Preparation and Characterization of an (Acylperoxo)iron(III) Porphyrin

Sir:

As model systems for cytochrome P-450 and the peroxidases,[1] synthetic metalloporphyrins have allowed the observation of nearly all intermediates in the proposed catalytic cycle of molecular oxygen activation.[2] Synthetic oxoiron(IV) models for compounds I[3] and II[4] of horseradish peroxidase have been realized. Recently, we have reported the transient formation of (acylperoxo)iron(III) porphyrin generated from the addition of *m*-chloroperoxybenzoic acid (mCPBA) to a hydroxoiron(III) precursor. The (acylperoxo)iron(III) species then decomposed to an oxoiron(IV) porphyrin cation radical.[5] We describe here a stable (acylperoxo)iron(III) complex, prepared from a sterically hindered iron(III) porphyrin, (5,10,15,20-tetrakis(2,4,6-triphenylphenyl)porphyrinato)iron(III), [Fe^{III}TTPPP].

The reaction of Fe^{III}TTPPP(OH)[6] (**1**) (1.1×10^{-5} M) with 2 equiv of mCPBA in CH_2Cl_2 at room temperature was found to be remarkably slow (Figure 1). After 40 min at room temperature this reaction gave a new species (**2a**) with a visible spectrum typical of a high-spin iron(III) porphyrin (λ_{max} = 444 nm).[7] The reaction was found to proceed smoothly through isosbestic changes from Fe^{III}TTPPP(OH) to **2a**. As shown in Figure 1, **2a** is distinct from an authentic sample of Fe^{III}TTPPP(mCB) (**3a**; mCB m-chlorobenzoate) (λ_{max} = 440 nm). Furthermore, a CH_2Cl_2 solution of **2a** decomposed slowly to **3a** at room temperature. By contrast, **1** reacted instantaneously with *m*-chlorobenzoic acid (mCBA) to give **3a**. When a dark green solution of **1** in CD_2Cl_2 (32 mg in 400 μL, 5×10^{-2} M) was added to a CD_2Cl_2 solution of peroxybenzoic-d_5 acid[8] (3.5 mg in 100 μL, 6.5×10^{-2} M) at −78 °C, a complete color change from dark green to brown was observed in a few seconds. The 360-MHz ^1H NMR spectrum of **2b** was typical for an iron(III) high-spin porphyrin[9] with two separated meta hydrogen resonances at δ 14.7 and 16.7 and the pyrrole protons at δ 63. The two meta protons of **2b** are different from those of **1**, which appear at δ 14.4 and 16.3 at −78 °C in CD_2Cl_2. When the the reaction mixture was warmed, **2b** decomposed to form **3b** (δ = 16.9 and 18.8; λ_{max} = 442 nm.)

These changes in chemical shift during the reaction of **1** with peroxyacid indicate that there are two five-coordinate iron(III) TTPPP species with different axial ligands. These results strongly support the first product **2** as a iron(III) peroxybenzoate that is still high-spin, as expected for a five-coordinate iron(III) complex. The EPR spectra of **2a** and **3a** also support this high-spin iron(III) assignment (**2a** g = 6.9; **3a**, g = 6.3).[10]

A 5-fold excess of mCPBA reacted with Fe^{III}TTPPP(Cl) (5×10^{-2} M) to afford the corresponding oxoiron(IV) porphyrin cation radical (**4**) as a green solution at −78 °C. The EPR

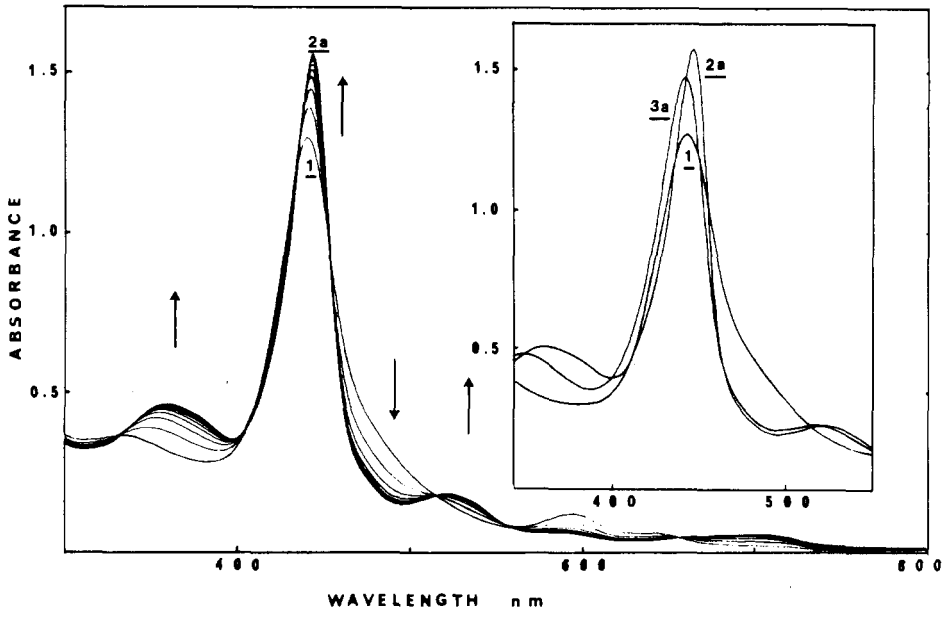
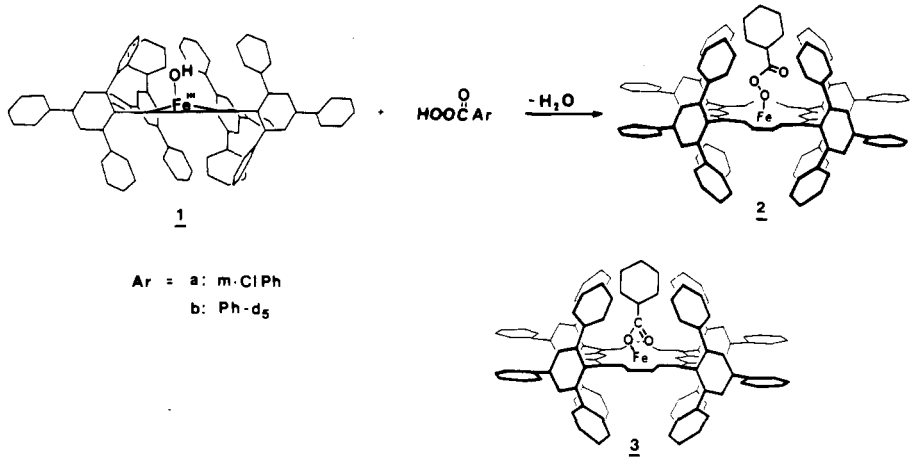


Figure 1. Reaction of FeTTPPP(OH) [1.1×10^{-5} M] in CH_2Cl_2 with 2 equiv of mCPBA at room temperature (cycle time 4 min). Inset: comparison of Fe^{III}TTPPP(OH) (**1**), Fe^{III}TTPPP(mCB) (**3a**), and **2a** [(a = 1.1×10^{-5} M) in CH_2Cl_2 at room temperature].

Scheme I



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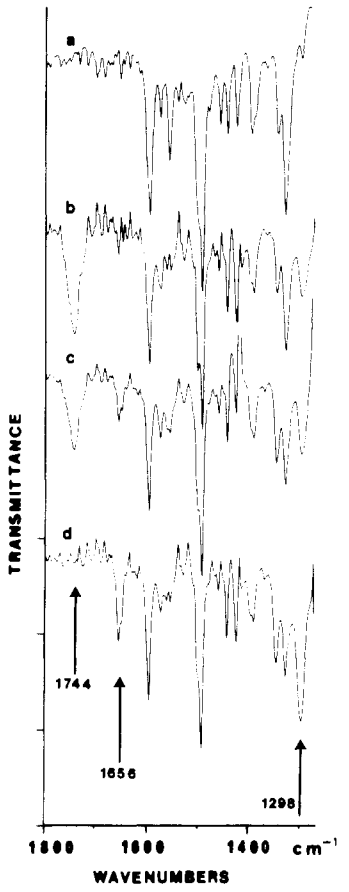

Figure 2. IR spectral changes during the reaction of Fe^{III}TTPPP(OH) and 0.9 equiv mCPBA in CH_2Cl_2 at −65 °C: (a) spectrum of Fe^{III}TTPPP(OH) (**1**); (b) spectrum of **1** + mCPBA; (c) spectrum after slight warming of the mixture used for spectrum b; (d) final spectrum.

spectrum of **4** showed a broad and very weak peak at $g = 4.4$, which is consistent with the earlier preparations of such complexes.[11] Solutions of **4** were not notably more stable than the corresponding tetramesityl derivative $[(O)Fe^{IV}TMP]^+$.[3]

Finally, we have obtained low-temperature FT-IR spectra of compounds **1**–**3**. Figure 2 shows the IR spectrum of **1** at −65 °C in CH_2Cl_2 (spectrum a). Treatment of this dark green solution (5×10^{-2} M) with 0.9 equiv of mCPBA at −55 °C afforded a brown solution in a few seconds whose spectrum at −65 °C is illustrated in Figure 2b. No peaks for free mCPBA were evident (1735 cm^{-1} (C=O); 1555, and 1419 cm^{-1} (C=C)); however, a new C=O stretching band at 1744 cm^{-1} and another peak at 1298 cm^{-1} have appeared. Slight warming of the reaction mixture caused the partial decomposition of **2a** (spectrum c). Continued warming afforded spectrum d with a strong band at 1656 cm^{-1}, which was identical with that of **3a** prepared by the reaction of **1** with mCBA. We interpret the large shift of the C=O band of **3a** to lower frequency to indicate replacement of the acylperoxo ligand of **2a** with benzoate[12a] in **3a** as depicted in Scheme I. A similar shift was also observed in Fe^{III}TMP(mCB) ($\nu_{C=O}$ = 1652 cm^{-1} in CH_2Cl_2). The appearance of the C=O band for **2a** at 1744 cm^{-1} clearly demonstrates that the reaction of **1** with mCPBA has formed an iron(III) *m*-chloroperoxybenzoate (**2a**), the carbonyl oxygen of which does not interact with iron.[12b]

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(6) (a) The ligand was prepared by a modification of the method we have reported for tetramesitylporphyrin. Cf.: Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 6243. λ_{max} in nm (log ϵ) (benzene): $TTPPPH_2$, 442.5 (5.49), 500.0 (3.53), 535.5 (4.12), 572.0 (3.88), 612 (3.62), 671 (3.38); $TTPPPH_4^{2+}$, 469.0 (5.22), 560.0 (3.48), 606.0 (3.93), 658.5 (4.31). (b) In our hands an earlier procedure produced a mixture of porphyrins with different spectroscopic properties. Cf.: Suslick, K. S.; Fox, M. M. *J. Am. Chem. Soc.* **1983**, *105*, 4261. (c) Cook, B. R.; Reinert, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986**, *108* 7281–7286. (d) Fe^{III}TTPPP(OH) was prepared by the reaction of Fe^{III}TTPPP(Cl) with NaOH(aq) in the presence of a catalytic amount of Me_4NOH in benzene under reflux condition for 5 h. λ (nm) in CH_2Cl_2 (log ϵ): 442.0 (503), 595.2 (4.07), 639.6 (3.72). ν_{O-H} = 3620 cm^{-1} in CH_2Cl_2. A preliminary X-ray crystal structure has confirmed this assignment. (e) The large variations in the rates of reaction of **1** were observed to result from changes in the concentrations of the reagents.

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(13) A portion of this work was also done at the Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109.

Department of Chemistry
Princeton University
Princeton, New Jersey 08540[13]

John T. Groves*
Yoshihito Watanabe

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