Kcal/mol, $\Delta H^{‡} = 3.6$ kcal/mol, and $-11 > \Delta S^{‡} > -25$ eu. While a detailed analysis of these activation parameters must await further study, it is clear that there is very little intrinsic barrier to the heterolytic O–O bond cleavage in an iron(III) peroxybenzoate. The large negagive entropy term suggests an associative reaction which could involve positioning the necessary proton and perhaps coordination of a sixth ligand on the iron.

In summary, by direct observations of the primary steps, the mechanism of iron(III) porphyrin oxidation by peroxy acids to form the corresponding oxo iron(IV) porphyrin cation radical (i) has been shown to involve prior coordination of the peroxy acid. (ii) the nature of the O–O bond cleavage step for peroxyacyliron(III) benzoates is heterolytic and acid catalyzed.

In the accompanying paper,[17] formation of an iron(III) porphyrin N-oxide from the same peroxyiron(III) precursor (**4**) in non-polar solvents and in the absence of acid is proposed to result from a homolytic O-O bond cleavage in **4**.

**Acknowledgment.** Support of this research by the National Institutes of Health (GM 36298) and the National Science Foundation is gratefully acknowledged. Portions of this research were carried out at the University of Michigan.

**Registry No. 3**, 77439-20-4; **4** (Ar = $CH_2Ph$), 104619-66-1; **4a**, 104619-67-2; **4b**, 104463-57-2; **4c**, 104619-68-3; **4d**, 104619-69-4; **5** (Ar = $CH_2Ph$), 104619-70-7; **5a**, 104619-71-8; **5b**, 104619-72-9; **5c**, 104619-73-0; **5d**, 104619-74-1; HOOCO*p*-$NO_2$Ph, 943-39-5; HOOCO*m*-ClPh, 937-14-4; HOOCOPh, 93-59-4; HOOCO*p*-$CH_3$Ph, 937-21-3; $HOOCOCH_2Ph$, 19910-09-9; peroxidase, 9003-99-0; cytochrome P-450, 9035-51-2; oxygen, 7782-44-7.

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[17] Groves, J. T.; Watanabe, Y., *J. Am. Chem. Soc.*, following paper in this issue.

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## Preparation and Characterization of an Iron(III) Porphyrin *N*-Oxide

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The nature of oxidized iron species in a variety of heme proteins has been clarified by the preparation of related synthetic iron porphyrin complexes. Thus, both an oxoiron(IV) porphyrin[1] and an oxoiron(IV) porphyrin cation radical[2] are now known. The latter of these is related to compound I of horse radish peroxidase and is the most attractive candidate for the ultimate oxidizing intermediate in the catalytic cycle of cytochrome P-450.[3] An alternative bridged iron porphyrin *N*-oxide has been suggested on the basis of the crystal structures of N-bridged iron porphyrin carbenes[4] and the existence of several metalloporphyrin *N*-oxides[5a–c] and an N-bridged nitrene.[5d] We describe here the preparation and characterization of the first iron porphyrin *N*-oxide and show that such species are chemically distinct from the formally isomeric oxoiron(IV) porphyrin cation radical complexes we have previously reported.

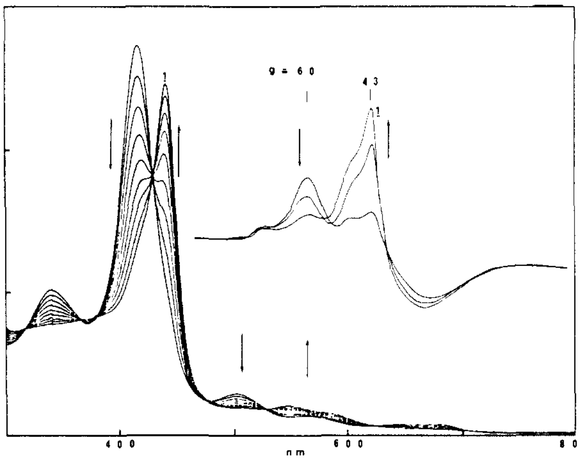

**Figure 1.** Visible spectral changes upon addition 0.25-equiv aliquots of mCPBA to $Fe^{III}(TMP)(mCB)$ ($1.27 \times 10^{-5}$ M) in toluene at 0 °C. Inset, EPR spectral changes upon addition of mCPBA to $Fe^{III}(TMP)(mCB)$ ($5.3 \times 10^{-4}$ M) to form **1**.

The slow addition of *m*-chloroperoxybenzoic acid (mCPBA) to a toluene solution of (5,10,15,20-tetramesitylporphyrinato)iron(III) *m*-chlorobenzoate [$Fe^{III}(TMP)(mCB)$] (ca. $10^{-4}$ M) at 0 °C gave a new species (**1**) with a dramatically red-shifted soret band (417 to 441 nm). The titration of $Fe^{III}(TMP)(mCB)$ with mCPBA showed that 2 equiv of mCPBA were required to complete the formation of **1** (Figure 1). The EPR spectrum of $Fe^{III}(TMP)(mCB)$ ($g = 6$) was replaced with strong new signals at $g = 4.3$ in the course of this titration (Figure 1 inset). The $^1H$ NMR spectrum of **1** at −50 °C showed broad resonances for the *m*-mesityl protons at $\delta$ 17.2, 15.0, and 13.8 (relative intensity 1:2:1) and *two p*-methyl peaks ($\delta$ 4.2 and 3.9). The pyrrole protons were not evident. The visible spectrum of **1** was uneffected by added olefins even at room temperature.

The demetalation of **1** with acetic acid–HCl (4:1) was remarkably facile; complete in 60 s at 0 °C. Neutralization and thin-layer chromatography of the resulting green solution afforded $H_2TMP$ *N*-oxide (**2**) in 25% yield and an equivalent amount of $H_2TMP$.[6] The structure of **2** was evident from its UV, $^1H$ NMR, and FAB mass spectra[7] and from its independent synthesis from $H_2TMP$.[5a] Complex **1** could not be prepared by the metalation of **2**.

The 20-nm red shift of the soret band of **1** and the facility of the demetalation reaction indicate that **1** has a substituent on the porphyrin pyrrole nitrogen.[8] The $^1H$ NMR spectrum of **1** supports a structure of *Cs* symmetry, and the meta protons are in a region typical for high-spin iron(III) porphyrins. The isolation of $H_2TMP$ *N*-oxide (**2**) upon demetalation points strongly to an iron(III) porphyrin *N*-oxide structure for **1**. The $g = 4.3$ signal in the EPR of **1** is similar to that reported recently for an analogous

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[1] (a) Chin, D.-H.; LaMar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 5845. (b) Balch, L. A.; Chan, Y.-W.; Cheng, R.-J.; LaMar, G. N.; Latos-Grazynski, L.; Renner, M. W. *Ibid.* **1984**, *106*, 7779–7785. (c) Schappacher, M.; Weiss, R.; Montiel-Montoya, R.; Trautwein, A.; Tabard, A. *Ibid.* **1985**, *107*, 3736–3738.

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[6] $H_2TMP$ *N*-oxide (**2**) decomposed slowly to $H_2TMP$ under these conditions and sometimes more than 80% of the recovered porphyrin was $H_2TMP$. The ratio of *N*-oxide and parent free base depended on the conditions of the dematalation reaction (cf. ref 5a).

[7] **2**: NMR ($CD_2Cl_2$) pyrrole, 8.53 (4 H, AB q, $J = 12.6$, 5.0 Hz) 8.40 (2 H, s) 7.49 (2 H, s); meta H, 7.36 (8 H, s); *p*-Me, 2.59 (12 H, s); *o*-Me, 1.88 (12 H, s), 1.86 (12 H, s); NH, 1.75 (2 H, s). UV (nm) (log $\epsilon$) (toluene) 417 (5.17), 544 (3.77), 602 (3.78), 696 (3.28). IR ($cm^{-1}$, Nujol) 1273, 864 (N–O). Mass spectrum (FAB), *m/e* 798 ($M^+$, 72%), 782 ($M^+ - O$, base).

[8] Jackson, A. H. *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 1, p 341.

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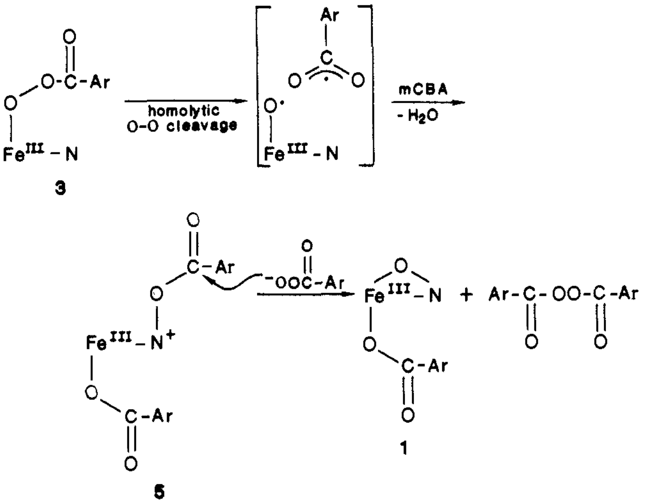
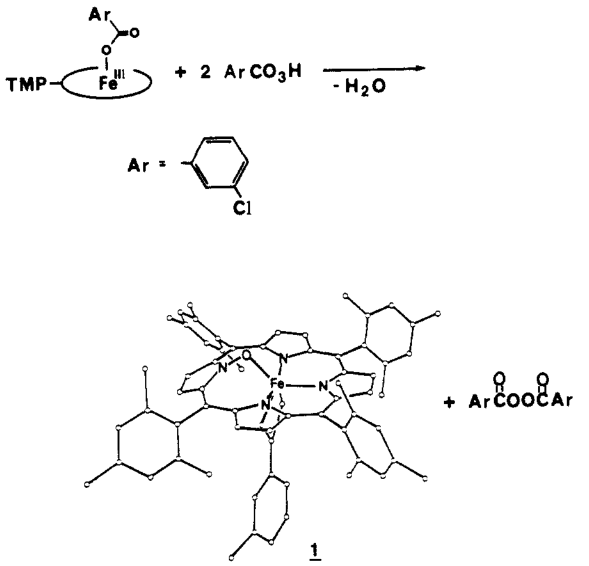
Scheme I



N-bridged iron(III) nitrene[5d] and is consistent with a rhombically distorted high-spin iron(III) electronic configuration for **1**. The solution magnetic susceptibility of **1** determined by the Evans method in toluene-$d_8$ at −25 °C was found to be 5.4 ± 0.1 $\mu_B$.

Inspection of the FT-IR spectrum in Nujol of the reaction mixture obtained upon addition of mCPBA to $\mathrm{Fe^{III}(TMP)(mCB)}$ showed bands for iron-coordinated *m*-chlorobenzoate (1660 $\mathrm{cm^{-1}}$) and prominant peaks for **bis(3-chlorobenzoyl) peroxide** (1796, 1771, 1216, 1012 $\mathrm{cm^{-1}}$). The intensities of these bands indicated that the diacyl peroxide had been produced in amounts equivalent to those of **1**. Additionally, no free *m*-chlorobenzoic acid was evident in the IR spectrum. When this reaction was performed with peroxybenzoic acid, dibenzoyl peroxide could be isolated from the reaction mixture. Accordingly, the stoichiometry for the formation of **1** is as indicated in eq 1.



(1)

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The reaction of $\mathrm{Fe^{III}(TMP)(OH)}$ ($10^{-4}$ M) with mCPBA at −50 °C in toluene showed the immediate formation of $\mathrm{Fe^{III}}$-(TMP)(*m*-chloroperoxybenzoate)[9] (**3**) and then a relatively slow decomposition to **1**. The oxidation of $\mathrm{Fe^{III}(TMP)(OH)}$ with phenylperoxyacetic acid under these conditions produced $\mathrm{(O){=}Fe^{IV}(TMP)}$[1] instead of **1**.[10] At higher concentrations or under more acidic conditions, the mCPBA oxidation of $\mathrm{Fe^{III}(TMP)(OH)}$ afforded the oxoiron(IV) porphyin cation radical species **4**,[2a] also via **3**. These observations indicate that there are two modes of iron(III)-mediated O–O bond cleavage. The stoichiometry of the formation of **1**, the concommitant formation of diacyl peroxide, and the decarboxylation of phenylperoxyacetic acid suggest a homolytic process leading to **1** as outlined in Scheme I. The intermediate *N*-(benzoyloxy) iron(III) porphyrin species **5** would be expected to be a good acylating agent, affording **1** and the diacyl peroxide in equimolar amounts. In the preceding paper we describe the acid-catalyzed heterolysis of the O–O bond in **3** to give **4**.[9,11]

That **1** and **4** should both result from **3** indicates that mechanistic implications derived from catalytic reactions must be interpreted with great care. Further, that **1** and **4** are independently isolable compounds suggests that while **4** is still the preferred model for highly oxidizing species in cytochrome P-450 and horse radish peroxidase, iron(III) *N*-oxides such as **1** must be considered for other systems, particularly those in which ligand stabilization of the iron(IV) oxo group may be absent.

**Acknowledgment.** Support of this research by the National Institutes of Health (GM 36298) and the National Science Foundation is gratefully acknowledged. EPR spectra were obtained by T. P. Radhakrishnan.

**Registry No.** **1**, 104463-56-1; **2**, 104439-49-8; **3**, 104463-57-2; **4**, 99688-03-6; $\mathrm{Fe^{III}(TMP)(mCB)}$, 104463-55-0; $\mathrm{H_2TMP}$, 56396-12-4; $\mathrm{Fe^{III}(TMP)(OH)}$, 77439-20-4; $\mathrm{(O)Fe^{IV}(TMP)}$, 93085-16-6.

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(9) (a) Groves, J. T.; Watanabe, Y., presented in part at the International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec 16–21, 1984. (b) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.*, preceding paper in this issue.

(10) GC analysis indicated 63% toluene, 19% benzyl alcohol, and 11% benzyaldehyde base on phenyl peroxyacetic acid.

(11) Evidence for homolytic and heterolytic O–O bond cleavage mediated by iron porphyrins has been deduced from catalytic systems. Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 513–514.

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## Characterization of Transition-Metal Molecular Hydrogen Complexes by Solid-State Proton NMR

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Recently it has been discovered that stable transition-metal complexes containing molecular hydrogen as a ligand can be prepared.[1] Current research under way in several laboratories[2–9] indicates that the $\eta^2$ mode of binding hydrogen is fairly common and even occurs in several polyhydrides previously believed to be classical in structure. These molecules have been cited as examples of an arrested oxidative addition of hydrogen to a metal complex, and the observed variations in physical properties seems to indicate that the addition is halted at different points. Characterization

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[†] Los Alamos National Laboratory, University of California, Los Alamos, NM 87545.

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