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Biomimetic Alkane Hydroxylations by an Iron(III) Porphyrin Complex with H_2O_2 and by a High-Valent Iron(IV) Oxo Porphyrin Cation Radical Complex

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Introduction

Iron(III) porphyrin complexes have been used as model compounds to mimic the chemistry of cytochrome P-450 enzymes that are capable of catalyzing a wide range of oxidation reactions including the remarkably difficult hydroxylation of unactivated C−H bonds of alkanes.[1] Previous studies for iron(III) porphyrin complex-catalyzed alkane hydroxylation reactions have been conducted extensively with oxidants such as PhIO, $KHSO_5$, NaOCl, ROOH, O_2, and ozone.[2,3] However, as far as we have been able to discern, *radical-free* (enzyme mimetic) hydroxylation of alkanes with a biologically important oxidant (i.e., H_2O_2) has been rarely observed in iron porphyrin-catalyzed oxygenation reactions.[4−6] Moreover, although high-valent iron(IV) oxo porphyrin cation radical species have been generally proposed as a reactive intermediate responsible for the C−H bond activation in cytochrome P-450 enzymes and iron porphyrin systems[1,2] and the presence of a high-valent iron oxo intermediate has been detected during the catalytic hydroxylation of ethylbenzene by ozone,[3] direct hydroxylation reactions by "isolated" high-valent iron(IV) oxo porphyrin cation radical complexes have been rarely reported.[7] In this note, we report that an electronegatively-substituted iron porphyrin complex efficiently catalyzes the hydroxylation of alkanes by H_2O_2 via *radical-free* oxidation reactions in aprotic solvent (i.e., CH_3CN) and that an "isolated" high-valent iron(IV) oxo porphyrin cation radical intermediate of the iron porphyrin complex is capable of activating C−H bonds of alkanes to give oxygenated products efficiently even at low temperature. We also present strong evidence that the hydroxylating intermediate generated in the catalytic H_2O_2 reaction is the high-valent iron(IV) oxo porphyrin cation radical species.

Results and Discussion

The reactions of $Fe(TF_4TMAP)^{5+}$ (**1**, TF_4TMAP = *meso*-tetrakis(2,3,5,6-tetrafluoro-4-*N*,*N*,*N*-trimethylaniliniumyl)porphyrinato)[8] with H_2O_2 (30% aqueous) in the presence of alkanes efficiently yielded the corresponding alcohols as major products with high alcohol to ketone ratios[9] in acetonitrile solution (Table 1). Interestingly, when the hydroxylation of cyclohexane was performed with ^{18}O-labeled hydrogen peroxide in air,[10] we found that the source of the oxygen incorporated into cyclohexanol was the oxidant $H_2{}^{18}O_2$, not molecular oxygen (eq 1). The alkane

$$\text{cyclohexane} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{Fe(TF_4TMAP)^{5+}/H_2{}^{18}O_2}} \underset{>93\%\ ^{18}\text{O-incorporation from }H_2{}^{18}O_2}{\text{cyclohexanol-}^{18}\text{O}} \qquad (1)$$

hydroxylation reactions were found to be highly stereospecific, since the hydroxylations of *cis*- and *trans*-1,2-dimethylcyclohexane afforded tertiary alcohol products with >99% retention.[11] Also, the kinetic isotope effect (KIE) for the cyclohexanol

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(4) It has been reported by Chauhan et al. that the oxidation of indole-3-acetic acid by a water-soluble iron porphyrin complex and H_2O_2 in aqueous buffer solution gives the formation of indole-3-carbinol. They suggested that the oxidation reaction occurs by forming a high-valent iron oxo porphyrin intermediate. However, no clear evidence for the proposed mechanism has been provided: Chauhan, S. M. S.; Mohapatra, P. P.; Kalra, B.; Kohli, T. S.; Satapathy, S. *J. Mol. Catal. A*: *Chem*. **1996**, *113*, 239−247.

(5) Although alkane hydroxylations by iron porphyrin complexes with H_2O_2 have not been reported, it has been shown that the reactions of electronegatively substituted iron porphyrins with H_2O_2 afford the formation of epoxide products in olefin epoxidation reactions: (a) Yang, S. J.; Nam, W. *Inorg. Chem*. **1998**, *37*, 606−607. (b) Traylor, T. G.; Kim, C.; Richards, J. L.; Xu, F.; Perrin, C. L. *J. Am. Chem. Soc*. **1995**, *117*, 3468−3474 and references therein. (c) Bartoli, J. F.; Battioni, P.; De Foor, W. R.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1994**, 23−24.

(6) Mansuy et al. showed that manganese porphyrin complexes efficiently catalyze the hydroxylation of alkanes by H_2O_2, giving the corresponding alcohols as a major product: Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc*. **1988**, *110*, 8462−8470 and references therein.

(7) A number of high-valent iron(IV) oxo porphyrin cation radical complexes have been prepared and characterized with a variety of spectroscopic methods at low temperature. The reactivities of the intermediates have been studied in olefin epoxidations, but not in alkane hydroxylations. For some examples, see: (a) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc*. **1981**, *103*, 2884−2886. (b) Fujii, H. *J. Am. Chem. Soc*. **1993**, *115*, 4641−4648. (c) Gross, Z.; Nimri, S. *J. Am. Chem. Soc*. **1995**, *117*, 8021−8022.

(8) La, T.; Miskelly, G. M.; Bau, R. *Inorg. Chem*. **1997**, *36*, 5321−5328 and references therein.

(9) Hydroxylation of alkanes by hydroxyl or alkoxyl radicals via free radical pathways affords equal amounts of alcohol and ketone products: (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (b) MacFaul, P. A.; Ingold, K. U.; Wayner, D. D. M.; Que, L., Jr. *J. Am. Chem. Soc*. **1997**, *119*, 10594−10598.

(10) Reaction conditions: $H_2{}^{18}O_2$ (7×10^{-3} mmol, diluted in 0.1 mL of CH_3CN, 92% ^{18}O enriched) was added dropwise to a reaction solution (CH_3CN, 0.9 mL) containing $Fe(TF_4TMAP)^{5+}$ (6.3×10^{-4} mmol) and cyclohexane (0.63 mmol). The reaction mixture was stirred for 5 min and then directly analyzed by GC/MS. The ^{16}O and ^{18}O compositions in cyclohexanol were determined by the relative abundances of mass peaks at $m/z = 57$ for ^{16}O and $m/z = 59$ for ^{18}O.

(11) Hydroxyl and alkoxyl radicals afford epimeric tertiary alcohol products in the hydroxylation of *cis*-1,2-dimethylcyclohexane: Khenkin, A. M.; Shilov, A. E. *New J. Chem*. **1989**, *13*, 659−667.

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Table 1. Hydroxylation of Alkanes by **1**/H_2O_2 at 25 °C and by **2** at −40 °C[a]

substrate	products	yield (%)[b]	
		1 + H_2O_2[c]	**2**
cyclohexane	cyclohexanol	33	40
	cyclohexanone	2	3
cyclooctane	cyclooctanol	50	60
	cyclooctanone	5	8
cis−1,2-dimethylcyclohexane	*cis*-1,2-dimethylcyclohexanol	54	55
	2,3- and 3,4-dimethylcyclohexanol[d]	9	14
trans−1,2-dimethylcyclohexane	*trans*-1,2-dimethylcyclohexanol	10	8
	2,3- and 3,4-dimethylcyclohexanol[d]	24	34

[a] See Experimental Section for detailed experimental procedures. Since the hydroxylation reactions were not affected by molecular oxygen, all the reactions were performed in air. [b] Based on the amount of oxidants used. [c] Less than 10% of the iron porphyrin complex was destroyed. [d] The yield of 3,4-dimethylcyclohexanol was determined with commercially available 2,3-dimethylcyclohexanol, with an assumption that the response factors for these alcohols are identical.

Table 2. Comparison of KIE Values Obtained in the Reactions of **1**/H_2O_2 at 25 °C, **2** at −40 °C, and **1**/*m*-CPBA at 25 °C and −40 °C[a]

	k_H/k_D		
temp, °C	**1** + H_2O_2[b]	**2**[c]	**1** + *m*-CPBA[d]
25	3.7 ± 0.3		3.9 ± 0.3
−40		6.6 ± 0.5	6.4 ± 0.5

[a] All reactions were run at least in triplicate, and the data reported represent the average of these reactions. [b] Reaction conditions were the same as described in the Experimental Section (for the reaction of $Fe^{III}(TF_4TMAP)^{5+} + H_2O_2$) except that a 1:5 mixture of cyclohexane (0.3 mmol) and cyclohexane-d_{12} (1.5 mmol) was used to improve the accuracy for measuring the amount of the deuterated cyclohexanol product. [c] Reaction conditions were the same as described in the Experimental Section (for the $[(TF_4TMAP)^{+\bullet}Fe^{IV}{=}O]^{5+}$ reaction) except that a mixture of cyclohexane (0.03 mmol) and cyclohexane-d_{12} (0.15 mmol) was used. [d] Reaction conditions: *m*-CPBA (7.5×10^{-3} mmol, diluted in a solvent mixture (0.02 mL) of CH_3CN/CH_2Cl_2 (1:1)) was added to a solution containing $Fe(TF_4TMAP)(CF_3SO_3)_5$ (5×10^{-4} mmol) and substrates (1:5 mixture of cyclohexane (0.08 mmol) and cyclohexane-d_{12} (0.4 mmol)) in a solvent mixture (1 mL) of CH_3CN/CH_2Cl_2 (1:1). The reaction mixture was stirred for 40 min, and PPh_3 was added to quench the reaction prior to the product analysis.

formation by **1**/H_2O_2 was determined to be 3.7 ± 0.3 (Table 2),[12] indicating that the C−H bond activation is involved in the rate-determining step.[13] All of the results[14] presented above clearly demonstrate that the reactive intermediate generated in the reaction of **1**/H_2O_2 is distinct from those found in typical radical-type of oxidation reactions (i.e., alkane hydroxylation by hydroxyl radical).[9a]

We also attempted the hydroxylation of alkanes by the high-valent iron(IV) oxo porphyrin cation radical complex of **1**. Surprisingly, we found that the iron oxo porphyrin complex $[(TF_4TMAP)^{+\bullet}Fe^{IV}{=}O]^{5+}$, **2**, is able to hydroxylate alkanes with high product yields at −40 °C (Table 1). In the alkane hydroxylations by **2**, we observed high alcohol to ketone ratios and stereospecific hydroxylations of *cis*- and *trans*-1,2-dimethylcyclohexane, as observed in the catalytic H_2O_2 reactions. The KIE value for the cyclohexanol formation by **2** was determined to be 6.6 ± 0.5 at −40 °C (Table 2).

We then focused our efforts on characterizing the nature of the reactive intermediate responsible for the hydroxylation of alkanes by **1**/H_2O_2. We first performed isotopically labeled water, $H_2{}^{18}O$, experiments, since it has been shown previously that high-valent iron oxo porphyrin complexes exchange oxygen atoms with $H_2{}^{18}O$, resulting in the incorporation of ^{18}O into oxygenated products.[15] When the hydroxylation of cyclohexane by H_2O_2 was performed in the presence of $H_2{}^{18}O$,[16] we observed 40% ^{18}O-incorporation from the labeled $H_2{}^{18}O$ (95% ^{18}O enriched) into the cyclohexanol product (eq 2), suggesting that a high-valent iron oxo intermediate is generated as a reactive species responsible for the cyclohexane hydroxylation.[15] Further

$$\text{cyclohexane} \xrightarrow[\text{in the presence of}\atop H_2{}^{18}O\text{ in }CH_3CN]{Fe(TF_4TMAP)^{5+}/H_2{}^{16}O_2} \begin{matrix}\text{cyclohexanol-}^{18}O\\ 40\%\ ^{18}O\text{ from }H_2{}^{18}O\end{matrix} \qquad (2)$$

supporting evidence for the intermediacy of **2** in the **1**/H_2O_2 reaction comes from the results of reactivity studies such as kinetic isotope effects (k_H/k_D)[13] and competitive hydroxylations. Since the reactions with **2** and **1**/H_2O_2 were run at different temperatures (i.e., −40 °C for **2** and 25 °C for **1**/H_2O_2), we considered temperature effect on the activation of C−H bonds.[13] We therefore conducted the reactivity studies with **1**/*m*-CPBA (*m*-chloroperoxybenzoic acid) at −40 and 25 °C, for comparison. The KIE values determined with **2** and **1**/*m*-CPBA at −40 °C were 6.6 ± 0.5 and 6.4 ± 0.5, respectively, and those obtained from **1**/H_2O_2 and **1**/*m*-CPBA at 25 °C were 3.7 ± 0.3 and 3.9 ± 0.3, respectively (Table 2). In the competitive hydroxylations performed with *cis*- and *trans*-1,2-dimethylcyclohexane, the ratios of *cis*- to *trans*-1,2-dimethylcyclohexanol products were determined to be 20 in the reactions of **2** and **1**/*m*-CPBA at −40 °C and 10 in the reactions of **1**/H_2O_2 and **1**/*m*-CPBA at 25 °C (Table 3).[17] Since the reactions of **1**/*m*-CPBA at −40 and 25 °C afford the formation of **2**,[18] the results

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(12) KIE values reported for alkane hydroxylations by hydroxyl radical are in the range 1−2: Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 513−886.

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(14) Additional supporting evidence that the oxygenating intermediate generated in the reaction of **1**/H_2O_2 was not the hydroxyl radical was obtained from the olefin epoxidation reactions, in which epoxides were formed predominantly with trace amounts of allylic oxidation products: Lee, Y. J.; Goh, Y. M.; Han, S.-Y.; Kim, C.; Nam, W. *Chem. Lett*. **1998**, 837−838.

(15) (a) Bernadou, J.; Meunier, B *J. Chem. Soc., Chem. Commun*. **1998**, 2167−2173. (b) Groves, J. T.; Lee, J.; Marla, S. S. *J. Am. Chem. Soc*. **1997**, *119*, 6269−6273. (c) Lee, K. A.; Nam, W. *J. Am. Chem. Soc*. **1997**, *119*, 1916−1922. (d) Balahura, R. J.; Sorokin, A.; Bernadou, J.; Meunier, B. *Inorg. Chem*. **1997**, *36*, 3488−3492. (e) Bernadou, J.; Fabiano, A.-S.; Robert, A.; Meunier, B. *J. Am. Chem. Soc*. **1994**, *116*, 9375−9376.

(16) Reaction conditions: Hydrogen peroxide (0.021 mmol, diluted in 0.3 mL of CH_3CN) was divided into three aliquots. An aliquot (7×10^{-3} mmol of H_2O_2 in 0.1 mL of CH_3CN) was slowly added over a period of 20 min to a stirred CH_3CN (0.9 mL) solution containing $Fe(TF_4TMAP)^{5+}$ (6.7×10^{-4} mmol), cyclohexane (0.67 mmol), and $H_2{}^{18}O$ (80 μL, 3.6 mmol, 95% ^{18}O enriched). The reaction mixture was stirred for 5 min at room temperature. Subsequently, the second aliquot was added over a period of 20 min and stirred for 5 min followed by addition of the third aliquot. Total reaction time was 75 min. Cyclohexanol (22% based on the H_2O_2 added) was the predominant product with a small amount of cyclohexanone formation (1.3%). See footnote 10 for the analysis of the ^{16}O and ^{18}O compositions in cyclohexanol.

(17) It has also been observed that *cis*-1,2-dimethylcyclohexane is more reactive than *trans*-1,2-dimethylcyclohexane in dioxirane-mediated hydroxylation reactions: Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc*. **1989**, *111*, 6749−6757.

(18) We have shown in the text that the reaction of **1**/*m*-CPBA at −40 °C affords the formation of **2**. We also found that significant amounts of ^{18}O were incorporated into the cyclohexanol product when the hydroxylations of cyclohexane by **1**/*m*-CPBA were carried out in the presence of $H_2{}^{18}O$ at −40 and 25 °C, indicating that **2** is generated as a hydroxylating intermediate in the reactions of **1**/*m*-CPBA at the temperatures (data not shown).

Table 3. Product Ratios Determined in the Competitive Hydroxylation Reactions Performed with **1**/H_2O_2 at 25 °C, **2** at −40 °C, and **1**/*m*-CPBA at 25 °C and −40 °C[a]

	ratio of *cis*- to *trans*-1,2-dimethylcyclohexanol		
temp, °C	**1** + H_2O_2[b]	**2**[c]	**1** + *m*-CPBA[d]
25	10 ± 1		10 ± 1
−40		20 ± 2	21 ± 2

[a] All reactions were run at least in triplicate, and the data reported represent the average of these reactions. [b] Reaction conditions were the same as described in the Experimental Section (for the reaction of $Fe^{III}(TF_4TMAP)^{5+}$ + H_2O_2) except that a 1:7 mixture of *cis*-1,2-dimethylcyclohexane (0.3 mmol) and *trans*-1,2-dimethylcyclohexane (2.1 mmol) was used to improve the accuracy for measuring the amount of the *trans*-1,2-dimethylcyclohexanol product. [c] Reaction conditions were the same as described in the Experimental Section (for the $[(TF_4TMAP)^{+\bullet}Fe^{IV}{=}O]^{5+}$ reaction) except that a 1:7 mixture of *cis*-1,2-dimethylcyclohexane (0.03 mmol) and *trans*-1,2-dimethylcyclohexane (0.21 mmol) was used. [d] Reaction conditions: *m*-CPBA (2.4×10^{-3} mmol, diluted in 20 μL of CH_3CN) was added to a solution containing $Fe(TF_4TMAP)(CF_3SO_3)_5$ (2.0×10^{-3} mmol) and substrates (1:7 mixture of *cis*-1,2-dimethylcyclohexane (0.03 mmol) and *trans*-1,2-dimethylcyclohexane (0.21 mmol)) in a solvent mixture of CH_3CN (0.6 mL) and CH_2Cl_2 (0.1 mL). The reaction mixture was stirred for 30 min, and PPh_3 was added to quench the reaction prior to the product analysis.

of the reactivity studies, after considering the temperature effect, strongly support the conclusion that the reaction of **1**/H_2O_2 generates **2** as a hydroxylating intermediate.[19,20]

In summary, we have shown that a synthetic iron(III) porphyrin complex containing highly electron-withdrawing substituents on the porphyrin ligand is able to conduct biomimetic alkane hydroxylations with a biologically important oxidant (i.e., H_2O_2)[21] and that its high-valent iron(IV) oxo porphyrin intermediate, prepared in situ by the reaction of the iron porphyrin complex with *m*-CPBA at low temperature, activates C−H bonds of aliphatic hydrocarbons to give alcohol products efficiently. The latter complex will provide a great opportunity to elucidate the detailed mechanisms of oxygen atom transfer from high-valent iron oxo porphyrin intermediates to alkanes (e.g., oxygen rebound, nonsynchronous concerted, or "agostic" substrate−catalyst complex mechanism).[22]

Experimental Section

Materials. Acetonitrile (anhydrous) was obtained from Aldrich Chemical Co. and used without further purification. All chemicals obtained from Aldrich Chemical Co. were of the best available purity and were used without further purification unless otherwise indicated. $H_2{}^{18}O$ (95% ^{18}O enrichment) and *m*-CPBA (65%) were purchased from Aldrich. H_2O_2 (30% aqueous) was purchased from Fluka. $Fe(TF_4TMAP)(CF_3SO_3)_5$[8] was obtained from Mid-Century Chemicals.

Instrumentation. Product analyses were performed on either a Hewlett-Packard 5890 II Plus gas chromatograph interfaced with a Hewlett-Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a FID detector. UV−vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer equipped with an *Optostat*^{DN} variable-temperature liquid-nitrogen cryostat (Oxford Instruments). ESR spectra were obtained on a Bruker ESP-300 spectrometer.

Catalytic Hydroxylation of Alkanes by $Fe(TF_4TMAP)^{5+}$ and H_2O_2. In order to avoid the fast reaction of $[(TF_4TMAP)^{+\bullet}Fe^{IV}{=}O]^{5+}$ with H_2O_2 that leads to the inhibition of hydroxylation of alkanes,[21,23] we added H_2O_2 extremely slowly to increase the yields of products. H_2O_2 (0.084 mmol, 30% aqueous, diluted in 1 mL of CH_3CN) was divided into four aliquots. An aliquot (0.021 mmol of H_2O_2 in 0.25 mL of CH_3CN) was slowly added over a period of 10 min to a stirred CH_3CN (2.7 mL, containing 0.1 mL of CH_2Cl_2) solution containing $Fe(TF_4TMAP)(CF_3SO_3)_5$ (2.0×10^{-3} mmol) and substrate (2.1 mmol), and the reaction mixture was stirred for 5 min at room temperature. Subsequently, the second aliquot was added over a period of 10 min and stirred for 5 min followed by addition of the third and the fourth aliquots. Total reaction time was 1 h. The reaction mixture was analyzed by GC or GC/MS with known authentic samples.

Stoichiometric Hydroxylation of Alkanes by $[(TF_4TMAP)^{+\bullet}Fe^{IV}{=}O]^{5+}$. The reaction of $Fe(TF_4TMAP)^{5+}$ with 1.2 equiv of *m*-CPBA in CH_3CN at −40 °C gave the formation of a green intermediate. A UV−vis spectrum of the intermediate showed a Soret band at 389 nm with decreased intensity and broad absorption bands around 550−700 nm ($\lambda_{max} = 652$ nm) (Supporting Information, Figure S1), characteristic of porphyrin cation radical complexes.[7b] The green intermediate showed no strong EPR signals at 10 K in frozen acetonitrile solution. Substrate (0.2 mmol, dissolved in a solvent mixture (0.2 mL) of CH_3CN/CH_2Cl_2 (1:1)) was added to a solution containing $[(TF_4TMAP)^{+\bullet}Fe^{IV}{=}O]^{5+}$, which was prepared by reacting $Fe(TF_4TMAP)^{5+}$ (2×10^{-3} mmol) with *m*-CPBA (2.4×10^{-3} mmol) in CH_3CN (0.5 mL) at −40 °C. After the reaction solution was stirred for 10 min at −40 °C, PPh_3 (0.01 mmol diluted in 0.1 mL of CH_2Cl_2) was added to quench the reaction followed by analysis of the resulting solution with GC or GC/MS.

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Supporting Information Available: Absorption spectrum of **2** (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Heme-containing enzymes react with H_2O_2 to form high-valent iron(IV) oxo porphyrin cation radical species, called compound I: Ozaki, S.-I.; Matsui, T.; Watanabe, Y. *J. Am. Chem. Soc*. **1997**, *119*, 6666−6667 and references therein.

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