The Diverse Reactivity of Peroxy Ferric Porphyrin Complexes of Electron-Rich and Electron-Poor Porphyrins

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Abstract: A systematic study of the properties and reactivities of iron(III) porphyrin peroxo complexes containing ligands with different electronic properties has been undertaken. While the spectral properties of the peroxo complexes do not show much variation, the stability of the complexes is dramatically increased by employing very electron-poor ligands such as 5,10,15,20-(pentafluorophenyl)porphyrin. The nucleophilicity of the peroxo moiety is decreased considerably by such electron-poor ligands: unlike all other iron(III) porphyrin peroxo complexes examined here, the perfluorinated peroxo complex does not epoxidize electron-poor olefins. However, this complex appears to have an unusually strong desire for a second axial ligand: it binds reversibly to triphenylphosphine. This interesting binding pattern is also observed for the perfluorinated iron−chloro complex. None of the complexes are capable of reacting with electron-rich olefins such as tetramethylethylene or with triphenylphosphine. Possible transition states for nucleophilic epoxidation are discussed.

Peroxy ferric heme complexes, generated by one-electron reduction of oxy heme intermediates analogous to oxymyoglobin, are implicated as key intermediates in oxidation reactions catalyzed by the cytochrome P450 family of enzymes.[1] However, the details of the reaction mechanisms occurring after formation of these peroxy ferric heme intermediates are unknown. In fact, three distinctly different modes of reaction of this intermediate have been postulated to account for the type of reactivity observed for different enzymes, i.e., (a) heterolytic O-O cleavage to generate a (porphyrin)Fe^{V}=O or (oxidized porphyrin)Fe^{IV}=O high-valent oxo species,[2] (b) homolytic O−O cleavage to generate a (porphyrin)Fe^{IV}=O,[2] and (c) direct nucleophilic attack on an enzyme-bound substrate.[3−5] Assuming that these three modes of reaction of the peroxy ferric heme intermediate do all occur in the different cytochrome P450-type enzymes, it is of considerable interest to elucidate the factors that determine which mode will be dominant in each oxidative process. Our laboratory had been studying synthetic analogs of the peroxy ferric heme intermediate for some time.[6−9] These complexes are prepared by oxidative addition of superoxide to synthetic ferrous porphyrin complexes to form high-spin ferric porphyrin peroxo complexes. Although there is as yet no crystal structure of such a complex, there is considerable evidence indicating that its structure is analogous to that of the corresponding manganic porphyrin peroxo complex, which is known to have the peroxo ligand bonded to Mn^{III} in a bidentate, triangular fashion.[10] The reactivity of these ferric porphyrin peroxo complexes is of great interest to us in our ongoing attempts to mimic the three different modes of reaction proposed for different members of the cytochrome P450 family. In order to have a better model of the ferric peroxo heme intermediate, we have now synthesized and characterized $[Fe^{III}(PPIXDME)(O_2)]^-$. PPIXDME, the dimethyl ester derivative of PPIX, the naturally occurring porphyrin in the cytochrome P450 family, is a relatively electron-rich porphyrin ligand. For comparative purposes, we have also prepared $[Fe^{III}(F_{20}TPP)(O_2)]^-$, the ferric peroxo complex of a particularly electron-poor porphyrin ligand. Halogenated electron-poor porphyrins have been the subject of extensive research because they are robust catalysts for the oxidation of hydrocarbons[11] with oxidants such as hydrogen peroxide, iodosylbenzene, and monoperoxysulfuric acid. Electron-poor porphyrins are particularly resistant toward oxidative degradation in these catalytic oxidations.[12]

Earlier studies of the ferric porphyrin peroxo complexes have established that these complexes are not themselves electrophilic, i.e., they do not oxidize typical olefins such as cyclohexene or

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styrene and they do not hydroxylate hydrocarbons.[9,13] Instead, nucleophilic reactivity has been found to be most characteristic of these complexes,[13−16] and we have recently discovered that this reactivity can be applied to the direct oxygenation of a substrate with our finding that $[Fe^{III}(TMP)(O_2)]^-$ epoxidizes electron-poor olefins such as cyclohexenone.[14] This nucleophilic oxygen transfer thus mimics the direct nucleophilic attack on enzyme-bound substrate proposed for certain types of the P450 enzymes. We report here the results of similar studies of the nucleophilic behavior of the more biologically relevant complex $[Fe^{III}(PPIXDME)(O_2)]^-$, and we compare these results with those obtained with $[Fe^{III}(TMP)(O_2)]^-$ and $[Fe^{III}(F_{20}TPP)(O_2)]^-$. The dramatic differences in reactivity observed for these complexes provide insight into the reactivity of the ferric heme peroxo intermediate in the cytochrome P450 enzymes.

Results

Synthesis and Characterization of Iron(III) Porphyrin Peroxo Complexes. Iron(III) porphyrin chloride complexes react smoothly in dry acetonitrile with 2 equiv of KO_2 in the presence of 2.6 equiv of either 18-Crown-6 or K222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) to form the corresponding iron(III) peroxo complexes via the reduced iron(II) porphyrin complex.[8,9] The characteristic UV/vis spectral properties for the peroxo complexes peroxoiron(III) tetramesitylporphyrin ($[Fe(III)(TMP)(O_2)]^-$, **2a**), peroxoiron(III)-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ($[Fe(III)(F_{20}TPP)(O_2)]^-$, **2b**),[17] and iron(III) protoporphyrin(IX) dimethyl ester ($[Fe(III)(PPIX)(O_2)]^-$, **2c**), as well as those of all other previously prepared iron(III) porphyrin peroxo complexes, are shown in Table 1. All peroxo complexes show low-energy Soret bands and two maxima between 500 and 600 nm as well as two shoulders on the latter peaks. The UV/vis spectra of the novel peroxo complexes are displayed in Figure 1.

Each of the novel complexes **2a**−**c** show a strong EPR signal between $g = 4.2$ and $g = 4.3$, as do the previously prepared complexes of this type, indicating that these compounds are high-spin iron(III) complexes with high rhombicity.[6,8]

For the complex peroxo-5,10,15,20-(tetrakis(pentafluorophenyl)porphyrinato)iron(III), (**2b**), we have been able to identify the ν_{OO} in the IR spectrum. This stretch occurs at 802 cm^{-1} (KBr pellet). During the decomposition of **2b** into a mixture of the μ-oxo dimer and the hydroxy complex upon addition of water (see below), this stretch disappears. For the complex peroxoiron(III) octaethylporphyrin, the ν_{OO} has been reported to be at 806 cm^{-1}.[8,9] For several peroxoiron(III) chlorin complexes, the ν_{OO} has been reported to occur at 806 cm^{-1} as well.[18]

Table 1. Spectral Properties of All Known Mononuclear Iron(III) Porphyrin Peroxo Complexes

compd	λ_{max} (Soret)[a] (nm)	α,β-region[a] (nm)	EPR[b]	ν_{OO} (cm^{-1})
$Fe^{III}(TMP)O_2^-$ (**2a**)[c,d]	434	549 (sh), 568, 595 (sh), 612	4.24	
$Fe^{III}(F_{20}TPP)O_2^-$ (**2b**)[c]	430	538(sh), 559, 612 (sh)	4.27	802[e]
$Fe^{III}(PPIXDME)O_2^-$ (**2c**)[c]	432	553, 581, 592 (sh)	4.26	
$Fe^{III}(OEP)O_2^-$[f]	423	530 (sh), 543, 569, 582 (sh)	4.23	806
$Fe^{III}(TPP)O_2^-$[f]	432	545 (sh), 563, 595 (sh), 606	4.24	

[a] In CH_3CN at room temperature. [b] At 90 K in CH_3CN. [c] This work. [d] Literature values for the UV/vis maxima of this complex: 435 nm (Soret), 571 nm, 637 nm (ref 15b). [e] KBr pellet. [f] See refs 8 and 9.

Stability of the Iron(III) Peroxo Complexes. Both the peroxoiron(III) protoporphyrin dimethyl ester complex (**2c**) and the peroxoiron(III)tetramesitylporphyrin complex (**2a**) are very unstable upon exposure to moisture, as are all other previously prepared iron(III) porphyrin peroxo complexes. Upon exposure to air, acetonitrile solutions of **2a** are converted within minutes to the corresponding hydroxy complex[19] and CH_3CN solutions of **2c** are converted to the corresponding μ-oxo dimer. In contrast, peroxo-5,10,15,20-(tetrakis(pentafluorophenyl)porphyrinato)iron(III) (**2b**) is considerably more stable; it has a half-life in acetonitrile of ca. 15 min when the solution is exposed to air. The product obtained from the decomposition of **2b** in the presence of moisture or in the presence of methanol is a mixture of the corresponding μ-oxo dimer ($\lambda_{max} = 398$ (Soret)) and the corresponding hydroxy complex $Fe(F_{20}TPP)OH$ ($\lambda_{max} = 418$ (Soret)). The UV/vis spectrum of this decomposition product mixture is identical to that of a mixture of $Fe(F_{20}TPP)OH$ and $Fe(F_{20}TPP)OFe(F_{20}TPP)$ prepared from concentrated base and $Fe(F_{20}TPP)Cl$.[19] Furthermore, acetonitrile solutions of **2b** can be stored under an inert atmosphere for several weeks without significant decomposition, whereas solutions of **2a**,**c** (as well as those of all other previously prepared peroxoiron(III) porphyrin complexes) decompose even under an inert atmosphere within 24 h. When the acetonitrile of a CH_3CN solution of **2b** is slowly removed under an inert atmosphere, complex **2b** is obtained as a black solid; upon redissolving this solid in acetonitrile, the characteristic UV/vis spectrum of **2b** is again obtained. Solid samples of **2b** have been stored for several weeks in the drybox without significant decomposition. Solid samples of peroxoiron(III) octaethylporphyrin have been prepared previously at −30 °C,[8,9] but this is the first case where a solid sample of a peroxoiron(III) porphyrin complex has been obtained at room temperature.

Reactivity of Iron(III) Peroxo Complexes with Electron-Poor Olefins. Both the tetramesityl derivative **2a** and the protoporphyrin(IX) dimethyl ester derivative **2c** epoxidize electron-poor olefins. The reaction of either **2a** or **2c** with the

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(17) Watanabe *et al*. report having prepared complex **2b** previously. The only characterization that was reported was the UV/vis maxima. These values differ substantially from the ones reported here: the Soret band reported by them is at 445 nm, 15 nm higher than our value; their Q-bands are also different from the ones reported here. These authors did not use any other spectroscopic techniques to confirm that the species they obtained was in fact the Fe(III) peroxo complex. Watanabe *et al*. have used slightly less than 1 equiv of 18-Crown-6 to solubilize the KO_2 and added a large excess of KO_2. We have repeated Watanabe's procedure and have obtained the iron(III) peroxo complex described in this paper with $\lambda_{max} = 430$ nm (Soret) under his conditions. If only 1 equiv of crown ether and KO_2 are reacted with **2a**, a species with $\lambda_{max} = 413$ nm (Soret) is formed. We believe that the latter species is the reduced Fe(II) complex derived from complex **2a**. If additional KO_2 is added to this compound, it is converted to complex **2b**, in agreement with the suggestion that the species is the reduced Fe(II) complex. See: (a) Watanabe, Y.; Ishimura, Y. *J. Am. Chem. Soc.* **1989**, *111*, 410. (b) Watanabe, Y.; Ishimura, Y. *J. Am. Chem. Soc.* **1989**, *111*, 8047.

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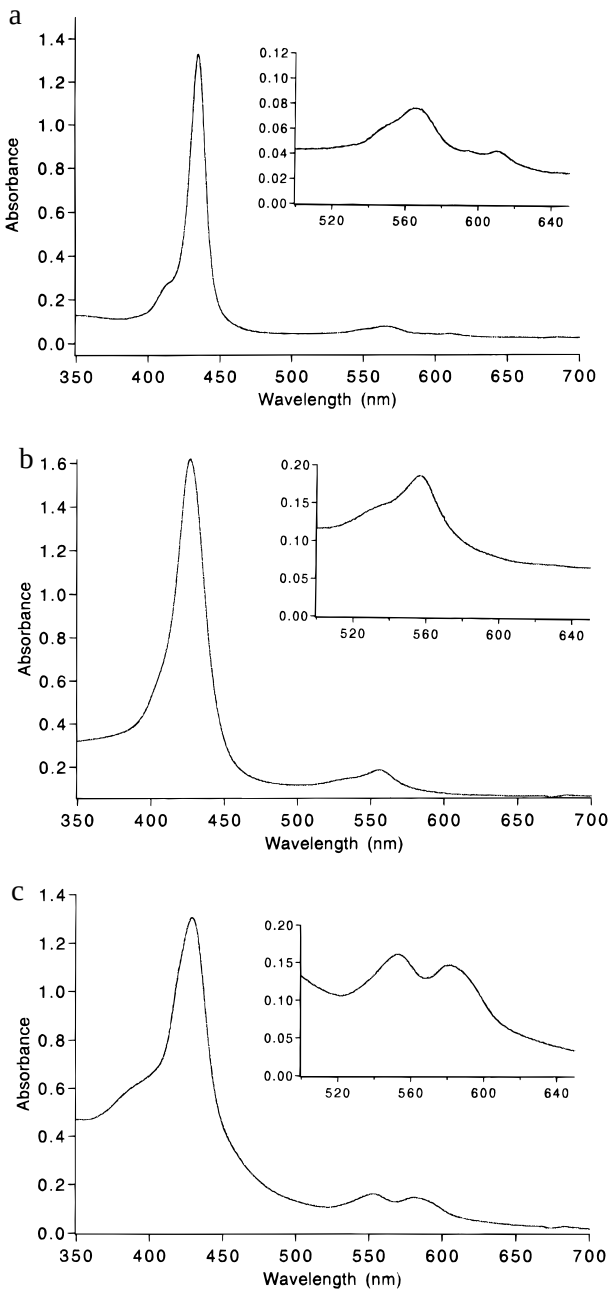

Figure 1. UV/vis spectra of the 1 mM solutions of the novel iron(III) porphyrin peroxo complexes in CH_3CN (0.1 mm pathlength): (a) complex **2a**; (b) complex **2b**; (c) complex **2c**.

very electron-poor olefin 2-methyl-1,4-naphthaquinone (menadione) gives menadione epoxide in about 75% yield (determined by HPLC). The reaction products of **2a** and menadione have also been analyzed by ^{1}H NMR. The peaks for the reaction product were identical to those from a sample of menadione epoxide prepared from H_2O_2/NaOH.[20] The yield of epoxide obtained from integration of the protons of the methyl groups of the menadione and the menadione epoxide was also 75%. The reaction of **2a**,**c** with the less electron-poor cyclohexenone results in only about 25% yield of cyclohexenone epoxide.

In contrast to complexes **2a**,**c**, peroxo-5,10,15,20-(tetrakis-(pentafluorophenyl)porphyrinato)iron(III) (**2b**) shows *no* interaction with electron-poor olefins. Addition of up to 20 equiv of menadione to an acetonitrile solution of **2b** did not result in any changes in the UV/vis spectrum (except for dilution effects).

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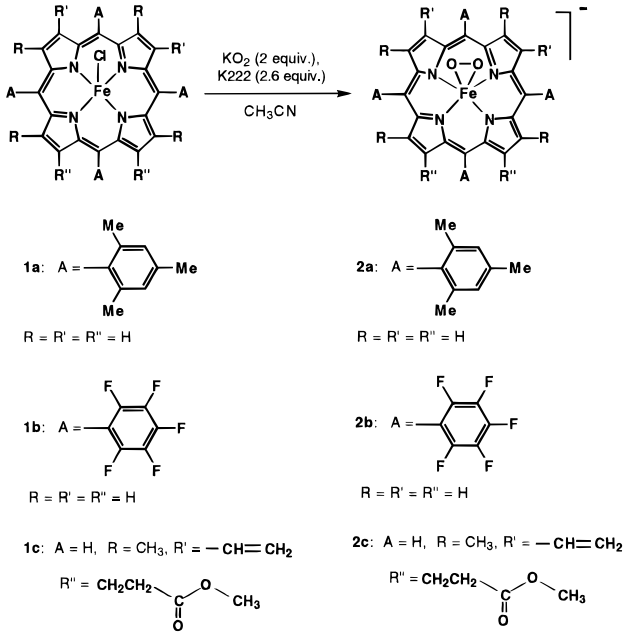
Scheme 1. Preparation of Novel Iron(III) Porphyrin Peroxo Complexes



Also, less than 3% menadione epoxide (i.e., less than in the KO_2 control experiments) was detected by HPLC, even after letting the reaction mixture stand for several hours.

Reaction with Triphenylphosphine and Electron-Rich Olefins. It has been previously reported that small amounts (13−30%) of triphenylphosphine oxide were obtained (determined by HPLC) upon reaction of peroxoiron(III) octaethylporphyrin with triphenylphosphine.[8,9] However, the triphenylphosphine was apparently not oxidized directly by the peroxo complex, since addition of triphenylphosphine did not result in any changes in the UV/vis spectrum of the peroxo complex.[8,9] We report here that none of the peroxo complexes **2a**−**c** are capable of oxidizing triphenylphosphine: When 2−5 equiv of PPh_3 is added to a sample containing 1−5 mmol of the peroxo complex in CD_3CN and the sample mixture is subsequently sealed in the drybox, *no* formation of PPh_3O is observed by ^{31}P NMR. When the peroxo complex is allowed to decompose under air in the presence of 2−5 equiv of PPh_3, however, ca. 40% (based on the Fe complex) of PPh_3O is obtained (by ^{31}P NMR). Addition of PPh_3 to solutions of complexes **2a**−**c** did not result in changes in the UV/vis spectra of the peroxo complexes; in the drybox, the fluorinated derivative **2b** was stable in the presence of 5 equiv of triphenylphosphine for 2 weeks!

In the course of this study, we noted that, when a ^{31}P NMR spectrum of PPh_3 in the presence of the fluorinated complex **2b** was taken, much of the phosphine "disappeared" (i.e., the signal-to-noise ratio was much worse than for a spectrum of PPh_3 without the presence of **2b**) and the peak was dramatically broadened. The PPh_3 resonance was also shifted downfield by 1−2 ppm; the exact magnitude of the downfield shift depended on the concentration of **2b** and PPh_3. The same effect could be observed for the fluorinated iron(III) chloro complex **1b**. Upon addition of pyridine to an acetonitrile solution of **2b** and PPh_3, the broadening of the PPh_3 resonance disappeared and the signal-to-noise ratio greatly improved. The UV/vis spectrum of the porphyrin complex obtained this way showed a Soret band at 420 nm and peaks in the α,β-region that were identical with the complex $Fe^{III}(F_{20}TPP)(Py)_2$ prepared from $Fe^{III}(F_{20}$-TPP)Cl and pyridine. The amount of line broadening of the phosphine observed for both complexes **1b** and **2b** depends on

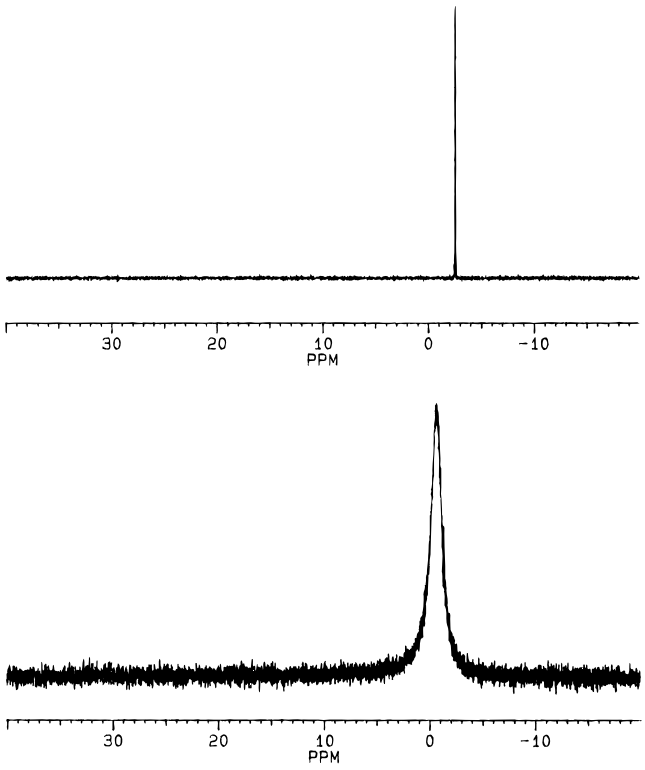


Figure 2. ^{31}P NMR spectra of [Fe(PPIXDME)(O_2)]$^-$ (**2c**) and PPh_3 (upper spectrum) and [Fe(F_{20}TPP)(O_2)]$^-$ (**2b**) and PPh_3 (lower spectrum). In both cases, 5 equiv of PPh_3 was employed and no signal due to PPh_3O at 29 ppm was observed.

both the concentration of the porphyrin complex and the amount of PPh_3 present; increases in the concentration of either substrate increase the line broadening. These results are consistent with very rapid formation of a weak bond between the iron complex and the phosphine. No such line broadening of the PPh_3 signal in the ^{31}P NMR was observed for any other of the iron(III) porphyrin peroxo complexes or their precursors. ^{31}P NMR spectra for PPh_3 in the presence of complex **2b** as well as in the presence of complex **2c** are shown in Figure 2. Bonding of very basic phosphine ligands as axial ligands to iron porphyrin complexes has been reported previously by several authors.[21] However, the complexes obtained by these authors are all diamagnetic Fe(II) species. The interaction of triphenylphosphine with complex **2b**, on the other hand, does not lead to displacement of the axial peroxo ligand, and there are no visible changes in the electronic spectrum of **2b**.

It was also tested whether any of the peroxo complexes **2a**−**c** are capable of oxidizing the electron-rich olefin tetramethylethylene (TME). In all cases, there was no reaction between the peroxo complex and TME, as monitored by UV/vis spectroscopy.

All reactions of the peroxo complexes **2a**−**c** are summarized in Table 2.

Discussion

The perfluorinated peroxo complex **2b** is most unusual in that it is far more stable than any other previously prepared iron(III) porphyrin peroxo complex. Apparently the strongly electron-withdrawing ligands stabilize the negatively charged iron(III) peroxo complexes. The increased stability of iron(III) peroxo complexes induced by electron-withdrawing groups is opposite to the behavior of many peroxo complexes derived from group VIII transition metals. For example, for complexes of the type M(CO)X(PPh_3)$_2O_2$ (M = Ir, Rh; X = F, Cl, Br, I), the kinetic stability increases with decreasing electron-withdrawing power of the ligand.[22] This difference in behavior can easily be rationalized by the different pathways of decomposition: for the peroxo complexes derived from group VIII transition metals, decomposition simply means reductive elimination of $^3O_2$, an option not available to the iron(III) peroxo complexes.

Cytochrome P450 aromatase converts androgen to estrogen[3] via a series of transformations that involve hydroxylation followed by aromatization. Graham-Lawrence *et al.*[3c] have recently suggested that *direct nucleophilic attack by an open peroxo species* may indeed be the key step in the aromatization step catalyzed by cytochrome P450 aromatase. They hypothesize that, during the hydroxylation step, O−O bond cleavage, rather than nucleophilic attack, occurs because of the availability of protons for the iron complex, while the direct nucleophilic attack in the aromatization step takes place because there are no accessible protons for the active site of the enzyme. The fact that the peroxo ferric heme complex **2c** is able to transfer an oxygen atom to electron-poor olefins is new powerful evidence that such direct nucleophilic attacks can occur in biological systems.

While complex **2b** is by far the most stable iron porphyrin peroxo complex prepared to date, its electronic spectrum as well as its O−O stretch in the IR spectrum are very similar to those of the more electron-rich porphyrin peroxo complexes. However, the reactivity of this complex is dramatically different, as evidenced by its failure to epoxidize electron-poor olefins. On the basis of the similar spectral properties and the different reactivity of **2b**, we hypothesize that the electron-withdrawing ligands affect the energy difference between the ground state iron peroxo complex and the transition state during the epoxidation reaction. Two possible transition states are depicted in Scheme 2.

Transition state **A** involves the closed triangular peroxo complex. The properties of this transition state would be expected to be very similar to those of the ground state. Specifically, if this were the transition state in the nucleophilic epoxidation reaction, there would be no reason why the perfluorinated complex **2b** would not also undergo this reaction, given that its ground state electronic properties are very similar to those of all the other ferric porphyrin peroxo complexes. We therefore favor transition state **B**, involving an open peroxo complex. Ring opening of η^2 peroxo complexes has been suggested in a number of oxidation reactions by such complexes. For example, in the reaction of η^2 peroxo complexes with SO_2, ^{18}O labeling studies have conclusively shown that prior ring opening of the peroxo complex is a necessary step for the formation of the peroxysulfite intermediate.[23] Also, it has recently been shown that, during the reductive elimination of dioxygen from some peroxo complexes derived from group VIII transition metals, the oxygen is in the triplet state,[22c,24] which implies that the two metal−oxygen bonds of the peroxo complex

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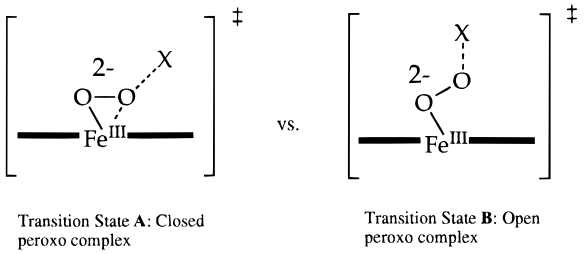
Table 2. Reaction of Mononuclear Iron(III) Peroxo Complexes

compd	menadione epoxide (% yield)	cyclohexenone epoxide (% yield)	reaction with triphenylphosphine	tetramethylethylene epoxide
$Fe^{III}(TMP)O_2^-$ (**2a**)[a]	76%	23%	no reaction	none detected
$Fe^{III}(F_{20}TPP)O_2^-$ (**2b**)	0[b]	0[b]	binds reversibly	none detected
$Fe^{III}(PPIXDME)O_2^-$ (**2c**)	73%	20%	no reaction	none detected

[a] See ref 14. [b] Trace amounts of the epoxide were detected by HPLC, but these amounts were smaller than those obtained during the control experiments.

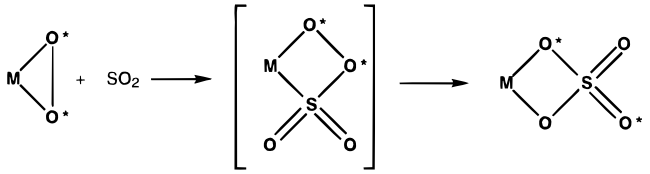
Scheme 2. Possible Transition States for Oxygen Transfer of Peroxo Ferric Heme Complexes



Transition State **A**: Closed peroxo complex

Transition State **B**: Open peroxo complex

Scheme 3. Formation of Sulfato Complexes from Peroxo Complexes and SO_2[a]



O* = ^{18}O; M = Ru Peroxy sulfite intermediate

[a] To form the peroxysulfite intermediate, one of the metal−oxygen bonds must be broken.

are not broken simultaneously and that hence an open peroxo complex must exist as an intermediate in these reactions.

The interaction of the perfluorinated peroxo complex **2b** with phosphines, although weak, clearly demonstrates that this complex is much more electron-poor than the other peroxo complexes studied in this work. The electron-withdrawing ligands increase not only the affinity of this complex for a second axial ligand but also are also expected to make the ring-opening step depicted in transition state **B** less favorable and hence decrease the reactivity. However, an "Umpolung" (i.e., switch from nucleophilicity to electrophilicity) of the reactivity of the peroxo functionality cannot be accomplished even by such extremely electron-withdrawing ligands as the pentafluorophenyl groups of complex **2b**. Like all other iron(III) porphyrin peroxo complexes, complex **2b** does not oxidize electron-rich olefins or triphenylphosphine.

This study thus shows that the peroxo complex of iron protoporphyrin(IX) dimethyl ester is a good nucleophile and that nucleophilic attack by an open peroxo complex is indeed a potential pathway for certain oxidation reactions catalyzed by cytochrome P450.

Experimental Section

General Procedure. All reactions involving the preparation and studies of the ferric peroxo complexes were carried out in an inert atmosphere chamber (Vacuum Atmospheres) under helium, except as noted otherwise. Solvents were rigorously dried before use: Acetonitrile was distilled from calcium hydride. It was then stirred over KO_2 (Aldrich) in the drybox for *ca.* 1 h and subsequently passed over Super I neutral alumina (Sigma). Deuterated acetonitrile (Cambridge Isotopes, 99.8+%) was stirred over KO_2 inside the drybox and then passed over Super I neutral alumina. ^1H NMR spectra were recorded on a Brucker 360 MHz spectrometer; ^{31}P NMR spectra were recorded on the same instrument, using an external $P(OMe)_3$ standard. FTIR spectra were recorded on a Nicolet 510P spectrometer and UV/vis spectra on a Cary 3 UV/vis spectrophotometer.

Preparation of the Peroxo Complexes 2a−c. An acetonitrile solution of 2−2.5 mmol of KO_2 and 2.5−3 mmol of K222 or 18-Crown-6 was stirred for *ca.* 1 h. Any undissolved KO_2 was removed by filtration. Complexes **1a−c** (1 mmol) were then added, and the resulting black-red solution was stirred for several minutes. Solutions of the perfluorinated peroxo **2b** complex could also be prepared by employing much larger concentrations (*ca.* 50 mmol of the starting complex **1b**).

Spectroscopic Analyses of Complexes 2a−c. (a) UV/Vis Spectroscopy. Samples of complexes **2a−c**, prepared as described above, were transferred inside the drybox into a 0.1 mm pathlength cell (Starna Cells Inc.), which was sealed with a rubber septum before being taken out of the box.

(b) EPR Spectroscopy. Samples containing *ca.* 1 mmol of the complexes were transferred into EPR tubes inside the box. The spectra were measured on an IBM (Brucker) 200D spectrometer at liquid nitrogen temperature. Four scans were accumulated per spectrum. The *g* value was determined at the zero crossing point of the derivative signal.

Reactivity Studies of Complexes 2a−c. General Procedure. Before each study was carried out, formation of the peroxo complex was confirmed by the checking the UV/vis spectrum of the solution.

(a) NMR Analyses of the Reaction with Menadione. To a 1−4 mmol sample of complex **2a−c** prepared as described above was added a 2−3-fold excess of menadione (Aldrich). The sample was stirred for 5 min in the drybox; the solvent was then evaporated in the drybox, and the residue was redissolved in $CDCl_3$. This solution was transferred to an NMR tube for analyses. The reaction was also carried out in deuterated acetonitrile; in this case, the reaction mixture was transferred directly to an NMR tube in the drybox.

(b) HPLC Analyses of the Reactions with Menadione and Cyclohexenone. To a 1−4 mmol sample of complex **2a−c** was added a 2−3-fold excess of menadione or cyclohexenone (Aldrich). The mixture was stirred for *ca.* 5 min and then injected into the HPLC (Beckmann 114M solvent delivery module, flow 1 mL/min, 65% acetonitrile/35% water, with a 165 variable wavelength detector set at 265 nm). Cyclohexenone and its epoxide were analyzed by GC−MS using decane as an internal standard. Epoxide yields were determined by comparison against standard curves.

(c) NMR Analyses of the Reaction with PPh_3. To a 1−4 mmol sample of complex **2a−c** in CD_3CN was added a 4−5-fold excess of triphenylphosphine. The sample was transferred into an NMR tube and sealed inside the drybox.

(d) UV/Vis Analyses of Reactions of 2a−c with PPh_3 and Tetramethylethylene (TME). Acetonitrile solutions (1 mmol) of **2a−c** were transferred to a 0.1 mm UV/vis cell in the drybox. The cells were sealed with a rubber septum. Solutions of PPh_3 or TME were added by syringe in portions varying from 0.5 to 2 equiv. Up to 20 equiv of substrate was added to the peroxo complex solution.

(e) Control Experiments. KO_2 (0.1 mmol) was reacted with 2 equiv of menadione for 10−15 min. The yield of epoxide was 8 ± 1%. KO_2 (3.4 mmol) was reacted with 2 equiv of menadione for 2−4 min prior to analyses by GC−MS. Less than 3% of the epoxide was detected.

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