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Communications

A High-Valent Iron(IV) Oxo Porphyrin Cation Radical Complex in Olefin Epoxidation Reactions

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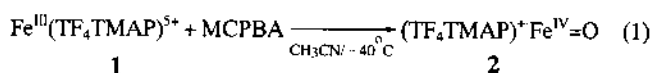
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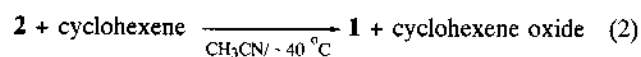
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Since it has been shown that high-valent iron(IV) oxo porphyrin π -cation radical complexes, called compound **1**, are the active species during the catalytic cycles of heme-containing enzymes such as peroxidases, catalases, and cytochrome P-450s, much attention was given to the preparation of the high-valent iron(IV) oxo porphyrin π -cation radical intermediates with synthetic iron(III) porphyrin complexes.¹ Groves *et al.* were the first to characterize a high-valent iron(IV) oxo porphyrin π -cation radical complex, (TMP)⁺Fe^{IV}=O (TMP=tetramesitylporphyrinato dianion).² Since then, a number of high-valent iron oxo porphyrin complexes have been prepared and characterized with various spectroscopic methods.³ However, most of the iron porphyrin complexes studied to generate the iron oxo intermediates contained electron-donating substituents on the porphyrin ligand. Moreover, there are few reports that present reactivity studies of such intermediates toward hydrocarbon oxygenations including olefin epoxidation.⁴ In this paper, we report the preparation of a new high-valent iron(IV) oxo porphyrin π -cation radical complex with highly electron-withdrawing substituents on the porphyrin ligand and the detailed reactivity studies of this intermediate in olefin epoxidation reactions.

The reaction of Fe(TF₄TMAP)⁵⁺ (**1**, TF₄TMAP=*meso*-tetrakis(2,3,5,6-tetrafluoro-4-*N,N,N*-trimethylaniliniumyl)porphyrinato, see Figure 1 for the structure of Fe(TF₄TMAP)⁵⁺)⁵ with 1.2 equiv of *m*-chloroperoxybenzoic acid (MCPBA) at -40 °C gave the formation of a green intermediate (eq. 1).



This species was identified to be a high-valent iron(IV) oxo porphyrin cation radical complex [(TF₄TMAP)⁺Fe^{IV}=O], **2**, by taking a visible spectrum of the green complex (Figure 2).² Upon the addition of cyclohexene to the green solution at -40 °C, the visible spectrum of **2** immediately reverted to the original spectrum of **1**, and analysis of the reaction solution with GC showed that a quantitative amount of cyclohexene oxide was formed, indicating that **2** is able to transfer its oxygen atom to olefin substrate to yield the oxide product (eq. 2).



We then studied epoxidation of various olefins with **2** in acetonitrile at -40 °C. As shown in Table 1, olefins were mainly converted to the corresponding oxide products. In the epoxidation of cyclohexene, cyclohexene oxide was the predominant product with only trace amounts of allylic oxidation products such as cyclohexen-2-ol. *cis*-Stilbene was predominantly oxidized to *cis*-stilbene oxide, as generally observed in iron(III) porphyrin complex-catalyzed olefin epoxidation reactions.⁶ Moreover, 1-octene, which is a rather difficult substrate to be oxidized, was also converted to 1,2-epoxyoctane with a high yield. We also tested the reaction of **2** with methanol, since it has been shown previously that the addition of methanol to the solution of (TDCPP)⁺Fe^{IV}=O (TDCPP=*meso*-tetrakis(2,6-dichlorophenyl)porphyrinato) generated a novel oxo-perferryl complex, (TDCPP)Fe^V=O.⁷ When methanol was added to the green solution of **2** at -40 °C, **2** was reduced to **1** instead of forming an oxo-perferryl complex of **1**. We presumed that **2** is a powerful oxidizing agent due to the

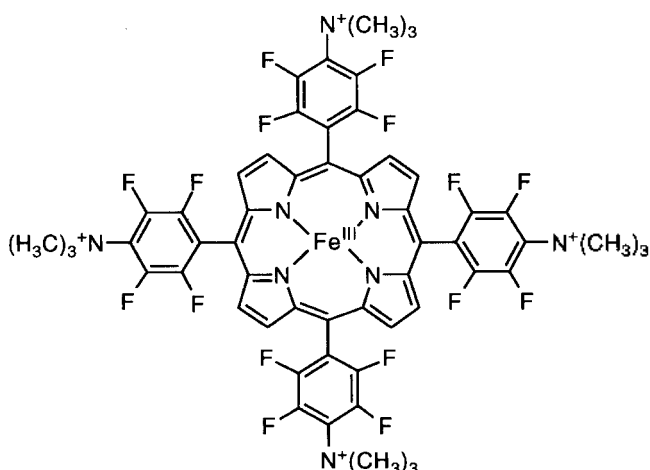


Figure 1. Structure of $\text{Fe}^{\text{III}}(\text{TF}_4\text{TMAP})^{5+}$ complex.

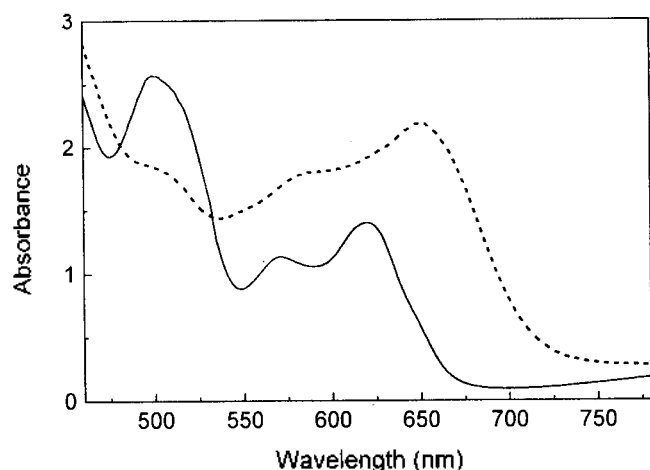


Figure 2. Absorption spectra of $[\text{Fe}^{\text{III}}(\text{TF}_4\text{TMAP})]^{5+}$ (solid line) and $(\text{TF}_4\text{TMAP})\text{Fe}^{\text{IV}}=\text{O}$ (dotted line). The high-valent iron(IV) oxo porphyrin cation radical was generated by reacting $\text{Fe}^{\text{III}}(\text{TF}_4\text{TMAP})(\text{CF}_3\text{SO}_3)_2$ (0.3 mM) with MCPBA (0.36 mM) in CH_3CN (3 mL) at -40°C .

Table 1. Epoxidation of Olefins by $(\text{TF}_4\text{TMAP})\text{Fe}^{\text{IV}}=\text{O}^a$

Substrate	Products	Yield (%) ^b
cyclooctene	cyclooctene oxide	85 ± 7
cyclohexene	cyclohexene oxide	65 ± 10
	cyclohexen-2-ol	4 ± 1
	cyclohexen-2-one	0
1-octene	1,2-epoxyoctane	35 ± 5
<i>cis</i> -stilbene	<i>cis</i> -stilbene oxide	45 ± 5
	<i>trans</i> -stilbene oxide	4 ± 1
	benzaldehyde	trace

^a Reaction conditions: Substrate (0.2 mmol, dissolved in a solvent mixture (0.2 mL) of $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ (1:1)) was added to a solution containing $(\text{TF}_4\text{TMAP})\text{Fe}^{\text{IV}}=\text{O}$, which was prepared by reacting $\text{Fe}(\text{TF}_4\text{TMAP})(\text{CF}_3\text{SO}_3)_2$ (2×10^{-3} mmol) with MCPBA (2.4×10^{-3} mmol) at -40°C in CH_3CN (0.5 mL). The reaction solution was stirred for 10 min at -40°C , and then products were analyzed by GC and HPLC with known authentic samples. ^b Based on the amount of oxidant used. All reactions were run at least in triplicate, and the data reported represent the average of these reactions.

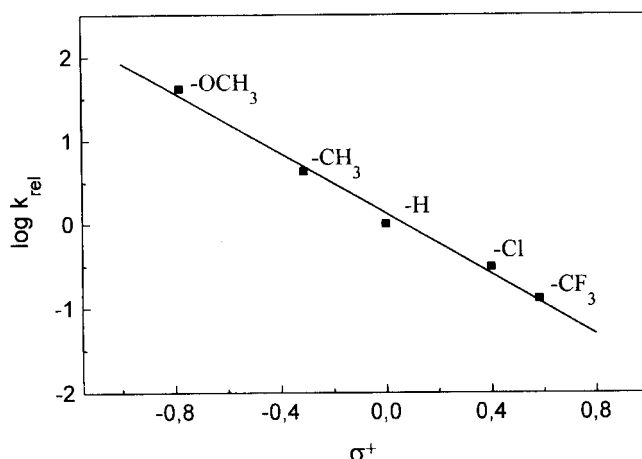


Figure 3. Hammett plot for relative reactivities of substituted styrenes to styrene. In a typical reaction, a mixture of styrene (5×10^{-3} mmol) and substituted X-styrene (5×10^{-3} mmol, X = *para*-OCH₃, *para*-CH₃, *meta*-Cl, and *para*-CF₃) in a solvent mixture (0.2 mL) of CH_3CN and CH_2Cl_2 (1:1) was added to the reaction solution containing $(\text{TF}_4\text{TMAP})\text{Fe}^{\text{IV}}=\text{O}$ (2.0×10^{-3} mmol) at -40°C . The reaction solution was stirred for 10 min at -40°C . The amounts of olefins before and after reactions were determined by GC. The relative reactivities were determined using the following equation: $k_i/k_j = \log(X_i/X_j)/\log(Y_i/Y_j)$ where X_i and X_j are the initial and final concentrations of substituted styrenes and Y_i and Y_j are the initial and final concentrations of styrene.

highly electron-deficient porphyrin ligand; therefore, **2** oxidizes methanol to give formaldehyde.

In order to study the influence of electrophilicity of olefin substrates, we examined the relative reactivities of *para*- and *meta*-substituted styrenes to styrene in the epoxidation reactions with **2**. As observed in other iron porphyrin systems,⁸ electron-donating substituents enhance the rate of the olefin epoxidation and electron-withdrawing substituents decrease the rate of the epoxidation. A Hammett treatment of the data gave a good correlation against σ^+ and the slope of the Hammett plot, ρ , was determined to be -1.9 (Figure 3). The large negative ρ value suggests that **2** attacks the double bond of olefin by electrophilic character and that a positive charge on the α -carbon atom of the styrene develops in the transition state.⁸ Further support for the electrophilicity of **2** was obtained from the result that electron poor olefins such as cyclohexen-2-one were not epoxidized at all.⁹

In summary, we have shown that an electronegatively-substituted iron(III) porphyrin complex reacts with MCPBA to give a stable high-valent iron(IV) oxo porphyrin cation radical intermediate *via* the heterolytic O-O bond cleavage of MCPBA and that this intermediate epoxidizes olefins efficiently at low temperature. Future studies will focus on using this novel high-valent iron(IV) oxo porphyrin π -cation radical complex in other oxidation reactions to mimic the chemistry of cytochrome P-450 enzymes.

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Crystal Structure of the Pentanuclear Complex Containing Ru₂(chp)₄⁺ Units Linked by Co(CN)₆³⁻

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Organic cyanides and metal cyanides have connected metal complexes to form one-, two-, or three-dimensional polymeric compounds.¹ Recently, the synthesis of polymeric compounds has expanded to metal-metal multiply-bonded compounds.² Organic cyanides, TCNE, bridge four Rh₂(O₂CCF₃)₄ units to form an extended two-dimensional layer³ or bridge two Rh₂(O₂CCH₃)₄ units to form either 1,1- or *trans*-1,2 type one-dimensional polymers.⁴ Metal cyanides, Co(CN)₆³⁻ also bridge four Rh₂(O₂CCH₃)₄ units to form a two-dimensional sheet.⁵ Jacobson mentioned that the Co(CN)₆³⁻ group acts like TCNE even though Co(CN)₆³⁻ can form three-dimensional polymer. We have interested in the diruthenium unit to study magnetic interactions through Co(CN)₆³⁻ bridging groups. The pentanuclear complex, K[{Ru₂(chp)₄]₂{Co(CN)₆}] (chp=6-chloro-2-hydroxypyridinato) has been synthesized and studied its structure and magnetic properties.

Reaction of a methanol solution of [Ru₂(chp)₄](PF₆) with an aqueous solution of K₃Co(CN)₆ gave purple precipitate with yield of 75.5%. [Ru₂(chp)₄](PF₆) was prepared by elimination of the axial chlorine atom from Ru₂(chp)₄Cl₆ with AgPF₆ in CH₂Cl₂ solution. The precipitate⁷ was not soluble in any solvent. Dark purple crystals were obtained from the direct diffusion technique. An aqueous solution of

K₃Co(CN)₆ was carefully layered by a methanol solution of [Ru₂(chp)₄](PF₆). The CN stretching modes were observed in the IR spectrum at 2133 cm⁻¹ which is shifted from 2129 cm⁻¹ of K₃Co(CN)₆. This blue shift indicates that the cobalt cyanide acts like a σ donor to diruthenium unit.

The Ru₂(chp)₄⁺ units are bridged by Co(CN)₆³⁻ to form a pentanuclear compound, K[{Ru₂(chp)₄]₂{Co(CN)₆}] (Figure 1). There are two formula units in the tetragonal cell. The ruthenium atoms and cobalt atom reside on a 4 axis at 0, 1/2, z, and do the C and N atoms of *trans*-CN groups of the bridging ligand. In contrast to the diruthenium-cobaltcyanide polymer, the diruthenium units are coordinated by only two CN groups of Co(CN)₆³⁻ that is *trans* each other. Chlorine atoms of the chp ligands block the one axial position of diruthenium unit and the bridging ligand, Co(CN)₆³⁻, connect only two diruthenium units to form a pentanuclear compound. The distances of Ru(1)-Ru(2) and Ru(3)-Ru(4) are 2.254 (4) and 2.241(4) Å, respectively. The distances between Co and C atoms of the bridging CN groups are different (2.09 (6) and 1.85 (5) Å, respectively) from Co-C(3) (other CN groups) distance (1.80 (3) Å).

Magnetic moments⁹ of the pentanuclear complex are shown in Figure 2. Also, the temperature dependence of the magnetic moments of Ru₂(O₂CC₃H₇)₄Cl¹⁰ is shown for