomel electrode (SCE)) in acetonitrile containing diphenyl sulfide (100 mM, 2), 1-methylimidazole (5 mM), and tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte with a reticulated vitreous carbon (RVC) cathode and bubbling O_2 gas, gave diphenylsulfoxide (12.6%—16.4%, 3) and diphenylsulfone (0.5%—1.5%, 4) in the presence of acetic acid/or tetramethylammonium hydroxide (5). In the absence of acetic acid or 5, compound 2 was not oxidized. The results of cyclic voltammetry and CPE at −0.4 V (*vs.* SCE) showed that the oxidant of 2 was an oxo-manganese (V) species which was generated from 1a and dissolved dioxygen by two-electron transfer and that the presence of H^+ was essential not only to cleave the O–O bond in the peroxo-manganese species, but also to transfer the second electron. This catalytic cycle is similar to that of P-450. The current efficiency was 79.1%.

CPE of dissolved O_2 was carried out at −1.0 V in acetonitrile and superoxide ion was detected by use of an electron spin resonance spectrometer in the frozen electrolyzed solution. Addition of potassium superoxide to acetonitrile containing 1a, 1-methylimidazole and 2 gave 3 (15.6%—26.7%) and 4 (0%—2.7%) in the presence of acetic acid or 5. A similar procedure in the absence of the acid or 5 did not give 3 or 4.

When the applied potential was −1.0 V, superoxide ion generated by cathodic reduction of dissolved oxygen in the electrolytic solution containing acetic acid was converted into hydrogen peroxide by the reaction with protons. The reaction of manganese (III) porphyrin with hydrogen peroxide produced an oxo-manganese (V) species, which is a strong oxidant and oxidized 2 and 3. This mechanism is similar to the shunt mechanism in the cytochrome P-450 catalytic cycle.

Keywords P-450 model; *meso*-tetraphenylporphyrinatomanganese (III) chloride; sulfoxide; superoxide; activated oxygen; hydrogen peroxide

The molecular mechanism of biological oxidation is of great interest because cytochrome P-450, an important drug-metabolizing enzyme for catalyzes a wide variety of oxygenations and has a unique catalytic cycle.[1] In the generally accepted catalytic cycle for cytochrome P-450, an oxo-iron(V) species or oxo-iron(IV) porphyrin π-cation radical is produced by transfer of two electrons and one dioxygen. Metalloporphyrins are often used as model compounds for P-450 and some reductants such as $NaBH_4$ or dihydrogen and colloidal platinum, are used as the electron source.[2-13] In the oxidation of sulfides, it is particularly important to choose the reductant carefully because the oxidation products of sulfides, sulfoxides, may be easily reduced to sulfides again. As the applied potential can be changed freely, controlled potential electrolysis is suitable for such a study. Electrodes were used as the H_2O_2 source as well as the electron source, but the mechanism of the latter has not been reported in detail.[14a-c] The aim of this study was to investigate biomimetic oxidation of sulfides by means of electrochemistry with *meso*-tetraphenylporphyrinatomanganese(III) chloride (**1a**) as a model compound, and to elucidate the mechanism more precisely.[2]

Results

Controlled Potential Electrolysis (CPE) CPE was carried out by use of a divided cell and reticulated vitreous carbon (RVC) electrode (glassy carbon with a porous structure having a free void volume of about 97% and a surface area of about 65 cm^2/cm^3).[15] A relatively small piece of it can provide an electrode with a substantial surface area owing to its low electrical resistance and physically continuous structure. Four kinds of electrolytic solution were prepared: acetonitrile containing compound **1a** (1 mM), 1-methylimidazole (5 mM) and tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte (**SA**); acetonitrile containing acetic acid (0.2 M), compound **1a** (1 mM), 1-methylimidazole (5 mM) and tetrabutylammonium perchlorate (0.1 M) (**SB**); acetonitrile containing tetramethylammonium hydroxide (0.2 M, **4**, a 15% aqueous solution was used), compound **1a** (1 mM), 1-methylimidazole (5 mM) and tetrabutylammonium perchlorate (0.1 M) (**SC**); acetonitrile containing H_2O (11%), compound **1a** (1 mM), 1-methylimidazole (5 mM) and tetrabutylammonium perchlorate (0.1 M) (**SD**). Diphenyl sulfide (100 mM) was added to each solution as the substrate. The results of CPE with bubbling O_2 gas are summarized in Table I.

Though −0.4 V was a sufficient potential to reduce **1a**, CPE at −0.4 V in **SA** gave no reaction product. CPE at −0.4 V in **SB** gave **3** selectively with high current efficiency (79.1%).[16] CPE in **SC** also gave **3** selectively but with lower current efficiency. Because compound **5** used in this study was in aqueous solution, the effect of H_2O on CPE in **SC** should also be examined. CPE in **SD** was carried out and the result was similar to that in **SA** except for an increase in the electricity consumed. Therefore, compound **5** plays a more important role in the oxidation of **2** than does H_2O.

The applied potential was increased to −1.0 V, at which potential dioxygen could be reduced to superoxide ion. In **SA**, though the consumed electricity was increased to 328.0 C, diphenyl sulfide was not oxidized at all and neither **3** nor **4** was formed. In **SB**, the yield of **3** was in-

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Table I. Results of Controlled Potential Electrolysis of Mn(III)TPPCl in the Presence of O_2 and Diphenyl Sulfide

Applied potential (V *vs.* SCE)	Added substance (solution)		Quantity of electricity[a] (C)	Products (%)		Current efficiency	Turnover
				Sulfoxide	Sulfone		
−0.4	—	**(SA)**	8.4	—	—	—	—
−0.4	CH_3COOH	**(SB)**	190.1	16.4	1.5	79.1	19.4
−0.4	$(CH_3)_4NOH$	**(SC)**	216.8	12.6	0.5	48.6	14.1
−0.4	$(CH_3)_4NOH$	**(SC)**[b]	163.6	5.4	—	25.5	5.4
−0.4	H_2O	**(SD)**	25.5	—	—	—	—
−1.0	—	**(SA)**	328.0	—	—	—	—
−1.0	CH_3COOH	**(SB)**	409.0	21.0	2.9	50.4	26.9
−1.0	$(CH_3)_4NOH$	**(SC)**	1158.1	24.7	13.6	34.6	51.9
−1.0	$(CH_3)_4NOH$	**(SC)**[b]	507.9	11.6	—	17.6	11.6

a) For 3 h. *b*) In the absence of 1-methylimidazole.

Table II. Results of Controlled Potential Electrolysis of Mn(III)TPPCl in the Presence of O_2 and Sulfide at −0.4 V (*vs.* SCE)

Sulfide	Added substance	Products (%)		Current efficiency	Turnover
		Sulfoxide	Sulfone		
Phenyl-*p*-tolylsulfide	CH_3COOH	17.2	—	58.5	17.2
	$(CH_3)_4NOH$	2.8	—	22.7	2.8
	$(CH_3)_4NOH$[a]	4.2	Trace	31.1	4.1
Thioanisole	CH_3COOH	11.7	0.5	65.3	12.8
	$(CH_3)_4NOH$	6.3	0.2	29.8	6.7
	$(CH_3)_4NOH$[a]	4.5	—	30.3	4.5

a) In the absence of 1-methylimidazole.

Table III. Results of Oxidation[a] of Diphenylsulfide with KO_2 in the Presence of Mn(III)TPPCl[b] as a Catalyst

Added substance	Quantity of added KO_2 (g)	Products (%)	
		Sulfoxide	Sulfone
—	0.32	—	—
18-Crown-6[c]	0.78	Trace	—
CH_3COOH	0.32	26.7	2.7
$(CH_3)_4NOH$	0.16	15.6	—
$(CH_3)_4NOH$	0.32	14.6	—
$(CH_3)_4NOH$[d]	0.32	20.0	—

a) For 3 h. *b*) 1 mm. *c*) 0.1 m. *d*) In the absence of 1-methylimidazole.

Table IV. Results of Cyclic Voltammetry of Mn(III)TPPCl (1 mm) under an N_2 Stream in Acetonitrile Solutions Containing Bu_4NClO_4

CH_3CN solution	E_p, V *vs.* SCE		$i_p v^{-1/2}$, μA $(mV/s)^{-1/2}$	
	E_{pc}	E_{pa}	i_{pc}	i_{pa}
—	−0.33	−0.23	1.60	1.40
SA[a]	−0.37	−0.26	1.50	1.30
SB[b]	−0.35	−0.24	1.60	1.40
SD[c]	−0.39	−0.30	1.39	1.22

a) Containing 1-methylimidazole (5 mm). *b*) Containing acetic acid (0.2 m) and 1-methylimidazole (5 mm). *c*) Containing H_2O (11%) and 1-methylimidazole (5 mm).

creased to 21.0%, but the current efficiency was decreased to 50.4%. In **SC**, the yield of **3** was considerably increased, but the yield of diphenylsulfone was increased to 13.6% and the selectivity was decreased.

CPE with other sulfides, gave similar results, as summarized in Table II.

Electron Spin Resonance (ESR) Spectroscopy Cathodic reduction of dioxygen was carried out at −1.0 V for 30 min in acetonitrile containing tetrabutylammonium perchlorate as a supporting electrolyte, and a part of the solution from the electrolysis was poured into the cell, followed by bubbling N_2 gas through the cell. The cell was immersed in liquid N_2 and the ESR spectrum (low-field $g=2.076$, high-field $g=1.983$) was obtained. It was similar to the ESR spectrum of superoxide ion in acetonitrile observed previously.[17] In most cases the ESR spectrum of superoxide ion has a low-field g value of about 2.08 and a high-field g value of about 2.00.[18]

Reaction with Potassium Superoxide Potassium superoxide (0.32 g) was added to **SA**-**SC** containing **2** (100 mm) without any supporting electrolyte. The reaction mixture was stirred for 3 h. The results are summarized in Table III.

No product was obtained in **SA**. Even in the presence of 18-crown-6 (0.1 m), which is a representative phase-transfer catalyst, only a trace of **3** was detected. In **SB** and **SC**, **3** and **4** were obtained in yields comparable to those of CPE.

Cyclic Voltammetry (CV) CV for **1a** was carried out in four kinds of acetonitrile solution: acetonitrile containing the supporting electrolyte, **SA**, **SB**, and **SD**, under an N_2 stream. **SC** was a heterogeneous solution and did not give a reproducible cyclic voltammogram. Glassy carbon was used as the working electrode and the scan rate was 150 mV/s. The results are summarized in Table IV.

CV in acetonitrile containing **1a** and the supporting electrolyte gave a quasi-reversible voltammogram, *i.e.*, the separation of peak potentials (anodic peak potential (E_{pa})-cathodic peak potential (E_{pc})) was 100 mV and the ratio of peak current (anodic peak current (i_{pa})/cathodic peak current (i_{pc})) was 0.88. E_{pa} and E_{pc} shifted to more negative potential by 30—40 mV upon addition of 1-methylimidazole (5 mm). When acetic acid was further added to the solution, E_{pa} and E_{pc} went back by 20 mV. These results show that the electron transfer step is scarcely affected by the presence of acetic acid or 1-methylimidazole in the electrolyte solution.

Cyclic voltammograms obtained when air was introduced into the solutions are shown in Fig. 1.

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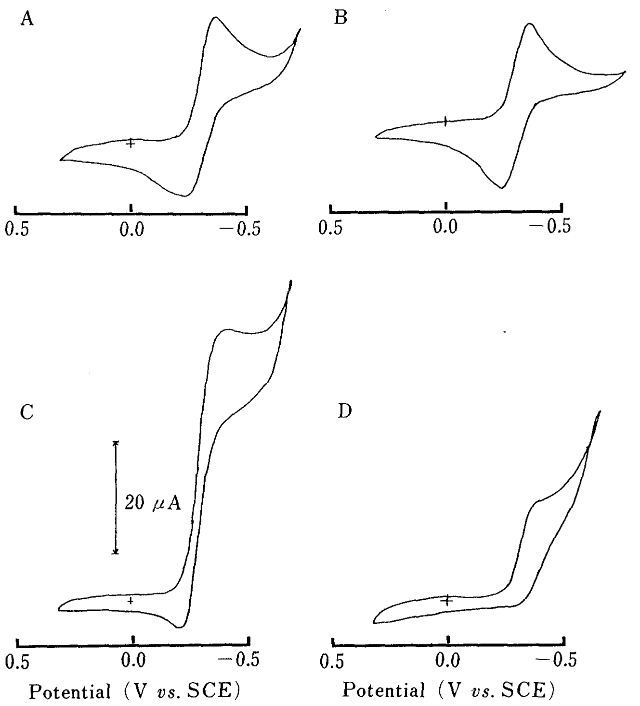


Fig. 1. Cyclic Voltammograms of *meso*-Tetraphenylporphyrinatomanganese (III) Chloride (1 mM, **1a**) in Acetonitrile (A), in **SA** (B), in **SB** (C), in **SD** (D) under Air

Tetrabutylammonium perchlorate was use as a supporting electrolyte. Glassy carbon cathode; voltage sweep rate, 150 mV/s; at 25 °C.

A small change was found in the cyclic voltammogram in the solution containing only **1a** and the supporting electrolyte (Fig. 1, A), *i.e.*, the separation of peak potentials and the ratio of peak currents were 150 mV and 0.65, respectively. However, no drastic change was found in the cyclic voltammogram in **SA** (Fig. 1, B), *i.e.*, the separation of peak potentials and the ratio of peak currents were 120 mV and 0.84, respectively. These facts suggest that a part of *meso*-tetraphenylporphyrinatomanganese (II) 1-methylimidazole (**6**) produced by the cathodic reduction of *meso*-tetraphenylporphyrinatomanganese (III) 1-methylimidazole (**1b**), which was formed by the exchange of the 5th ligand of **1a** from Cl^- to 1-methylimidazole, reacted irreversibly with O_2. A drastic change was seen in the cyclic voltammogram in **SB** (Fig. 1, C), *i.e.*, the cathodic peak current increased to more than twice that in other solutions and the corresponding anodic wave almost disappeared. These facts suggest that two-electron reduction occurred in the presence of acid. No anodic wave was seen in the cyclic voltammogram in **SD** (Fig. 1, D). The fact that the presence of a proton source such as acetic acid or H_2O quenches the anodic wave suggests that protons play an important role in the homogeneous chemical reaction following heterogeneous electron transfer on the electrode. However, the homogeneous chemical reaction following heterogeneous electron transfer on the electrode is not clearly seen in **SD**.

The results of CV when the scan range was extended to $-1.5-+0.5\,\mathrm{V}$ are shown in Fig. 2. In this range,

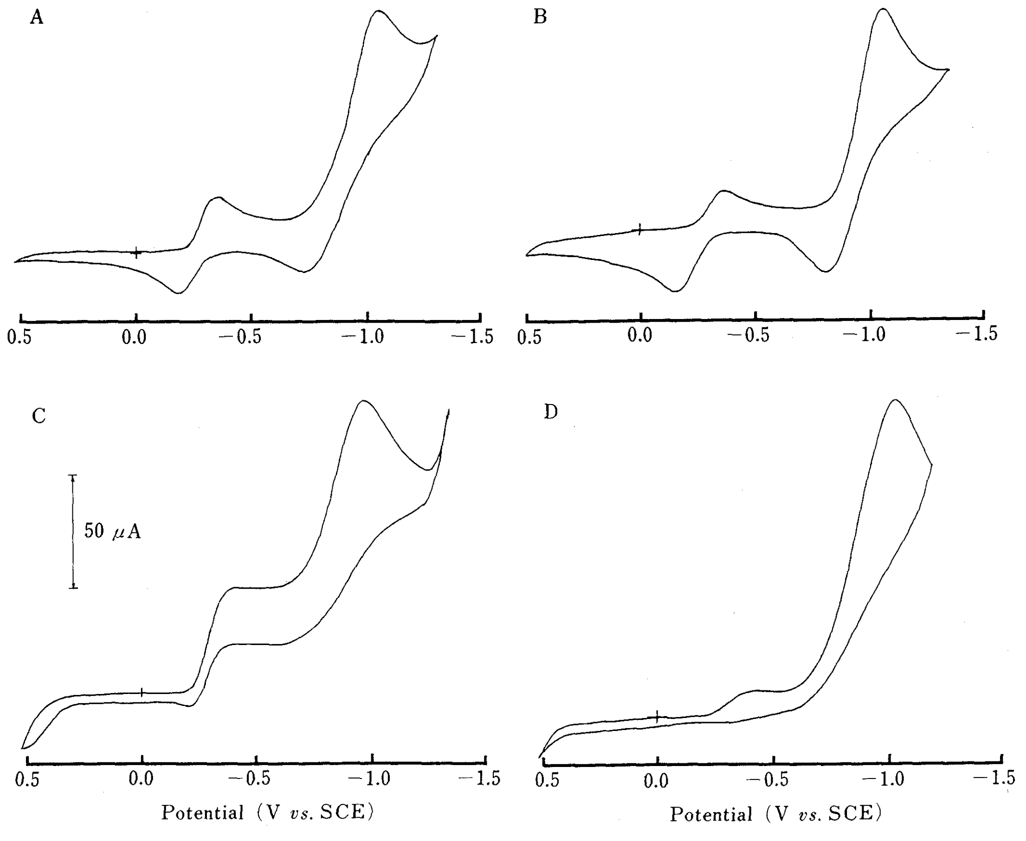
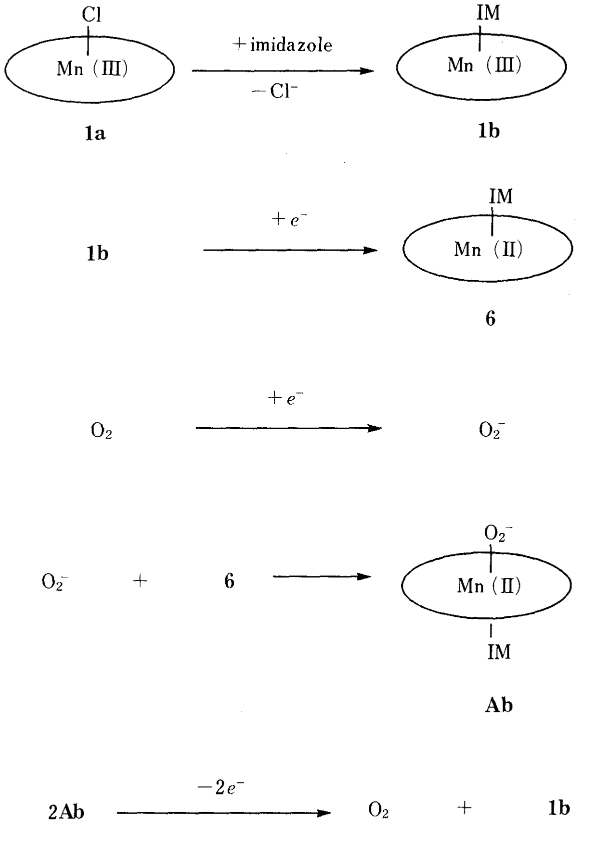


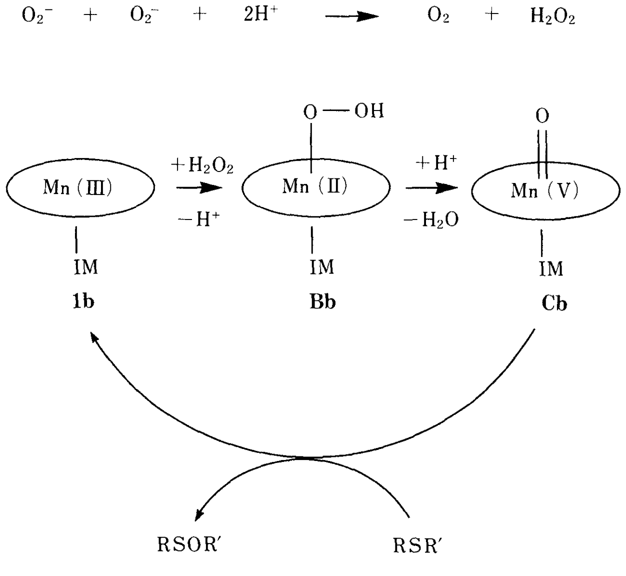
Fig. 2. Cyclic Voltammograms of *meso*-Tetraphenylporphyrinatomanganese(III) Chloride (1 mM, **1a**) in Acetonitrile (A), in **SA** (B), in **SB** (C), in **SD** (D) under Air

Tetrabutylammonium perchlorate was use as a supporting electrolyte. Glassy carbon cathode; voltage sweep rate, 150 mV/s; at 25 °C.



IM = 1-methylimidazole

Chart 1



IM = 1-methylimidazole

Chart 2

superoxide ion is generated by the electrochemical reduction of O_2. Though the first cathodic waves and the corresponding anodic waves in the solution containing **1a** and supporting electrolyte, **SB** and **SD**, scarcely changed, those in **SA** showed some changes. The separation of peak potentials was increased to 210 mV and the ratio of peak currents was 1.58. The unusual value of the ratio of peak currents can be explained on the basis of the presence of superoxomanganese (II) species (**Ab**) in close vicinity to the working electrode, as shown in Chart 1.

In **SA**, compound **1b** was reduced to **6** in the first cathodic wave and the dissolved O_2 was reduced to superoxide ion in the second cathodic wave. The reaction of superoxide ion with **6** produced superoxomanganese (II) species (**Ab**).[19] Unreacted superoxide ion was oxidized to O_2 in the first anodic wave and **Ab** was oxidized to **1b** and O_2 by two-electron transfer in the second anodic wave.

Visible Spectrometry Visible spectra were obtained in dry acetonitrile. The soret band was seen at 474.6 nm in the visible spectrum of compound **1a**. Addition of 1-methylimidazole and acetic acid to the solution containing **1a** changed the spectra slightly, but addition of **5** caused a drastic change. Namely, the Soret band shifted to 432.8 nm. These results suggest that the 5th ligand should be replaced with a hydroxyl ion.

Discussion

A P-450 model system consisting of **1a**, O_2 and electrochemical reduction seems to react very slowly as a value of 11 turnovers of the porphyrin catalyst in 6 h was reported by Creager *et al.*[14b] Therefore, RVC was used as the working electrode to obtain a large electrode area. As a result, a value of 51.9 turnovers in 3 h was obtained.

There are two mechanisms for the electrolytic P-450 model depending on the applied potential. When the applied potential is −1.0 V, most of the current is consumed in the reduction of dissolved O_2 owing to the difference of concentrations of O_2 and **1b**. As a result, a lot of superoxide ion is produced in the electrolyte solution. In the presence of acetic acid, disproportionation of superoxide ions generates hydrogen peroxide and dioxygen, as shown in Chart 2.[20]

Hydrogen peroxide affords protonated peroxomanganese species (**Bb**), and O–O bond cleavage catalyzed by protons affords oxomanganese (V) species (**Cb**). The later oxidizes sulfide and is reduced to **1b**. This catalytic cycle is the so-called shunt pathway.

The reaction mechanism in **SC** is shown in Chart 3.

As can be seen from the results of visible spectrometry, the 5th ligand of **1a** was replaced with OH ion and *meso*-tetraphenylporphyrinatomanganese (III) hydroxide (**1c**) was formed in **SC**. Compound **1c** was reduced to *meso*-tetraphenylporphyrinatomanganese (II) hydroxide (**7**) by the electrode and/or superoxide ion. The reaction of superoxide ion with **7** afforded the superoxomanganese (II) species (Ac). The 5th ligand of **Ac** was OH, the push effect of which on the O–O bond cleavage may explain the formation of **Cc**.[21] In this case OH ion was generated concomitantly. The origin of the hydrogen atom of the OH ion was H_2O, which was introduced into the electrolyte solution when the 15% aqueous solution of **5** was added to the electrolyte solution. Active oxidant **Cc** oxidizes sulfide and is reduced to **1c**.

In **SA**, **Ab** is produced as shown in Chart 1. Lack of H^+ to cleave the O–O bond of **Ab** prevents the formation of an oxidant such as the oxomanganese (V) species.

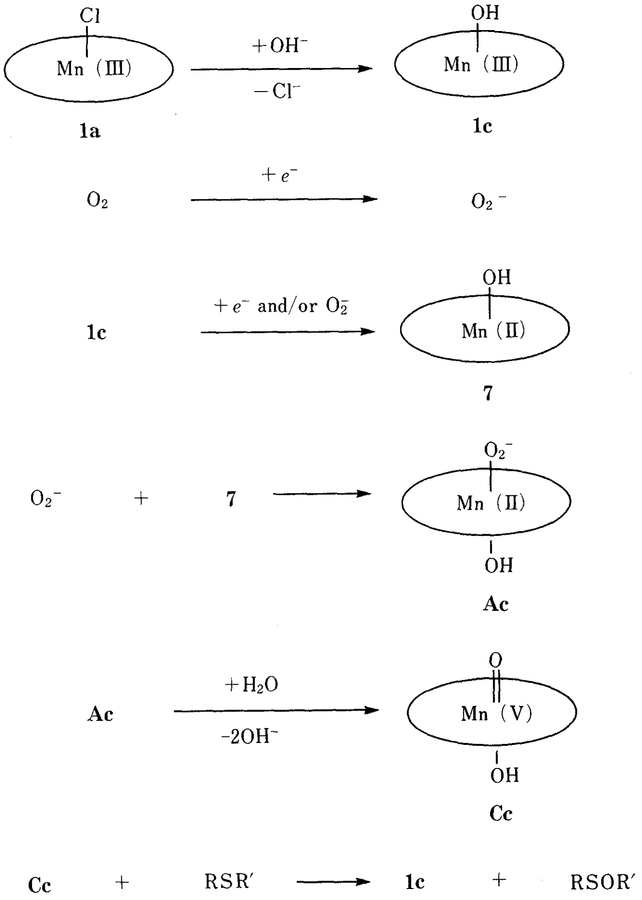
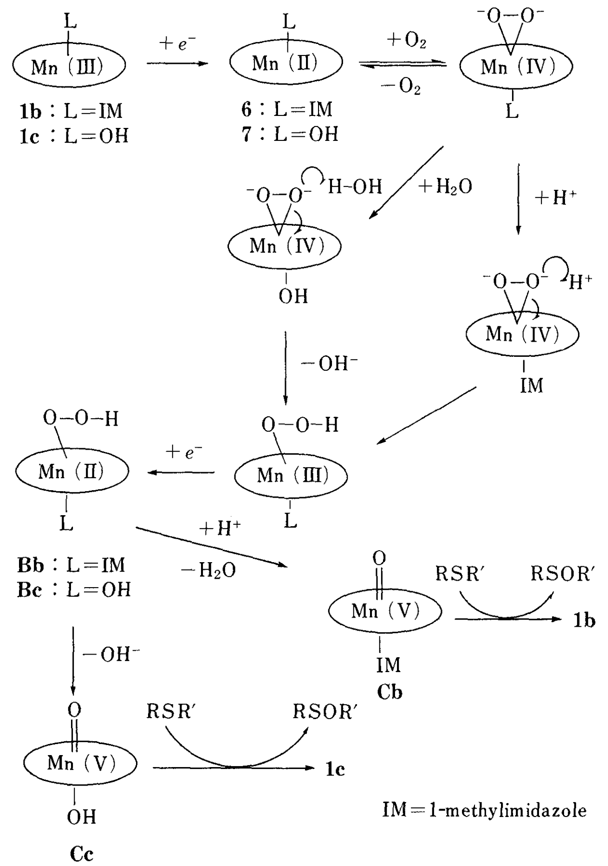


Chart 3



IM=1-methylimidazole

Chart 4

Therefore no oxidation product was obtained in **SA**. The fact that the reactions with KO_2 gave similar results to those of CPE supports this mechanism.

Though diphenylsulfone is the oxidation product of diphenyl sulfide, sulfides tend to be oxidized by electrophilic oxidants owing to the lone electron pair, while sulfoxides were not oxidized by electrophilic oxidants but were by nucleophilic ones owing the positive charge.[2] OH^- is more basic than 1-methylimidazole, so **Cc** has higher nucleophilicity. This is responsible for the lower selectivity.

The reaction mechanism when the applied potential was −0.4 V is shown in Chart 4.

In **SA**, **SB** and **SD**, **6** (a one-electron reduction product of **1b**) coordinates to dioxygen reversibly, and the O_2–adduct (Mn–O_2) has the side-on geometry.[22] In the presence of a proton source such as acetic acid or H_2O, the geometry of Mn–O_2 is changed to end-on type and in this step one electron on Mn is transferred to the O_2 moiety following the second electron transfer from the electrode to the metal in the porphyrin ring. As a result, **Bb** is produced. In **SB** a proton catalyzes the O–O bond cleavage of **Bb** and the oxomanganese (V) species (**Cb**) is produced. The latter oxidizes sulfide and is reduced to **1b**.

In **SC**, **Bc** is derived from **1c** through a similar mechanism to that of **Bb** in **SB**. The push effect of the 5th ligand of **Bc** on the O–O bond affords the oxomanganese (V) species (**Cc**) and OH^-.

Oxomanganese (IV) species might be formed but neither CV nor CPE data could distinguish whether the oxidant is oxomanganese (V) species or oxomanganese (IV) species.[23a,b]

In **SD** there are not enough protons to catalyze the O–O bound cleavage nor the push effect of the 5th ligand, so **Cc** was not generated.

Tabushi pointed out that two-electron transfer is necessary to activate dioxygen in P-450 model systems, but third and fourth electron transfers waste oxomanganese (V) species to produce H_2O.[24] The tetraphenylporphyrintetrasulfonate–Mn complex/NADH analog/FMN/*N*-methylimidazole/$(PhCO)_2O/O_2$ system was developed by Tabushi and Kodera in order to prevent third electron transfer, and good efficiency of the reductant (50%) was obtained.[9,24] A higher efficiency of 79.1% was obtained in our P-450 model system because the metalloporphyrin **Bb** or **Bc** left the surface of the electrode during the O–O bond cleavage and avoided the third electron transfer.

Experimental

Materials Acetonitrile was purified as described previously.[25] Tetrabutylammonium perchlorate was prepared by a known method.[26] Potassium superoxide, 18-crown-6, 15% tetramethylammonium hydroxide solution and 1-methylimidazole were reagent grade chemicals and were used without further purification. *meso*-Tetraphenylporphyrinatomanganese (III) chloride was prepared as described previously.[2]

Apparatus Gas chromatography was carried out with a Shimadzu GC-14A equipped with an AOC-14 auto injector and C-R6A Chromatopac. ESR spectra were obtained as described previously.[27] The working electrode used for voltammetry was purchased (BAS, GCE, diameter 3.0 mm). The reference electrode system was described previously.[28] A BAS CV-1B voltammetry control unit and a Riken

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Denshi F-3F X-Y recorder were used for cyclic voltammetry. A Hokuto Denko HF-102 coulombmeter and HA-104 or HA-151 potentiostat were used for controlled potential electrolysis.

Controlled Potential Electrolysis A typical example of the procedure is given below. A divided cell, a reference electrode system and a RVC electrode were used.[15] The electrolytic solution was acetonitrile (40 ml) containing diphenyl sulfide (0.75 ml, 100 mM), **1a** (28 mg, 1 mM), 1-methylimidazole (16 μl, 5 mM), acetic acid (0.48 ml, 0.2 M), and tetrabutylammonium perchlorate (0.1 M) as a supporting electrolyte. CPE was carried out at -0.4 V for 3 h with O_2 gas bubbling through the solution, and 2 ml aliquots were diluted with acetonitrile containing diphenyl (35.36 mg in 25 ml) as an internal standard to 5 ml. The products and substrate were monitored by GC (column, Silicon OV-101, Uniport HP).

Reaction with Potassium Superoxide A typical example of the procedure is given below. Potassium superoxide (0.317 g) was added to acetonitrile (40 ml) containing compound **1a** (28 mg, 1 mM), 1-methylimidazole (16 μl, 5 mM), and **2** (100 mM) and the reaction mixture was stirred for 3 h. Two ml aliquots were diluted to 5 ml with acetonitrile containing diphenyl (35.36 mg in 25 ml) as a internal standard. The products and substrate were determined by GC (column, Silicon OV-101, Uniport HP).

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