Formation, Characterization, and Reactivity of the Oxene Adduct of [Tetrakis(2,6-dichlorophenyl)porphinato]iron(III) Perchlorate in Acetonitrile. Model for the Reactive Intermediate of Cytochrome P-450

Hiroshi Sugimoto, Hui-Chan Tung, and Donald T. Sawyer*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received March 12, 1987*

Abstract: Combination of [tetrakis(2,6-dichlorophenyl)porphinato]iron(III) perchlorate with pentafluoroiodosobenzene, *m*-chloroperbenzoic acid, or ozone in acetonitrile at -35 °C yields a green porphyrin-oxene adduct. This species, which has been characterized by spectroscopic, magnetic, and electrochemical methods, cleanly and stereospecifically epoxidizes olefins (>99% *exo*-norbornene oxide). The reaction chemistry and electronic characterization of the adduct are consistent with an oxygen atom covalently bound to an iron(II)-porphyrin radical center [$(Por^{\bullet -})Fe^{II}(O)^+$]. The latter has the spectral, magnetic, and redox characteristics of compound I of horseradish peroxidase (HRP) and the selective stereospecific oxygenase character of the reactive intermediate for cytochrome P-450. Reduction of the green species by one electron equivalent yields a red species, $PorFe^{II}(O)$, which has the spectral characteristics and reactivity of compound II of HRP. The iron(III)-porphyrin is an efficient catalyst for (a) the stereospecific epoxidation of olefins and (b) the oxidative cleavage of α-diols by F_5PhIO and *m*-ClPhC(O)OOH; with H_2O_2, there is extensive attack on the porphyrin ring and no significant reaction with olefins or α-diols.

Although there has been persistent and compelling evidence that the reactive intermediates of horseradish peroxidase (HRP-I and HRP-II)[1-5] and of cytochrome P-450[6-14] involve a heme oxygen group (derived from $Fe^{III}Por^+$ plus H_2O_2 and $O_2 + 2H^+ + 2e^-$, respectively), the electronic density and nature of the bonding between the porphyrin, iron, and oxygen are not established. The proposed valence of the iron in the reactive intermediates ranges from Fe(V) to Fe(III), of the porphyrin from $Por^{\bullet -}$ to Por^{2-}, and of the oxygen from O^{2-} to O^0. The unique chemistry of the reactive intermediate of cytochrome P-450[6-21] [(a) stereospecific epoxidation of olefins, (b) demethylation of dimethylaniline, (c) oxidative cleavage of α-diols, and (d) insertion of an oxygen atom in C-H bonds of hydrocarbons] is consistent with that expected of singlet-state atomic oxygen. However, the dominant contemporary fomulation of the reactive intermediate for this protein is $(RS^-)(Por^{\bullet -})Fe^{IV}(O^{2-})$, with a thiolate anion[22,23] and an oxo dianion coordinated to an iron(IV)-porphyrin radical center.

The interaction of horseradish peroxidase [an iron(III) heme that has a proximal imidazole] with hydrogen peroxide results in the formation of a green reactive intermediate known as compound I. This is reduced by one electron to give a red reactive intermediate, compound II.[24-26] Both of these intermediates contain a single oxygen atom from H_2O_2, and compound I is two oxidizing equivalents above the iron(III)-heme state with a magnetic moment equivalent to three unpaired electrons ($S = {}^3/_2$). Electron nuclear double resonance (ENDOR),[27] Mössbauer,[28-30] ESR,[31] NMR,[32] and EXAFS[33,34] measurements have been used (in conjunction with formal electron count) in support of the formulation of compound I as a low-spin iron(IV)-oxo dianion-porphyrin radical species $[(Por^{\bullet -})Fe^{IV}(O^{2-})]^+$ and compound II (its one-electron-reduction product) as $(Por^{2-})Fe^{IV}(O^{2-})$. A recent EXAFS study[33] concludes that compound I and compound II contain an oxoferryl group (Fe=O) with a bond length of 1.64 Å.

During the past decade there have been numerous efforts via iron-porphyrin models to form and characterize compounds I and

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II. An early effort involved the low-temperature oxygenation of (TPP)Fe^{II} (TPP = tetraphenylporphyrin dianion) with O_2 to form a transiently stable binuclear species [(TPP)Fe(O–O)Fe(TPP)], which dissociates homolytically to give a product that exhibits the spectroscopic properties associated with compound II of HRP and is formulated as $(TPP^{2-})Fe^{IV}(O^{2-})$.[35,36] Other studies have made use of various derivatives of (TPP)Fe^{III}Cl and (OEP)Fe^{III}Cl (OEP = octaethylporphyrin dianion) with peracids,[37,38] iodosobenzene,[37,38] 4-cyano-*N*,*N*-dimethylaniline *N*-oxide,[39] and hypochlorite[40] to oxidize and oxygenate cytochrome P-450 model substrates. On the basis of the close parallel with the products from the enzyme-catalyzed reactions and the net two oxidizing equivalents of the catalytic cycles for cytochrome P-450/(O_2 + $2H^+$ + $2e^-$) and HRP/H_2O_2, a general consensus has developed that the reactive intermediate is like compound I and is best formulated as $(Por^{\bullet-})Fe^{IV}(O^{2-})^+$. In particular, the proposed mechanism for the epoxidation of olefins by this intermediate invokes electrophilic attack of an unsaturated carbon by the high-valent iron center with electron transfer to give a carbonium ion that combines with the O^{2-} group.[37-39] Similar conclusions have resulted when $(Por^{2-})Mn^{III}(ClO_4)$ models are used; the reactive intermediate is formulated as $(Por^{2-})Mn^{IV}(O^{2-})$.[40-46]

All contemporary work indicates that the reactive intermediate for HRP-I and cytochrome P-450 is an oxygen atom adduct of (imid)$(Por^{2-})Fe^{III}$ and $(RS^-)(Por^{2-})Fe^{III}$.[6,33] The common belief is that atomic oxygen invariably removes two electrons from iron(III) and/or (Por^{2-}) to achieve an oxo (O^{2-}) state. Although this convention (or misconception) is general for the oxygen compounds of transition metals, there is no thermodynamic, electronegativity, or theoretical reason to exclude stable $M(O^{\bullet-})$ and M(O) species.[47] Thus, the atomic oxygen adduct of $(Por^{2-})Fe^{III}(B)^+$ should be viewed as the resonance hybrid of several valence-bond formulations

$$[(Por^{2-})Fe^{V}(O^{2-})^+ \leftrightarrow (Por^{\bullet-})Fe^{IV}(O^{2-})^+ \leftrightarrow (Por^{0})Fe^{III}(O^{2-})^+ \leftrightarrow (Por^{2-})Fe^{IV}(O^{\bullet-})^+ \leftrightarrow (Por^{\bullet-})Fe^{III}(O^{\bullet-})^+ \leftrightarrow (Por^{0})Fe^{II}(O^{\bullet-})^+] \leftrightarrow (Por^{2-})Fe^{III}(O)^+ \leftrightarrow (Por^{\bullet-})Fe^{II}(O)^+]$$

with the last of these simple O atom adducts without intramolecular electron transfer but stabilized by d–p orbital overlap [similar to the addition of [O] to CO to give O=C=O or O_2 to heme Fe(II) to give heme $Fe^{II}(O_2)$].[48]

Many model studies have endeavored to match spectroscopic data and product profiles for model substrates with the chemical character inferred by one or more of these valence-bond formulations. However, these have been frustrated by (a) the reactivity of the solvent, (b) the insolubility of the model porphyrins [(TPP)Fe^{III}Cl] in inert solvents, (c) the insolubility of the source of atomic oxygen (PhIO), (d) the instability and incomplete formation of the reactive intermediate, and (e) the susceptibility of the porphyrin ring to destructive oxidation. The present study has optimized the experimental conditions and the solvent/oxygen atom source/$(Por^{2-})Fe^{III}X$ combination to make possible the stoichiometric formation of a transiently stable oxygen atom adduct of the iron(III)–porphyrin. This species has been characterized by spectroscopy, cyclic voltammetry, and magnetic measurements and by its reactivity and products when combined with model substrtates. Whereas previous .studies[35,36,49,50] of compound I models have been limited to −78 °C or colder in CH_2Cl_2 or MePh, the present system permits solution-phase experiments at −35 °C in an inert solvent (MeCN) and in the absence of chloride ion.

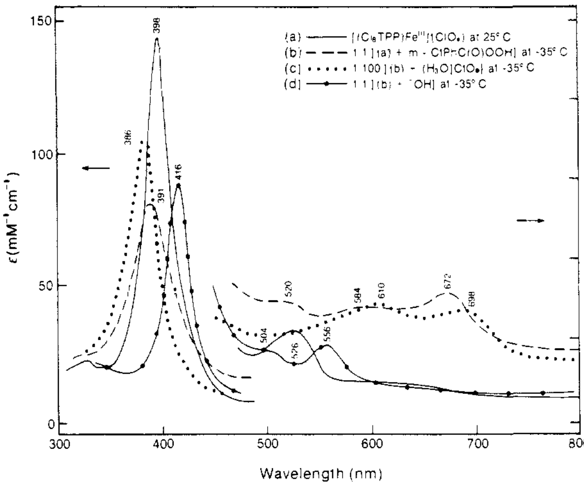

Figure 1. Absorption spectra for (a) 1 mM $[(Cl_8TPP)Fe^{III}](ClO_4)$, (b) the product from its 1:1 combination with *m*-ClPhC(O)OOH at −35 °C, (c) the product from the addition of excess protons to the green species of solution b, and (d) the product from the 1:1 addition of ^-OH to the green species of solution b.

Experimental Section

Chemicals and Reagents. Pentafluoroiodosobenzene (F_5PhIO) was prepared[51] and purified just prior to its use. *m*-Chloroperbenzoic acid (85% pure) (Aldrich) was assayed by iodometry. Norbornene, 1-octene, *cis*- and *trans*-2-heptene, *cis*- and *trans*-stilbene, (+)-1-phenyl-1,2-ethanediol, and phenylglyoxal monohydrate were obtained from Aldrich and were purified by distillation or recrystallization before use. Acetonitrile (Burdick and Jackson Laboratories, "distilled in glass grade", <0.003% H_2O) was kept free of oxygen under an argon atmosphere. Tetraethylammonium perchlorate (TEAP) was purchased from G. Frederick Smith and was dried under vacuum before use as the supporting electrolyte for the electrochemical investigations.

Synthesis of $(Cl_8TPP)Fe^{III}(ClO_4)$. 5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphine (Cl_8TPPH_2) was synthesized from 2,4,6-collidine[38a,52] and was used to prepare $(Cl_8TPP)Fe^{III}Cl$.[53] Reaction of the latter with NaOH made it possible to isolate $(Cl_8TPP)Fe^{III}(^-OH)$.[38a] Both materials were purified by alumina column chromatography; their UV-vis spectra were identical with those of the respective complexes.[38a,54] The perchlorate salt, $(Cl_8TPP)Fe^{III}(ClO_4)$, was prepared by the addition of $HClO_4$ (in acetonitrile) to a dispersion of $(Cl_8TPP)Fe^{III}(^-OH)$ in acetonitrile until the complex dissolved. The solvent was evaporated slowly by a rotary evaporator at <10 °C until purple-black cubic crystals formed. The crystals were collected and dried under vacuum at room temperature. Anal. Calcd for $(C_{44}N_4H_{20}Cl_8)(FeClO_4)(H_2O)_3$: C, 48.15; H, 2.38; N, 5.10. Found: C, 48.44, H, 2.39; N, 5.10. IR: 3500 (coordinated water), 1100–1000 cm^{-1} (perchlorate). UV-vis: 398 nm (144

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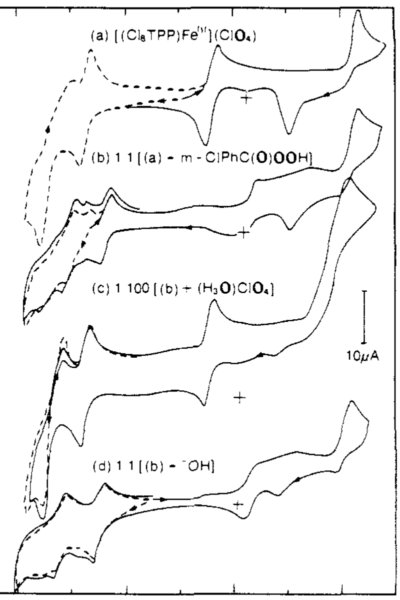

Figure 2. Cyclic voltammograms at a glassy carbon electrode in acetonitrile (0.1 M tetraethylammonium perchlorate) at −35 °C for (a) 1 mM $[(Cl_8TPP)Fe^{III}](ClO_4)$, (b) the product from its 1:1 combination with *m*-ClPhC(O)OOH, (c) the product from the addition of excess protons to the green species (**1**) of solution b, and (d) the product from the 1:1 addition of ^-OH to the green species (**1**) of solution b; scan rate 0.1 V s^{-1}.

mM^{-1} cm^{-1}), 526 (11.3). Magnetic moment in MeCN (−35–25 °C): 4.8 μ_B. ESR (77 K, frozen MeCN): *g*, 4.5 [spectrum similar to those of intermediate-spin iron(III)–porphyrins).[55,56]

Equipment. The cyclic voltammetric measurements were accomplished with a three-electrode potentiostat (Bioanalytical Systems, CV-27) and Houston Instruments Model 100 Omnigraphic X-Y recorder. The electrochemical measurements were made with a Bioanalytical Systems microcell assembly (10-mL capacity) that was adapted to use a platinum or glassy carbon inlay working electrode, a platinum-wire auxiliary electrode, and an Ag/AgCl reference electrode (filled with aqueous tetramethylammonium chloride solution and adjusted to 0.000 V vs SCE)[57] with a solution junction via a glass tube closed with a cracked-glass bead that was contained in a luggin capillary. The low-temperature experiments were made via a dry ice–acetonitrile bath. The UV-vis spectrophotometric measurements were made with a Hewlett Packard HP 8450A diode array spectrophotometer.

Methods. A mixture of oxidant (*m*-ClPhC(O)OOH, F_5PhIO, or HOOH) and substrate in MeCN (0.5 mL) was added to a solution of $(Cl_8TPP)Fe^{III}(ClO_4)$ in MeCN (0.5 mL) at −10 °C. The initial concentrations after mixing were the following: oxidant, 40–60 mM; substrate, 100–150 mM; $(Cl_8TPP)Fe^{III}(ClO_4)$, 0.5–1.0 mM. After a reaction time of 5–10 min, the mixture was added to 5 mL of H_2O, extracted with diethyl ether, and analyzed by capillary GC, GC/MS, and/or HPLC. Control experiments were done under the same conditions in the absence of $(Cl_8TPP)Fe^{III}(ClO_4)$.

Magnetic susceptibilities of the complexes and their oxygen adducts were determined by the Evans method.[58]

Results

The combination of $(Cl_8TPP)Fe^{III}(ClO_4)$ with *m*-ClPhC(O)OOH in acetonitrile at −35 °C results in the rapid and stoichiometric formation of a green product species (**1**), which is illustrated by the spectral transformations in Figure 1 and the cyclic voltammograms of Figure 2. The same product with identical spectroscopy and electrochemistry results when a 20-fold excess of F_5PhIO is added to the iron(III)–porphyrin (only small amounts of **1** are formed for a 1:1 combination).

The spectrum for **1** includes distinct new visible bands at 672 and 584 nm (curve, b, Figure 1), and its electrochemical rest potential is shifted to +1.35 V vs SCE [from +0.6 V for $(Cl_8TPP)Fe^{III}(ClO_4)$] with a new reduction peak at +1.25 V (curve b, Figure 2). At −35 °C the green species (**1**) has an approximate half-life of 1 h; combination of the reagents at room temperature results in a transient green color prior to the rapid degradation of the porphyrin. For all conditions the addition of anhydrous H_2O_2 to $(Cl_8TPP)Fe^{III}(ClO_4)$ fails to yield even trace amounts of **1** and rapidly degrades the porphyrin. However, the transient addition of O_3 at −35 °C (10-s exposure, 0.03 atm of O_3 in O_2, followed by an argon purge of the solution) to the iron(III)–porphyrin results in its stoichiometric conversion to **1** (Figure 3).

The addition of excess $(H_3O)ClO_4$ to **1** (at −35 °C in MeCN) yields an intense blue species (**2**) (curve c, Figure 1) that exhibits the electrochemistry (curve c, Figure 2) of oxidized iron(III)–porphyrin $[Fe^{III}(Cl_8TPP^0)^{3+}]$. The new redox couples for **1** are absent from the cyclic voltammogram for **2**, which is equivalent to that for $(Cl_8TPP)Fe^{III}(ClO_4)$ (curve a, Figure 2). Species **2** has two distinctive visible bands at 698 and 610 nm.

The addition of 1 equiv of $(Bu_4N)OH$ to a solution of **1** in MeCN at −35 °C results in the formation of a red species (**3**) with visible absorption bands at 556 and 504 nm (curve d, Figure 1). The spectroscopy and electrochemistry for **3** (curve d, Figure 2) are identical with those observed for the product from the controlled-potential one-electron reduction of the green species (**1**) in MeCN at −35 °C. After the preparation of a pure solution of species **3**, subsequent addition of 1 equiv of $(H_3O)ClO_4$ results in the formation of a blue-green species (**4**) that has spectroscopy and electrochemistry that are the same as the product $[(Cl_8TPP^{\cdot-})Fe^{III}(ClO_4)^+]$ from the one-electron oxidation of $(Cl_8TPP)Fe^{III}(ClO_4)$.

The magnetic moments (μ_B) for the various iron–porphyrin species in MeCN at −35 °C have been determined by the Evans method:[58] $(Cl_8TPP)Fe^{III}(ClO_4)$, 4.8 ± 0.4 μ_B; **1** (green), 4.8 ± 0.4 μ_B; **2** (blue), 5.6 ± 0.4 μ_B; **3** (red), 3.1 ± 0.4 μ_B.

Reactivity of 1. After the formation of **1** in MeCN at −35 °C [via *m*-ClPhC(O)OOH], addition of norbornene results in the stoichiometric formation of *exo*-norbornene oxide and Fe^{III}-$(Cl_8TPP)^+$. Because the reaction occurs at mixing rates, quantitative kinetic analysis has not been possible.

The catalytic activity of 0.7 mM $(Cl_8TPP)Fe^{III}(ClO_4)$ for the activation of 50mM *m*-ClPhC(O)OOH and F_5PhIO (via formation of **1**) to epoxidize olefins (125 mM) and to cleave oxi-

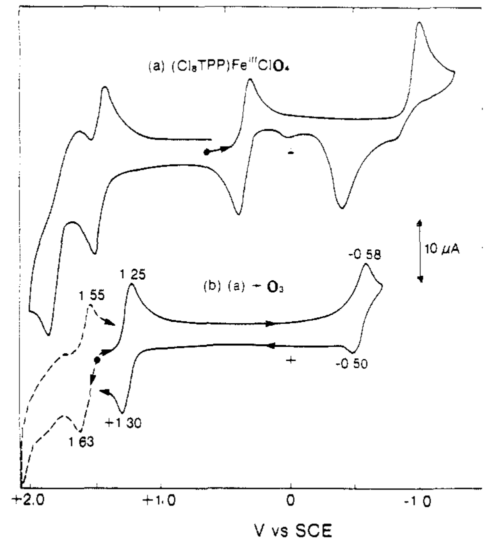

Figure 3. Cyclic voltammograms at a glassy carbon electrode in acetonitrile (0.1 M tetraethylammonium perchlorate) at −35 °C for (a) 1 mM $[(Cl_8TPP)Fe^{III}](ClO_4)$ and (b) the product from its exposure for 10 s to 0.03 atm of O_3 in O_2 (followed by a purge of the solution with Ar); scan rate 0.1 V s^{-1}.

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Table I. Products, Conversion Efficiencies, and Turnover Numbers for the $[(Cl_8TPP)Fe^{III}](ClO_4)$-Catalyzed Epoxidation of Olefins and Oxidative Cleavage of Diols by *m*-ClPhC(O)OOH and F_5PhIO in Acetonitrile[a]

substrate	presence of catalyst	oxidant	reaction conv effic,[b] %	net catalytic turnover[c]	products
			A. Olefins		
norbornene	with	*m*-ClPhC(O)OOH	100	57	*exo*-epoxide (99%), *endo*-epoxide (1%)
		F_5PhIO	70	50	*exo*-epoxide (89%), *endo*-epoxide (11%)
		F_5PhIO	83 (−15 °C)	59	*exo*-epoxide (91%), *endo*-epoxide (9%)
	without				
		m-ClPhC(O)OOH	20		*exo*-epoxide (100%)
		F_5PhIO	0		
1-octene	with	*m*-ClPhC(O)OOH	55	25	epoxide (76%), others (24%)
		F_5PhIO	53 (10 min)	38	epoxide (89%), others (11%)
	without				
		m-ClPhC(O)OOH	20		epoxide (100%)
		F_5PhIO	0 (10 min)		
cis-2-heptene	with	*m*-ClPhC(O)OOH	100	54	*cis*-epoxide (100%)
		F_5PhIO	74	53	*cis*-epoxide (99%), others (1%)
	without				
		m-ClPhC(O)OOH	25		*cis*-epoxide (100%)
		F_5PhIO	0		
trans-2-heptene	with	*m*-ClPhC(O)OOH	70 (10 min)	39	*trans*-epoxide (90%), others (10%)
		F_5PhIO	76	54	*trans*-epoxide (95%), others (5%)
	without				
		m-ClPhC(O)OOH	15 (10 min)		*trans*-epoxide (100%)
		F_5PhIO	0		
cis-stilbene	with	*m*-ClPhC(O)OOH	50	25	*cis*-epoxide (100%)
		F_3PhIO	90	64	*cis*-epoxide (60%), *trans*-epoxide (19%), PhCH(O) (7%); others (14%)
	without				
		m-ClPhC(O)OOH	15		*cis*-epoxide (100%)
		F_5PhIO	0		
trans-stilbene	with	*m*-ClPhC(O)OOH	20	11	PhCH(O) (98%)
		F_5PhIO	10	7	PhCH(O) (100%)
	without				
		m-ClPhC(O)OOH	5		*trans*-epoxide (100%)
		F_5PhIO	0		
			B. 1,2-Diols		
$PhCH(OH)CH_2OH$	with	*m*-ClPhC(O)OOH	100	71	[PhCH(O) + $H_2C(O)$] (100%)
		F_5PhIO	100	71	[PhCH(O) + $H_2C(O)$] (100%)
	without				
		m-ClPhC(O)OOH	0		
		F_5PhIO	0		
PhC(Me)(OH)C(Me)(OH)Ph	with	*m*-ClPhC(O)OOH	100	71	PhC(O)Me (90%), others (10%)
		F_5PhIO	100	71	PhC(O)Me (92%), others (8%)
	without				
		m-ClPhC(O)OOH	0		
		F_5PhIO	0		

[a] Reaction conditions: All materials at −10 °C; oxidant added to substrate and catalyst to give initial concentrations of oxidant (50 mM), substrate (125 mM), and $[(Cl_8TPP)Fe^{III}(ClO_4)]$ (0.7 mM); reaction time 5 min. [b] 100% represents one substrate conversion per oxidant added. [c] Net turnover number = $[[\text{substrate converted}]_{cat} - [\text{substrate converted}]_{uncat}]/[(Cl_8TPP)Fe^{III}(ClO_4)]$.

datively α-diols (125 mM) is illustrated by the results in Table I. For each substrate (a) the reaction conversion efficiency (relative to equivalents of oxidant), (b) the net catalytic turnover (net equivalents of substrate converted per equivalent of catalyst), and (c) the reaction products have been determined.

During the course of the catalyzed reaction of olefins and diols with oxidant [*m*-ClPhC(O)OOH or F_5PhIO], the solution has a green to greenish brown color, which indicates that species **1** is the reactive intermediate. If excess protons are present in the olefinic reaction mixture, a diverse group of products are formed with only a small fraction of epoxide (the product profile is characteristic of radical processes).

When anhydrous HOOH is used as the oxidant with olefinic substrates, no epoxide is formed and the catalyst is degraded. Table II summarizes and compares the $(Cl_8TPP)Fe^{III}(ClO_4)$-catalyzed reactivity of *m*-ClPhC(O)OOH and of HOOH with a variety of organic substrates. Both F_5PhIO and HOOH are inert toward these substrates in the absence of catalyst, but *m*-ClPhC(O)OOH epoxidizes olefins (about 3 times less reactive than with the catalyst, Table I).

The use of base (2,4,6-Me_3Py) in combination with $(Cl_8TPP)Fe^{III}(ClO_4)$ and anhydrous HOOH at −35 °C results in the stoichiometric formation of the red species (**3**); its half-life is about 1 h. When **3** is formed in the presence of excess norbornene or 1-heptene, limited amounts of epoxide are produced as the only substrate product. The process is not catalytic, and one $Cl_8TPPFe^{III}(^-OH)$ and one oxidized Me_3Py are formed per epoxide product.

Discussion and Conclusions

The spectroscopy (Figure 1), electrochemistry (Figures 2 and 3), magnetic measurements, and reaction chemistry (Tables I and II) for the green species (**1**) are consistent with the formation of an oxene adduct of $(Cl_8TPP)Fe^{III}(ClO_4)$ via O atom transfer from *m*-ClPhC(O)OOH, F_5PhIO, or O_3 (Table III). The results do not provide any support for hypervalent iron. A recent theoretical study[59] concludes that within CrO^+ (a nominal d^5 oxene system) the charge density on oxygen is 0.5 electron. When the much more electropositive nature of d^5 iron(III) than d^5 chromium(I) is given, an iron(III)–oxene or $(Por^{\bullet -})Fe^{II}$–oxene charge distribution is predicted for **1**. The conversion of **1** to the blue species (**2**) (fully oxidized porphyrin) via the addition of protons is particularly impressive and would not be expected if **1** contained hypervalent iron. Table III summarizes the formation reaction and reactivity

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Table II. Comparison of *m*-ClPhC(O)OOH and HOOH as Oxidants for the $[(Cl_8TPP)Fe^{III}](ClO_4)$-Catalyzed Oxidation of Organic Substrates in MeCN[a]

	m-ClPhC(O)OOH		H_2O_2	
substrate	reaction conv effic,[b] %	products	reaction conv effic,[b] %	products
norbornene	100	*exo*-epoxide (99%), *endo*-epoxide (1%)	<1	oxidized catalyst[c]
cis-2-heptene	100	*cis*-epoxide (100%)	0	oxidized catalyst
$PhCH(OH)CH_2OH$	100	$[PhCH(O) + H_2C(O)]$ (100%)	0	oxidized catalyst
Me_2CHOH	100	Me_2CO	0	oxidized catalyst
PhCH(O) (1 M)	80	PhC(O)OH	5[d]	oxidized catalyst
cyclohexane (1.2 M)	10		0	oxidized catalyst
PhMe	0		0	oxidized catalyst
PhH	0		0	oxidized catalyst
CH_2Cl_2	20[e]	Cl^- [f]	0	oxidized catalyst
$PhNHNH_2$	100	PhH, N_2, H_2O		

[a] Reaction conditions: all materials at −10 °C; oxidant added to substrate and catalyst to give initial concentrations of oxidants (50 mM), substrate (125 mM), and $(Cl_8TPP)Fe^{III}(ClO_4)$ (0.7 mM); reaction time 5 min. [b] 100% represents one substrate conversion per oxidant added. [c] After 15 min the color of the solution changes to pale yellow. [d] PhCH(O) is oxidized by H_2O_2 at 25 °C in the absence of catalyst. [e] At room temperature (25 °C), 100% conversion efficiency. [f] Catalyst converted to $[(Cl_8TPP)Fe^{III}Cl]$.

Table III. Reactions and Redox Chemistry for $[(Cl_8TPP)Fe^{III}](ClO_4)$ and Its Oxene Adduct at −35 °C in MeCN

A. Reactions[a]

$$[(Cl_8TPP^{2-})Fe^{III}](ClO_4) + m\text{-}ClPhC(O)OOH \rightarrow [(Cl_8TPP^{\bullet-})Fe^{II}(O)]^+ + m\text{-}ClPhC(O)OH + ClO_4^-$$

orange-brown; λ_{max} 398, 526 nm; 4.8 μ_B ($S = {}^3/_2, {}^5/_2$) — **1**: green; λ_{max} 391, 520, 584, 672 nm; 4.8 μ_B ($S = {}^3/_2, {}^5/_2$)

$$(Cl_8TPP^{\bullet-})Fe^{II}(O)^+ + 2H^+ \rightarrow (Cl_8TPP^0)Fe^{III}(OH_2)^{3+}$$

2: blue; λ_{max} 386, 610, 698 nm; 5.6 μ_B ($S = {}^5/_2$)

$$(Cl_8TPP^{\bullet-})Fe^{II}(O)^+ + {}^-OH \rightarrow (Cl_8TPP^{2-})Fe^{II}(O) + {}^1/_2H_2O_2$$

3: red; λ_{max} 416, 504, 556 nm; 3.1 μ_B ($S = {}^2/_2$)

$$(Cl_8TPP^{2-})Fe^{II}(O) + 2H^+ \rightarrow [(Cl_8TPP^{\bullet-})Fe^{III}(OH_2)^{2+}] \rightarrow {}^1/_2(Cl_8TPP^{2-})Fe^{III}(OH_2)^+ + {}^1/_2\mathbf{2}$$

4: blue-green; λ_{max} 386, 604, 684 nm

B. Redox Reactions[b]

reactions	$E^{0\prime}$ vs NHE,[b] V
$[(Cl_8TPP^{2-})Fe^{III}](ClO_4) + e^- \rightarrow (Cl_8TPP^{2-})Fe^{II} + ClO_4^-$	+0.56
$(Cl_8TPP^{\bullet-})Fe^{II}(O)^+ + e^- \rightarrow (Cl_8TPP^{2-})Fe^{II}(O)$	+1.51
$(Cl_8TPP^{2-})Fe^{II}(O) + m\text{-}ClPhC(O)OH + e^- \rightarrow (Cl_8TPP^{2-})Fe^{III}({}^-OH) + m\text{-}ClPhC(O)O^-$	+0.16
$(Cl_8TPP^{2-})Fe^{II}(O) + e^- \rightarrow (Cl_8TPP^{2-})Fe^{II}(O^{\bullet-})^-$	−0.30
$(Cl_8TPP^0)Fe^{III}(OH_2)^{3+} + e^- \rightarrow (Cl_8TPP^{\bullet-})Fe^{III}(OH_2)^{2+}$	+1.96
$(Cl_8TPP^{\bullet-})Fe^{III}(O)^{2+} + e^- \rightarrow (Cl_8TPP^{\bullet-})Fe^{II}(O)^+$	+1.83
$(Cl_8TPP^{\bullet-})Fe^{III}(OH_2)^{2+} + e^- \rightarrow (Cl_8TPP^{2-})Fe^{III}(OH_2)^+$	+1.70
$O(g) + H^+ + e^- \rightarrow \cdot OH$	+2.64
$\cdot OH + H^+ + e^- \rightarrow H_2O$	+3.24
$O(g) + e^- \rightarrow O^{\bullet-}$	+0.67
$O^{\bullet-} + H_2O + e^- \rightarrow 2{}^-OH$	+0.59

C. Apparent Redox Thermodynamics[a]

reactions	$E^{0\prime}$ vs NHE,[b] V
$(Cl_8TPP^{\bullet-})Fe^{II}(O)^+ + 2H^+ + 2e^- \rightarrow (Cl_8TPP^{2-})Fe^{III}(OH_2)^+$	+1.94
$(Cl_8TPP^{2-})Fe^{II}(O) + 2H^+ + 2e^- \rightarrow (Cl_8TPP^{2-})Fe^{II} + H_2O$	+1.30
$(Cl_8TPP^{\bullet-})Fe^{II}(O)^+ + e^- \rightarrow (Cl_8TPP^{\bullet-})Fe^{II}(O^{\bullet-})$	+0.82
$O(g) + 2H^+ + 2e^- \rightarrow H_2O$	+2.94
$O(g) + H_2O + 2e^- \rightarrow 2{}^-OH$	+0.63
$O_3(g) + 2H^+ + 2e^- \rightarrow O_2(g) + H_2O$	+2.59

[a] Reference 47. [b] SCE = +0.244 V vs NHE.

of **1** as well as the redox thermodynamics for various iron–oxene species. The shift in the two-electron-reduction potential for O(g) (from +0.63 V vs NHE in a neutral unbuffered solution to +2.94 V in acidic media, Table IIIC) is analogous to that observed when protons are added to the green iron–oxene species (**1**). The reversible reductions of **1** to **3** (+1.51 vs NHE) and of **3** to $[(Cl_8TPP^{2-})Fe^{II}(O^{\bullet-})^-]$ (−0.30 V) that are illustrated by Figure 3 are assigned to porphyrin radical and oxene centers, respectively.

The data in Table I indicate that terminal olefins are less reactive with **1** than inner olefins, which is consistent with the electrophilic character of the reactive species. The cis isomer of 2-heptene is much more reactive than the trans, and both react stereospecifically to give the corresponding epoxide. Although *cis*-stilbene reacts cleanly with **1** to give the *cis*-epoxide, the trans isomer undergoes C=C bond cleavage to give benzaldehyde. These results confirm that the reactive species (**1**) is highly stereoselective and are consistent with the concerted insertion of a singlet oxygen atom by **1** into the olefinic bond to produce an epoxide with the same stereoconfiguration. When steric hindrance precludes this mechanism, epoxide is not produced.

Because the addition of 1 equiv of ^-OH to **1** produces the same red species (**3**) as the addition of an electron to **1** (Figure 3), species **3** is formulated as an iron(II)–oxene (Table III). Production of this species by the combination $(Cl_8TPP)Fe^{III}(ClO_4)$, Me_3Py, and HOOH and its limited epoxidation of olefins are consistent with an iron(II)–oxene (versus iron(III)–$O^{\bullet-}$) formulation. Finally, the estimated reduction potential for an iron(III)–(O)/iron(III)–($O^{\bullet-}$) couple is +0.82 V vs NHE, whereas the observed potential for **1** $[(Por^{\bullet-})Fe^{II}(O)^+]$ is +1.51 V vs NHE.

Addition of protons to **3** promotes an intramolecular two-electron transfer to the oxene oxygen [one from the porphyrin ring and one from iron(II)] to give $(Cl_8TPP^{\bullet-})Fe^{III}(OH_2)^{2+}$ (**4**) (Table

III). If species **3** contained hypervalent iron, such a transformation with proton addition would not be expected.

The results in Table II indicate that CH_2Cl_2 is oxidized by **1** to give chloride ion, which is susceptible to further oxidation to chlorine atoms. Hence, previous studies[37-45,50] with CH_2Cl_2 as the solvent may have given results with solvent participation. Even at −78 °C the electrochemical oxidation of the hydroxide derivatives of several iron(III)–porphyrins in CH_2Cl_2 is complicated by solvent reactions.[49]

The formation of **3** rather than **1** from the combination of $(Cl_8TPP)Fe^{III}(ClO_4)$, 2,4,6-Me_3Py, and HOOH indicates that the latter is unable to transfer an O atom to the iron(III) center. With HOOH alone there is rapid degradation of the porphyrin ring. Thus, the formation process for **3** requires a base and reducing agent (2,4,6-Me_3Py) to cause HOOH to act as an $(O^{\bullet -})$-transfer agent to iron(III) with subsequent intramolecular electron transfer (eq 1). Olefins are epoxidized by **3** to give the iron(II)–porphyrin

$$(Cl_8TPP^{2-})Fe^{III}(ClO_4) + 2Me_3Py + HOOH \rightarrow \underset{\mathbf{3}}{(Cl_8TPP^{2-})Fe^{II}(O)} + Me_3PyH^+ + (1/n)[Me_3Py(^{\bullet}OH)]_n \quad (1)$$

(eq 2), which reacts with HOOH to give inactive catalyst (eq 3).

$$(Cl_8TPP^{2-})Fe^{II}(O) + \text{norbornene} \rightarrow exo\text{-norbornene oxide} + (Cl_8TPP^{2-})Fe^{II} \quad (2)$$

$$(Cl_8TPP^{2-})Fe^{II} + HOOH + Me_3Py \rightarrow (Cl_8TPP^{2-})Fe^{III}(^{-}OH) + (1/n)[Me_3Py(^{\bullet}OH)]_n \quad (3)$$

The reaction chemistry of Table I confirms that **1** acts as an oxygen atom transfer agent toward olefins. The stereospecificity for the epoxidation of norbornene is consistent with the concerted insertion[34] of a singlet oxygen atom into the π-bond (analogous to the stereospecific transfer of a singlet oxygen atom from uncatalyzed *m*-ClPhC(O)OOH to norbornene; Table I). If **1** contained hypervalent iron, an electron-transfer mechanism would be favored, which results in a mixture of *exo*- and *endo*-epoxides.[38,60]

The magnetic moments for **1** ($S = {}^3/_2, {}^5/_2$) and for **3** ($S = {}^2/_2$) indicate extensive coupling between the ground-state triplet p-orbitals of atomic oxygen and the half-filled d-orbitals of iron(II). In terms of valence-bond considerations overlap by the metal d and oxygen p orbitals will result in the formation of a metal–oxygen σ-bond and a metal–oxygen π-bond. The two-electron-reduction potentials under acidic conditions for **1** (+1.94 V vs NHE) and O(g) (+2.94 V) provide an approximate measure of the bond energy for the $(Por^{\bullet -})Fe^{II}{=}O$ covalent double bond; BE $= \Delta E \times n \times 23.1$ kcal = 46.2 kcal (Table III). Likewise, the two-electron-reduction potential for **3** (+1.30 V vs NHE) relative to that for O(g) (+2.94 V) provides an indication of the bond energy for the $(Por^{2-})Fe^{II}{=}O$ covalent double bond; BE = +1.64 × 2 × 23.1 = 76 kcal. Thus, the much lower reactivity of **3** with olefins is consistent with the greater stabilization of (O) by the iron(II) center.

The spectroscopy, electrochemistry, and magnetic properies of **1** indicate that its iron center is equivalent to that of compound I of HRP. Recent EXAFS studies[33,34] of compound I confirm that it contains an Fe=O double bond (bond distance 1.64 Å) and that its conversion to compound II (via one-electron reduction) gives a species with an Fe=O group that has the same iron–oxygen bond distance.[33,61] Again, the spectroscopic, electrochemical, and magnetic properties of **3**, and its reduced reactivity with olefins, indicate that the electronic structure of its iron–oxygen center is analogous to that of compound II of HRP.[62-64] The inability to produce species **1** with HOOH may indicate that nature makes use of an intermediary O atom cofactor (a carboxylic acid or an imidazole)[11,65] to achieve compound I from HOOH.

The ability of **1** to epoxidize olefins stereospecifically and to cleave α-diols closely parallels the chemistry of the active center of cytochrome P-450 (Table I). The present results indicate that **1** contains a stabilized oxygen atom, and the parallel chemistry with the active form of cytochrome P-450 prompts us to propose that it also contains a stabilized oxygen atom. Experiments with $(Cl_8TPP)Fe^{III}(ClO_4)$ and thiol ligands are in progress to test this proposition and to achieve the formation and characterization of the reactive intermediate of cytochrome P-450.

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