Bull. Chem. Soc. Jpn., 63, 1374—1380 (1990) [Vol. 63, No. 5

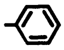
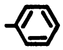
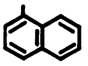
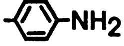
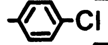
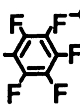
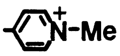
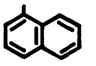
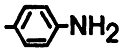
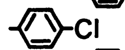
Catalytic Epoxidation of Cyclooctene with Oxygen Using Electrochemically Reduced Metalloporphyrins

Fumihiro Ojima, Nagao Kobayashi, and Tetsuo Osa*
Pharmaceutical Institute, Tohoku University, Aobayama,
Aoba-ku, Sendai 980
(Received November 20, 1989)

Epoxidation of cyclooctene with molecular oxygen was achieved using electrochemically reduced metalloporphyrins in *N,N*-dimethylformamide (DMF) containing acetic anhydride as an electrophile. Turnover numbers 5—7 based on moles of cyclooctene oxide produced per moles of porphyrin were obtained by the use of [5,10,15,20-tetrakis(pentafluorophenyl)porphinato]iron(III) chloride and [5,10,15,20-tetra(1-naphthyl)porphinato]manganese(III)chloride. The effects of central metals and substituents on phenyl groups of matalloporphyrins were also investigated. Rate constants (*k*) were estimated by way of digital simulation of cyclic voltammograms based on a simple ECE reaction mechanism. The reaction mechanism in the presence of cobalt(II) complexes seemed to be somewhat different from that in the presence of iron(III) or manganese(III) complexes.

The cytochrome P-450 monooxygenase[1–3] is a heme-containing porphyrin which is capable of oxygenating hydrocarbons in a catalytic way, yielding alcohols from alkanes and epoxides from alkenes. Its physiological significance and unique mechanism have attracted much interest of many chemists and biochemists since its discovery by Omura and Sato in 1962.[4] The reaction systems using synthetic metalloporphyrins and several oxygen sources have served as models[5,6] for cytochrome P-450 monooxygenase enzymes. Groves and co-workers[7] first found that (5,10,15,20-tetraphenylporphinato)iron(III) chloride (abbreviated as [Fe(tpp)]Cl) catalyzes the oxygen atom transfer from iodosylbenzene to olefins. Since then, many model systems have appeared on the metalloporphyrin-catalyzed oxidations and their reaction mechanisms also have beed discussed. As oxygen sources, the following compounds or systems have been utilized: iodosylbenzene,[8,9] hypochlorites,[6,9–12] amine oxides,[13] peroxycarboxylic acids,[14,17] hydrogen peroxide,[18,19]

Table 1. The Abbreviations for Various Metalloporphyrins Used in This Paper

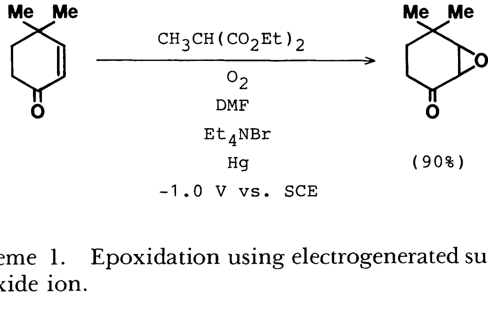
Porphyrin		Metal	R(meso-)	Ligand anion	Free anion
TPP[a)]	**(1)**	—		—	—
[Fe(tpp)]Cl[b)]	**(2)**	Fe(III)		Cl⁻	—
[Fe(tnp)]Cl[c)]	**(3)**	Fe(III)		Cl⁻	—
[Fe(tampp)]Cl[d)]	**(4)**	Fe(III)		Cl⁻	—
[Fe(tchpp)]Cl[e)]	**(5)**	Fe(III)		Cl⁻	—
[Fe(tmcpp)]Cl[f)]	**(6)**	Fe(III)		Cl⁻	—
[Fe(tpfpp)]Cl[g)]	**(7)**	Fe(III)		Cl⁻	—
[Fe(tmpyp)]PCl[h)]	**(8)**	Fe(III)		ClO_4^-	ClO_4^-
[Mn(tpp)]Cl[i)]	**(9)**	Mn(III)		Cl⁻	—
[Mn(tnp)]Cl[j)]	**(10)**	Mn(III)		Cl⁻	—
[Co(tpp)][k)]	**(11)**	Co(II)		—	—
[Co(tampp)][l)]	**(12)**	Co(II)		—	—
[Co(tchpp)][m)]	**(13)**	Co(II)		—	—
[Co(tpyp)][n)]	**(14)**	Co(II)		—	—

a) 5,10,15,20-Tetraphenylporphyrin. b) (5,10,15,20-Tetraphenylporphinato)iron(III) chloride. c) [5,10,15,20-Tetra(1-naphthyl)porphinato]iron(III) chloride. d) [5,10,15,20-Tetrakis(4-aminophenyl)porphinato]iron(III) chloride. e) [5,10,15,20-Tetrakis(4-chlorophenyl)porphinato]iron(III) chloride. f) [5,10,15,20-Tetrakis[4-(methoxycarbonyl)phenyl]porphinato]iron(III) chloride. g) [5,10,15,20-Tetrakis(pentafluorophenyl)porphinato]iron(III) chloride. h) [5,10,15,20-Tetrakis(1-methyl-4-pyridinio)porphinato]iron(III) pentaperchlorate. i) (5,10,15,20-Tetraphenylporphinato)manganese(III) chloride. j) [5,10,15,20-Tetra(1-naphthyl)porphinato]-manganese(III) chloride. k) (5,10,15,20-Tetraphenylporphinato)cobalt(II). l) [5,10,15,20-Tetrakis(4-aminophenyl)porphinato]cobalt(II). m) [5,10,15,20-Tetrakis(4-chlorophenyl)porphinato]cobalt(II). n) [5,10,15,20-Tetra(4-pyridyl)porphinato]cobalt(II).

and alkyl hydroperoxides,[20,21] or molecular oxygen in the presence of reducing agents such as sodium tetrahydroborate,[22] hydrogen and colloidal platinum,[23] or zinc powder and acetic acid,[24] and potassium superoxide.[25] In the most systems so far reported, central metals of metalloporphyrins were reduced by electrons from some chemical species generated during the reactions, and these reduced porphyrins functioned as catalysts. But considerably less works have been reported on the use of electrochemical methods,[26–28] which reduce central metals of metalloporphyrins directly. Recently, Creager et al.[26] have reported a cytochrome P-450 model utilizing an electrochemically reduced manganese porphyrin. In this report, we have studied, using electrochemical methods, the activity and stability of various iron(III), manganese(III), and cobalt(II) porphyrins (Table 1) as catalysts for the epoxidation of cyclooctene in the presence of molecular oxygen and acetic anhydride. We also present the mechanism of this reaction on the basis of the results of cyclic voltammetry (CV) and controlled potential macro-electrolyses. In the present system using molecular oxygen and acetic anhydride, superoxide ion ($O_2^{\cdot -}$) could be generated under electrolysis as shown in Eq. 1:

$$O_2 + e^- \rightleftharpoons O_2^{\cdot -} \qquad (1)$$

Although one of the most promising reactions of electrogenerated $O_2^{\cdot -}$ is the epoxidation of olefins, epoxidation using electrogenerated $O_2^{\cdot -}$ is not well-known and, of course, the number of reports on this subject is very limited. Baizer et al.[29–31] reported that electrogenerated $O_2^{\cdot -}$ reacted, in the presence of carbon acid such as diethyl methylmalonate, with olefins activated by the attached electron-withdrawing groups to yield the epoxides (Scheme 1). We have similarly attempted the epoxidations of various kinds of olefins by the use of electrogenerated $O_2^{\cdot -}$, but could not have obtained expected results because of low reactivity of electrogenerated $O_2^{\cdot -}$ with inactivated olefins. In this study, we have achieved the epoxidation of cyclooctene using oxygen in solution and electrochemically reduced matalloporphyrins as catalysts.



Scheme 1. Epoxidation using electrogenerated superoxide ion.

Experimental

TPP (Wako Chemicals) and [Fe(tpfpp)]Cl (Aldrich Chem. Co.) were obtained commercially. Other porphyrins were prepared by methods described in the literature.[32–37] The metals, such as iron(III), manganese(III), and cobalt(II), were inserted by the procedure of Adler et al.[38]

Cyclic Voltammetry. Cyclic voltammetry was carried out in a DMF solution containing 0.1 M (1 M=1 mol dm^{-3}) tetraethylammonium perchlorate (TEAP) as a supporting electrolyte. A glassy carbon (GC) disk (area ca. 0.71 cm^2) and a platinum wire were employed as a working electrode and a counter electrode, respectively. The working electrode surface was polished with a 0.05 μm alumina/water slurry on a felt surface, and sonicated in distilled water, thoroughly washed with acetone, and dried before electrochemical measurements. The cathode potentials were referred to Ag/Ag$^+$ (0.05 M $AgNO_3$ and 0.1 M TEAP in acetonitrile). Cyclic potential sweeps were generated by a Hokuto Denko Model HAB-151 potentiostat/galvanostat. Cyclic voltammograms were recorded on a Graphtec Model WX-1200 X-Y recorder. All electrochemical measurements were carried out at room temperature.

Controlled Potential Macro-Electrolysis. Cyclooctene (130.4 μl, 1 mmol) and acetic anhydride (94.4 μl, 1 mmol) were dissolved in DMF (10 ml), containing TEAP (0.459 g, 2 mmol). From this solution, 6 ml was transferred to an H-type cell in which cathodic and anodic chambers were separated by a fine-porosity sintered-glass frits, and 3 ml to a trap through which O_2 gas was bubbled into the catholyte solution. A metalloporphyrin (3 μmol) was placed only in the cathodic chamber. For controlled potential macro-electrolysis, a GC plate with a surface area of ca. 4.8 cm^2 was used as the cathode, and a platinum plate was used as the anode. The cathode potential was controlled with a Hokuto Denko Model HA-305 potentiostat/galvanostat. The electrolyses were carried out at room temperature and the quantity of passed electricity was measured with a Hokuto Denko Model HF-201 coulomb/amperehour meter. Quantitative analyses and identification of the main products were performed by gas chromatography on a Carbowax 20M (2 m×3 mmϕ) column. Identification of by-products was attempted by GC-MS spectroscopy on a Silicone OV-101 (2 m×3 mmϕ) column.

Results and Discussion

Cyclic Voltammetry of Metalloporphyrins. The first one-electron reduction peak potentials (E_p^1) of central metals of metalloporphyrins measured by CV method are listed in Table 2. As typical cyclic voltammograms, those of TPP (**1**), [Fe(tpp)]Cl (**2**), [Mn(tpp)]Cl (**9**), and [Co(tpp)] (**11**) are demonstrated in Fig. 1. As seen in this Figure, iron(III), manganese(III), and cobalt(II) TPP complexes are reduced at −0.61, −0.62, −0.17 V vs. Ag/Ag$^+$, respectively. The E_p^1 values of iron(III) in iron porphyrins having electron-withdrawing substituents on phenyl groups shift to more positive direction than that in [Fe(tpp)]Cl which has no substituents on phenyl rings: the electron-withdrawing effects[39,40] of the phenyl rings are in the order of **7**>**3**>**6**>**5**>**2**>**4**. This may be derived from the fact that the electron-withdrawing groups reduce electron density on the central iron atom.[41] Decrease of the electron density facilitates the reduction of the central iron(III).

Controlled Potential Macro-Electrolysis. The results of the controlled potential macro-electrolyses of cyclooctene with oxygen in the presence of metalloporphyrins and acetic anhydride are summarized in Table 3. Substantially all the metalloporphyrins except cobalt(II) porphyrins (**11** and **13**) showed low current efficiency. The turnover numbers (defined as the mole ratio: [product]/[catalyst]) shown in Table 3 are not necessarily high. This can be rationalized by the facile decomposition of the metalloporphyrins during the electrolyses, since the rate of the formation of metal oxo porphyrin complexes is very slow.[6,10,11,17] Actually the decomposition of **2** was spectroscopically confirmed in the presence of oxygen and acetic anhydride in a DMF solution, i.e., the Soret band of **2** at 415 nm faded away during the electrolysis. Also, after macro-electrolyses, the CV response corresponding to $\mathrm{Fe}^{\mathrm{III/II}}$ redox couple of **2** disappeared. Furthermore, the dual actions of the catalysts in the reaction may shorten their lifetime. That is to say, the reduced form of the catalysts is used to transfer electrons to molecular oxygen to generate superoxide ion[42] (Scheme 2). In addition, the catalysts react with oxygen and acetic anhydride to yield metal oxo porphyrin complexes, which epoxidize the substrate[43] (Scheme 3). On the other hand, cobalt(II) porphyrins (**11** and **13**) showed high current efficiency over 100%. This suggests that the epoxidation mechanism in cobalt(II)-system is different from that in iron(III) and manganese(III)-systems. Detailed description about cobalt(II)-system is given in the later paragraph of **"Determination of Simple Rate Constatns"**.

Table 2. Reduction Peak Potentials of Porphyrins[a]

Porphyrin	E_p^1	E_p^2	E_p^3
1	—	−1.52	−1.91
2	−0.61	−1.45	−2.02
3	−0.54	−1.41	−1.99
4	−0.83	−1.57	—
5	−0.60	−1.50	−2.05
6	−0.58	−1.46	−2.00
7	−0.46	−1.21	−1.77
8	−0.31	−1.28, −1.42	−1.73, −1.84
9	−0.62	−1.74	—
10	−0.37	−1.45, −1.58	—
11	−0.17	−1.16	—
12[b]	—	—	—
13	−0.20	−1.17	—
14[c]	—	—	—

a) E/V vs. Ag/Ag+, solvent: DMF, supporting electrolyte: TEAP, working electrode: GC, counter electrode: Pt. b) [Co(tampp)] was insoluble in DMF. c) No reduction peak was observed ranging from 0 V to −2.1 V.

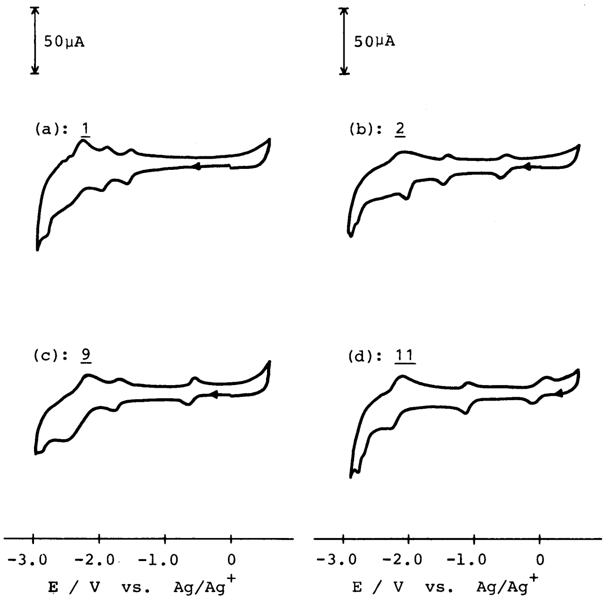
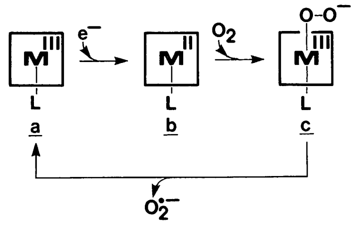


Fig. 1. Cyclic voltammograms for the reduction of 0.5 mM **1**, **2**, **9**, and **11** in 0.1 M TEAP/ DMF at a GC disk electrode. Sweep rate: 0.2 V s^{-1}. (a): **1**, (b): **2**, (c): **9**, (d): **11**.

Table 3. Metalloporphyrin Catalyzed Epoxidation of Cyclooctene

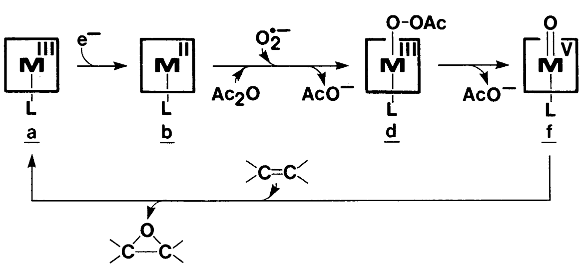
Catalyst No.	Cathodic potential	Charge passed	Current efficiency	Selectivity	Turnover number[a]
	E/V	F mol^{-1}	%	%	
2	−0.75	0.478	22.5	69	3.70
3	−0.75	0.876	15.7	62	4.30
4	−0.90	0.460	13.7	72	2.31
5	−0.75	0.304	9.4	100	1.41
6	−0.75	0.210	28.9	100	3.05
7	−0.65	0.538	12.9	100	6.89
8	−0.65	0.394	12.0	100	2.37
9	−0.75	1.256	2.8	35	0.63
10	−0.75	0.968	11.5	92	5.10
11	−0.50	0.086	295	100	2.53
13	−0.50	0.142	328	100	2.33

a) Defined as the mole ratio of [epoxide]/[porphyrin]. Yields (%) based on moles of porphyrin used are given as "turnover number" ×100.



□=PORPHYRIN DIANION, **M**=Fe or Mn, L=Cl

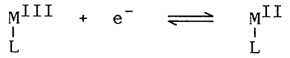
Scheme 2. A generation cycle of superoxide ion.



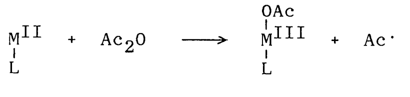
□=PORPHYRIN DIANION, **M**=Fe or Mn, L=Cl

Scheme 3. A formation cycle of high-valent metal oxo porphyrin complex.

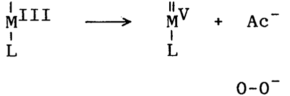
In iron(III)-system, addition of excess amounts of acetic anhydride increased the current efficiency and the turnover number. When acetyl bromide was used instead of acetic anhydride, the current efficiency was found to be very low. When acetic anhydride was not present in the solution, electricity consumption by the electrolysis was very small, and practically no reaction occurred. In the absence of oxygen, however, the epoxidation proceeded in the current efficiency of more than 100%. These facts indicate that acetic anhydride is necessary to form metal oxo porphyrin complexes from electrochemically reduced metalloporphyrin (Eqs. 2—4, M=Fe or Mn; L=Cl) and promote the change from metal peroxo porphyrin compelxes to metal oxo porphyrin complexes (Eqs. 5—7).



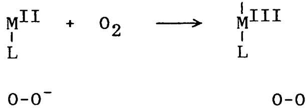
$$\underset{L}{M^{III}} + e^- \rightleftharpoons \underset{L}{M^{II}} \qquad (2)$$



$$\underset{L}{M^{II}} + Ac_2O \longrightarrow \underset{L}{\overset{OAc}{M^{III}}} + Ac\cdot \qquad (3)$$



$$\underset{L}{\overset{OAc}{M^{III}}} \longrightarrow \underset{L}{\overset{O}{\overset{\|}{M^{V}}}} + Ac^- \qquad (4)$$



$$\underset{L}{M^{II}} + O_2 \longrightarrow \underset{L}{\overset{O\text{-}O^-}{M^{III}}} \qquad (5)$$

$$\underset{L}{\overset{O\text{-}O^-}{M^{III}}} + Ac_2O \longrightarrow \underset{L}{\overset{O\text{-}OAc}{M^{III}}} + AcO^- \qquad (6)$$

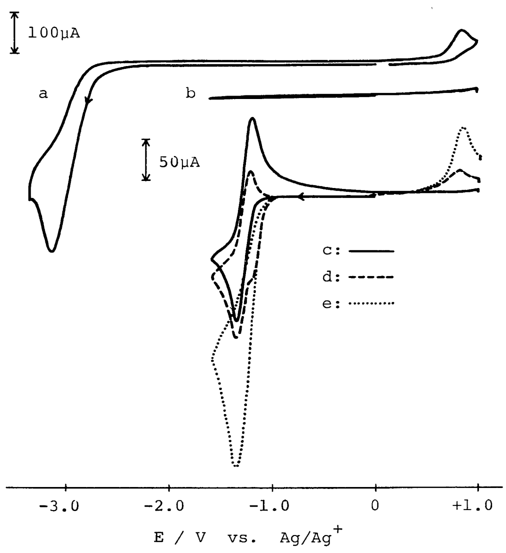
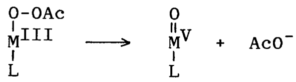


Fig. 2. Cyclic voltammograms of acetic anhydride (AA) in 0.1 M TEAP/DMF at a GC disk electrode. Sweep rate: 0.1 V s^{-1}. Curve a: 30 mM AA under N_2, curve b: the same condition as curve a, but different scanning range from curve a; curves c, d, and e: 0, 3, 15 mM AA under O_2, respectively.



$$\underset{L}{\overset{O\text{-}OAc}{M^{III}}} \longrightarrow \underset{L}{\overset{O}{\overset{\|}{M^{V}}}} + AcO^- \qquad (7)$$

When oxygen was directly reduced by electrolysis at −1.5 V vs. Ag/Ag$^+$ in the system with acetic anhydride and without catalyst, trace amounts of epoxide were detected by gas chromatography. Accordingly, it can be conceivable that the electrogenerated $O_2^{\bullet -}$ attacks acetic anhydride nucleophilically to form acetylperoxyl radical (Eq. 8) and/or acetylperoxide ion (Eq. 9).

$$Ac_2O + O_2^{\bullet -} \longrightarrow AcOO\cdot + AcO^- \qquad (8)$$

$$AcOO\cdot + e^-(O_2^{\bullet -}) \longrightarrow AcOO^- \ (+\ O_2) \qquad (9)$$

These facts were confirmed by CV (Fig. 2). Acetic anhydride uptook electrons at −3.1 V in the absence of oxygen and an oxidation peak at +0.84 V appeared (Fig. 2, curve a; reductive cleavage reaction: Eq. 10). This oxidation peak is assumed to correspond to the formation of acetyl radical from acetyl anion (Eq. 11).

$$Ac_2O + 2e^- \longrightarrow Ac^- + AcO^- \qquad (10)$$

$$Ac^- \longrightarrow Ac\cdot + e^- \qquad (11)$$

The reductive cleavage reaction was accelerated in the presence of oxygen (Fig. 2, curves c—e; Eqs. 12—14). Especially, the catalytic current of oxygen reduction can be explained in Eqs. 9, 12, and 14. The intermediate species of acetylperoxyl radical or acetylperoxide ion react with cyclooctene to yield cyclooctene oxide (Eq. 15).

$$\mathrm{Ac_2O} + \mathrm{O_2^{\cdot -}} \longrightarrow \mathrm{Ac_2O^{\cdot -}} + \mathrm{O_2} \qquad (12)$$

$$\mathrm{Ac_2O^{\cdot -}} \longrightarrow \mathrm{Ac^{\cdot}} + \mathrm{AcO^{-}} \qquad (13)$$

$$\mathrm{Ac^{\cdot}} + e^{-}(\mathrm{O_2^{\cdot -}}) \longrightarrow \mathrm{Ac^{-}} \; (+\ \mathrm{O_2}) \qquad (14)$$

(15)

Metalloporphyrins were supposed to be electrochemically stable even in the presence of oxygen. Tsuchiya et al.[44] obtained a high turnover number of 580 in the epoxidation of cyclooctene with hydrogen peroxide using [Fe(tpfpp)]Cl[19] as a catalyst. In the present study, [Fe(tpfpp)]Cl (**7**) lost its catalytic activity at turnover number of ca. 7. The reason for such a big difference between two systems is not clear, but some intermediate species formed in our system might easily decompose the metalloporphyrin structures and easily inactivate the metalloporphyrins. Electron-withdrawing groups on the phenyl rings seem to make not only the $E_{\mathrm{p}}^{\frac{1}{}}$ values more positive but also the stability of porphyrin skeleton higher.

Determination of Simple Rate Constant. In order to clarify each reaction rate of metalloporphyrins with oxygen or acetic anhydride, rate constants have been estimated based on a simple ECE reaction mechanism. The values listed in Table 4 are determined by the use of the digital simulation method which simulates the ratio of the cathodic peak current of catalyst reduction in the presence of oxygen or acetic anhydride to that in their absence. The results indicate the following:

1. The catalysts (except **5** and **8**) react with oxygen faster than with acetic anhydride.
2. The rates of reaction between oxygen and catalysts are faster in the order of **7**≒**8**>**2**>**10**>**6**>**5**>**3**≒**9**. This order indicates that the effect of electron-withdrawing substituents on phenyl groups is not remarkable.
3. The rates of reaction between acetic anhydride and catalysts are faster in the order of **8**>**7**>**5**>**2**>**3**>**6**>**9**>**10**. This order shows that iron porphyrins react with acetic anhydride faster than manganese porphyrins.

Table 4. Reaction Rates of Metalloporphyrins with Oxygen or Acetic Anhydride

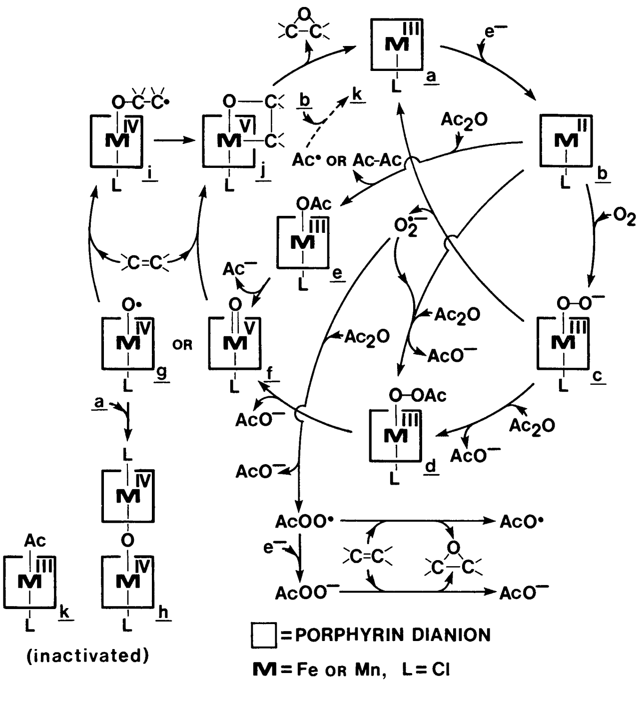
Porphyrin	Rate constant k/M^{-1} s^{-1}	
	Oxygen	Acetic anhydride
2	2.1×10^4	9.7×10^3
3	6.0×10^3	4.8×10^3
4[a]	—	—
5	7.2×10^3	4.0×10^4
6	8.9×10^3	4.1×10^3
7	7.6×10^4	4.5×10^4
8	7.3×10^4	8.7×10^5
9	5.9×10^3	3.2×10^3
10	1.3×10^4	1.9×10^3
11[b]	—	—
13[b]	—	—

a) The reaction of **4** with oxygen or acetic anhydride was exceedingly slow and could not be simulated. b) The reaction mechanism of Co complexes with oxygen or acetic anhydride seemed to be different from that of Fe or Mn complexes with oxygen or acetic anhydride.

In addition, the rate constant for the reaction of electrogenerated $\mathrm{O_2^{\cdot -}}$ with acetic anhydride has been determined by the digital simulation method. The value estimated is 4.3×10^4 M^{-1} s^{-1}, which is larger than the rate constants for the reactions of the catalysts (except **7** and **8**) with oxygen or acetic anhydride. That is, once superoxide ion is electrocatalytically generated, two possibilities arise concerning its reaction: i.e., it may react with both metalloporphyrin and acetic anhydride. If the reaction of metalloporphyrin with $\mathrm{O_2^{\cdot -}}$ is more rapid than the reaction of acetic anhydride with $\mathrm{O_2^{\cdot -}}$, the main active intermediates of epoxidation would be metal oxo porphyrin complexes. Moreover, electrochemically reduced species of metalloporphyrins are considered to react directly with acetic anhydride to produce metal oxo porphyrin complexes, so that the oxo complexes will epoxidize cyclooctene more effectively than other active intermediates such as acetylperoxy radical and acetylperoxide ion. Superoxide ion rarely reacted with cyclooctene directly: the reduction peak current of oxygen hardly increased even in the presence of 30 mM cyclooctene. Metalloporphyrins did not also react with cyclooctene directly so long as we judge from the cyclic voltammograms. On the other hand, the rate constants for cobalt(II) complexes could not be obtained because the reaction mechanism of Co(II) complexes with oxygen or acetic anhydride seemed to be different from that of Fe(III) or Mn(III) complexes with oxygen or acetic anhydride. In the case of Fe(III) or Mn(III) complexes, the addition of oxygen or acetic anhydride to the electrolyte solution containing the catalysts resulted in the increase of reduction peak current of the catalyst, but in the case of Co(II) complexes (**11** and **13**), the addition of oxygen or acetic anhydride brought about the decrease of reduction peak current of the complexes. In spite of the phenomena, the current efficiency was ca. 300%. This suggests that the epoxidation with Co(II) complexes proceeds in a chain reaction mechanism as well as an electrochemical one. The unusual reaction with Co(II) complexes might be due to some kinds of chemical reactions preceding electron transfer and/or reductive cleavage of acetic anhydride.

Reaction Mechanism. Many reports have been published with respect to mechanisms and rate-determining steps for epoxidation of alkenes with metalloporphyrins and various oxidants. Propositions about those are different from system to system: i.e., differences in central metals of metalloporphyrins, porphyrin skeletons, (with/without) ligands, (organic/aqueous) solvents, oxidants, and chemical methods or electrochemical methods. In chemical methods, two main conflicting opinions exist with regard to rate-determining steps. One is that rate-determining step is the formation of metal oxo porphyrin complexes,[6,10,11,17,45] and the other is that the rate-determining step is the decomposition of metallaoxetanes (**j**)[5,8,12] which form from olefins and metal oxo porphyrin complexes. In addition to these two intermediates, a new intermediate, *N*-alkylated metalloporphyrin complex, has been proposed recently.[46] Further advanced investigations about epoxidation have suggested an intermediate carbonium ion arising from caged pair collapse or metallacycle opening.[47,48] On the other hand, detailed kinetic and mechanistic studies have not appeared on the metalloporphyrin-catalyzed epoxidation by electrochemical methodology.[26–28] Our results suggest that metalloporphyrins are prone to be inactivated easier in the electrochemical systems than in the chemical systems. For instance, the electrochemical systems may be accompanied with formation of an unreactive dimer (**h**) assumed as (Por)M^{IV}–O–M^{IV}(Por) (M=Fe or Mn),[10,21] formation of inactivated metalloporphyrin (**k**) which is formed from **b** and acetyl radical, and/or decomposition of a porphyrin skeleton, under electrolyses. The following is the proposed reaction mechanism in our system (Scheme 4).

We suppose that electrochemical epoxidation in our system has two simultaneously proceeding reaction pathways. One is the pathway in which an active intermediate is high-valent metal oxo porphyrin complex, and the other is that in which an active intermediate is acetylperoxyl radical or acetylperoxide ion. However, the latter contribution must be smaller than the former one, because the yield of epoxidation without the metalloporphyrins was low. These pathways are considered to be reasonable for iron(III) and manganese(III)-systems. However, the epoxidation mechanism in cobalt(II)-system is not definite at the present. Further advanced investigations will be necessary to explain it.



Scheme 4. Mechanism of electrochemical epoxidation with metalloporphyrin.

Conclusion

Epoxidation of cyclooctene was achieved with molecular oxygen using electrochemically reduced metalloporphyrins in DMF containing acetic anhydride as an electrophile. Cyclooctene oxide was obtained as a main product with a high selectivity. Compared with the chemical systems reported to date, electrocatalytic systems presented here are simpler and cleaner. In fact, we could detect only one by-product, cyclooctanone, by GC-MS spectroscopy. However, unfortunately, the durability of the metalloporphyrins is relatively low in the electrochemical systems. As shown in Table 3, the obtained turnover numbers were not high. Hence, the next subject in electrochemical systems will be the improvement of the durability of the catalysts. In addition, the detailed mechanistic elucidation in cobalt(II)-system will be an important next subject.

References

1) M. Klingenberg, *Arch. Biochem. Biophys.*, **75**, 376 (1958).

2) D. Garfinkel, *Arch. Biochem. Biophys.*, **77**, 493 (1958).

3) F. P. Guegerich and T. L. Macdonald, *Acc. Chem. Res.*, **17**, 9 (1984) and references cited therein.

4) T. Omura and R. Sato, *J. Biol. Chem.*, **237**, 1375 (1962).

5) J. P. Collman, J. I. Brauman, B. Meunier, T. Hayashi, T. Kodadek, and S. A. Raybuck, *J. Am. Chem. Soc.*, **107**, 2000 (1985).

6) A. W. van der Made, P. M. F. C. Groot, R. J. M. Nolte, and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **108**, 73 (1989).

7) J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Am. Chem. Soc.*, **101**, 1032 (1979).

8) T. G. Traylor and A. R. Miksztal, *J. Am. Chem. Soc.*, **109**, 2770 (1987).

9) H. Sugimoto, H.-C. Tung, and D. T. Sawyer, *J. Am. Chem. Soc.*, **110**, 2465 (1988).

10) J. A. S. J. Razenberg, R. J. M. Nolte, and W. Drenth, *J. Chem. Soc., Chem. Commun.*, **1986**, 277.

11) R. J. M. Nolte, J. A. S. J. Razenberg, and R. Schuurman, *J. Am. Chem. Soc.*, **108**, 2751 (1986).

12) H. Amatsu, T. K. Miyamoto, and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **61**, 3193 (1988).

13) W. -H. Wong, D. Ostovic, and T. C. Bruice, *J. Am. Chem. Soc.*, **109**, 3428 (1987).

14) J. T. Groves, Y. Watanabe, and T. J. McMurry, *J. Am. Chem. Soc.*, **105**, 4489 (1983).

15) T. G. Traylor and R. Miksztal, *J. Am. Chem. Soc.*, **109**, 2770 (1987).

16) J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, **109**, 3812 (1987).

17) T. G. Traylor and F. Xu, *J. Am. Chem. Soc.*, **110**, 1953 (1988).

18) P. Battioni, J.-P. Renaud, J. F. Bartoh, M. Reina-Artiles, M. Fort, and D. Mansuy, *J. Am. Chem. Soc.*, **110**, 8462 (1988).

19) S. Tsuchiya and M. Seno, *Chem. Lett.*, **1989**, 263.

20) P. N. Balasubramanian, J. R. L. Smith, M. J. Davies, T. W. Kaaret, and T. C. Bruice, *J. Am. Chem. Soc.*, **111**, 1477 (1989).

21) R. D. Arasasingham, C. R. Cornman, and A. L. Balch, *J. Am. Chem. Soc.*, **111**, 7800 (1989).

22) I. Tabushi and N. Koga, *J. Am. Chem. Soc.*, **101**, 6456 (1979).

23) I. Tabushi and K. Morimitsu, *J. Am. Chem. Soc.*, **106**, 6871 (1984).

24) P. Battioni, J. F. Bartoli, P. Leduc, M. Fontecave, and D. Mansuy, *J. Chem. Soc., Chem. Commun.*, **1987**, 791.

25) E. McCandlish, A. R. Miksztal, M. Nappa, A. Q. Sprenger, J. S. Valentine, J. D. Strong, and T. G. Spiro, *J. Am. Chem. Soc.*, **102**, 4268 (1980).

26) S. E. Creager, S. A. Raybuck, and R. W. Murray, *J. Am. Chem. Soc.*, **108**, 4225 (1986).

27) L. Geng and R. W. Murray, *Inorg. Chem.*, **25**, 3115 (1986).

28) P. Moisy, F. Bedioui, Y. Robin, and J. Devynck, *J. Electroanal. Chem.*, **250**, 191 (1988).

29) M. Sugawara, M. M. Baizer, W. T. Monte, R. D. Little, and U. Hess, *Acta Chem. Scand., B*, **37**, 509 (1983).

30) M. Sugawara and M. M. Baizer, *Tetrahedron Lett.*, **24**, 2223 (1983).

31) M. Sugawara and M. M. Baizer, *J. Org. Chem.*, **48**, 4931 (1983).

32) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 5111 (1959).

33) E. B. Fleischer, *Inorg. Chem.*, **1**, 493 (1962).

34) A. D. Adler, F. R. Longo, J. D. Finarell, J. Goldmacker, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **33**, 476 (1967).

35) G. H. Barnet, M. F. Hudson, and K. M. Smith, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 1401.

36) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975).

37) F. L. Harris and D. L. Toppen, *Inorg. Chem.*, **17**, 71 (1978).

38) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

39) M. Tezuka, Y. Ohkatsu, and T. Osa, *Bull. Chem. Soc. Jpn.*, **49**, 1435 (1976).

40) P. S. Traylor, D. Dolphin, and T. G. Traylor, *J. Chem. Soc., Chem. Commun.*, **1984**, 279.

41) Y. Tatsuno, A. Sekiya, K. Tani, and T. Saito, *Chem. Lett.*, **1986**, 889.

42) T. Kuwana, P. A. Forshey, N. Kobayashi, and T. Osa, *Adv. Chem. Ser.*, **201**, 601 (1982).

43) J. T. Groves, Y. Watanabe, and T. J. McMurry, *J. Am. Chem. Soc.*, **105**, 4489 (1983).

44) S. Tsuchiya and M. Seno, *Chem. Lett.*, **1989**, 263.

45) C. M. Dicken, T. C. Woon, and T. C. Bruice, *J. Am. Chem. Soc.*, **108**, 1636 (1986).

46) T. G. Traylor, T. Nakano, A. R. Miksztal, and B. E. Dunlap, *J. Am. Chem. Soc.*, **109**, 3625 (1987).

47) T. G. Traylor, W. A. Lee, and D. V. Stynes, *J. Am. Chem. Soc.*, **106**, 755 (1984).

48) T. G. Traylor, T. Nakano, B. E. Dunlap, P. S. Traylor, and D. Dolphin, *J. Am. Chem. Soc.*, **108**, 2782 (1986).