September, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***61***, *3193—3198 (1988)*

Olefin Epoxidation Catalyzed by Sterically Bulky Metalloporphyrins (Metal=Fe,Mn) by Use of Sodium Hypochlorite as an Oxygen Source—A Kinetic Study

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(Received April 6, 1988)

Substituents around an active center give a variety of effects on metalloporphyrin catalyses. In order to examine the effects of a substituent on the kinetic parameters, several olefins (styrene derivatives, cyclooctene and 1-octene) have been epoxidized by iron(III) and manganese(III) complexes of *meso*-tetrakis(2,6-dimethylphenyl)porphyrin or *meso*-tetrakis(2,6-dichlorophenyl)porphyrin in the presence of sodium hypochrolite as an oxidant. As previously reported for a manganese porphyrin system, the rate-profile of an iron complex can be described by the Michaelis–Menten equation. Several examples of an anomalous rate dependence on the olefin concentration have been observed. The ortho substituents have little influence on the binding affinity of the oxo–iron complex to olefin, in contrast to the case of manganese complexes. It is additionally proposed that the *N*-alkylation of an iron porphyrin has some correlation to the kinetic parameters.

Metalloporphyrins, especially iron and manganese complexes, are capable of oxygenating hydrocarbons in a catalytic way, yielding alcohols from alkanes and epoxides from olefins. In these catalyses, several oxygen sources, either single oxygen donors such as iodosylbenzenes,[1—10] amine oxides,[11—13] and alkyl hydroperoxides,[14,15] or molecular oxygen in the presence of reducing agents such as sodium tetrahydroborate,[16] hydrogen and colloidal platinum,[17,18] or zinc powder and acetic acid[19] have been used. These reaction systems not only serve as models to cytochrome P-450 monooxygenase enzymes,[20] but have promising possibilities as catalysts. Several studies have been made to develop efficient metalloporphyrin catalysts for high-turnover oxygenation,[8,21,22] and to control the chemo-,[1,5,30,34] regio-,[1,23—26] and stereoselectivity.[27,28]

The use of manganese porphyrins with hypochlorite oxidant has recently been well-established for olefin epoxidation.[29—41] Nitrogen bases, such as pyridines and *N*-substituted imidazoles, enhance the reaction rate.[29,33,34,38] Kinetic studies have demonstrated that the rate can be described by the Michaelis–Menten equation and that the breakdown of an oxo–olefin intermediate (a proposed structure is a metallaoxetane **2**) is the rate-determining step of the catalytic cycle[35] (Fig. 1). The manganese–hypochlorite system has several advantages. First, sodium hypochrolite is a cheap oxidant and its concentration in solution can be determined by simple titration. Second, the rate is easy to measure since the reaction stops without adding a quencher when the aqueous and organic phases are separated. The observed kinetic parameters give information concerning catalyst-substrate interactions.

Although few iron porphyrins have been successful in oxygenation with hypochlorite, we found that a low catalytic activity results from an oxidative destruction of the catalysts and that the introduction of the electron-withdrawing substituents into the

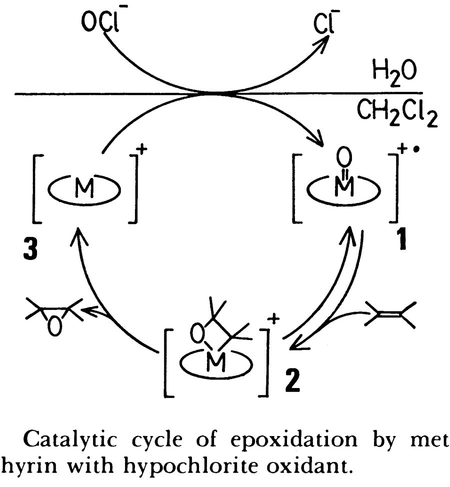
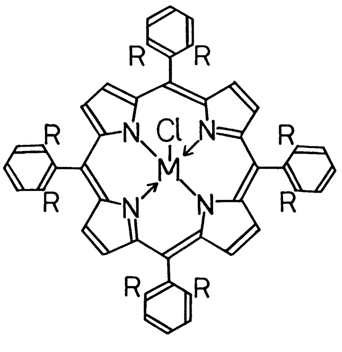


Fig. 1. Catalytic cycle of epoxidation by metalloporphyrin with hypochlorite oxidant.



R=Me, Cl
M=Fe, Mn

Fig. 2. The porphyrin complexes used as catalysts. Abbreviations: TPP=*meso*-tetraphenylporphyrin dianion; TMP=*meso*-tetramesitylporphyrin dianion; FeMe=[*meso*-tetrakis(2,6-dimethylphenyl)porphyrinato]iron(III) chloride; FeCl=[*meso*-tetrakis(2,6-dichlorophenyl)porphyrinato]iron(III) chloride; MnMe=[*meso*-tetrakis(2,6-dimethylphenyl)porphyrinato]manganese(III) chloride; MnCl=[*meso*-tetrakis-(2,6-dichlorophenyl)porphyrinato]manganese(III) chloride.

ortho-position(s) of phenyl rings of TPP[42] reduces the catalyst decomposition; especially, an iron *meso*-tetrakis(2,6-difluorophenyl)porphyrin complex shows a sufficient epoxidation capability[39–41] (Fig. 2: R=F).

In order to obtain a greater undertstanding of olefin epoxidation by metalloporphyrin–hypochlorite systems, we used iron(III) and manganese(III) TPP derivatives carrying methyl- or chloro groups in the 2,6-positions of the phenyl rings (FeMe, FeCl, MnMe, and MnCl: Fig. 2).

Experimental

meso-Tetrakis(2,6-dimethylphenyl)porphyrin[42] and *meso*-tetrakis(2,6-dichlorophenyl)porphyrin[21] were prepared by methods described in the literature. The metals, iron(III) and manganese(III), were inserted by the procedure of Adler et al.[43]

Standard Conditions for Kinetics. A metalloporphyrin catalyst (4.6×10^{-5} M[44]), olefin (styrenes, cyclooctene, or 1-octene; 0.17 M), internal standard (*p*-dichlorobenzene; 0.014 M), phase-transfer reagent (benzyldimethyltetradecylammonium chloride; 0.010 M) were dissolved in 10 ml of dichloromethane. When manganese porphyrins were used, the addition of 4′-(1-imidazolyl)acetophenone was necessary; in the absence of the base, the reaction was too slow to obtain kinetic data. Sodium hypochlorite solution (20 ml, 0.42 M) was layered over the organic phase. The reaction was initiated by vigorous stirring. The temperature was maintained at 22 °C. The products were monitored periodically by gas chromatography.

Results and Discussion

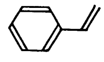
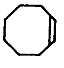
Stabilities of Catalysts. When styrene was oxygenated catalytically by four metalloporphyrins (FeMe, FeCl, MnMe, and MnCl), phenylacetaldehyde could not be detected as a by-product. The same results were obtained in the styrene epoxidation, both by $[(\mathrm{Mn(TMP)}]^+$–*N*-base–hypochlorite system[35] and by $[\mathrm{Fe(TMP)}]^+$–iodosylbenzene system,[35] and by $[\mathrm{Fe(TMP)}]^+$–iodosylbenzene system,[5] however, $[\mathrm{Mn(TPP)}]^+$ produced a relatively large amount of phenylacetaldehyde (ca. 15%).[39–41] This tendency indicates that the steric hindrance of ortho substituents around the active site contributes to product selectivity.

In order to evaluate the ortho-substituent effect on the porphyrin catalyst stability, we measured the maximum yields of epoxides (Table 1). The reaction was continued until the catalyst was completely bleached or the epoxide formation stopped. (Both olefin and sodium hypochlorite were added, if necessary.) In Table 1, the yield of epoxide is expressed in turnovers (mol of produced epoxide per mol of catalyst). In styrene and cyclooctene epoxidation, all complexes, except for FeMe, showed quite high yields of the epoxidation compared with $[\mathrm{Fe(TPP)}]^+$ and $[\mathrm{Mn(TPP)}]^+$. In 1-octene epoxidation, all of the catalysts show low yields. In view of the fact that the TPP complexes have no reactivity, however, the R groups must contribute to the catalyst stability to a small extent.

It is well-known that metalloporphyrin, itself, suffers from oxidation at the meso-positions, followed by ring opening.[45] The ortho substituents of the meso-phenyl rings protect the meso-position from a bimolecular oxidative process, sterically or electronically (when the R is electron-withdrawing substituent). As far as iron porphyrin complexes are concerned, steric protection by the methyl groups is not efficient in stabilizing the catalyst against oxidative degradation.

Reaction Mechanism. The reaction rate was found to be first-order in the concentration of the iron or manganese porphyrin ($0-1\times10^{-4}$ M) and independent of the hypochlorite concentration (0.0043—0.42 M). With respect to the olefin concentration (0.002—2 M), the reaction order varied from zero to one. Plotting the reciprocal of the initial velocity vs. the reciprocal of the olefin concentration gave a straight line (Fig. 3). These results suggest that the mechanism of iron porphyrin-catalyzed epoxidation follows Michaelis–Menten kinetics, which has been proposed for the epoxidation by manganese complex–

Table 1. The Maximum Yields in Turnovers

M	R			
	H	300$^{a)}$	300$^{a)}$	ca. 0
Fe	Me	450	2300	80
	Cl	9500	28000	350
Mn	H$^{b)}$	5000$^{a)}$	600$^{a)}$	20
+	Me	37000	8200	360
N-base	Cl	21000	10500	400

a) Ref. 41. b) Bromide complex was used. All the others are chlorides.

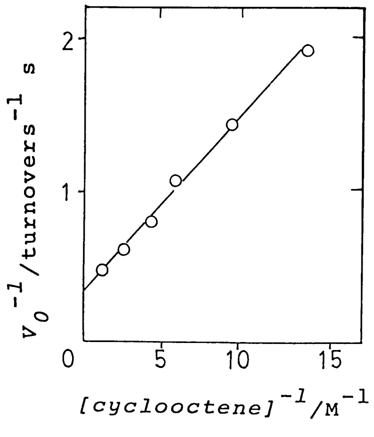


Fig. 3. Reciprocal plot of the initial velocity (V_0) vs. reciprocal of the cyclooctene concentration. catalysis by FeCl.

hypochlorite system,35) i.e., the high valent oxo-iron complex and olefin reversibly interact to form an oxo-olefin intermediate. A breakdown of the intermediate to epoxide is the rate-determining step.

Since the ortho-substituents prevent μ-oxo dimerization, a by-pass mechanism can be avoided. During the catalytic cycle all porphyrin molecules serve as a single catalyst.46)

Although the epoxidation rate essentialy fitted Michaelis-Menten kinetics, we observed two anomalies of the rate dependence on the olefin concentration. One is the case using FeMe as a catalyst. As shown in Fig. 4, rate saturation was not found, even in the concentration range [cyclooctene]>1 M. An analogous rate dependence on the substrate concentration was found for styrene and 1-octene epoxidation. The other is the case of a MnCl catalyst, particularly for cyclooctene epoxidation (Fig. 5). The rate remarkably decreased with an increase in the concentration of the olefin above 0.2 M. A similar behavior was observed for styrene or 1-octene epoxidation. In the presence of cyclooctene in large excess, the UV-vis spectra of organic aliquots from the reaction mixtures showed a Soret band at 437 nm. This band could not be assigned to a common high valent manganese porphyrin which usually has a Soret band at 420—425 nm.47—50) The observed kinetic behavior would result from the formation of a low reactive unknown intermediate under conditions of excess olefin. At present, we can not characterize this intermediate.51)

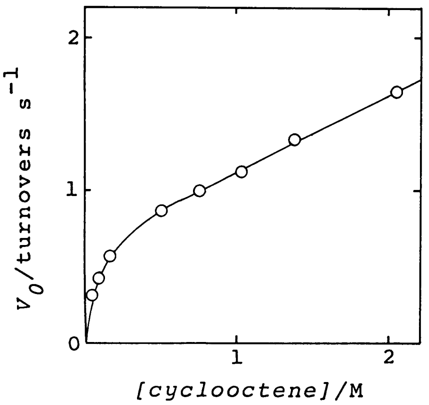


Fig. 4. Plot of initial velocity vs. cyclooctene concentration for FeMe-catalyzed epoxidation. The kinetic parameters were obtained from the linear part of double reciprocal plots at low cyclooctene concentration region.

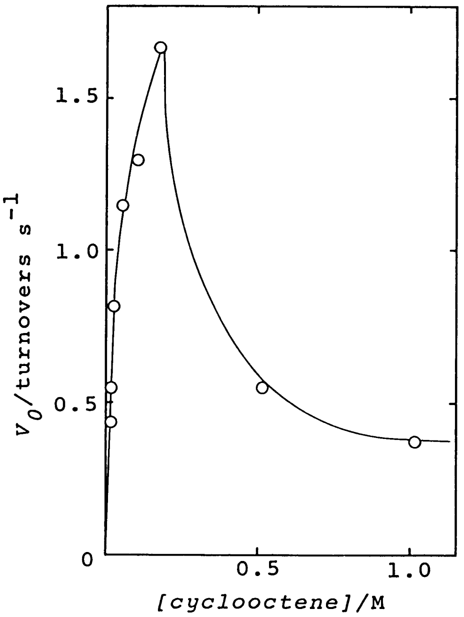


Fig. 5. Plot of initial velocity vs. cyclooctene concentration for MnCl-catalyzed epoxidation. The kinetic parameters were obtained from the linear part of double reciprocal plots at low cyclooctene concentration region.

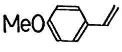
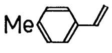
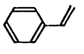
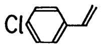
Kinetic Parameters. In the Michaelis-Menten equation, the parameter V_{max} gives the rate-determining constant. The Michaelis constant K_m is a measure of the binding affinity of the olefin to a high valent metal-oxo complex: a large binding affinity corresponds to a low K_m value.

The values of V_{max} and K_m were calculated from the intercept and the slope of the straight line obtained by the Lineweaver-Burk plotting.53)

In general, both the steric and electronic factors of porphyrin catalysts must govern the reactivity. On the assumption that both the methyl- and chloro-group would be nearly equal in steric hindrance, we expected to be able to obtain information concerning the electronic effect on the reaction. According to recent measurements of the CV redox potentials of iron porphyrin,54) oxo $Fe^{IV}Cl^{+\cdot}$ is more oxidative than oxo $Fe^{IV}Me^{+\cdot}$ by 250 mV, reflecting the fact that the electron-withdrawing chloro groups might enhance the electrophilicity of the oxo-iron complex.

The above consideration encouraged us to examine the substituent effect on the binding affinity of the oxo-iron complex toward olefins. Table 2 gives the K_m values for the epoxidation of para-substituted styrenes(substituents: MeO-, Me-, H-, Cl-) by FeMe and FeCl. The K_m values decrease (i.e., the affinity toward the styrenes increases) as the styrene substituents become increasingly electron-donative, suggesting that the oxo-iron complexes are electrophilic.

Table 2. K_m Values for Para-Substituted Styrenes Epoxidation Catalyzed by Porphyrin Complexes

M	R				
		K_m/M	K_m/M	K_m/M	K_m/M
Fe	Me	0.0052	0.0095	0.40	0.5
	Cl	0.0077	0.017	0.065	0.6

The logarithm of the K_m values could be correlated with Hammett substituent constants σ_p (Fig. 6). The difference between the K_m values for FeMe and FeCl is small and the slopes of the two straight lines are almost equal; the difference in the ρ values is small. These results demonstrate that the difference between the methyl- and chloro-groups in the ortho-positions of TPP has little influence on the binding affinity of an oxo-iron complex to olefins. In other words, the electronic effect of oxo-iron complexes is not an important factor in epoxidation kinetics.

It is highly desirable that epoxidation by manganese catalyst should be carried out in the absence of an *N*-base, in comparison with that of iron catalysts. In all cases concerning our manganese system, the addition of an *N*-base was, however, required in order to monitor the reaction by gas chromatography. Moreover,in epoxidation by MnMe a determination of the initial velocity was very difficult because of the peculiar time course for epoxide production without any catalyst or *N*-base loss (Fig. 7). (The behavior has not yet been rationalized.) This prevented us from carrying out a manganese catalyzed epoxidation of a series of para substituted styrenes. In a calculation of the kinetic parameters for MnMe (Table 3), the initial velocities were obtained from the tangent slopes of the time course curves at time T=0.

The V_{max} and K_m values for the epoxidation of three different olefins to the four iron and manganese porphyrins are also listed in Table 3. Although large differences in the K_m values between the two different metals or between the two different subsituents to each olefin were not observed, a slight tendency is noticeable, as described below.

When iron porphyrins are used for olefin epoxidation, the difference in the K_m values between FeMe and FeCl to each olefin is not very large, compared with the difference obtained by using manganese complexes. This result indicates a small electronic effect

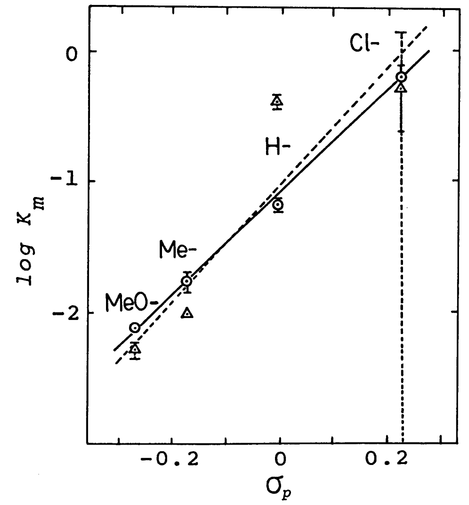


Fig. 6. Plot of log K_m for para-substituted styrenes vs. Hammett substituent constants σ_p for iron porphyrin-catalyzed epoxidation: —O— for FeCl catalyst; ---Δ— for FeMe catalyst. The two straight lines are drawn by the least squares method.

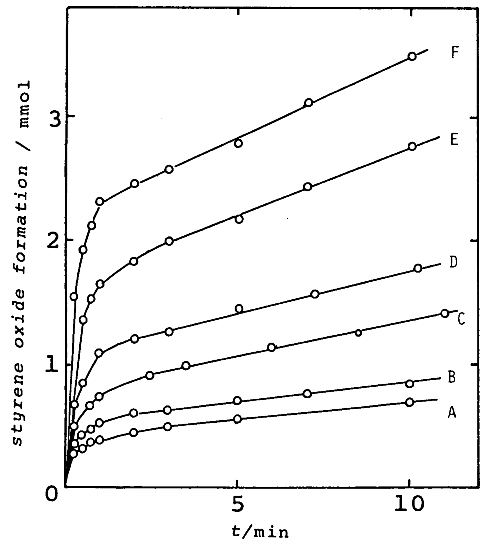
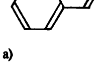
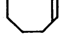
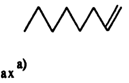


Fig. 7. Time course for styrene oxide production catalyzed by MnMe. [styrene]=A 0.21; B 0.31; C 0.75; D 1.3; E 2.7; F 3.9 M. By use of other complexes the plots of time course for epoxide production give straight lines.

Table 3. Kinetic Parameters for Epoxidation Catalyzed by Iron and Manganese Porphyrin Complexes

M	R						
		V_{max}[a)]	K_m	V_{max}[a)]	K_m	V_{max}[a)]	K_m
		turnovers s^{-1}	M	turnovers s^{-1}	M	turnovers s^{-1}	M
Fe	Me	1.3	0.40	1.1	0.16	0.13	0.26
	Cl	1.4	0.065	2.8	0.30	0.37	0.06
Mn + *N*-base	Me	10.3	0.51	3.8	0.051	4	2
	Cl	2.8	0.06	1.9	0.036	2.1	0.09

a) V_{max} (in turnovers s^{-1}) here is identical to the rate-determining constant k_2.[35)] on the binding affinity of oxo–iron complex to olefin, as mentioned above. With respect to the manganese complexes, the K_m value for MnCl to each olefin is smaller than that of MnMe (by a factor of 8.5 for styrene; 22 for 1-octene). The electron-withdrawing chloro groups enhance the binding affinity of the oxo–manganese complex to olefin.

Taking all these facts together, we presently propose a speculative mechanism. One possible explanation for the difference between the iron and the manganese catalysts is that steric interactions between an ortho substituent and the olefin differ. According to previous EXAFS results regarding oxo-metal complexes, the distance Fe–O is 1.64 Å⁵⁵⁾ and Mn–O is 1.84 Å.⁵⁶⁾ Fe–O is shorter than Mn–O by 0.2 Å. Thus, when olefin approaches the oxygen atom of an oxo-metal complex, a relatively large steric interaction between the olefin and ortho substituents of oxo–iron complexes would be expected, compared with the case of manganese complexes. In iron complexes, owing to a large steric interaction, the electronic effect of the ortho-substituents has little influence on the binding affinity to the olefins. On the other hand, in manganese complexes, the steric interaction is not so large that the electronic effect reflects the binding affinity.

***N*-Alkylation of an Iron Porphyrin.** Both cytochrome P-450 enzymes[57] and iron porphyrin–iodosylarene systems[58–62] undergo an *N*-alkylation of porphyrin in the epoxidation of 1-olefins. Although *N*-alkylation causes a "suicide" inactivation of P-450, a reduced activity is still retained in a model system.[59]

We observed an *N*-alkylaiton of FeCl in the course of the epoxidation of 1-octene. Under hypochlorite oxidant conditions FeCl and excess 1-octene were stirred for 4 min. The organic phase turned green. The UV-vis spectrum (λ_{max} 435, 578, 641 nm) was similar to that of the previously reported iron *N*-alkylporphyrins.[58,59]

For each of the two iron porphyrins the difference of K_m values among the three different olefins is small, as shown in Table 3. The V_{max} values for 1-octene are, however, about 1/10 of the V_{max} values for other two olefins. These kinetic data suggest that the oxo-1-octene intermediate has a relatively long lifetime. Therefore, a rearrangement of the intermediate may occur while affording *N*-alkylporphyrin.

Conclusively, we have demonstrated that: (1) the mechanism for the catalytic reaction by iron porphyrins is the Michaelis-Menten type as well as that by manganese complexes, (2) the differences of the metals or the ortho substituents give effects on oxidative catalyst destruction and on the Michaelis-Menten parameters, V_{max} and K_m, and (3) *N*-alkylation of an iron porphyrin has a relationship to the kinetic parameters.

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 61470041) from the Ministry of Education, Science and Culture.

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