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Factors Affecting the Catalytic Epoxidation of Olefins by Iron Porphyrin Complexes and H_2O_2 in Protic Solvents

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Abstract: The catalytic epoxidation of cyclohexene by iron(III) porphyrin complexes and H_2O_2 has been investigated in alcohol solvents to understand factors affecting the catalyst activity in protic solvents. The yields of cyclohexene oxide and the $Fe^{III/II}$ reduction potentials of iron porphyrin complexes were significantly affected by the protic solvents, and there was a close correlation between the product yields and the reduction potentials of the iron porphyrin catalysts. The role of alcohol solvents was proposed to control the electronic nature of iron porphyrin complexes that determines the catalyst activity in the epoxidation of olefins by H_2O_2. We have also demonstrated that an electron-deficient iron porphyrin complex can catalyze the epoxidation of olefins by H_2O_2 under conditions of limiting substrate with high conversion efficiency in a solvent mixture of CH_3OH and CH_2Cl_2.

The importance of iron(III) porphyrin complexes as chemical models of heme-containing enzymes and their use as catalysts for selective and controlled oxygenation reactions have prompted extensive studies of their reactions with a variety of oxidants including iodosylbenzene, peracids, hypochlorite, and hydroperoxides.[1] In particular, the reactions of iron porphyrin complexes with hydrogen peroxide have attracted much attention in the communities of bioorganic, bioinorganic, and oxidation chemistry, since H_2O_2 is a biologically important and environmentally clean oxidant. Traylor and co-workers demonstrated for the first time that electron-deficient iron porphyrin complexes are capable of catalyzing epoxidation of olefins by H_2O_2 in a solvent mixture of $CH_2Cl_2/CH_3OH/H_2O$.[2] It has been proposed that protic solvents function as general-acid catalysis which facilitates O−O bond heterolysis, resulting in the generation of high-valent oxoiron(IV) porphyrin π-cation radicals.[2−4] Recently, we[5] and others[6,7] have shown that olefin epoxidation and alkane hydroxylation by H_2O_2 can be achieved in aprotic solvents (e.g., CH_3CN) when highly electron-deficient iron porphyrins are used as catalysts. In the studies, oxygenation reactions were found to depend significantly on the electronic nature of iron porphyrin catalysts. More recently, we have shown that simple counterions of iron porphyrins (e.g., X = Cl or CF_3SO_3 in Fe(Porp)X) and the presence of imidazoles as axial ligands also affect the oxygenation reactions in aprotic solvents.[8,9] Other factors[10] such as pHs in aqueous solution,[11] the presence of a proton-shuttle group on porphyrin ligand,[12] and the robustness of iron porphyrin catalysts[13] were reported to play important roles in the reactions of iron porphyrin complexes and H_2O_2. In the

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TABLE 1. Yields of Cyclohexene Oxide Formed in the Epoxidation of Cyclohexene by Iron(III) Porphyrin Complexes and H_2O_2 and the $Fe^{III/II}$ Reduction Potentials of the Iron Porphyrin Complexes[a]

A. Effect of Alcohol Solvents[b]

	CF_3CH_2OH	CH_3OH	CH_3CH_2OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$
product yield[e,f] (%)	17 ± 2	71 ± 6	67 ± 5	65 ± 5	3 ± 1
$E°$ vs ferrocene, V[g,h]	−0.11	−0.33	−0.34	−0.35	−0.49

B. Effect of 5-Chloro-1-methylimidazole as an Axial Ligand[b,c]

	CF_3CH_2OH	CH_3OH	CH_3CH_2OH	$(CH_3)_2CHOH$	$(CH_3)_3COH$
product yield[e,f] (%)	70 ± 5	72 ± 6	69 ± 6	68 ± 5	35 ± 3
$E°$ vs ferrocene, V[g,h]	−0.23	−0.20	−0.20	−0.20	−0.23

C. Effect of Electronic Nature of Iron(III) Porphyrins[d]

	1	**2**	**3**	**4**	**5**	**6**	**7**
product yield[e,f] (%)	0	0	41 ± 3	64 ± 5	71 ± 6	46 ± 3	11 ± 2
$E°$ vs ferrocene, V[g,h]	−0.61	−0.56	−0.50	−0.45	−0.33	−0.17	0.02

[a] See the Experimental Section for detailed reaction conditions. [b] Fe(TPFPP)Cl was used as a catalyst. [c] 5-Chloro-1-methylimidazole (0.1 mmol) was present in reaction solutions. [d] Reactions were run in CH_3OH/CH_2Cl_2 (3:1). [e] Only small amounts (<3% based on H_2O_2 used) of cyclohexenol and cyclohexenone were formed. [f] Based on the amounts of H_2O_2 added. [g] Experimental details for electrochemical measurements have been described previously.[3a] [h] In V versus Fc/Fc^+ (ferrocene/ferrocinium) couple.

present work, we have studied the catalytic epoxidation of olefins by iron porphyrin complexes and H_2O_2 in protic solvents, to understand factors affecting the catalyst activity in protic solvents. We found from the studies that the yields of epoxide product and the $Fe^{III/II}$ reduction potentials of iron porphyrin complexes are significantly influenced by the protic solvents and that there is a close correlation between the product yields and the reduction potentials of the iron porphyrin catalysts. These results led us to propose that alcohol solvents coordinating to iron porphyrins as axial ligands control the electronic nature of iron porphyrin complexes and determine the catalyst activity in the epoxidation of olefins by H_2O_2.

We first explored the effect of alcohol solvents on the catalytic epoxidation of cyclohexene by an electron-deficient iron(III) porphyrin complex, Fe(TPFPP)Cl (TPFPP = *meso*-tetrakis(pentafluorophenyl)porphinato dianion), and H_2O_2 in a solvent mixture of alcohol/CH_2Cl_2 at room temperature.[2] The results in Table 1A show that the yields of cyclohexene oxide were markedly influenced by alcohol solvents; the yields were high in CH_3OH, CH_3CH_2OH, and $(CH_3)_2CHOH$, whereas only small amounts of cyclohexene oxide were yielded in $(CH_3)_3OH$ and CF_3CH_2OH. In addition, when the $Fe^{III/II}$ reduction potentials of Fe(TPFPP)Cl were determined with cyclic voltammetry under the identical reaction conditions employed in the epoxidation reactions,[3a] the $Fe^{III/II}$ reduction potentials were found to vary significantly depending on the alcohol solvents; the $E°$ values were similar in CH_3OH, CH_3CH_2OH, and $(CH_3)_2CHOH$ but quite different in $(CH_3)_3OH$ and CF_3CH_2OH (see Table 1A). The $Fe^{III/II}$ reduction potentials of the $Fe(TPFPP)^+$ complex also indicate that the electron-richness of the iron porphyrin complex in alcohol solvents is in the order of $(CH_3)_3OH$ > $(CH_3)_2CHOH \cdot CH_3CH_2OH \cdot CH_3OH$ > CF_3CH_2OH. Since it has been demonstrated previously that alcohols bind to metalloporphyrins as axial ligands,[14,15] we propose that the effect of alcohol solvents on the catalyst activity and the $Fe^{III/II}$ reduction potentials results from the coordination of alcohols as axial ligands (vide infra).

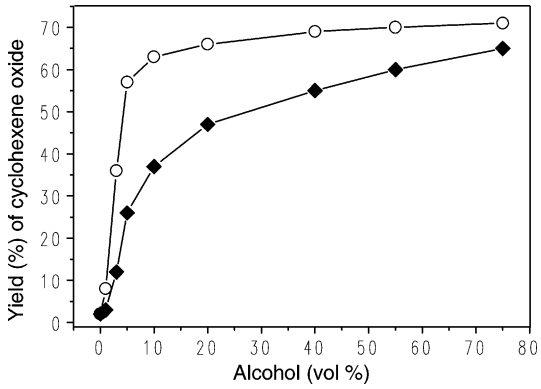

FIGURE 1. Plot of the percent yields of cyclohexene oxide formed in the catalytic epoxidation of cyclohexene by Fe(TPFPP)Cl and H_2O_2 vs volumes (%) of alcohols in the solvent mixture of alcohol/CH_2Cl_2: ○, CH_3OH; ♦, $(CH_3)_2CHOH$.

Then, the effect of alcohol concentration on the epoxidation of cyclohexene by Fe(TPFPP)Cl and H_2O_2 was investigated in CH_3OH and $(CH_3)_2CHOH$. Figure 1 shows that epoxide yields increased with the increase of alcohol concentrations and the increase of the product yields was faster in CH_3OH than in $(CH_3)_2CHOH$. In addition, the increase of alcohol concentratons shifted the $Fe^{III/II}$ reduction potentials to less negative values (Supporting Information, Table S1), indicating that the iron porphyrin complex became more electron-deficient with the increase of the amounts of alcohols in reaction solutions. As we have discussed above, the results of the concentration effect on the product yields and the $Fe^{III/II}$ reduction potentials are illustrated with the axial ligand effect. Indeed, it has been reported that the reduction potentials of Mn(TPP)Cl (TPP = *meso*-tetraphenylporphinato dianion) were dependent on methanol concentrations, and this phenomenon was illustrated with the replacement of an axial chloride ligand by CH_3OH upon the increase of methanol concentrations.[16]

To probe that the alcohol solvent effect was resulted from the coordination of alcohol solvents as axial ligands,

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the catalytic epoxidation of cyclohexene by Fe(TPFPP)Cl and H_2O_2 was carried out in the presence of 5-chloro-1-methylimidazole (5-Cl-1-MeIm) in alcohol solvents.[8b] The binding of 5-Cl-1-MeIm to the $Fe(TPFPP)^+$ complex was monitored by taking UV−vis spectra of the reaction solutions (data not shown).[3b,17] The results in Table 1B show that when the epoxidation reactions were carried out in the presence of 5-Cl-1-MeIm, the yield of cyclohexene oxide increased from 17% to 70% in CF_3CH_2OH solution and high yields of epoxide product were obtained in CH_3OH, CH_3CH_2OH, and $(CH_3)_2CHOH$. In $(CH_3)_3OH$ solution, the yield of cyclohexene oxide increased from 3% to 35%, and this result was ascribed to a fast degradation of the Fe(TPFPP)Cl catalyst under the reaction condition (data not shown). In addition, the $Fe^{III/II}$ reduction potentials of the imidazole-bound low-spin Fe(TPFPP)(5-Cl-1-MeIm)$_2$ were identical within experimental error in all alcohol solvents (see Table 1B). When 1-methylimidazole (1-MeIm) was used instead of 5-Cl-1-MeIm, the yields of epoxide product were low (about 15% based on H_2O_2 used) and the $Fe^{III/II}$ reduction potentials of the imidazole-bound low-spin Fe(TPFPP)(1-MeIm)$_2$ were identical (~ -0.32 V) in all alcohol solvents.[8b] On the basis of the observations that the alcohol solvent effect disappeared when the axial positions of the $Fe(TPFPP)^+$ complex were coordinated by imidazoles, we conclude that the chloride ligand of Fe(TPFPP)Cl is replaced by alcohol solvents and the $Fe(TPFPP)^+$ complexes binding different alcohols show different reactivities in the epoxidation of olefins by H_2O_2.[18]

The electronic effect of iron porphyrin complexes on the catalytic epoxidation of cyclohexene by H_2O_2 was also investigated with iron porphyrins bearing different substituents on *meso*-phenyls and pyrrole positions of porphyrin ligand in CH_3OH (Supporting Information, Figure S1 for the structures of iron porphyrin complexes).[19] As we have shown previously,[3a] electron-rich iron porphyrins did not produce cyclohexene oxide in the epoxidation of cyclohexene by H_2O_2 (see data of **1** and **2** in Table 1C). As the iron porphyrin catalysts became electron-deficient, the yields of cyclohexene oxide increased (see data of **3**−**5** in Table 1C). Interestingly, the epoxide yields diminished as the iron porphyrins became more electron-deficient (see data of **6** and **7** in Table 1C).[20] These results indicate that iron complexes of electron-rich or too electron-deficient porphyrin ligands are poor catalysts. This trend is also seen in the studies of alcohol solvent effect, in which the $Fe(TPFPP)^+$ complex in $(CH_3)_3OH$ and CF_3CH_2OH is the most electron-rich and -deficient, respectively, and in these solvents, the yields of epoxide product are low (see Table 1A). On the basis of the results, we conclude that alcohol solvents coordinating as axial ligands play an important role in controlling the electronic nature of iron porphyrin complexes and that the electronic nature of iron porphyrin catalysts is an important factor in determining the catalyst activity.[21]

TABLE 2. Catalytic Epoxidation of Olefins by Fe(TPFPP)Cl and H_2O_2 under Conditions of Limiting Substrate[a]

substrate	conversion[b] (%)	products	yields[b] (%)
cyclohexene	99 ± 1	cyclohexene oxide	90 ± 5
		cyclohexenol	5 ± 1
		cyclohexenone	∼0
cyclooctene	99 ± 1	cyclooctene oxide	95 ± 5
cis-stilbene	99 ± 1	*cis*-stilbene oxide	95 ± 4
		trans-stilbene oxide	2 ± 1
		benzaldehyde	<1

[a] See the Experimental Section for detailed reaction conditions. [b] Based on the amount of substrates used.

Finally, the catalytic epoxidation of olefins by Fe(TPFPP)Cl and H_2O_2 was attempted under conditions of limiting substrate (catalyst/substrate/H_2O_2 = 1:2000:2400), since the development of efficient and practical methods that utilize environmentally benign and inexpensive H_2O_2 as a terminal oxidant is an important objective in preparative oxidation chemistry.[22] Treatment of olefins with 1.2 equiv of H_2O_2 in the presence of 0.05 mol % catalyst in a solvent mixture of CH_3OH/CH_2Cl_2 afforded the complete conversion of olefins with high product yields and stereoselectivity (Table 2). By taking UV−vis spectra of reaction solutions before and after the addition of the oxidant, the destruction of the iron porphyrin catalyst was found to be minimal (i.e., less than 5%). These results demonstrate that the Fe(TPFPP)Cl complex can catalyze the epoxidation of olefins by H_2O_2 efficiently and selectively under conditions of limiting substrate.

In summary, we have shown here that the electronic nature and catalytic activity of iron porphyrin complexes are markedly influenced by alcohol solvents. This phenomenon was illustrated with the binding of alcohols as axial ligands that controls the electronic nature of iron porphyrin complexes. We have also demonstrated that the electronic nature of iron porphyrin catalysts is an important factor in determining the catalyst activity and that an electron-deficient iron porphyrin complex can catalyze the epoxidation of olefins by H_2O_2 under conditions of limiting substrate with high conversion efficiency.

Experimental Section

Materials and Instrumentation. All reagents purchased from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated.

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(18) When the anionic chloride ligand of Fe(TPFPP)Cl was replaced by nonligating anions such as $CF_3SO_3^-$ and ClO_4^-, the catalytic efficiency of the iron porphyrin complex increased markedly and the yields of oxygenated products were high in olefin epoxidation and alkane hydroxylation reactions by H_2O_2 in aprotic solvents.

(19) Abbreviations of porphyrin ligands: β-Cl_8TPFPP = β-octachloro-*meso*-tetrakis(pentafluorophenyl)porphinato dianion; β-Cl_8TDCPP = β-octachloro-*meso*-tetrakis(2,6-dichlorophenyl)porphinato dianion; TDFPP = *meso*-tetrakis(2,6-difluorophenyl)porphinato dianion; TDCPP = *meso*-tetrakis(2,6-dichlorophenyl)porphinato dianion; TMP = *meso*-tetramesitylporphinato dianion.

(20) In these reactions, the iron catalysts degraded at a fast rate, confirming a previous observation that iron porphyrin complexes bearing halogen-substituents on pyrrole positions lose their stability against oxidative degradation: Porhiel, E.; Bondon, A.; Leroy, J. *Tetrahedron Lett*. **1998**, *39*, 4829−4830.

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Methanol (anhydrous) and dichloromethane (anhydrous) were purified by distillation over CaH_2 prior to use. H_2O_2 (30% aqueous) was purchased from Aldrich. Fe(TPFPP)Cl and Fe(TPP)Cl were purchased from Aldrich Chemical Co. Other iron(III) porphyrin complexes were obtained from Mid-Century Chemicals. The purity of the iron porphyrins was examined by ^1H NMR in CD_2Cl_2.

Product analyses were performed on either a Hewlett-Packard 5890 II Plus gas chromatograph equipped with a FID detector using 30-m capillary column (Hewlett-Packard, HP-1 and HP-5) or a SUMMIT HPLC (DIONEX) with a variable-wavelength UVD 170S and a Phenomenex LUNA C18 reversed-phase column. UV−vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. ^1H NMR spectra were recorded on a Bruker AM 250. All electrochemical experiments were performed under N_2 atmosphere in a glovebox using BAS 50W voltammetric analyzer.

Reaction Conditions. Reactions were performed at ambient temperature under argon atmosphere unless otherwise indicated. All reactions were run in at least triplicate, and the data reported represent the averages of these reactions. In general, an iron porphyrin complex (1.25×10^{-3} mmol) was dissolved in a solvent mixture (2.5 mL) of alcohol/CH_2Cl_2 (3:1) containing cyclohexene (1 mmol). H_2O_2 (0.1 mmol, 30% aqueous, diluted in 0.2 mL of CH_3OH/CH_2Cl_2 (3:1)) was slowly added to the reaction solution over a period of 3 min, and the resulting solution was stirred for 10 min. An aliquot of the reaction mixture was directly analyzed by GC or GC/MS, and product yields were determined by comparison against standard curves prepared with known authentic samples.

The catalytic epoxidation reactions under conditions of limiting substrate were carried out as follows: H_2O_2 (3 mmol, diluted in a solvent mixture (0.5 mL) of CH_3OH/CH_2Cl_2 (3:1)) was added via syringe pump over 40 min to a reaction solution containing Fe(TPFPP)Cl (1.25×10^{-3} mmol) and substrate (2.5 mmol) in a solvent mixture (5 mL) of CH_3OH/CH_2Cl_2 (3:1). The reaction mixture was further stirred for 10 min and directly analyzed by GC or HPLC.

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Supporting Information Available: Table S1 reports the yields of cyclohexene oxide and the $Fe^{III/II}$ reduction potentials of Fe(TPFPP)Cl determined in different alcohol concentrations. Figure S1 shows structures of iron(III) porphyrin complexes used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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