propriate substituents, pyrolysis leading to the elimination of some small molecule (H_2, HCl, or Me_3SiCl) might reasonably lead to cluster formation.[17]

Acknowledgment. D.A.J. acknowledges support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., and the State University of New York Research Foundation. T.F.G. acknowledges support from the Office of Naval Research and the National Science Foundation under Grant No. CHE-9016789.

Registry No. $C_{12}B_{24}N_{24}$, 137720-14-0.

---

(17) For examples of elimination reactions of this type by similar systems, see ref 14. See also: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1980; Chapters 4 and 5.

Department of Chemistry
College at Fredonia
State University of New York
Fredonia, New York 14063

James R. Bowser*
Daniel A. Jelski

Departments of Chemistry and Physics
Washington State University
Pullman, Washington 99164

Thomas F. George

Received August 1, 1991

Push Effect on the Heterolytic O–O Bond Cleavage of Peroxoiron(III) Porphyrin Adducts

In the oxygen activation mechanisms by P-450, peroxidases, and catalase, a heterolytic O–O bond cleavage process of (hydroperoxo)iron(III) porphyrin complexes is believed to afford oxoferryl (O=Fe^{IV}) porphyrin cation radical intermediates.[1] In fact, the reactive species called "compound I" is observable in some peroxidase reactions.[2] For these heme enzymes, it has been proposed that the proximal ligands (thiolate,[3] imidazolate,[4] and phenolate[5]) are crucial to the heterolytic process by serving as a strong internal electron donor to destabilize the O–O bond of a (hydroperoxo)iron(III) porphyrin (*push effect*).[6] In addition, distal histidine residues in some cases are considered to serve as a general acid/general base to assist heterolytic O–O bond cleavage as shown below (*pull effect*).[6]

$$\underset{push}{:B\rightarrow}\underset{Por}{Fe^{III}}-\underset{OH}{O}\overset{pull}{\cdots H-Im} \longrightarrow :B\rightarrow \underset{Por^{+\bullet}}{Fe^{IV}}=O + H_2O \qquad (1)$$

The push–pull mechanism has been examined by several model systems.[7-9] For instance, the catalytic oxidation of tri-*tert*-butylphenol by synthetic iron porphyrin complex/peracid (or hydroperoxide) systems was enhanced by added buffers and by covalently attached bases.[7] Further, Bruice et al. also reported general-acid/general-base effects by using similar catalytic systems.[8] Kinetic studies of the reactions indicate the oxidation being first order in [peracid (or hydroperoxide)] and [iron porphyrin] under the reaction conditions.[7,8] While these observations are very important to understand biological manipulation of hydrogen peroxide against the Fenton type radical process by utilizing the push–pull effects, observed second-order rate constants (k_{obs}) do not represent the O–O bond cleavage step (k_{dec}) since k_{obs} apparently includes preequilibrium constants (K_{eq}) as shown in eq

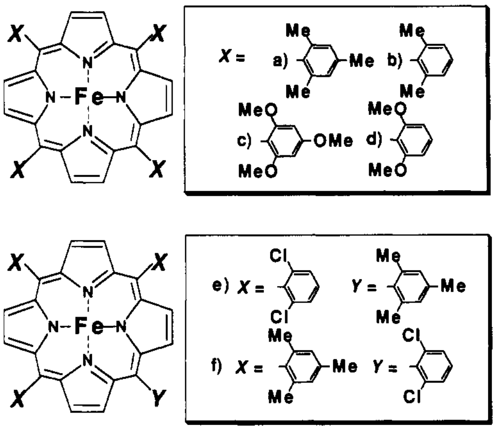


Figure 1. Structures of the porphyrin core of various substituted iron porphyrin complexes (**a–f**) employed in this study. Axial ligands have been omitted for simplicity.

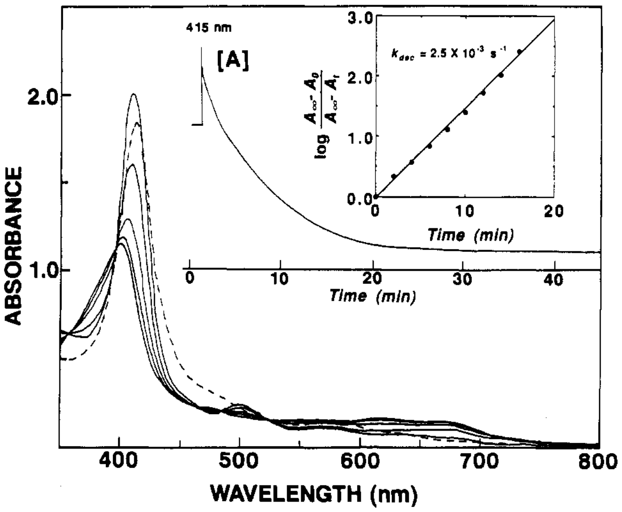


Figure 2. Visible spectral changes in the reaction of 2.0×10^{-5} M hydroxoiron(III) porphyrin (**3b**) and 3 equiv of *p*-nitroperoxybenzoic acid in methylene chloride at –80 °C. The spectrum of **4b** was recorded immediately after the addition of *p*-nitroperoxybenzoic acid. Line A represents the time-dependent change of absorbance at 415 nm. Inset: Plots of log $[(A - A_0)/(A - A_t)]$ at 415 nm vs time for the formation of **5b** by the reaction of **3b** with 3 equiv of *p*-nitroperbenzoic acid in CH_2Cl_2 at –80 °C.

---

(1) For example: (a) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *50*, 315–356. (b) Dawson, J. H. *Science* **1988**, *240*, 433–439.

(2) Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J.; Felton, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1971**, *68*, 614–618.

(3) (a) Poulos, T. L.; Finzel, B. C.; Gunsalus, I. C.; Wagner, G. C.; Kraut, J. *J. Biol. Chem.* **1985**, *260*, 16122–16130. (b) Poulos, T. L.; Finzel, B. C.; Howard, A. J. *Biochemistry* **1986**, *25*, 5314–5322. (c) Poulos, T. L.; Howard, A. J. *Biochemistry* **1987**, *26*, 8165–8174.

(4) Thanabal, V.; de Ropp, J. S.; La Mar, G. N. *J. Am. Chem. Soc.* **1988**, *110*, 3027–3035.

(5) Murthy, M. R. N.; Reid, T. J., III; Sicignano, A.; Tanaka, N.; Rossmann, M. G. *J. Mol. Biol.* **1981**, *152*, 465–499.

(6) (a) Dawson, J. H.; Holm, R. H.; Trudell, J. R.; Barth, G.; Linder, R. E.; Bunnenberg, E.; Djerassi, C.; Tang, S. C. *J. Am. Chem. Soc.* **1976**, *98*, 3707–3709. (b) Poulos, T. L. *Adv. Inorg. Biochem.* **1987**, *7*, 1.

(7) (a) Traylor, T. G.; Lee, W. A.; Stynes, Dennis V. *J. Am. Chem. Soc.* **1984**, *106*, 755–764. (b) Traylor, T. G.; Popovitz-Biro, R. *J. Am. Chem. Soc.* **1988**, *110*, 239–243.

(8) (a) Zipplies, M. Z.; Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 4433–4445. (b) Yuan, L.-C.; Bruice, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1643–1650. (c) Bruice, T. C.; Balasubramanian, P. N.; Lee, R. W.; Lindsay Smith, J. R. *J. Am. Chem. Soc.* **1988**, *110*, 7890–7892.

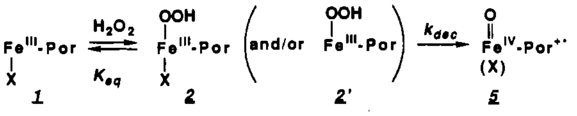
(9) (a) Groves, J. T.; Watanabe, Y. *Inorg. Chem.* **1986**, *25*, 4808–4810. (b) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7834–7836. (c) Labeque, R.; Marnett, L. J. *J. Am. Chem. Soc.* **1989**, *111*, 6621–6627. (d) Higuchi, T.; Uzu, S.; Hirobe, M. *J. Am. Chem. Soc.* **1990**, *112*, 7051–7053. (e) Robert, A.; Loock, B.; Momenteau, M.; Meunier, B. *Inorg. Chem.* **1991**, *30*, 706–711.

Table I. Substituent Effect on First-Order Rate Constants for the Heterolytic O–O Bond Cleavage of **4** in CH_2Cl_2 at −80 °C

	10^3k_{dec}, s^{-1} (log k_{rel}[c])	
compds[b]	*m*-CPBA[d]	*p*-NO_2PBA[e]
4a	3.2 (0.00)	11.2 (0.00)
4b	0.7 (−0.64)	2.5 (−0.65)
4c	16.6 (0.72)	50.8 (0.66)
4d	4.0 (0.10)	14.5 (0.11)
4e	*a*	0.6 (−1.28)
4f	0.5 (−0.77)	2.2 (−0.71)

[a] Not available. [b] See Figure 1. [c] k_{rel} is the relative rate constant based on that of **4a**. [d] 3 equiv of *m*-chloroperoxybenzoic acid were used. [e] 3 equiv of *p*-nitroperoxybenzoic acid were used.

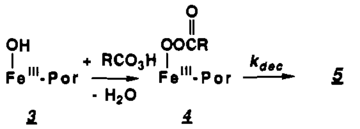
2. Furthermore, a possible intermediate, **2** or **2′**, has never been observed in these catalytic systems.



$$\underset{\underline{1}}{\underset{X}{Fe^{III}\text{-Por}}} \underset{K_{eq}}{\overset{H_2O_2}{\rightleftharpoons}} \underset{\underline{2}}{\overset{OOH}{\underset{X}{Fe^{III}\text{-Por}}}} \left(\text{and/or } \underset{\underline{2'}}{\overset{OOH}{Fe^{III}\text{-Por}}}\right) \xrightarrow{k_{dec}} \underset{\underline{5}}{\overset{O}{\underset{(X)}{Fe^{IV}\text{-Por}^{+\cdot}}}} \quad (2)$$

$$k_{obs} = k_{dec}[\underline{2} \text{ (or } \underline{2}')] = k_{dec}\cdot K_{eq}[\underline{1}][H_2O_2]$$

In order to understand the push effect on the O–O bond cleavage reaction of the (hydroperoxo)iron(III) porphyrin complex, we have examined the reactivity of a series of (acylperoxo)iron(III) porphyrins (**4**) by changing substituents at the *meso* positions of the porphyrin ring. The substituted porphyrins listed in Figure 1 were prepared according to the methods reported.[10]



$$\underset{\underline{3}}{\overset{OH}{Fe^{III}\text{-Por}}} \xrightarrow[-\,H_2O]{+\,RCO_3H} \underset{\underline{4}}{\overset{OOC(=O)R}{Fe^{III}\text{-Por}}} \xrightarrow{k_{dec}} \underline{5} \quad (3)$$

In a typical reaction, a methylene chloride solution of hydroxoiron porphyrin (**3b**, 2.0 × 10^{-5} M) was cooled to −80 °C in a UV–vis cuvette. Introduction of 3 equiv of *p*-nitroperbenzoic acid to the solution immediately afforded (acylperoxo)iron(III) porphyrin (**4b**), which exhibits a typical visible spectrum for five-coordinated high-spin iron(III) porphyrins but different from that for the hydroxide complex (Figure 2).[11] The following transformation of **4b** to an oxoferryl porphyrin cation radical[12] (**5b**) was also directly observed as shown in Figure 2. Trace A in Figure 2 shows the time course of absorbance change of **3b** at 415 nm upon the addition of 3 equiv of *p*-nitroperoxybenzoic acid. Similar spectral changes were also observed in the reaction of **3a,c–f** with peracids under the conditions described above. From an analysis of the spectral changes, the O–O bond cleavage of **4** was found to be first-order in [**4**] (d[**5**]/d*t* = k_{dec}[**4**]) as shown in Figure 2 (inset), consistent with recent observation by Groves and Watanabe.[13] Values of the rate constants (k_{dec}) for several substituted porphyrins are summarized in Table I. As expected for the heterolytic O–O cleavage in **4**, *p*-nitroperbenzoato)iron(III) porphyrin complexes decompose faster than the *m*-chloroperbenzoate derivatives (pull effect).[13,14] At the same time, electron-donating groups at the *meso* positions of a porphyrin ring were found to accelerate the O–O bond cleavage step, whereas electron-withdrawing substituents retarded the formation of **5**. A Hammett plot of log k_{rel} vs the summation of Hammett σ's of the substituents gives a slope ρ of −0.53 (correlation coefficient: 0.92). These observations demonstrate that the electron donor at the *meso* positions of a porphyrin ring accelerates the heterolytic O–O bond cleavage reaction effectively.

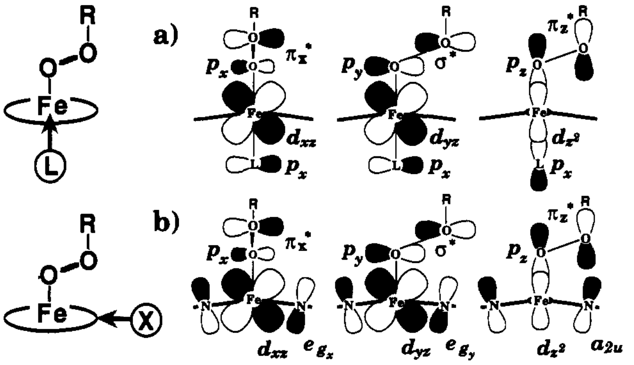


Figure 3. Idealized orbital interaction diagrams for peroxoiron(III) porphyrin complexes: (a) interaction among the sixth ligand's p orbitals, iron d orbitals, and peroxo p orbitals; (b) interaction among the porphyrin ligand's orbitals, iron d orbitals, and peroxo p orbitals.

Implication of the Push Effect of Substituents on a Porphyrin Ring. Figure 3 shows the orbital interaction diagrams among iron, porphyrin, axial ligand, and peroxide. The oxygen p orbitals (σ* and π*) of the iron-bound peroxide are overlapped with iron d_{xz}, d_{yz}, and d_{z^2} orbitals, which also interact with the p orbitals of an axial ligand (Figure 3a). Thus, the push effect by the axial ligand on the heterolytic O–O bond cleavage depicted in eq 1 can be explained by the orbital interaction between the ligand and peroxide through iron. Since the porphyrin e_g and a_{2u} orbitals on the pentacoordinated domed porphyrin ring, in which large electron densities are localized at the pyrrole nitrogens and the *meso* carbons, interact with iron d_{xz}, d_{yz}, and d_{z^2} orbitals, *meso* substituents on a porphyrin ring as well as the axial ligand are also expected to affect the rate of the heterolytic O–O bond cleavage. These considerations are consistent with the experimental results shown in Table I.

In conclusion, it has been shown that the internal electron donor to destabilize the O–O bond (push effect) is important in the heterolytic O–O bond cleavage process of *meso*-substituted (acylperoxo)iron(III) porphyrin complexes to form the corresponding oxoiron(IV) porphyrin cation radicals.

Division of Molecular Engineering
Graduate School of Engineering
Kyoto University
Kyoto 606, Japan

Kazuya Yamaguchi
Yoshihito Watanabe
Isao Morishima*

Received October 30, 1991

Environmentally Induced Multiple Intervalence Transitions in a Symmetrically Substituted Analogue of the Creutz–Taube Ion

Intervalence transition energies for class II (valence localized) mixed-valence systems are known to be a sensitive function of molecular environment[1] (i.e. solvent,[2] ionic strength,[3-5] etc.). Class

---

(10) (a) Lindsey, L. S.; Wagner, R. W. *J. Org. Chem.* **1989**, *54*, 828–836. (b) Kobayashi, H.; Higuchi, T.; Kaizu, Y.; Osada, H.; Aoki, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3137.

(11) (a) Woon, T. C.; Shirazi, A.; Bruice, T. C. *Inorg. Chem.* **1986**, *25*, 3845–3846. (b) Groves, J. T.; Watanabe, Y. *Inorg. Chem.* **1987**, *26*, 785–786.

(12) Formation of oxoferryl porphyrin cation radicals was also confirmed by NMR spectroscopy in comparison with the result of Groves et al.; see ref 15.

(13) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8443–8452.

(14) Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 513–514.

(15) (a) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884–2886. (b) Gold, A.; Jayaraj, K.; Doppelt, P.; Weiss, R.; Bill, E.; Ding, X.-Q.; Bominaar, E. L.; Trautwein, A. X.; Winkler, H. *New J. Chem.* **1989**, *13*, 169–172.

(1) For a general review, see: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(2) See, for example: Brunschwig, B. S.; Ehrenson, S.; Sutin, N. *J. Phys. Chem.* **1986**, *90*, 3657 and references therein.

(3) (a) Hammack, W. S.; Drickamer, H. G.; Lowery, M. D.; Hendrickson, D. N. *Chem. Phys. Lett.* **1986**, *132*, 231. (b) Lowery, M. D.; Hammack, W. S.; Drickamer, H. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 8019.

0020-1669/92/1331-0157$03.00/0