

Preparation and Reactivity of Oxoiron(IV) Porphyrins

John T. Groves,* Zeev Gross,[†] and Michael K. Stern[‡]

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

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Oxoiron(IV) porphyrins were conveniently prepared by ligand metathesis of stable iron(III) porphyrin cation radicals over moist basic alumina. The formation of oxoiron(IV) porphyrins by electrochemical oxidation of the corresponding hydroxoiron(III) porphyrin was shown to be an EC process, with initial oxidation of the porphyrin ring followed by elimination of HClO₄ and rearrangement. Oxo(tetramesitylporphyrinato)iron(IV), (TMP)Fe^{IV}=O (**1**), was found to be stable at room temperature in relatively unreactive solvents such as benzene. (TMP)-Fe^{IV}=O (**1**) reacted readily with substituted styrenes with a selectivity which was very much unlike that observed for (TMP⁺)Fe^{IV}=O (**4**). Kinetic data and product analyses in benzene indicate that the first and rate limiting step is attack of the ferryl oxygen of **1** on the olefin π -bond to form a carbon radical intermediate (**5**), followed by a fast reaction with molecular oxygen to form benzaldehydes or ring closure to afford epoxides with loss of the configuration of the starting olefin. In more polar solvents the results indicated a disproportionation of **1** to afford **4** as the reactive intermediate.

Introduction

Oxoiron(IV) or ferryl porphyrin intermediates have been widely invoked in the catalytic cycles of heme-dependent enzymes. Thus, for the peroxidases, an oxoiron(IV) porphyrin cation radical formulation has been accepted for "compound I" while for "compound II" an oxoiron(IV) structure is preferred.¹ A ferryl species analogous to compound I has been generally proposed for the reactive oxygenating intermediate of cytochrome P-450,² and an oxoiron(IV) complex similar to compound II has been detected recently during the energy transduction cycle of cytochrome oxidase.³ Terminal oxoiron complexes are rare, the first reported examples being the oxoiron(IV) porphyrin described by Balch⁴ and the oxoiron(IV) porphyrin cation radical prepared in our laboratories.⁵ Studies of the characterization and reactivity of these species have served both to illuminate biological strategies for the manipulation of oxygen and to offer new prospects for practical catalysis.^{5d, 6}

One convenient route to iron(IV) porphyrins is via the internal electron transfer that accompanies ligand metathesis of the corresponding iron(III) porphyrin cation radicals. Thus, (TMP⁺)-Fe^{III}(ClO₄)₂ (TMP = 5,10,15,20-tetramesitylporphyrin dianion, TMP⁺ = the corresponding π -cation radical of TMP, a monoanion overall), was converted quantitatively to (TMP)-Fe^{IV}(OCH₃)₂ by treatment with sodium methoxide.⁷ The electrochemical oxidation of hydroxoiron(III) precursors to oxoiron(IV) porphyrins has been studied by several groups.^{8 a,b,9,10} While the first oxidation wave observed for a variety of iron(III) porphyrins has been found to be porphyrin-centered,^{8a} it is apparent that oxo and alkoxy groups stabilize iron(IV) with respect to the iron(III) porphyrin cation radical.

We describe here the investigation of several aspects of the chemistry of oxoiron(IV) porphyrins. These include (i) the development of a simple procedure for the preparation and isolation of thermally stable oxoiron(IV) porphyrins, (ii) an examination of the mechanism of their formation by electrochemical oxidation of hydroxoiron(III) porphyrins and (iii) the first kinetic studies of hydrocarbon oxygenation by isolated oxoiron(IV) porphyrins. The results show that the electrochemical conversion of hydroxoiron(III) porphyrins to oxoiron(IV) porphyrins is a multistep process initiated by oxidation of the macrocycle. Further, the reactivity of oxoiron(IV) porphyrins toward olefins is shown to be unexpected high and mechanistically distinct in analogy with the reactivity we have reported for oxomanganese(IV) porphyrins.¹¹

Results

Preparation of Oxoiron(IV) Porphyrins. The preparation of (TMP)Fe^{IV}=O (**1**), via the corresponding iron(III) porphyrin cation radical (TMP⁺)Fe^{III}(ClO₄)₂ (**2**) is summarized in Scheme 1.

The chloroiron(III) porphyrin **3-Cl** was treated with wet basic alumina until its characteristic 510 nm UV band had disappeared, providing the green hydroxoiron(III) complex (TMP)-Fe^{III}OH (**3-OH**). Treatment of **3-OH** with solid Fe(ClO₄)₃ in

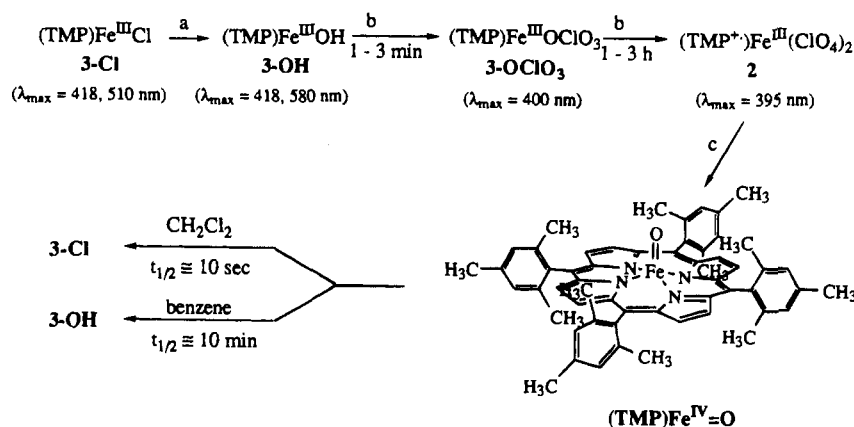
* Author to whom correspondence should be addressed.

[†] Current address: Department of Chemistry, Israel Institute of Technology, Technion City, Haifa 32000, Israel.[‡] Current address: Monsanto Chemical Co., St. Louis, MO.[⊗] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

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Scheme 1



^a Key: (a) CH_2Cl_2 , alumina/10% H_2O . (b) CH_2Cl_2 , $\text{Fe}(\text{ClO}_4)_3$. (c) Solutions of **2** in CH_2Cl_2 or benzene filtered through basic alumina/20% H_2O at room temperature.

CH_2Cl_2 afforded first $(\text{TMP})\text{Fe}^{\text{III}}\text{OCIO}_3$ (**3-OCIO₃**) and then $(\text{TMP}^+)\text{Fe}^{\text{III}}(\text{ClO}_4)_2$ (**2**) in a convenient one-pot preparation.⁷ Conversion of **3-OH** to **3-OCIO₃** was complete in a few minutes, indicated by a color change from green to deep red. The subsequent oxidation of **3-OCIO₃** to **2** took place in 1–3 h accompanied by the appearance of the characteristic brilliant green color of the porphyrin radical cation. Corresponding changes were observed in the UV spectra (λ_{max} values for **3-OH**, **3-OCIO₃**, and **2** are 418, 400, and 395 nm, respectively).

The formation of $(\text{TMP})\text{Fe}^{\text{IV}}=\text{O}$ (**1**) from **2** via ligand metathesis was performed by treating solutions of **2** in organic solvents with moist, basic alumina (20% water). The UV spectra of **2** ($\lambda_{\text{max}} = 395, 505 \text{ nm}$) and **1** ($\lambda_{\text{max}} = 418, 540 \text{ nm}$, Figure 1, inset) are very different, making it easy to follow the reaction course by these changes. Thus, fast filtration of a cold CH_2Cl_2 solution of **2** through basic alumina afforded **1** in the eluant. It was essential to keep solutions of **1** in methylene chloride cold since the formation of **3-Cl** was apparent in less than a minute, as signaled by the formation of a UV band at 510 nm and the loss of the 540 nm band. By contrast, solutions of **1** in benzene were much more stable and in the absence of substrates the conversion to **3-OH** took about 1 h at ambient temperature.

The same procedure in CD_2Cl_2 was convenient for the preparation of NMR samples. As shown in Figure 1, the formation of $(\text{TMP})\text{Fe}^{\text{IV}}=\text{O}$ (**1**) was indicated by the characteristic resonances in the diamagnetic region of the spectrum⁴ accompanied only by resonances corresponding to traces of iron(III) porphyrin (**3**). Samples of **1** prepared in this manner in the deuterated solvent were noticeably more stable than those in CH_2Cl_2 and were still robust at 0°C .^{8d} The addition of 3 equiv of cyclohexene at -60°C showed no effect. However, cyclohexene oxide, cyclohexen-3-one and cyclohexene-3-ol were formed in a ratio of 14: 9: 1 above 0°C .

The high stability of iron(IV) porphyrins in benzene could be used for synthesis of $(\text{TMP})\text{Fe}^{\text{IV}}(\text{OCH}_3)_2$ ⁷ as well. Thus, treatment of a benzene/methanol solution of **3** with iodosylbenzene at room temperature resulted in conversion to $(\text{TMP})\text{Fe}^{\text{IV}}(\text{OCH}_3)_2$. The analogous reaction in CH_2Cl_2 /methanol proceeded as well, but again, the product was stable only at low temperatures.

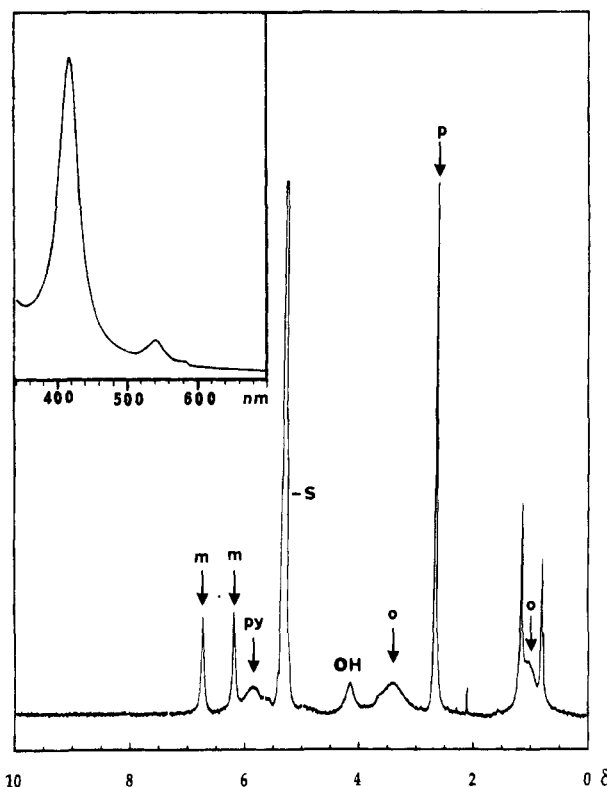


Figure 1. ^1H NMR of $(\text{TMP})\text{Fe}^{\text{IV}}=\text{O}$ (**1**) in CD_2Cl_2 at -78°C . The peaks marked p, m and o are the *p*-methyls, meta hydrogens, and the *o*-methyls of **1** and the peak marked OH is due to the *p*-methyls of **3-OH**. Inset: UV spectrum of **1** in benzene at room temperature.

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$\text{Fe}^{\text{IV}}(\text{OCH}_3)_2$. The analogous reaction in CH_2Cl_2 /methanol proceeded as well, but again, the product was stable only at low temperatures.

Electrochemical Formation of $(\text{TMP})\text{Fe}^{\text{IV}}=\text{O}$ (1**) from $(\text{TMP})\text{Fe}^{\text{III}}\text{OH}$ (**3-OH**).** The electrochemical oxidation of the chloroiron(III) and hydroxoiron(III) complexes of tetramesitylporphyrin, tetrakis(4-*tert*-butyl-2,6-dibromophenyl)porphyrin and tetrakis(2,6-dibromo-4-methoxyphenyl)porphyrin were examined in CH_2Cl_2 . The $E_{1/2}$ values obtained by cyclic voltammetry (vs SCE) were 1.13, 1.29, and 1.27 V, respectively, for the chloro complexes and 1.01, 1.18, and 1.16 V for the corresponding hydroxo complexes. Special care was taken during the synthesis of the hydroxoiron(III) compounds since they converted easily to the corresponding chlorides by even traces of HCl present in chlorinated solvents. Purity was

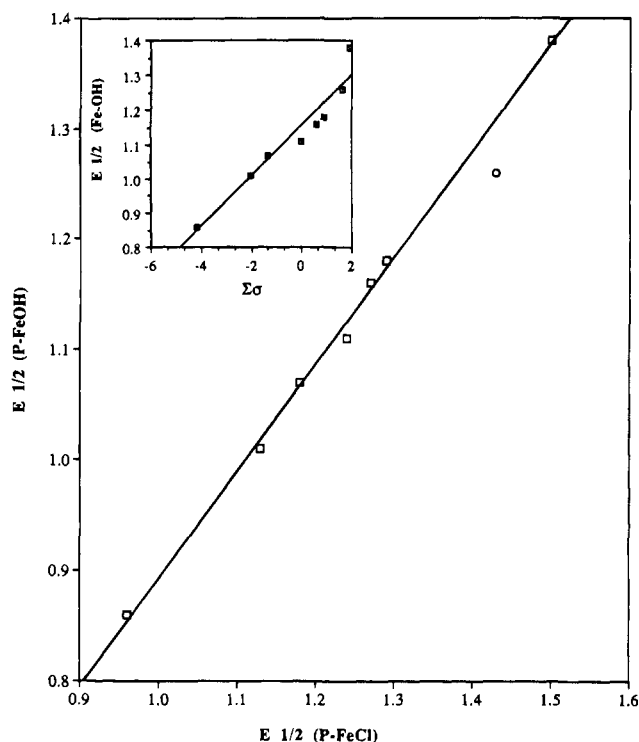


Figure 2. Plot of the $E_{1/2}$ values (V) of ring-substituted (tetraphenylporphyrinato) iron(III) hydroxides (Fe-OH) vs the same values of the corresponding iron chlorides (Fe-Cl). The least-squares fit has a slope of 0.97 ± 0.02 , ignoring the point at $E_{1/2} = 1.43$. Inset: Hammett plot for the $E_{1/2}$ values (V) of Fe-OH, $\rho = 0.073$. σ_{para} values are from Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191, σ_{ortho} values from Taft, R. W. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 3.

monitored by UV and NMR (CD_2Cl_2) prior to use and again after preparing the solutions for CV. Solutions prepared in this way did not exhibit a discernible shoulder at 500–520 nm in the UV (all chloroiron(III) porphyrins have a λ_{max} at about 510 nm).

The $E_{1/2}$ values of these three hydroxoiron(III) complexes and five additional porphyrinato iron(III) hydroxides⁹ were plotted against the values of the corresponding porphyrinato iron(III) chlorides. As shown in Figure 2, these data correlated linearly with a unit slope (0.97 ± 0.02). The inset of Figure 2 shows a Hammett plot for the hydroxoiron(III) complexes, the ρ value for both the hydroxide and the chloride ligated iron porphyrins being 0.075 ± 0.005 . We also observed a closely spaced (100 mV higher) second oxidation wave for **3-OH**, which has been reported previously. The presence of the second oxidation wave was found to be dependent upon the scan rate. Thus, at slow scan rates, two anodic waves were observed at 1.0 and 1.1 V. When the scan rate was increased from 0.02 to 1.0 V/s, the oxidation wave at 1.1 V gradually disappeared, while the first oxidation peak at 1.0 V was not affected by these changes.

Reactivity of (TMP)Fe^{IV} = O (1) with Olefins. (TMP)Fe^{IV} = O (**1**) was found to react with olefins readily at room temperature. *cis*- β -Methylstyrene was oxidized to mixtures of *trans*- and *cis*- β -methylstyrene oxide under a variety of conditions. Special attention was paid to the observed variations in the *cis/trans* epoxide ratio. Solutions of (TMP⁺)Fe^{IV}(O)(Cl) (**4**), produced by oxidizing **3-Cl** with MCPBA at $-78^\circ C$, reacted very rapidly to afford largely the *cis*-epoxide (*cis/trans* = 11.3). Electrocatalytic oxidations of *cis*- β -methylstyrene during bulk electrolysis of **3-OH** under basic conditions¹⁰ afforded a *cis/trans* epoxide ratio in the range 2.3–3.3. For

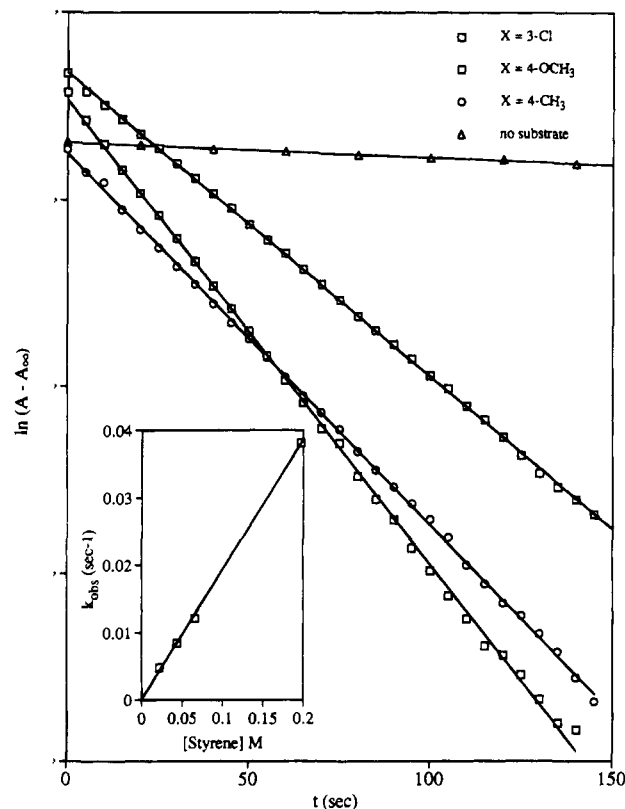


Figure 3. Kinetic data for the reaction of (TMP)Fe^{IV} = O (**1**) with 0.075 M substituted styrene in benzene at 25 °C. Second-order rate constants for the reactions of ring-substituted styrenes with **2** in benzene at 25 °C, k , $M^{-1} s^{-1}$ (substrate): 1.10 (4-NO₂), 0.69 (3-NO₂), 0.29 (4-Cl), 0.23 (3-Cl), 0.19 (H), 0.23 (4-CH₃), and 0.33 (4-OCH₃). The rate constants were obtained by following the changes in the UV spectra due to the conversion of **1** ($\lambda_{max} = 540$ nm) to **3-OH** ($\lambda_{max} = 580$ nm). Each kinetic run was repeated at least three times. The accuracy of the kinetic values is better than $\pm 5\%$. Inset: The variation of the observed rate constant in the reaction of styrene with **1** as a function of the concentration of styrene.

(TMP)Fe^{IV} = O (**1**), isolated by the various approaches described here, that ratio was only 1.0–1.3.

The stability of solutions of (TMP)Fe^{IV} = O (**1**) in benzene allowed a direct examination of the reaction of **1** with a series of substituted styrenes. Attempts to monitor this reaction in CH_2Cl_2 were not successful because of the competitive reaction of **1** with the solvent. The addition of excess olefin to benzene solutions of **1** resulted in its quantitative conversion to **3-OH** at rates between 10-fold and 100-fold faster than in the absence of substrate. The kinetic behavior of the reactions was studied by following the corresponding changes in the visible spectra with respect to time as a function of olefin concentration. Typical kinetic data for the reaction of **1** with several substrates in benzene are compared to the background decay of **1** in Figure 3. Each single run was strictly first order in **1** and the observed rate constants (k_{obs}) were directly related to the olefin concentration (Figure 3, inset). In this way the second-order rate constants for reaction of **1** with a series of substituted styrenes were obtained. The corresponding Hammett plot is shown in Figure 4.

Larger scale reactions were examined by GC analysis of the organic products from the oxidation of the substituted styrenes by **1**. With benzene as solvent, the principal products (>90%) were the corresponding benzaldehydes and the product ratios in competitive reactions of substituted styrenes with **1** were as predicted from their rate constants. In 1,2-dichlorobenzene or nitrobenzene under otherwise identical conditions, the major

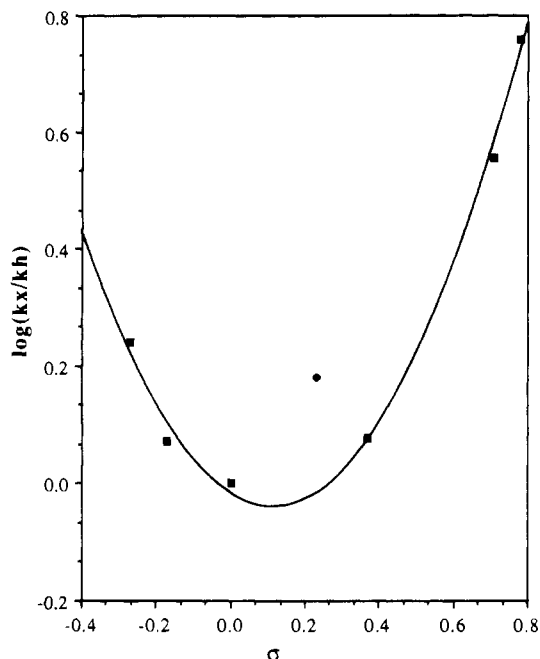


Figure 4. Hammett plot of the rate constants of ring-substituted styrenes with **1** in benzene. The curve was drawn while neglecting the deviating point at $\sigma = 0.23$.

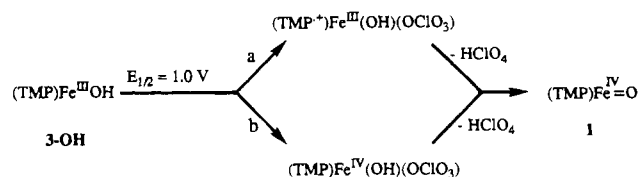
products were styrene oxides and phenylacetaldehydes. However, the product ratios in competitive reactions of substituted styrenes with **1** were *not* as predicted from their rate constants derived from benzene solution. Rather, the more electron rich styrenes were found to be considerably more reactive. A typical example is the competition reaction between 4-NO₂-styrene and styrene which in benzene gave mostly 4-NO₂-benzaldehyde, whereas in 1,2-dichlorobenzene the sole detected product was styrene oxide.

Discussion

In the present study we have described a facile and efficient procedure for the preparation and isolation of oxoiron(IV) porphyrins by ligand metathesis of the corresponding iron(III) porphyrin cation radicals. The mechanism of formation of oxoiron(IV) porphyrins by electrochemical oxidation of the corresponding hydroxoiron(III) porphyrins has been examined and the direct reaction of oxoiron(IV) porphyrins with olefins has been observed.

Preparation of an Oxoiron(IV) Porphyrin from an Iron(III) Porphyrin Cation Radical. The iron(IV) oxidation state in metalloporphyrins has been shown to be stabilized by oxygen and fluoride ligands,¹² a common phenomenon for high oxidation states of transition metals. Iron(III) porphyrin cation radicals and iron(IV) porphyrins are formally at the same oxidation level, and accordingly, it is possible to alternate between these two formulations by ligand metathesis. This principle was demonstrated experimentally by formation of dimethoxoiron(IV) and dimethoxomanganese(IV) porphyrins by treatment of the corresponding metalloporphyrin cation radicals with sodium methoxide.^{12a, 13} We have shown that a suitable source of hydroxide ions allows the conversion of iron(III)

Scheme 2



porphyrin cation radicals into the corresponding oxoiron(IV) porphyrins. This route has not explored previously as a preparative route, but is suggested by the electrochemical behavior of hydroxoiron(III) porphyrins.^{8a,b, 9, 10}

The transformation of (TMP⁺)Fe^{III}(ClO₄)₂ (**2**) to (TMP)Fe^{IV}=O (**1**) over moist, basic alumina succeeded in all the organic solvents examined. Significantly, the product was collected as a rapidly moving band, suggesting that it was a neutral species free of excess hydroxide or other counter ions. The stability of **1** varied significantly from solvent to solvent. In CD₂Cl₂, **1** was stable only at subzero temperatures (Figure 1). At room temperature and especially in non-deuterated CH₂Cl₂, its lifetime was very short, and examination of the visible and NMR spectra revealed that **1** was fully converted to **3-Cl**. As the only possible source for the chloride ligand of **3-Cl** was the solvent and because of the significant difference of stability of **1** in CD₂Cl₂ vs CH₂Cl₂, we examined several solvents without readily abstractable hydrogens. In benzene, as well as in bromo-, 1,2-dibromo-, and nitrobenzene, **1** was found to be much more stable and could be characterized at room temperature (Figure 1, inset). Stable benzene solutions of the related dimethoxoiron(IV)-(TMP), which was previously prepared by treating **2** with sodium methoxide in CH₂Cl₂ at low temperatures,^{12a} were also prepared in this way.¹⁴

Electrochemical Oxidation of Hydroxoiron(III) Porphyrins. The first electrochemical oxidation of haloiron(III) porphyrins is generally accepted to be porphyrin centered.^{8,15,16} Convincing evidence in favor of that assignment was the successful isolation and characterization of ferric porphyrin cation radicals obtained by oxidation of iron(III) porphyrins.¹⁷ By contrast, the products of electrochemical oxidation of hydroxoiron(III) porphyrins have been shown to be oxoiron(IV) porphyrins.⁷⁻¹⁰ It is not clear, however, whether the first oxidation wave in these cases represents an iron-centered or porphyrin-centered oxidation. In both cases a chemical reaction (elimination of HClO₄) is required in order to obtain the ferryl group observed in the product (Scheme 2).

The results obtained in this study can differentiate between these two possibilities. In Figure 2 the $E_{1/2}$ values of eight hydroxoiron(III) porphyrins are plotted against the $E_{1/2}$ values of the corresponding chloroiron(III) porphyrins. Not only is the correlation very high but also the slope is unity (0.97 ± 0.02), clearly indicating that the hydroxoiron and chloroiron

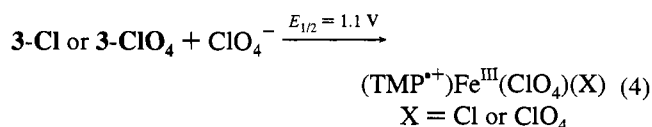
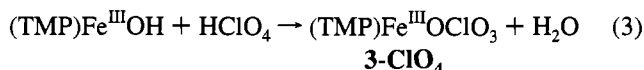
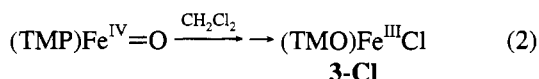
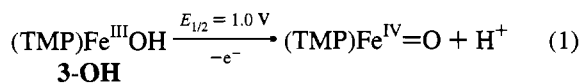
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porphyrins respond to the *same* substituent effect. This is very informative since it has been shown in series of metalloporphyrins that substituent effects on oxidation or reduction potentials are much higher for porphyrin than for metal centered reactions.¹⁸ As it is generally agreed that the oxidation of haloiron(III) porphyrins is porphyrin-centered, the conclusion is that the same must be true for the hydroxoiron(III) porphyrins as well. Furthermore, the Hammett ρ value for both the hydroxide and the chloride ligated iron porphyrins was 0.075 ± 0.005 (Figure 2, inset). This is in the range of $\rho = 0.07 \pm 0.01$ observed for ring oxidation of several other metalloporphyrins, whereas ρ values for metal oxidation are in the range 0.02–0.05 (for the Fe^{II}/Fe^{III} couple $\rho = 0.04$).^{8a} Thus, the results indicate that the first oxidation wave of hydroxoiron(III) porphyrins represent a (P)Fe^{III}OH/(P⁺)Fe^{III}OH couple similar to other iron porphyrins with more innocent ligands (halide, perchlorate, etc.).

Evidence in favor of a metal-centered electrochemical oxidation of hydroxoiron(III) porphyrins has been inferred from the fact that two oxidation waves are observed in the CV of hydroxoiron porphyrins in the region where the corresponding haloiron porphyrins display only one wave.⁹ Two oxidation waves were observed for **3-OH** with values of 1.0 and 1.1 V. However, the intensity of the second oxidation wave, whose $E_{1/2}$ is identical to that of the corresponding haloiron porphyrin **3-Cl**, was found to depend on the CV scan rate. At fast scan rates (500–1000 mV/s) and in very carefully dried CH₂Cl₂, the second oxidation wave was not observed. This behavior is very similar to the findings of Kadish et al., who have shown that the second oxidation wave for **3-OH** vanished at low temperatures.^{8b} Such behavior indicates the formation of a metastable species at the first oxidation wave which produces a new species with a higher oxidation potential at the electrode surface.

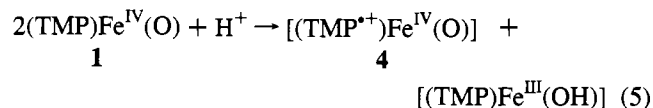
Thus, the results are best explained by the scenario shown in eqs 1–4. First, **3-OH** is oxidized at 1.0 V to **1** and HClO₄ (eq 1), which can react further to produce **3-Cl** and **3-ClO₄** respectively (eqs 2 and 3) in accord with the reactivity of **2** we have described above. Both species have identical $E_{1/2}$ values (1.1 V) and are responsible for the second oxidation wave (eq 4). The reactions described in eqs 2 and 3 are relatively slow, and accordingly, the process described in eq 4 is not observed when fast CV scan rates or low temperatures are applied. Accordingly, at high temperatures or slow scan rates, two oxidation waves are observed due to oxidation of **3-OH** at 1.0 V and **3-Cl** or **3-ClO₄** at 1.1 V, which derive from this ECE process.



We conclude that the first oxidation of **3-OH** is porphyrin-centered, similar to all other iron(III) porphyrins. The sole difference is that the initially formed hydroxo-iron(III) por-

phyrin cation radicals are unstable and convert immediately to oxoiron(IV) porphyrins and HClO₄ (pathway a in Scheme 2). Depending on the conditions under which the CV's are examined, these products can react with solvent and/or the starting material to produce new species whose oxidation potentials are about 100 mV higher than the corresponding hydroxoiron(III) porphyrins (eqs 2–4).

Oxygenation of Hydrocarbons by (TMP)Fe^{IV}(O) (1). The reactivity of **1** with olefins was investigated in several regimes. First, we reexamined the oxidation of *cis*- β -methylstyrene under conditions for the electrochemical oxidation of **3-OH**. We had previously observed the electrocatalytic epoxidation of this substrate under these conditions.¹⁰ *cis*- β -methylstyrene was chosen as the diagnostic substrate because it is known to be oxidized stereoselectively to its *cis*-oxide in the iododisilbenzene/iron porphyrin catalysis system and because significant mechanistic information was obtained from this substrate in oxomanganese oxidation reactions.^{2a,11} Comparison of the electrochemical results with those obtained for *cis*- β -methylstyrene oxidation by isolated [(TMP⁺)Fe^{IV}(O)] (**4**), which had been prepared by reaction of **3-Cl** with MCPBA at -78°C ,⁵ and by **1** isolated in CH₂Cl₂ at low temperatures was revealing. In its reaction with **4**, the ratio of *cis*/*trans* β -methylstyrene oxide was 11.3, as expected, whereas that ratio was only 1.0–1.3 when **1** was used directly as oxidant. In the electrochemical oxidation the *cis*/*trans* epoxide ratio was 2.3–3.3. We conclude that (TMP)-Fe^{IV}(O) (**1**) reacted with *cis*- β -methylstyrene with very low stereoselectivity, in marked contrast to the high selectivity observed with [(TMP⁺)Fe^{IV}(O)] (**4**). Accordingly, in the electrochemical experiments, direct reaction of **1** must be the major pathway for olefin oxidation together with some contribution from **4** formed by the disproportionation of **1** (eq 5).^{5d}

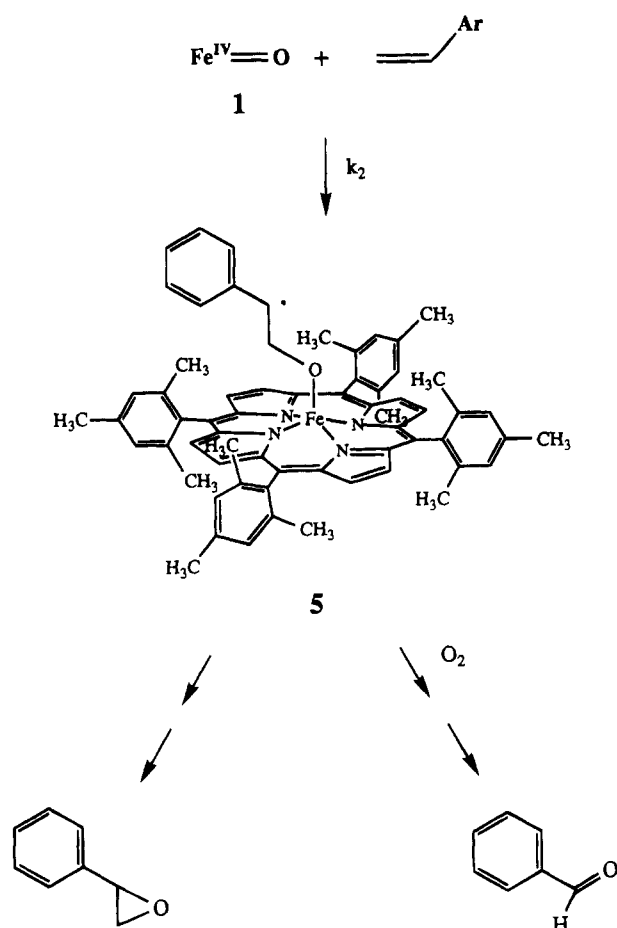


The second system investigated was the reaction of olefins with CH₂Cl₂ solutions of **1**, prepared from **2** and basic alumina as described above. Attempts to study the reaction of **1** with styrene in CH₂Cl₂ by varying the olefin concentration and temperature resulted in the conclusion that the reaction of **1** with CH₂Cl₂ masked a major part of the reaction with styrene. However, since the stability of **1** was significantly increased in CD₂Cl₂, its NMR spectrum could still be obtained at up to 0 °C. Under these conditions a pronounced reactivity toward cyclohexene was observed. Cyclohexene oxide, cyclohexen-3-one, and cyclohexen-3-ol were identified in a ratio of 14:9:1. These products began to appear only at temperatures higher than 0 °C. It is apparent that the high reactivity of **1** toward CH₂Cl₂ and its comparatively low reactivity toward olefins at low temperatures has obscured the reactivity of oxoiron(IV) porphyrins toward olefins described here.

The third system studied was the reaction of (TMP)Fe^{IV}(O) (**1**) in benzene with substituted styrenes. The increased life time of **1** in benzene has permitted a detailed kinetic investigation at room temperature. The addition of excess olefin to benzene solutions of **1** resulted in its quantitative conversion to **3-OH**. The background decomposition of **1** under these conditions was 1–2 orders of magnitudes slower in the absence of substrate. The kinetic behavior of the reactions was studied by following the corresponding changes in the visible spectra with respect to time as a function of olefin concentration. Repetitive scans showed ideal isosbestic points and the reaction kinetics followed

(18) Kadish, K. M.; Morrison, M. M. *Inorg. Chem.* **1976**, *15*, 980.

Scheme 3



at wavelengths corresponding to disappearance of **1** (540 nm) and for appearance of **3-OH** (580 nm) gave identical results. Each single run was strictly (pseudo) first order in **1** (Figure 3) and the observed rate constants (k_{obs}) were directly related to the olefin concentration (Figure 3, inset), confirming that the rate determining step was first order in each reagent.

The inspection of the second-order rate constants for the reaction of **1** with the series of substituted styrenes reveals that the rate constants of *all* substituted styrenes were higher than that of styrene. This results in the concave (upward) Hammett plot shown in Figure 4. The curved Hammett plot and the overall small differences in the rate constants are characteristic of reactions in which a neutral carbon radical is formed,¹⁸ but very different from the reactivity of $(\text{TMP}^+)\text{Fe}^{\text{IV}}=\text{O}$ (**4**) with the same substrates in which a linear Hammett plot with a large slope ($\rho = -1.9$) was observed.^{5b} The results indicate that the rate-determining step for the reaction of **1** with substituted styrenes is the addition of the ferryl oxygen to the double bond to afford the iron porphyrin-bound carbon radical **5** as shown in Scheme 3. Electron transfer without C–O bond formation to form an olefin π -cation radical would be expected to exhibit a much larger substituent effect as observed in other cases.^{5b}

To confirm that the conversion of $(\text{TMP})\text{Fe}^{\text{IV}}(\text{O})$ (**1**) to **3-OH** was indeed due to reaction with the olefins (and not with antioxidant stabilizers or other impurities), larger scale reactions were performed and followed by GC analysis of the organic products. With benzene as solvent, the principal products (>90%) were the corresponding benzaldehydes and the product ratios in competitive reactions of substituted styrenes with **1** were as predicted from their rate constants. Because of the small differences in reactivity, the competition results were quite

reliable. Thus, we can quite safely conclude that the small scale kinetic results and the larger scale reactions proceed by the same mechanism.

Very different results were obtained when the solvent was changed from benzene to 1,2-dichlorobenzene or nitrobenzene, however. Under otherwise identical conditions (ring substituted) styrene oxides and phenylacetaldehydes became the major products with only small amounts of benzaldehydes and the product ratios in competitive reactions of substituted styrenes with **1** were no longer as predicted from their rate constants. Rather, the more electron rich styrenes reacted faster, without exception, and with very large rate differences between the substrates. A typical example is the competition reaction between 4- NO_2 -styrene and styrene where in benzene 4- NO_2 -benzaldehyde was observed as the major product, but in 1,2-dichlorobenzene the sole detected product was styrene oxide.¹⁹

We suggest a mechanism which is compatible with all the results obtained in the different solvents. For the reaction of **1** with olefins, two pathways must exist. One pathway involves the direct reaction of **1** with styrene to form a carbon radical intermediate, **5**. Closure of the carbon–oxygen bond in **5** would necessarily form an epoxide coordinated to $(\text{TMP})\text{Fe}^{\text{II}}$. Precedent for this kind of process can be found in the chemistry of epoxide complexes of ruthenium(II) porphyrins.²⁰ The facile *cis*–*trans* isomerization of epoxides observed in this case has been shown by us to proceed through a ruthenium intermediate exactly analogous to **5**. Further, iron(III) thiolates are known to react with thioalkyl radicals to produce alkyl disulfides and iron(II),²¹ again in analogy to the ring closure of **5**. Such a process would be expected to afford an opportunity for loss of configuration of the starting olefin, as observed. The same radical intermediate, **5**, would be expected to react readily with dioxygen to form benzaldehyde. This is in good agreement with the direct kinetic results and the results from competition reactions of **1** with substituted styrenes in benzene.

Epoxides must be formed by a different mechanism in the more polar solvents, however. The higher polarity and, possibly, the presence of more water in 1,2-dichlorobenzene and nitrobenzene could encourage the formation of epoxides from **5**. However, the substrate selectivity would be expected to be similar in all solvents if **5** is formed in the first step. Since a dramatic change in selectivity in favor of electron-rich olefins was observed in the reactions performed in 1,2-dichlorobenzene and nitrobenzene, the reaction cannot proceed by the direct reaction of **1** with the olefin to afford **5**. It seems reasonable that the increased polarity serves in these cases to favor the disproportionation of $(\text{TMP})\text{Fe}^{\text{IV}}=\text{O}$ (**1**) to **3-OH** and the more electrophilic $(\text{TMP}^+)\text{Fe}^{\text{IV}}=\text{O}$ (**4**), shown in eq 5. Since the selectivity of **4** is known to be very high ($\rho = -1.9$), that electrophilic intermediate must be the stoichiometrically important oxidant in the reactions of **1** in 1,2-dichlorobenzene and nitrobenzene. This would explain both the high selectivity toward electron-rich olefins and the formation of epoxides as major products.

Thus, oxoiron(IV) porphyrins do react with olefins and by a mechanism that is both kinetically and stereochemically distinct from that observed with oxoiron(IV) porphyrin cation radicals,

(19) For the three solvents used there is a considerable difference in the solubility of water which may favor the disproportionation of **1**: 0.06% in benzene, 0.24% in nitrobenzene, and 0.31% in 1,2-dichlorobenzene. Riddick, J. A.; Bunger, W. B.; Sakano, T. K. In *Organic Solvents, Techniques of Chemistry, Volume II*, 4th ed; Weissberger, A., Ed.; John Wiley & Sons Inc.: New York, 1986; pp 136, 509, 581.

(20) Groves, J. T.; Ahn, K.-H.; Quinn, R. *J. Am. Chem. Soc.* **1988**, *110*, 4217–4220.

(21) Dawson, J. H.; Holm, R. H.; Trudell, J. R.; Barth, G.; Linder, R. E.; Bunnenberg, E.; Djerassi, C. *J. Am. Chem. Soc.* **1976**, *98*, 3707.

a situation which is exactly analogous to the parallel reactivity of oxomanganese(IV) and oxomanganese(V) porphyrins.^{11a} The disproportionation of oxoiron(IV) porphyrins to the more reactive oxoiron(IV) porphyrin cation radicals in polar solvents suggests catalytic schemes for olefin epoxidation and alkane hydroxylation using mild oxidants such as dioxygen.

Summary. Oxoiron(IV) porphyrins such as $(\text{TMP})\text{Fe}^{\text{IV}} = \text{O}$ (**1**) can be conveniently prepared by ligand metathesis of the corresponding iron(III) porphyrin cation radicals over basic alumina. The formation of **1** by electrochemical oxidation of **3-OH** was shown to be an EC process, with initial oxidation of the porphyrin ring followed by elimination of HClO_4 and rearrangement. $(\text{TMP})\text{Fe}^{\text{IV}} = \text{O}$ (**1**) was found to be quite stable at room temperature in relatively unreactive solvents such as benzene. $(\text{TMP})\text{Fe}^{\text{IV}} = \text{O}$ (**1**) reacted readily with substituted styrenes with a selectivity which was very much unlike that observed for $(\text{TMP}^+)\text{Fe}^{\text{IV}} = \text{O}$ (**4**). In benzene the kinetic data and product analysis has lead us to suggest that the first and rate limiting step is a radical attack of the ferryl oxygen of **1** on the olefin π -bond, followed by a fast reaction with molecular oxygen to form benzaldehydes or ring closure to afford epoxides with loss of the configuration of the starting olefin. In solvents with a higher water content **1** disproportionated to **3-OH** and **4** resulting the reactivity pattern of that more electrophilic species. Clearly, the reactivity of **1** toward olefins reported here and its facile interconversion with **4** need to be considered when assigning mechanisms in catalytic regimes. We continue to explore the relationships between the structure and reactivity of oxoiron(IV) porphyrins.²²

Experimental Section

Materials. *cis*- β -Methylstyrene was purchased from K&K, and all other olefins were purchased from Aldrich. Olefins were purified twice by basic alumina chromatography, analyzed by GC, and used the same day. Analytical grade CH_2Cl_2 was washed twice with 5% NaOH, dried over solid KOH and solid Na_2CO_3 , and finally distilled over CaH_2 . Other solvents were analytical grade and used as received unless specified.

Preparation of $(\text{TMP})\text{Fe}^{\text{III}}\text{OH}$, **3-OH.** $(\text{TMP})\text{Fe}^{\text{III}}\text{Cl}$ (**3-Cl**) was dissolved in a minimum of CH_2Cl_2 and eluted through a 10% water-basic alumina column with purified CH_2Cl_2 . The green organic phase was evaporated immediately and dried by heating to about 60 °C to give a quantitative yield of $(\text{TMP})\text{Fe}^{\text{III}}\text{OH}$ (**3-OH**). $^1\text{H NMR}$ ($\text{CD}_2\text{-Cl}_2$): δ 80.6 (pyr H), 12.46, 11.47 (meta H), 3.50 (*p*- CH_3). **3-OH** was extremely sensitive to traces of acids in common solvents. Crystallization from equal volumes of CH_2Cl_2 and hexane resulted in crystals of **3-Cl**, whereas crystals of **3-OCH}_3** were formed by recrystallization from CH_2Cl_2 and MeOH. Crystals of **3-OH** were obtained only when CH_2Cl_2 , containing tetrabutylammonium hydroxide ((TBA)OH), and hexane were used for the recrystallization.

Preparation of $(\text{TMP}^+)\text{Fe}^{\text{III}}(\text{ClO}_4)_2$, (2**).** An 8 mg sample of **3-OH** was dissolved in 10 mL CH_2Cl_2 and 80 mg of solid $\text{Fe}(\text{ClO}_4)_3$ (anhydrous, non-yellow) was added with stirring. The color changed from green to deep red in seconds, signaling the formation of **3-OCIO}_3**. Stirring was continued for 2 h. The color changed to brilliant green within about 20 min with the formation of **2**. The solution was freed from inorganic salts by filtration and dried over Na_2SO_4 , and an equal amount of hexane was added. The solvent was removed until solid started to separate and the mixture was transferred to a -20 °C freezer. $(\text{TMP}^+)\text{Fe}^{\text{III}}(\text{ClO}_4)_2$, (**2**) (6 mg) separated as a green-black solid.

Preparation of $(\text{TMP})\text{Fe}^{\text{IV}}(\text{O})$, **1.** A 2.1 mg sample of **2** was dissolved in 0.6 mL of CD_2Cl_2 and cooled in an dry ice-acetone bath. This solution was transferred through a short (0.5 \times 1 cm) column

containing basic alumina/20% H_2O at ambient temperature, directly into a NMR tube placed in the cooling bath. The $^1\text{H NMR}$ of the resulting solution (Figure 2) showed that **1** was formed with only traces of **3-OH**; $^1\text{H NMR}$ (CD_2Cl_2 , -78 °C): δ 5.85 (pyr H), 6.20 and 6.75 (meta H), 3.40 and 1.05 (*o*- CH_3), 2.70 (*p*- CH_3). In the deuterated solvent **1** was stable and afforded a good spectrum up to 0 °C. $^1\text{H NMR}$ (CD_2Cl_2 , 0 °C): δ 7.30 (pyr H), 6.35 and 6.70 (meta H), 2.80 and 1.25 (*o*- CH_3), 2.60 (*p*- CH_3).

Preparation of Chloro- and Hydroxo(5,10,15,20-tetrakis(4-*tert*-butyl-2,6-dibromophenyl)porphyrinato)iron(III), $(\text{TBOB})\text{Fe}^{\text{III}}\text{Cl}$ and $(\text{TBOB})\text{Fe}^{\text{III}}\text{OH}$. A 150 mg sample of 5,10,15,20-tetrakis(4-*tert*-butyl-2,6-dibromophenyl)porphyrin²³ and 0.4 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were refluxed overnight in 100 mL of DMF. A total of 100 mL of 10% HCl was added in several portions to the cool solution and the precipitated solid was collected on a Buchner funnel and washed with 10% HCl. This solid was dissolved in CH_2Cl_2 , extracted with 10% HCl and saturated NaCl, dried over Na_2SO_4 , and evaporated to dryness to afford a brown solid which was recrystallized from CH_2Cl_2 /hexanes to afford 60 mg of purple crystals of the iron chloride complex $(\text{TBOB})\text{Fe}^{\text{III}}\text{Cl}$. $^1\text{H NMR}$ (CDCl_3): δ 80.5 (pyr), 13.9 and 12.7 (meta H), 2.3 (*p*-*tert*-butyl). $^1\text{H NMR}$ (CD_2Cl_2): δ 14.0 and 12.85 (meta H), 2.3 (para *tert*-butyl). $^1\text{H NMR}$ (C_6D_6): δ 81.5 (pyr), 13.75 and 12.6 (meta H), 1.9 (*p*-*tert*-butyl). The hydroxo complex, $(\text{TBOB})\text{Fe}^{\text{III}}\text{OH}$, was prepared by dissolving the iron chloride complex in (TBA)OH-saturated CH_2Cl_2 . This solution was filtered and left to stand over pentane vapors for several days, after which black crystals were formed. $^1\text{H NMR}$ (CDCl_3): δ 80.2 (pyr), 11.4 and 10.7 (meta H), 1.92 (*p*-*tert*-butyl). $^1\text{H NMR}$ (CD_2Cl_2): δ 11.5 and 10.75 (meta H), 2.0 (*p*-*tert*-butyl). $^1\text{H NMR}$ (C_6D_6): δ 80.4 (pyr), 11.30 and 10.65 (meta H), 1.56 (*p*-*tert*-butyl).

Preparation of Chloro- and Hydroxo(5,10,15,20-tetrakis(2,6-dibromo-4-methoxyphenyl)porphyrinato)iron(III) $(\text{TBOMe})\text{Fe}^{\text{III}}\text{Cl}$ and $(\text{TBOMe})\text{Fe}^{\text{III}}\text{OH}$. A 36 mg sample of 5,10,15,20-tetrakis(2,6-dibromo-4-methoxyphenyl)porphyrin²⁰ (0.026 mmol) and 33 mg of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (0.166 mmol, 6.4 equiv) were refluxed in 50 mL of DMF overnight. Slow addition of 35 mL of 10% HCl to the cool solution, filtration of the solid, and extraction of the solid with CH_2Cl_2 and 10% HCl followed by evaporation of the solvent resulted in a mixture (~4:1) of free base and iron chloride complex. By chromatographic elution with CH_2Cl_2 on silica, 25 mg of free base was separated. Elution by 1:3 MeOH/ CH_2Cl_2 followed by extraction with 10% HCl and recrystallization from CH_2Cl_2 /MeOH resulted in 6 mg of purple crystals of the pure chloroiron(III) porphyrin $(\text{TBOMe})\text{Fe}^{\text{III}}\text{Cl}$. UV/vis ($\text{CH}_2\text{-Cl}_2$): 421 (Soret) and 512, 584, 645 nm in decreasing order of intensity; $^1\text{H NMR}$ (CDCl_3): δ 80.5 (pyr), 13.3 and 12.2 (meta H), 4.8 (para OCH_3). Quantitative conversion of the chloro complex to its hydroxo complex was carried out as for $(\text{TMP})\text{Fe}^{\text{III}}\text{OH}$ to afford $(\text{TBOMe})\text{-Fe}^{\text{III}}\text{OH}$. UV/vis (CH_2Cl_2): 419 (Soret) and 580 nm. $^1\text{H NMR}$ (CDCl_3): δ 80.0 (pyr), 10.95 and 10.35 (meta H), 4.5 (*p*- OCH_3).

Reaction of $(\text{TMP})\text{Fe}^{\text{IV}} = \text{O}$, **1, with Cyclohexene.** Addition of 3 equiv of cyclohexene to an NMR tube containing **1** in CD_2Cl_2 at -60 °C and inspection of the $^1\text{H NMR}$ spectrum showed no changes below 0 °C. When the tube reached room temperature, resonances due to **1** were transformed into those of **3-OH** and **3-Cl** and the formation of cyclohexene oxide and cyclohexen-3-one was clearly evident. GC analysis of this mixture revealed that the ratio of [cyclohexene oxide]:[cyclohexen-3-one]:[cyclohexen-3-ol] was 14.9:1.

Reactions of **1 with *cis*- β -Methylstyrene. (a) Reaction with $(\text{TMP}^+)\text{Fe}^{\text{IV}} = \text{O}$, **4**.** A 0.9 mg sample (1.2 equiv) of MCPBA was added to 4.0 mg of **3-Cl** dissolved in 0.4 mL of CH_2Cl_2 at -78 °C, to obtain the characteristic green color of **4**. Then 10 μL of *cis*- β -methylstyrene in 25 μL of methanol was added and the reaction was quenched after 15 min with tetrabutylammonium iodide. The ratio of *cis*/*trans* oxides was 11.5 by GC with a 25% yield (internal reference).

(b) Reaction by Electrochemical Oxidation. The conditions described in ref 10, which gave a *cis*/*trans* epoxide product ratio of 2.7, were repeated and gave a ratio of 2.3 and when performed with (TBA)OH gave a ratio of 3.30.

(c) Reaction with $(\text{TMP})\text{Fe}^{\text{IV}} = \text{O}$, **1.** A solution of **1** was prepared in CH_2Cl_2 at ca. -70 °C by several methods: by adding excess (TBA)-

(22) We have shown recently that the axial ligand in **4-X** affects its reactivity with cyclohexene: Groves, J. T.; Gross, Z. In *Bioinorganic Chemistry: An Inorganic Perspective of Life*; Kessissoglou, D. P., Ed., Kluwer Academic Publishers: Dordrecht, The Netherlands, in press.

(23) The free base porphyrin was prepared and designed by Mr. R. J. Nick according to the Lindsey method.

OH to a solution of **4** and mixing until the color changed from green to red, from **2** and basic alumina (similar to the NMR experiment described above), from **2** and (TBA)OH, or by chromatographic treatment (20% H₂O/basic alumina, ethyl acetate and CH₂Cl₂ eluents, $T = -78$ °C) of the electrochemically generated **1**. After the addition of *cis*- β -methylstyrene, the solutions were allowed to warm to room temperature and analyzed by GC after dissipation of the red color of **1**. The *cis/trans* β -methylstyrene product ratios for several runs were in the range of 1.0–1.5.

Reactions of **1 with Substituted Styrenes.** A 0.6 mL sample of about 3 mg of **1** in benzene (or nitrobenzene or 1,2-dichlorobenzene) was filtered through a pipet-type column containing 20% water/basic alumina into a reaction vessel containing about 20 μ L of the (freshly purified and GC analyzed) olefinic substrate(s). GC analysis were performed after the color change from red (**1**) to green (**3-OH**) was complete (1–10 min). Products were identified by comparison to authentic samples. For the competition reactions, the mixture of the substrates was analyzed by GC just before the reaction.

Kinetic Measurements. About 0.1 mL of concentrated benzene

solution of **2** was filtered through a pipet-type column with 20% water/basic alumina into water-saturated benzene. A 2 mL aliquot of the resulting red solution was transferred to a 1 cm UV cuvette, and 5–25 μ L of substituted styrene was added. The conversion of **1** to **3-OH** was followed at 540 and 580 nm, the λ_{max} of the reactant and the product respectively. The spectrophotometer used was a Hewlett-Packard 8452A diode array spectrophotometer. The kinetic data was analyzed with optimization of the infinity point.

Cyclic Voltammograms. The half-wave potentials of the chloroiron(III) and hydroxoiron(III) porphyrins were measured by a BAS-100 electrochemical analyzer for 10⁻³ M solute and 0.1 M (TBA)OH in CH₂Cl₂. Special attention was given to the purity of the Fe–OH solutions by monitoring the UV spectra as described in the Results section.

Acknowledgment. Financial support of this research by the National Institutes of Health (Grant GM-36298) is gratefully acknowledged.