Evidence for the Participation of Two Distinct Reactive Intermediates in Iron(III) Porphyrin Complex-Catalyzed Epoxidation Reactions

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Abstract: We have studied the competitive epoxidations of olefins with *cis*- and *trans*-stilbenes and with cyclooctene and *trans*-stilbene in iron porphyrin complex-catalyzed epoxidation reactions by H_2O_2, *tert*-butyl hydroperoxide (*t*-BuOOH), and *m*-chloroperoxybenzoic acid (*m*-CPBA) in protic solvent (i.e., a solvent mixture of CH_3OH and CH_2Cl_2) and aprotic solvent (i.e., a solvent mixture of CH_3CN and CH_2Cl_2) at room temperature under catalytic reaction conditions. The competitive epoxidations were also carried out with in situ generated high-valent iron(IV) oxo porphyrin cation radical complexes in aprotic solvent under stoichiometric reaction conditions. By determining the ratios of epoxide products formed in the competitive epoxidations, we were able to conclude unambiguously that the reactive species generated in protic solvent are high-valent iron(IV) oxo porphyrin cation radical complexes **3** and the intermediates formed in aprotic solvent are oxidant−iron porphyrin intermediates **2**. A protic solvent such as methanol is proposed to function as a general-acid catalyst, thereby increasing the rate of O−O bond cleavage of **2** to form **3**. In the absence of general-acid catalysis such as in aprotic solvent, the rate of O−O bond cleavage of **2** is relatively slow and **2** transfers its oxygen to olefins prior to the formation of **3**. To further examine the effect of the general-acid catalysis on the nature of epoxidizing intermediates, we carried out competitive epoxidations in the solvent mixtures of alcohol/CH_2Cl_2 using alcohols of varying pK_a values and in the presence of an acid (i.e., $HClO_4$) in aprotic solvent. The product ratios were found to vary depending on the strength of the solvent acidity, demonstrating that the reaction of **2** with olefin competes with the O−O bond cleavage of **2** that leads to the formation of **3**. We also reported for the first time that a high-valent iron(IV) oxo porphyrin cation radical intermediate containing electron-deficient porphyrin ligand shows an unexpected preference for *trans*-stilbene over *cis*-stilbene in the competitive epoxidations of *cis*- and *trans*-stilbenes.

Introduction

Elucidation of the structures of reactive intermediates responsible for oxygen atom transfer in catalytic oxygenation reactions by heme and nonheme iron monooxygenase enzymes and their model compounds has been the major goal of biological and bioinorganic chemistry for the past three decades.[1,2] In heme-containing enzymes and their iron(III) porphyrin models, it has been generally believed that high-valent iron(IV) oxo porphyrin cation radical intermediates **3** are the only reactive species responsible for the oxygenation of hydrocarbons (Scheme 1).[1] A number of high-valent iron oxo porphyrin complexes have been prepared at low temperature, characterized with a variety of spectroscopic methods, and directly used in the reactivity studies of oxygen atom transfer reactions such as olefin epoxidation, alkane hydroxylation, and N-demethylation.[3] Also, there is direct and indirect evidence that strongly supports the involvement of **3** as the reactive species in the catalytic oxygenation of hydrocarbons by heme-containing enzymes and iron porphyrin complexes.[4,5]

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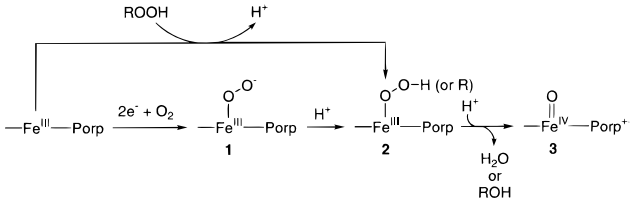
Scheme 1. Reactive Intermediates Capable of Oxygenating Organic Substrates in Heme-Containing Enzymes and Iron Porphyrin Models



In addition to the intermediacy of **3**, recent studies provided strong evidence that oxidant−iron(III) porphyrin intermediates **2** are capable of transferring their oxygen to hydrocarbons prior to the formation of **3** (Scheme 1).[6−8] Notably, Vaz et al. reported elegant results that iron(III)−hydroperoxide (Fe^{III}-OOH) and iron(III)−hydrogen peroxide (Fe^{III}-H_2O_2) intermediates function as electrophilic oxidants in olefin epoxidation and alkane hydroxylation reactions by cytochrome P-450 enzymes and their mutants.[6] In the mutants lacking threonine in the active site of cytochromes P-450, the lifetime of iron(III)−hydroperoxide species is increased, and this intermediate is capable of oxygenating hydrocarbons prior to the formation of **3**. The involvement of **2** as reactive intermediates has also been suggested in iron porphyrin complex-catalyzed oxygenations of hydrocarbons by oxidants such as hydrogen peroxide and peracids,[4c,7,8] especially in the epoxidation of olefins by peracids at low temperature.[8] When the rate of O−O bond cleavage of **2** becomes slow such as in the cases where the reactions are performed with electron-deficient iron porphyrin complexes,[7a,8a] in nonpolar solvents (e.g., toluene),[8a] or at low temperature,[4c] **2** is able to transfer its oxygen to easily oxygenated organic substrates such as olefins prior to the O−O bond cleavage of **2**. Another reactive intermediate that has been proposed to effect the oxidations of organic substrates in cytochrome P-450 enzymes and iron porphyrin models is an iron(III) peroxo porphyrin complex **1** (Scheme 1).[9−12] Valentine and co-workers reported elegant results recently that in situ generated iron(III) peroxo porphyrin complexes are powerful nucleophiles capable of epoxidizing electron-deficient olefins.[9] In cytochrome P-450 2B4 and aromatase enzymes, there is growing evidence that **1** is the reactive species responsible for the aldehyde deformylation and aromatization reactions.[11,12]

Although it has been shown in a number of reports that intermediates such as **2** and **3** are involved in iron(III) porphyrin complex-catalyzed oxygenations of hydrocarbons, it is not completely clear which reactive species (e.g., **2**, **3**, or both **2** and **3** at the same time) are responsible for oxygen atom transfer in the catalytic oxygenation reactions performed *at room temperature* and what factors are important to determine the nature of the reactive intermediates in iron porphyrin model systems. In this paper, we report the results of the competitive epoxidations studied with *cis*- and *trans*-stilbenes and with cyclooctene and *trans*-stilbene in iron(III) porphyrin-catalyzed epoxidation of olefins by oxidants such as H_2O_2, *tert*-butyl hydroperoxide (*t*-BuOOH), and *m*-chloroperoxybenzoic acid (*m*-CPBA) in protic and aprotic solvents at room temperature. We found from the studies that both the intermediates (i.e., **2** and **3**) *indeed* function as reactive species in the epoxidation of olefins by iron porphyrins *at room temperature* and that the participation of **2** and **3** as reactive epoxidizing intermediates is found to be controlled by the factors such as the solvent system (i.e., protic and aprotic solvents), the presence of a proton source in aprotic solvent, and the acidity of alcohol solvents. Furthermore, we report for the first time that a high-valent iron(IV) oxo porphyrin cation radical intermediate containing nonbulky *ortho*-fluoro substituents at the phenyl groups of electron-deficient porphyrin ligand shows an unexpected preference for *trans*-stilbene over *cis*-stilbene in the competitive epoxidations of *cis*- and *trans*-stilbenes.

Results and Discussion

We have studied competitive epoxidations with iron(III) porphyrin complexes such as (*meso*-tetrakis(pentafluorophenyl)-porphinato)iron(III) chloride [Fe(TPFPP)Cl], (*meso*-tetrakis(2,6-difluorophenyl)porphinato)iron(III) chloride [Fe(TDFPP)Cl], and (*meso*-tetrakis(2,6-dichlorophenyl)porphinato)iron(III) chloride [Fe(TDCPP)Cl] (see Figure 1 for the structures of iron(III) porphyrin complexes) and with oxidants such as *m*-CPBA, H_2O_2, and *t*-BuOOH in protic solvent (i.e., a solvent mixture of CH_3-OH and CH_2Cl_2) and aprotic solvent (i.e., a solvent mixture of CH_3CN and CH_2Cl_2) at room temperature under catalytic reaction conditions. Two sets of competitive epoxidations were carried out with *cis*- and *trans*-stilbenes (eq 1) and with cyclooctene and *trans*-stilbene (eq 2), and the yields of the epoxide products and the product ratios are listed in Tables 1 and 2. We also carried out control reactions with *cis*-stilbene

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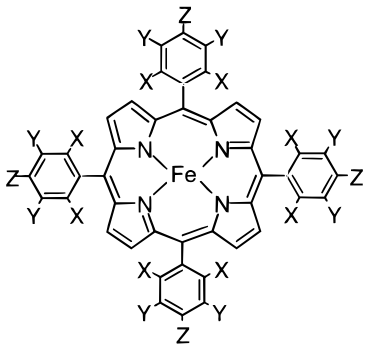
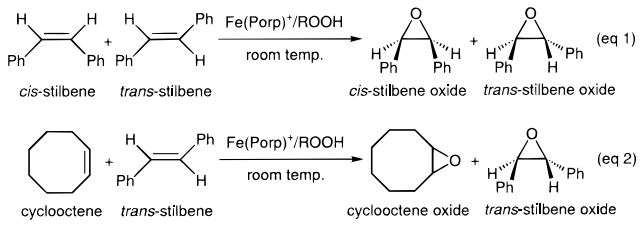


Iron(III) porphyrins	X	Y	Z
Fe(TPFPP)Cl	F	F	F
Fe(TDFPP)Cl	F	H	H
Fe(TDCPP)Cl	Cl	H	H

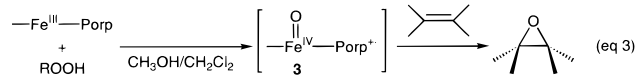
Figure 1. Structures of iron(III) porphyrin complexes used in this study.

and *trans*-stilbene individually, to ensure that no isomerized products were formed in the epoxidations of *cis*- and *trans*-stilbenes under the reaction conditions employed, since the



formation of isomerized products (e.g., the formation of *trans*-stilbene oxide in the epoxidation of *cis*-stilbene) would result in giving false product ratios in the competitive epoxidation reactions. The control reactions showed at most only trace amounts of isomerized *trans*-stilbene oxide formation in the *cis*-stilbene epoxidations and no formation of *cis*-stilbene oxide in the *trans*-stilbene epoxidations (Supporting Information, Table S1). In addition, an intriguing observation that we made in the control reactions was that the yields of *trans*-stilbene oxide formed in the epoxidations of *trans*-stilbene by Fe(TPFPP)Cl and Fe(TDFPP)Cl *in protic solvent* were unusually high and comparable to the yields of *cis*-stilbene oxide formed in the epoxidation of *cis*-stilbene by the iron porphyrin complexes (Table S1; compare the yields of *cis*-oxide in *cis*-stilbene epoxidation with the yields of *trans*-oxide in *trans*-stilbene epoxidation in the first column).[13] In the absence of the iron porphyrin catalysts, no epoxide formation was observed in the reactions of H_2O_2 and *t*-BuOOH. The epoxidations of olefins by *m*-CPBA carried out in the presence of iron porphyrin complexes are iron porphyrin complex-catalyzed reactions.[14]

Competitive Epoxidations in Protic Solvent. The competitive epoxidations of *cis*- and *trans*-stilbenes and of cyclooctene and *trans*-stilbene were first carried out in a protic solvent system (i.e., a solvent mixture of CH_3OH and CH_2Cl_2) at room temperature. As the results of the competitive epoxidations of *cis*- and *trans*-stilbenes are shown in Table 1 (see the column of protic solvent, catalytic reaction), the ratios of *cis*- to *trans*-stilbene oxides formed in the reactions of *m*-CPBA, H_2O_2, and *t*-BuOOH were identical in each iron porphyrin complex within experimental error (entries 1−3 for Fe(TPFPP)Cl, entries 4−6 for Fe(TDFPP)Cl, and entries 7−9 for Fe(TDCPP)Cl). Also, the ratios of cyclooctene oxide to *trans*-stilbene oxide formed in the competitive epoxidations of cyclooctene and *trans*-stilbene by *m*-CPBA, H_2O_2, and *t*-BuOOH were identical in each iron porphyrin complex (Table 2; see the column of protic solvent, catalytic reaction). These results clearly demonstrate that the reactions of the iron porphyrin complexes with the oxidants generate **3** as reactive epoxidizing intermediates in a protic solvent system (eq 3).[4c,f] If the reactive interemdiates generated in the reactions of *m*-CPBA, H_2O_2, and *t*-BuOOH were different, then the ratios of the oxide products formed in the competitive epoxidations would be different (vide infra).



Interestingly, the ratios of *cis*- to *trans*-stilbene oxides formed in the competitive epoxidations of *cis*- and *trans*-stilbenes were found to depend significantly on the nature of the iron porphyrin complexes (Table 1, ratios of ∼0.5, ∼2, and >15 in the reactions of Fe(TPFPP)Cl, Fe(TDFPP)Cl, and Fe(TDCPP)Cl, respectively), and these results are interpreted in terms of the steric and electronic effects of the iron porphyrins on the cis−trans selectivity. The high ratio of *cis*- to *trans*-stilbene oxides observed in the Fe(TDCPP)Cl reaction is ascribed to the steric effect of the bulky *ortho*-chloro substituents at the phenyl groups of the porphyrin ligand, since the approach of *trans*-stilbene to the iron oxo moiety is difficult due to the steric hindrance between the phenyl groups of *trans*-stilbene and the phenyl groups of the porphyrin ligand.[15] The relatively low ratios of *cis*- to *trans*-stilbene oxides observed in the reactions of Fe(TPFPP)Cl and Fe(TDFPP)Cl may be due to the fact that the size of the *ortho*-fluoro substituents at the phenyl groups of the porphyrin ligands is smaller than that of the *ortho*-chloro substituents at the Fe(TDCPP)Cl complex. In addition, the *cis*- to *trans*-epoxide ratios obtained in the reactions of Fe(TPFPP)Cl (i.e., ratio of ∼0.5) and Fe(TDFPP)Cl (i.e., ratio of ∼2) were different as well. Since these two iron porphyrins contain the same *ortho*-fluoro substituents at the phenyl groups of the porphyrin ligands, we suggest that the different *cis*- to *trans*-epoxide ratios are caused by the different electronic properties of the iron porphyrin complexes. The results also indicate that the intermediate of the more electron-deficient iron porphyrin complex (i.e., $(TPFPP)^{+\bullet}Fe^{IV}{=}O$) shows an unexpected preference for *trans*-stilbene over *cis*-stilbene (i.e., *cis*- to *trans*-epoxide ratio of 0.5), and, to the best of our knowledge, this is the first time to observe the preference of *trans*-stilbene over *cis*-stilbene in iron porphyrin-catalyzed competitive epoxidations of *cis*- and *trans*-stilbenes (vide infra).[15]

Competitive Epoxidations in Aprotic Solvent. When the identical competitive epoxidations were carried out in an aprotic solvent system (i.e., a solvent mixture of CH_3CN and CH_2Cl_2),

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Table 1. Competitive Epoxidations of *cis*- and *trans*-Stilbenes by Iron(III) Porphyrin Complexes with Various Oxidants in Protic and Aprotic Solvents under Catalytic Reaction Conditions and by in Situ Generated $(Porp)^{+\bullet}Fe^{IV}=O$ Complexes in Aprotic Solvent under Stoichiometric Reaction Conditions[a]

			protic solvent, catalytic reaction			aprotic solvent, catalytic reaction			$(Porp)^{+\bullet}Fe^{IV}=O$ in aprotic solvent		
			product yields (%)[b]		ratio of *cis*-	product yields (%)[b]		ratio of *cis*-	product yields (%)[b]		ratio of *cis*-
entry	iron porphyrin	oxidant	*cis*-oxide[c]	*trans*-oxide[c]	to *trans*-oxide	*cis*-oxide[c]	*trans*-oxide[c]	to *trans*-oxide	*cis*-oxide[c]	*trans*-oxide[c]	to *trans*-oxide
1	Fe(TPFPP)Cl	*m*-CPBA	28	59	**0.5** ± 0.1	88	11	**8** ± 1	18	41	**0.5** ± 0.1
2		H_2O_2	18	45	**0.4** ± 0.1	17[d]	29[d]	**0.6** ± 0.2[d]			
3		*t*-BuOOH	18	48	**0.4** ± 0.1	nd[e]	nd[e]	nd[e]			
4	Fe(TDFPP)Cl	*m*-CPBA	62	31	**2.0** ± 0.2	86	7	**12** ± 2	34	14	**2.4** ± 0.4
5		H_2O_2	46	20	**2.3** ± 0.4	48[d]	12[d]	**4** ± 1[d]			
6		*t*-BuOOH	39	18	**2.2** ± 0.4	nd[e]	nd[e]	nd[e]			
7	Fe(TDCPP)Cl	*m*-CPBA	76	trace[f]	>**15**	80	trace[f]	>**15**	48	trace[f]	>**15**
8		H_2O_2	44	trace[f]	>**15**	36[d]	trace[d,f]	>**15**[d]			
9		*t*-BuOOH	30	trace[f]	>**15**	nd[e]	nd[e]	nd[e]			

[a] See Experimental Section for detailed experimental procedures. All reactions were run at least in triplicate, and the data reported represent the average of these reactions. [b] Based on the amounts of oxidants used. [c] *cis*-Oxide and *trans*-oxide stand for *cis*-stilbene oxide and *trans*-stilbene oxide, respectively. [d] Reactions were run in the presence of 5-chloro-1-methylimidazole (0.1 mmol), since the epoxidation of olefins by H_2O_2 in aprotic solvent did not yield the oxide products in the absence of the imidazole.[23] [e] Not determined due to either low product yields or formation of isomerized *trans*-stilbene oxide product in the epoxidation of *cis*-stilbene. [f] Yields were less than 3% based on oxidants used.

Table 2. Competitive Epoxidations of Cyclooctene and *trans*-Stilbene by Iron(III) Porphyrin Complexes with Various Oxidants in Protic and Aprotic Solvents under Catalytic Reaction Conditions and by in Situ Generated $(Porp)^{+\bullet}Fe^{IV}=O$ Complexes in Aprotic Solvent under Stoichiometric Reaction Conditions[a]

			protic solvent, catalytic reaction			aprotic solvent, catalytic reaction			$(Porp)^{+\bullet}Fe^{IV}=O$ in aprotic solvent		
			product yields (%)[b]		ratio of co-	product yields (%)[b]		ratio of co-	product yields (%)[b]		ratio of co-
entry	iron porphyrin	oxidant	co-oxide[c]	*trans*-oxide[c]	to *trans*-oxide	co-oxide[c]	*trans*-oxide[c]	to *trans*-oxide	co-oxide[c]	*trans*-oxide[c]	to *trans*-oxide
1	Fe(TPFPP)Cl	*m*-CPBA	10	87	**0.1** ± 0.05	87	8	**11** ± 3	3	31	**0.1** ± 0.05
2		H_2O_2	8	71	**0.1** ± 0.05	11[d]	36[d]	**0.3** ± 0.1[d]			
3		*t*-BuOOH	7	60	**0.1** ± 0.05	nd[e]	nd[e]	nd[e]			
4	Fe(TDFPP)Cl	*m*-CPBA	31	53	**0.58** ± 0.15	92	4	**23** ± 5	22	27	**0.8** ± 0.2
5		H_2O_2	21	36	**0.58** ± 0.20	40[d]	25[d]	**1.6** ± 0.4[d]			
6		*t*-BuOOH	17	32	**0.53** ± 0.20	nd[e]	nd[e]	nd[e]			
7	Fe(TDCPP)Cl	*m*-CPBA	67	trace[f]	>**15**	93	trace[f]	>**15**	59	trace[f]	>**15**
8		H_2O_2	36	trace[f]	>**15**	66[d]	trace[d,f]	>**15**[d]			
9		*t*-BuOOH	24	trace[f]	>**15**	nd[e]	nd[e]	nd[e]			

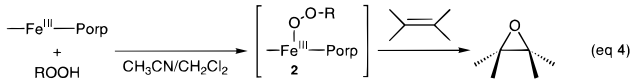
[a] See Experimental Section for detailed experimental procedures. All reactions were run at least in triplicate, and the data reported represent the average of these reactions. [b] Based on the amounts of oxidants used. [c] Co-oxide and *trans*-oxide stand for cyclooctene oxide and *trans*-stilbene oxide, respectively. [d] Reactions were run in the presence of 5-chloro-1-methylimidazole (0.1 mmol).[23] [e] Not determined due to the low yields of epoxide products. [f] Yields were less than 3% based on oxidants used.

the product ratios were found to be changed dramatically, especially in the reactions of Fe(TPFPP)Cl and Fe(TDFPP)Cl with *m*-CPBA (Tables 1 and 2; compare the product ratios in the columns of protic solvent and aprotic solvent). The ratios of *cis*- to *trans*-stilbene oxides obtained in the competitive epoxidations of *cis*- and *trans*-stilbenes in aprotic solvent were much higher than those obtained in protic solvent (Table 1, see the column of aprotic solvent, catalytic reaction). The ratio of ~0.5 in protic solvent was changed to 8 in aprotic solvent for the reactions of Fe(TPFPP)Cl with *m*-CPBA and the ratio of ~2.0 in protic solvent was changed to 12 in aprotic solvent for the reactions of Fe(TDFPP)Cl with *m*-CPBA (Table 1; compare entries 1 and 4 in the columns of protic solvent and aprotic solvent). The same trend was observed in the competitive epoxidations of cyclooctene and *trans*-stilbene, in which the ratios of cyclooctene oxide to *trans*-stilbene oxide were much higher in aprotic solvent than in protic solvent (Table 2). For examples, the ratios of 0.1 and ~0.6 in protic solvent were changed to 11 and 23 in aprotic solvent for the reactions of Fe(TPFPP)Cl and Fe(TDFPP)Cl with *m*-CPBA, respectively (Table 2; compare entries 1 and 4 in the columns of protic solvent and aprotic solvent). The finding of the dependence of the product ratios on the solvent systems (i.e., protic versus aprotic solvents) leads us to suggest that the reactive intermediates formed in aprotic solvent are different from the high-valent iron(IV) oxo porphyrin cation radical intermediates generated in protic solvent. If the reactive epoxidizing intermediates generated in the protic and aprotic solvents were the same species (e.g., **3**), we would expect to observe that the product ratios would be similar in both solvent systems (vide infra).

Another intriguing observation that we made in aprotic solvent was the dependence of the epoxide product ratios on the kinds of oxidants used. For example, the ratios of *cis*- to *trans*-stilbene oxides formed in the competitive epoxidations of *cis*- and *trans*-stilbenes by Fe(TPFPP)Cl were 8 and 0.6 for the reactions of *m*-CPBA and H_2O_2, respectively (Table 1, entries 1 and 2 in the column of aprotic solvent), and the ratios obtained with Fe(TDFPP)Cl were 12 and 4 for the reactions of *m*-CPBA and H_2O_2, respectively (Table 1, entries 4 and 5 in the column of aprotic solvent). The dependence of the product ratios on the structures of the oxidants was also observed in the competitive epoxidations of cyclooctene and *trans*-stilbene, in which the product ratios obtained in the reactions of *m*-CPBA and H_2O_2 were greatly different (Table 2; compare the product ratios in entries 1 and 2 for the Fe(TPFPP)Cl reactions and entries 4 and 5 for the Fe(TDFPP)Cl reactions in the column of aprotic solvent). These results further support that a common intermediate such as **3** is not responsible for the olefin epoxidations in aprotic solvent, since the generation of the common intermediate in the reactions of *m*-CPBA and H_2O_2

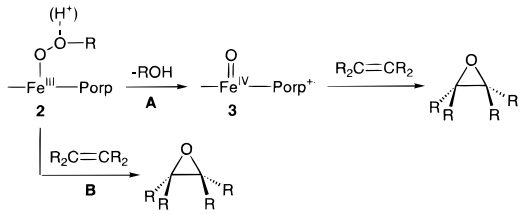
should give the same ratios of epoxide products, as we have observed in the protic solvent system.

We have suggested above that the different product ratios observed in protic and aprotic solvents are due to the presence of two different reactive intermediates in the protic and aprotic solvents. However, since we could not rule out a possibility that the different product ratios in the protic and aprotic solvents are caused by the difference of solvents, we therefore prepared high-valent iron(IV) oxo porphyrin cation radical complexes[4a,16] and directly used the in situ generated iron oxo intermediates in the competitive epoxidations *in aprotic solvent*.[17] As shown in Tables 1 and 2 (see the columns of $(Porp)^{+\bullet}Fe^{IV}=O$ in aprotic solvent), the ratios of *cis*- to *trans*-stilbene oxides and cyclooctene oxide to *trans*-stilbene oxide obtained with $(TPFPP)^{+\bullet}Fe^{IV}=O$ and $(TDFPP)^{+\bullet}Fe^{IV}=O$ were different from those obtained in aprotic solvent but the same as those obtained in protic solvent. These results lead us to conclude that the reactive species generated in the protic solvent are **3** as we have suggested above and that the intermediates generated in the aprotic solvent are not **3** but, possibly, **2** even at room temperature (eq 4).[8]



On the basis of the results that **2** may be the reactive epoxidizing intermediate in aprotic solvent, the observation of the high ratios of *cis*-olefin oxides to *trans*-stilbene oxide observed in the reactions of *m*-CPBA with Fe(TPFPP)Cl and Fe(TDFPP)Cl in aprotic solvent (Tables 1 and 2; see entries 1 and 4 in the column of aprotic solvent) is attributed to the steric effect of the bulky *m*-CPBA bound to the iron porphyrins, since the approach of *trans*-stilbene to **2** is highly restricted by the steric hindrance between the phenyl groups of *trans*-stilbene and the bulky *m*-CPBA bound to iron.[8a] Also, the relatively low ratios of *cis*-olefin oxides to *trans*-stilbene oxide observed in the H_2O_2 reactions, compared to the product ratios obtained in the *m*-CPBA reactions, are due to the fact that the size of the hydrogen atom in iron(III) hydroperoxide porphyrin intermediate (e.g., R = H in $(Porp)Fe^{III}-OOR$, **2**) is much smaller than that of the acyl group in acylperoxo−iron(III) porphyrin complex (e.g., R = C(O)(3-Cl-Ph) in $(Porp)Fe^{III}-OOR$, **2**). In addition, it is worth noting that both the postulated $(Porp)Fe^{III}-OOH$ intermediate and the high-valent iron(IV) oxo porphyrin cation radical intermediate containing nonbulky *ortho*-fluoro substituents at the phenyl groups of highly electron-deficient porphyrin ligand (i.e., $(TPFPP)Fe^{III}-OOH$ and $(TPFPP)^{+\bullet}Fe^{IV}=O$) show a selectivity of *trans*-stilbene over *cis*-olefins in the competitive epoxidations of *cis*- and *trans*-olefins. As we have noted in the previous section, this is the first time to observe that *trans*-stilbene is more reactive than *cis*-stilbene in iron porphyrin-catalyzed competitive epoxidations of *cis*- and *trans*-stilbenes.[15] These results further suggest that the previous interpretation that the preference of *cis*-stilbene over *trans*-stilbene in the competitive epoxidations of *cis*- and *trans*-stilbenes by the reactions of iron(III) porphyrin complexes with iodosylbenzene (e.g., the ratio of 15 for the selectivity of *cis*-stilbene over *trans*-stilbene in the reactions of Fe(TPP)Cl and PhIO)[15a] was due to the steric hindrance between the phenyl groups of *trans*-stilbene and the phenyl groups of the porphyrin ligand of high-valent iron oxo intermediate might not be correct. Instead, we propose that the selectivity of *cis*-stilbene over *trans*-stilbene in the PhIO reactions may be due to the generation of iodosylbenzene-iron porphyrin adducts as reactive epoxidizing intermediate in aprotic solvents such as CH_2Cl_2[2i,8a,18,19] and that the selectivity of *cis*-stilbene by the iodosylbenzene−iron porphyrin intermediates is caused by the steric hindrance between the phenyl groups of *trans*-stilbene and the bulky PhIO bound to iron.

Scheme 2. Proposed Mechanism for Olefin Epoxidation in Protic and Aprotic Solvents



Effect of General-Acid Catalysis on the Rate of O−O Bond Cleavage of 2. We have demonstrated above that **3** is the common reactive intermediate in protic solvent, whereas **2** is a potent reactive species in aprotic solvent. Then, how are two different reactive species responsible for olefin epoxidations in protic and aprotic solvents? A plausible explanation is that protic solvent functions as general-acid catalysis.[20] In the presence of general-acid catalysis, the rate of O−O bond cleavage of **2** is accelerated, resulted in forming **3** as the reactive species in a fast rate (Scheme 2, pathway A). In the absence of general-acid catalysis such as in aprotic solvent, the rate of O−O bond cleavage of **2** is relatively slow and **2** transfers its oxygen to olefins prior to the formation of **3** even at room temperature (Scheme 2, pathway B). To further examine the effect of general-acid catalysis on the formation of two different reactive intermediates such as **2** and **3**, we first carried out the competitive epoxidations of *cis*- and *trans*-stilbenes and of cyclooctene and *trans*-stilbene in the presence of an acid (i.e., $HClO_4$) in aprotic solvent and found that the product ratios changed dramatically and became similar to those obtained with $(Porp)^{+\bullet}Fe^{IV}=O$ complexes (Table 3; see data in 1-A and 2-A). These results clearly indicate that the presence of proton in aprotic solvent accelerates the rate of the O−O bond cleavage of **2** to form **3** as epoxidizing oxidant (Scheme 1, pathway A).[21] We also studied the competitive epoxidations in the solvent mixtures of alcohol/CH_2Cl_2 using alcohols of varying pK_a values, since it has been shown by Traylor and co-workers that the rate of hydroperoxide O−O bond cleavage is significantly affected by the alcohol acidity.[20] As shown in Table 3 (see data in 1-C and 2-C), the ratios of *cis*- to *trans*-oxides and cyclooctene oxide to *trans*-stilbene oxide gradually increased as the acidity of the alcohols decreased, demonstrating that the rate of the O−O bond cleavage of **2** is affected by the strength

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(17) Although we tried to prepare acylperoxo-iron(III) porphyrin complexes to use the intermediates directly in the competitive epoxidation reactions, we failed to prepare the acylperoxo-iron(III) porphyrin complexes by reacting Fe(TPFPP)OH and Fe(TDFPP)OH with *m*-CPBA at −45 °C in aprotic solvent.[8a] Instead, we observed the formation of ferryl-oxo porphyrin complexes, $(Porp)Fe^{IV}=O$, in the reactions.

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(19) The ratios of *cis*- to *trans*-stilbene oxides formed in the competitive epoxidations of *cis*- and *trans*-stilbenes by PhIO catalyzed by Fe(TPFPP)-Cl and Fe(TDFPP)Cl in aprotic solvent were 4 and 7, respectively, indicating that the reactive species generated in the PhIO reactions are not high-valent iron(IV) oxo porphyrin cation radical complexes such as $(TPFPP)^{+\bullet}Fe^{IV}=O$ and $(TDFPP)^{+\bullet}Fe^{IV}=O$: Nam, W.; Han, H. J.; Lee, H. J.; Kim, C. Unpublished results.

(20) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc*. **1990**, *112*, 178−186.

(21) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc*. **1988**, *110*, 8443−8452.

Table 3. Effects of Proton and Alcohol Acidity on the Ratios of Epoxide Products Formed in the Competitive Epoxidations of *cis*- and *trans*-Stilbenes and of Cyclooctene and *trans*-Stilbene Studied with Fe(TPFPP)Cl and Fe(TDFPP)Cl as Catalyst and *m*-CPBA as an Oxidant under Catalytic Reaction Conditions[a]

	cis-stilbene versus *trans*-stilbene			cyclooctene versus *trans*-stilbene		
	yields (%) of products[b]		ratio of	yields (%) of products[b]		ratio of
	cis-oxide[c]	*trans*-oxide[c]	*cis*- to *trans*-oxide	cyclooctene oxide	*trans*-oxide[c]	cyclooctene oxide to *trans*-oxide
1. Fe(TPFPP)Cl as the Catalyst						
A. proton effect in aprotic solvent[d]						
presence of $HClO_4$						
no	88	11	**8** ± 1	87	8	**11** ± 3
yes	30	41	**0.7** ± 0.1	9	40	**0.2** ± 0.1
B. $(TPFPP)^{+\bullet}Fe^{IV}{=}O$ as an oxidant[e]	18	41	**0.5** ± 0.1	3	31	**0.1** ± 0.05
C. effect of alcohol acidity in protic solvent[f,g]						
CH_3OH/CH_2Cl_2	30	50	**0.6** ± 0.1	18	59	**0.3** ± 0.1
CH_3CH_2OH/CH_2Cl_2	40	40	**1.0** ± 0.1	28	48	**0.6** ± 0.1
$(CH_3)_2CHOH/CH_2Cl_2$	62	23	**2.7** ± 0.5	53	27	**2.0** ± 0.4
$(CH_3)_3COH/CH_2Cl_2$	86	13	**6.6** ± 0.8	78	12	**6.3** ± 0.8
2. Fe(TDFPP)Cl as the Catalyst						
A. proton effect in aprotic solvent[d]						
presence of $HClO_4$						
no	86	7	**12** ± 2	92	4	**23** ± 5
yes	43	16	**2.7** ± 0.3	36	18	**2.3** ± 0.7
B. $(TPFPP)^{+\bullet}Fe^{IV}{=}O$ as an oxidant[e]	34	14	**2.4** ± 0.4	22	27	**0.8** ± 0.2
C. effect of alcohol acidity in protic solvent[f,g]						
CH_3OH/CH_2Cl_2	54	27	**2.0** ± 0.2	35	42	**0.8** ± 0.2
CH_3CH_2OH/CH_2Cl_2	53	26	**2.0** ± 0.3	40	45	**0.9** ± 0.2
$(CH_3)_2CHOH/CH_2Cl_2$	57	27	**2.1** ± 0.3	35	40	**0.9** ± 0.2
$(CH_3)_3COH/CH_2Cl_2$	85	11	**7.7** ± 0.5	86	11	**8** ± 2

[a] General reaction conditions were the same as described in Tables 1 and 2 unless otherwise indicated. [b] Based on the amounts of oxidants used. [c] *cis*-Oxide and *trans*-oxide stand for *cis*-stilbene oxide and *trans*-stilbene oxide, respectively. [d] Reactions were run in the presence of $HClO_4$ (5×10^{-3} mmol). [e] Data were obtained from Tables 1 and 2. [f] Reactions were run in a solvent mixture (total volume of 2.5 mL) of alcohol and CH_2Cl_2 (3:1). Since alcohols used as solvent may function as an axial ligand and it has been reported that there is a significant axial ligand effect on the reactivity of **3**,[3h] the studies of the alcohol acidity effect were performed by blocking the axial position of iron porphyrin complex with an imidazole (5-chloro-1-methylimidazole, 0.1 mmol) to eliminate a possibility of the axial ligand effect. [g] See ref 20 for the pK_a values of the alcohols.

of the alcohol acidity and that the rate of the O−O bond cleavage of **2** slows down as the acidity of the alcohols decreases. Furthermore, the results of the effect of alcohol acidity on the product ratios imply that the reaction of **2** with olefin (Scheme 1, pathway B) is competing with the O−O bond cleavage of **2** that leads to the formation of **3** (Scheme 1, pathway A) and that, in some cases, both the intermediates, **2** and **3**, effect the olefin epoxidation at the same time, depending on the acidity of the alcohol solvents functioning as general-acid catalysis.

In conclusion, we have demonstrated unambiguously (1) that two intermediates, **2** and **3**, are involved as reactive species in iron porphyrin complex-catalyzed epoxidation reactions at room temperature and (2) that an important factor to determine the nature of reactive intermediates by controlling the rate of the O−O bond cleavage of **2** is general-acid catalysis. The present results are relevant to those recently reported by Vaz et al. that several reactive intermediates can effect the functionalization of organic substrates by cytochrome P-450 enzymes and that **2** becomes the reactive epoxidizing intermediate by disrupting the presumed proton-transfer pathway in site-directed mutants.[6,11] Also, there is growing evidence that both iron(III)-hydroperoxide and high-valent iron oxo intermediates are capable of oxygenating hydrocarbons in methane monooxygenases and non-porphyrin iron complexes, depending on the reactivities of hydrocarbons such as olefins and alkanes.[2] Furthermore, the significant effect of the general-acid catalysis on the rate of the O−O bond cleavage of **2** has been well documented in peroxidase enzymes that the distal histidine residue functions as general-acid catalysis that increases the rate of formation of compound **I**.[22] Finally, our present results suggest that the previous results of the kinetic and mechanistic studies of oxygen atom transfer reactions that had been performed with an assumption that **3** was the reactive intermediate in iron porphyrin-catalyzed oxygenation reactions should be reevaluated because the reactive species responsible for oxygen atom transfer in the catalytic reactions in aprotic solvent might not be **3** but **2** in some cases.

Experimental Section

Materials. Methanol (anhydrous), dichloromethane (anhydrous), and acetonitrile (anhydrous) were obtained from Aldrich Chemical Co. and purified by distillation over CaH_2 prior to use. All reagents purchased from Aldrich Chemical Co. were the best available purity and used without further purification unless otherwise indicated. *m*-CPBA purchased from Aldrich Chemical Co. was purified by washing with phosphate buffer (pH 7.4) followed by water and then dried under reduced pressure. H_2O_2 (30% aqueous) and *tert*-butyl hydroperoxide (*t*-BuOOH, 70% aqueous) were purchased from Fluka and Sigma, respectively. Fe(TPFPP)Cl was obtained from Aldrich. Fe(TDFPP)Cl and Fe(TDCPP)Cl were obtained from Mid-Century Chemicals. Fe(TPFPP)(CF_3SO_3), Fe(TDFPP)(CF_3SO_3), and Fe(TDCPP)(CF_3SO_3) were prepared by stirring equimolar amounts of the chloride iron(III) porphyrins with $Ag(CF_3SO_3)$ followed by filtering through a 0.45 μM filter. The resulting solution was used immediately for further studies.

Instrumentation. Product analyses for the epoxidations of *cis*- and *trans*-stilbenes were performed on an *Orom Vintage 2000* HPLC equipped with a variable wavelength UV-200 detector. Detection was made at 215 nm. Products were separated on a Waters Symmetry C18 reverse phase column (4.6 × 250 mm), eluted first with 50% methanol in water for 15 min and then with 85% methanol in water for 10 min at a flow rate of 1 mL/min. The yields of cyclooctene oxide were determined by a Hewlett-Packard 5890 II Plus gas chromatograph equipped with a FID detector using a 30-m capillary column (Hewlett-

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Packard, HP-5). UV−vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer equipped with an *Optostat*^{DN} variable-temperature liquid-nitrogen cryostat (Oxford Instruments).

Catalytic Competitive Epoxidations in Protic and Aprotic Solvents. 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 average of these reactions.

The competitive epoxidations of *cis*- and *trans*-stilbenes and of cyclooctene and *trans*-stilbene in protic solvent were carried out as follows: oxidants (0.05 mmol, diluted in 0.3 mL of CH_3OH/CH_2Cl_2 (3:1)) were slowly added over a period of 20 min to a stirred solution containing an iron porphyrin complex (1×10^{-3} mmol) and equal amounts of competing olefins (0.15 mmol each) in a solvent mixture (2.2 mL) of CH_3OH and CH_2Cl_2 (3:1). The reaction mixture was further stirred for 10 min and directly analyzed by HPLC and/or GC. Product yields were determined by comparison against standard curves.

The reaction conditions in aprotic solvent were as follows: oxidants (0.05 mmol, diluted in 0.3 mL of CH_3CN/CH_2Cl_2 (1:1)) were slowly added over a period of 20 min to a stirred solution containing an iron porphyrin complex (1×10^{-3} mmol) and equal amounts of competing olefins (1.0 mmol each) in a solvent mixture (2.2 mL) of CH_3CN and CH_2Cl_2 (1:1). The competitive epoxidations studied with H_2O_2 were carried out in the presence of 5-chloro-1-methylimidazole (0.1 mmol), since the epoxidation of olefins by iron porphyrin complexes and H_2O_2 in aprotic solvent did not yield epoxide products in the absence of the imidazole.[23] The reaction mixture was further stirred for 10 min and directly analyzed by HPLC and/or GC with known authentic samples.

(23) Nam, W.; Lee, H. J.; Oh, S.-Y.; Kim, C.; Jang, H. G. *J. Inorg. Biochem*. Accepted for publication.

Competitive Epoxidations Studied with in Situ Generated High-Valent Iron(IV) Oxo Porphyrin Cation Radical Complexes. The reactions of triflate iron(III) porphyrin complexes (1.0×10^{-3} mmol) with 2 equiv of *m*-CPBA in a solvent mixture (0.5 mL) of CH_3CN and CH_2Cl_2 (1:1) at −45 °C gave the formation of green intermediates. The formation and stability of the intermediates were confirmed by taking low-temperature UV−vis spectra of the green solutions. The spectra showed broad absorption bands around 550−750 nm, characteristic of porphyrin cation radical complexes (Supporting Information, Figure S1).[4a,16] After substrates (equal amounts of competing olefins, 0.03 mmol each, diluted in 0.2 mL of CH_2Cl_2) were added to a reaction solution containing in situ generated $(Porp)^{+\bullet}Fe^{IV}{=}O$ (1.0×10^{-3} mmol) at −45 °C, the reaction mixture was stirred for 10 min at −45 °C and then directly analyzed by HPLC and/or GC.

Acknowledgment. Financial support for this research from the Korea Science and Engineering Foundation (96-0501-01-01-3, 1999-2-122-002-4), Brain Korea 21 Project, and the Ministry of Education of Korea (BSRI-98-3412) is gratefully acknowledged.

Supporting Information Available: Figure S1 displays UV−vis spectra of high-valent iron(IV) oxo porphyrin cation radical complexes and Table S1 contains data of control reactions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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