$$Tl_2O_3(s) + 2(H^+\text{-}Zeo^-) \xrightarrow[600\ ^\circ C]{} 2(Tl^+\text{-}Zeo^-) + H_2O + O_2 \qquad (4)$$

in C. Moreover, its dissolution by HF followed by a starch iodide test for Tl(III) gave a negative result and confirmed the complete reduction of Tl(III) to Tl(I) upon calcination of B. Note that this thermal decomposition is inconsistent with published observations[16] on anhydrous Tl_2O_3. The facile thermal decomposition of hydrated Tl_2O_3 at <100 °C has been reported by Hüttig et al.[17]

Exposure of C to moist ozone for 8 h regenerated the brown Tl_2O_3 surface. The particles were again ~76 Å, and the TEM (Figure 1D) X-ray powder diffraction pattern and ESCA (Figure 2D) of the product, D, are qualitatively similar to the original ozonation product, B. However, iodometric titration of the HF/H_2SO_4 solution of D showed that only 82% of the total Tl_2O_3 present in B underwent reoxidation on the calcination/ozonation cycle. This number agrees well with the 86% reoxidation value obtained by both quantitative ESCA and area measurements of the Tl_2O_3 X-ray powder pattern peaks. Thus, although the observed thallium oxidation and migration can be reversed thermally or chemically (vide infra), the extent of Tl_2O_3 formation decreased with each subsequent redox cycle. The source of this degradation is not obvious. Careful quantitative comparison of X-ray peak areas and intensities of A and C revealed no experimentally significant changes, so gross zeolite structural collapse had apparently not occurred. Limited or partial collapse and trapping of Tl^+ inside pores or at sites with different charge densities cannot, however, be ruled out, because the powder diffraction pattern may be insensitive to these changes.

The brown Tl_2O_3-coated solids B and D reacted with organic reagents to form oxidized products and Tl(I). ESCA and X-ray powder patterns confirmed the reduction of Tl_2O_3 and the location of Tl(I) within the zeolite framework. When B was slurried with a CH_2Cl_2 solution of phenol at room temperature and at dry ice/acetone temperature, brown oxidation products (quinones and oxidatively coupled phenols)[18,19] were formed. The reduced zeolite, E, was reozonized to give brown Tl_2O_3-coated F. After pumping in vacuo to remove excess ozone, F was used in both a flow-through and closed system to oxidize moist propylene at 25 °C.[20] Acetone[20-22] was the only organic product detected by GC/MS. The white zeolite product had ESCA binding energies and an X-ray powder pattern identical with E and A. Iodometric titration also confirmed the total absence of Tl(III). However, the total thallium present was unchanged.

Laboratory oxidations of organic compounds with Tl(III) have been studied by McKillop and Taylor[23] and their coworkers. The potential commercial use of these reactions for the manufacture of epoxides, carbonyl compounds, and aromatic derivatives is evidenced by a large number of pertinent patents[20,24-26] and articles. Patents claiming the use of immobilized Tl(III) reagents[27] or of Tl_2O_3[22,28] for selective oxidations have also been granted. Despite this interest, however, commercialization has only been minimal, if at all. The principal technical drawback has been the absence of a cost-effective method of reoxidizing the stoichiometric amounts of Tl(I) formed back to Tl(III). Regeneration with hydroperoxide,[29] peracids,[24] and Ce(IV)[30] has been proposed. Oxygen or air effects the change only at high temperatures and pressures.[31,32]

The standard reduction potential for the half-cell $Tl^{3+} + 2e^- \rightarrow Tl^+$ is 1.25 V. This value is 0.02 V greater than the standard electrode potential for the oxygen half-cell. That the electrode potential for ozone reduction is 0.82 V above that for thallium indicates that regeneration of Tl(III) by ozonation is thermodynamically favorable at 25 °C. Prior to our work on the ozonation of Tl-zeolites, we established the kinetic feasibility of thallium oxidation by ozone by effecting >95% conversion of $TlNO_3$ to Tl_2O_3 in 45 min at 25 °C with 2% O_3 in O_2. Heretofore, only limited use[33] has been made of this thermodynamic and kinetic advantage. Our results show that regeneration with ozone yields an easily accessible surface oxidant, but the partial reversibility of the redox-migration phenomenon limits the utility of ozonation as a method of regeneration for thallium reagents immobilized in zeolites. Ozone can conceivably still function as a regenerant if the immobilization is done as described by Taylor et al.[27] Treatment with trimethoxymethane or other dehydrating agent will be necessary in order to avoid thermal decomposition of Tl_2O_3 under realistic reaction conditions.[22]

Acknowledgment. The authors thank Union Carbide Corp. for support and for permission to publish this paper. The technical assistance of and useful discussions with Janet Cohen, Herb Hillery, Paul Kasai, and Don McLeod are also acknowledged.

Registry No. Tl, 7440-28-0; Tl_2O_3, 1314-32-5; O_3, 10028-15-6.

---

(16) (a) D. Cubicciotti and F. J. Keneshea, *J. Phys. Chem.*, **71**, 808 (1967); (b) A. G. Lee, "The Chemistry of Thallium", Elsevier, New York, 1971.

(17) A. F. Huttig and R. Mytyzek, *Z. Anorg. Allg. Chem.*, **192**, 187 (1930).

(18) A. McKillop, A. Turrell, and E. Taylor, *J. Org. Chem.*, **42**, 764 (1977).

(19) A. McKillop, D. Perry, M. Edwards, et al., *J. Org. Chem.*, **41**, 282 (1976).

(20) W. M. Krus, U. S. Patent 3 641 067, 1972.

(21) R. J. Ouellette, "Oxidation in Organic Chemistry", Academic Press, New York, 1973, Part B, pp 143-146.

(22) T. Honda, H. Tanaka, and I. Watanabe, *Chem. Abstr.*, **77**, 115046*b* (1972).

(23) A. McKillop and E. C. Taylor, *Endeavor*, **35**, 88 (1976).

(24) J. A. Walker, U. S. Patent 4 135 051 (1979).

(25) J. J. Leonard, U. S. Patent 4 031 196 (1977).

(26) W. F. Brill, U. S. Patent 4 021 453 (1977).

(27) J. F. White and E. C. Taylor, U. S. Patent 4 067 823 (1978).

(28) H. Zondler, D. Trachsler, and F. Lohse, *Ger. Offen.*, **GER. OFFEN. 2,602,157** (1976).

(29) W. F. Brill, U. S. Patent 4 115 421 (1978).

(30) A. F. McLean and A. L. Stautzenberger, U. S. Patent 3 479 262 (1969).

(31) W. F. Brill, U. S. Patent 4 115 420 (1978).

(32) R. A. Johnson, U. S. Patent 4 113 756 (1978).

(33) G. Kauffmann and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **347**, 318 (1966).

Contribution from the Department of Chemistry,
University of Iowa, Iowa City, Iowa 52242

Investigation of Axial Anionic Ligand and Porphyrin Substituent Effects on the Oxidation of Iron(III) Porphyrins: Porphyrin-Centered vs. Metal-Centered Oxidation

Martin A. Phillippi, Eric T. Shimomura, and Harold M. Goff*

Received August 24, 1979

The electrochemical behavior of iron porphyrins is of current interest due to their diverse biological functions as redox catalysts. Iron porphyrins may exhibit formal oxidation states of +4, +3, +2, and +1,[1] with iron(II) and iron(III) porphyrins being characterized in high-, low-, and intermediate-spin states.[2-5] In nonaqueous solvents many metalloporphyrins

---

(1) Fuhrhop, J.-H. *Struct. Bonding* (*Berlin*) **1974**, *18* 1.

(2) Smith, K. M. "Porphyrins and Metalloporphyrins"; Elsevier: New York, 1975.

may be oxidized and reduced in single, reversible, one-electron steps.[1] A Hammett linear free-energy relationship between the half-wave potentials and σ constants of phenyl and β-pyrrole substituents for iron(III) tetraphenylporphyrin chloride has been demonstrated.[6-9] Potential shifts are much smaller for phenyl substituents than for those attached at the β-pyrrole carbon atoms. As expected, oxidation waves shift cathodically when electron-releasing groups are present and anodically with electron-withdrawing groups present. A relationship between reduction half-waves and porphyrin ring basicity has also been recognized.[10]

Interest in examination of oxidized iron porphyrins is derived from the observation of iron(IV) and possible π-cation radical intermediates in the catalytic cycle of hemoproteins such as horseradish peroxidase.[11] Felton et al. have reported the preparation and partial solution characterization of iron porphyrins oxidized to the formal iron(IV) state.[12] Our attempts at improved electrochemical synthesis of oxidized iron porphyrin species prompted cyclic voltammetric examination of various high-spin iron(III) derivatives in hopes of minimizing oxidation potentials. Oxidation potentials are remarkably insensitive to the nature of axial ionic ligands. This previously unexplained observation[13] was reaffirmed by other investigators during conclusion of our work.[14,15] Supporting spectroscopic measurements reported here serve to explain the insensitivity of oxidation potentials as being due to electron abstraction from a porphyrin-centered rather than a metal-centered molecular orbital.

Experimental Section

Iron(III) tetraphenylporphyrin chloride (Fe(TPP)Cl) was prepared by literature methods.[16,17] Iron(III) octaethylporphyrin chloride (Fe(OEP)Cl) was prepared by total pyrrole synthesis, iron insertion, and chromatographic purification.[17,18] Natural-derivative iron(III) porphyrin dimethyl ester complexes were prepared as described elsewhere.[19] All iron(III) porphyrins were converted to the μ-oxo-bridged dimer by base hydrolysis with 1 M sodium hydroxide or by passage through a deactivated alumina column. Acid hydrolysis of the μ-oxo-bridged dimers with the appropriate acid yields monomeric iron(III) porphyrins with various axial ligands.[20] Synthesis of the previously unreported SO_4^{2-}, HSO_4^-, NO_3^-, and p-$CH_3C_6H_4SO_3^-$ adducts by this acid cleavage method will be reported in detail elsewhere.[21,22] All compounds have been characterized by proton and carbon-13 NMR spectroscopy.

Table I. Half-Wave Oxidation Potentials for the Voltammetric Oxidation of Synthetic Iron(III) Porphyrins[a]

	$E_{1/2}$		
	Fe(TPP)X		Fe(OEP)X
X^-	first	second	first
F^-	1.09	1.36	1.01
Cl^-	1.11	1.38	1.01
Br^-	1.10	1.35	1.00
I^-	1.09	1.38	
ClO_4^-	1.09	1.35	1.01
SO_4^{2-}	1.11	*b*	1.03
NO_3^-	1.10	1.33	
N_3^-	1.08	1.38	
NCS^-	1.10	1.38	
OPh^-	1.08	1.44	
p-$CH_3C_6H_4SO_3^-$	1.11	1.37	
HSO_4^-	1.09	1.35	
H_2TPP[c]	1.02	1.27	
ZnTPP	0.76	1.07	
NiTPP[c]	1.05	*d*	
$CoTPP^+$[c]	1.00	1.20	
Mn(TPP)Cl	1.06	*d*	

[a] Referenced to SCE, uncertainties ±0.02 V, CH_2Cl_2 solvent, 0.1 M TBAP, 2 mM iron porphyrin, 25 °C. [b] Complicated behavior. [c] Reference 8. [d] Beyond potential range of solvent.

All electrochemical studies were carried out in methylene chloride solvent with 0.1 M tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte and iron porphyrin typically 2 mM in concentration. The TBAP (Eastman Chemicals) was dried under vacuum before use. Solutions were deoxygenated by bubbling solvent-saturated argon through the solution for 20 min.

A conventional three-electrode system was used with platinum working (bead) and platinum auxiliary (wire) electrodes. All potentials in this study were recorded vs. a Ag, $AgNO_3$ (0.01 M) in acetonitrile reference electrode at 25 °C. Reported potentials are corrected to the SCE electrode. The experimentally determined conversion factor was found to be 0.33 V (potentials vs. SCE are 0.33 V more positive) by running several compounds with each reference electrode (SCE purchased from PAR). Cyclic voltammetric measurements were made with a Princeton Applied Research (PAR) Model 173 potentiostat driven by the Model 175 universal programmer. Typical scan rates were 50 mV/s, and IR compensation was provided by the positive feedback unit in the Model 176 coulometer. Reported CV waves were reversible, and half-wave potentials are given as the midpoint of anodic and cathodic peak separations.

Solvents were purified by published procedures[23] and stored over molecular sieves, as traces of water (in the absence of acid) will convert certain monomeric iron(III) porphyrin species to μ-oxo-bridged dimers. Likewise, HCl in chlorinated solvents will displace the more weakly bound anionic ligands. Thus, methylene chloride was routinely washed with 1 M Na_2CO_3 solution, washed with water, dried, distilled, and stored over activated 3-Å molecular sieves (protected from light).

Results and Discussion

Half-wave potentials for the first, one-electron oxidation of various high-spin iron(III) porphyrin derivatives are listed in Table I. As is apparent, potentials are surprisingly insensitive to the nature of the anionic ligand for Fe(TPP)X and Fe(OEP)X compounds. A reasonable explanation would involve displacement of the intended axial ligand with that of perchlorate ion from the supporting electrolyte. However, only for authentic perchlorate complexes was a reduction wave [Fe(III) → Fe(II)] at 0.14 V observed, indicating that perchlorate does not effectively compete with the anionic ligands.

---

(3) Goff, H.; La Mar, G. N.; Reed, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 3641.

(4) Goff, H.; Shimomura, E. *J. Am. Chem. Soc.* **1980**, *102*, 31.

(5) Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.

(6) Kadish, K. M.; Morrison, M. M.; Constant, L. A.; Dickens, L.; Davis, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 8387.

(7) Ni, S.; Dickens, L.; Tappan, J.; Constant, L.; Davis, D. G. *Inorg. Chem.* **1978**, *17*, 228.

(8) Kadish, K. M.; Morrison, M. M. *Bioinorg. Chem.* **1977**, *7*, 107.

(9) Giraudeau, A.; Callot, H. J.; Jordan, J.; Ezhar, I.; Gross, M. *J. Am. Chem. Soc.* **1979**, *101*, 3857.

(10) Kadish. K. M.; Larson, G. *Bioinorg. Chem.* **1977**, *7*, 95.

(11) Dunford, H. B.; Stillman, J. S. *Coord. Chem. Rev.* **1976**, *19*, 187.

(12) (a) Felton, R. H.; Owen, G. S.; Dolphin, D.; Fajer, J. *J. Am. Chem. Soc.* **1971**, *93*, 6332. (b) Felton, R. H.; Owen, G. S.; Dolphin, D.; Forman, A.; Borg, D. C.; Fajer, J. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 504.

(13) Wolberg, A. *Isr. J. Chem.* **1974**, *12*, 1031.

(14) Cohen, I. A.; Lavallee, D. K.; Kopelove, A. B. *Inorg. Chem.* **1980**, *19*, 1098.

(15) Kadish, K. M.; Bottomley, L. A. *Inorg. Chem.* **1980**, *19*, 832. In this reference the ratio of chloride to perchlorate binding, K_{ex}, is at one point listed as 10.5, when properly log K_{ex} = 10.5.

(16) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(17) Adler, A. D.; Longo, F. R.; Varadi, V. *Inorg. Synth.* **1976**, *16*, 213.

(18) Fuhrop, J.-H.; Smith, K. M. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; pp 765-769.

(19) O'Keeffe, D. H.; Barlow, C. H.; Smythe, G. A.; Fuchsman, W. H.; Moss, T. H.; Lilienthal, H. R.; Caughey, W. S. *Bioinorg. Chem.* **1975**, *5*, 125.

(20) Torrens, M. A.; Straub, D. K.; Epstein, L. *J. Am. Chem. Soc.* **1972**, *94*, 4162.

(21) Phillippi, M. A.; Goff, H. M. *J. Chem. Soc., Chem. Commun.* **1980**, 455.

(22) Phillippi, M. A.; Baenziger, N.; Goff, H. M., submitted for publication.

(23) Perrin, D. D.; Armarego, W. L. F.; Perrin, O. R. "Purification of Laboratory Chemicals"; Pergamon Press: New York, 1966.

Variation of reduction potentials among the anionic complexes examined further demonstrates species integrity in the presence of TBAP. This is confirmed by other workers[15,24] and our proton NMR studies of these complexes in the presence of 0.1 M TBAP. Under such conditions the pyrrole resonance for all Fe(TPP)X complexes listed in Table I exhibits a downfield isotropic shift of 64–70 ppm[21,22] except in the perchlorate complex where the pyrrole peak is at 3.8 ppm (in CD_2Cl_2 at 299 K).[4]

Unexplained insensitivity of oxidation potentials has been noted previously in limited cases for Fe(TPP)X where X = ClO_4^-, Br^-, Cl^-, F^-, and BF_4^- [13-15] and for Fe(OEP)X where X = Cl^- and ClO_4^-.[15] We have considerably expanded this list. (Note that X = OH^- is not found in Table I as there is no evidence for its existence in these monomeric complexes—hydrolysis of simple iron(III) porphyrins results in μ-oxo dimer formation.[2]) Constancy of oxidation potentials is largely unexpected, as axial ligands are known to dictate a variety of magnetic and spectroscopic properties of high-spin iron(III) porphyrins.[25,26] Diverse ligand types are represented in Table I. Halide complexes demonstrate "pure" high-spin character, whereas the perchlorate derivative is best described as a quantum mechanically admixed $S = {}^5/_2, {}^3/_2$ species.[4,5] Our recent X-ray structure determination reveals that nitrate ion serves as a bidentate ligand,[22] and it is also expected that sulfate and toluenesulfonate derivatives behave similarly. The solution molecular and electronic structures of these oxyanionic species are clearly perturbed with respect to halide derivatives.

Independence of ligand type on oxidation potentials appears to reflect the site of electron abstraction (i.e., from a porphyrin vs. a metal-based molecular orbital). Hückel calculations assign the $d_{x^2-y^2}$ orbital of high-spin iron(III) and iron(IV) species as the HOMO and LUMO, respectively.[12,27] Nature of the axial ligand would thus be expected to affect the potential required to remove the electron from a bonding or an antibonding iron d orbital. However, absence of ligand dependence suggests electron abstraction from a nonbonding metal orbital or from the porphyrin π system. Furthermore, the higher energy $d_{x^2-y^2}$ orbital of Fe(TPP)ClO_4 (associated with $S = {}^3/_2$ character) should dictate more facile oxidation of this species vs. pure high-spin complexes,[28] if electrons were being removed from a metal-based molecular orbital.

We have reported proton NMR results used to characterize the one- and two-electron oxidation products of μ-oxo-bis-(5,10,15,20-tetraphenylporphinato)iron(III).[29] The doubly oxidized dimer is cleaved by acid to give a monomeric oxidized species. The same compound may be generated by direct electrolysis of Fe(TPP)Cl[29,30] to yield Fe(TPP)Cl^+, which shows the following ^{1}H NMR resonances in CD_2Cl_2 referenced to internal Me_4Si at 299 K: pyrrole H, 66.1; ortho H, 37.6, 34.4; meta H, −12.4; para H, 29.5 ppm. Downfield isotropic shifts (positive spin density) for pyrrole protons of Fe(TPP)Cl^+ and ring methyl/methylene groups of oxidized iron mesoporphyrin dimethyl ester chloride demand single-electron occupation of the $d_{x^2-y^2}$ orbital. Mn(TPP)Cl is isoelectronic with Fe(TPP)Cl^+ and its pyrrole resonance is found upfield at −23 ppm (5 mM in $CDCl_3$ referenced to internal Me_4Si at 302 K) consistent with depopulation of $d_{x^2-y^2}$ in the Mn(III) ion. Large phenyl proton isotropic shifts alternating in sign are further suggestive of porphyrin π-radical character with large spin density at the meso position. It is of interest that the ESR hyperfine constant for the phenyl protons of the π-cation radical Zn(TPP)ClO_4 was found to be 0.316 G,[31] which would yield an isotropic ^{1}H NMR shift of 23 ppm at 298 K (or observed resonances as far as 31 ppm downfield or 15 ppm upfield). This isotropic shift value approximates those observed for Fe(TPP)Cl^+, further suggesting radical character in the oxidized iron porphyrin.

Table II. Half-Wave Oxidation Potentials for Chloride Monomers and μ-Oxo-Bridged Dimers of Natural-Porphyrin Dimethyl Ester Derivatives[a]

2,4-position *substituents*	$E_{1/2}$	
	Cl monomers	*dimers*
CH_3CH_2	0.99	0.71
H	1.07	0.74
$CH_2{=}CH$	1.03	0.71
CH_3CO	1.20	0.87
Br	1.20	0.91

[a] See legend of Table I.

Detailed electronic structural assignments for the oxidized monomeric compounds are not yet available. Magnetic moments corresponding to $S = 2$[12b,29] could be explained by very strong antiferromagnetic coupling of radical and metal spins. However, such an interaction is thought to be quite small.[32] Moreover, strong coupling would seemingly preclude observation of radical-type spin density in the proton NMR shift pattern for phenyl protons. Moderately strong antiferromagnetic coupling ($J \approx -75$ cm^{-1}) would result in large susceptibility and NMR Curie law deviations, but, over the accessible temperature range investigated (200–300 K), no significant deviations were apparent. Effects of configuration interaction or large zero field splitting for iron(III) should be considered in attempting to understand the magnetic properties of oxidized iron porphyrins.

Earlier electrochemical evidence serves to support, but does not prove, a π-cation radical formulation.[1] The Hammett reaction constant, ρ, for the formation of the π-anion radical of phenyl-substituted FeTPP(p-R) is essentially equivalent to those obtained for the first- and second-oxidation waves of Fe(TPP)Cl in butyronitrile but very different from those found for the metal-centered reduction to iron(II) and iron(I).[6] Also, the Hammett constant is very similar for the oxidation of free-base TPP and the oxidation of Fe(TPP)Cl. The difference between the first- and second-oxidation waves for Fe(TPP)Cl and Fe(OEP)Cl of 0.24 V is taken as support for ring oxidation.[33]

Table I also lists oxidation potentials for H_2TPP and Zn(II), Ni(II), Co(III), and Mn(III) complexes[8] for comparative purposes. It is interesting to note that the free ligand is more easily oxidized than the iron(III) derivative (this is also true for OEP complexes[1]). The above-mentioned Zn(II), Ni(II), and Co(III) TPP derivatives likewise undergo one-electron oxidation to the corresponding π-cation radicals at potentials below those of the iron(III) derivatives.

The invariance of $E°$ would be expected if the iron(III) complexes were 1:1 electrolytes,[34] but this does not appear to

---

(24) Lexa, D.; Momenteau, M.; Mispelter, J.; Lhoste, J. M. *Bioelectrochem. Bioenerg.* **1974**, *1*, 108.

(25) Phillippi, M. A.; Shimomura, E. T.; Goff, H. M., unpublished results.

(26) (a) Caughey, W. S.; Johnson, L. F. *J. Chem. Soc. D* **1969**, 1362. (b) Caughey, W. S.; Eberspaecher, H; Fuchsman, W. H.; McCoy, S.; Alben, J. O. *Ann. N.Y. Acad. Sci.* **1969**, *153*, 722. (c) Brackett, G. C.; Richards, P. L.; Caughey, W. S. *J. Chem. Phys.* **1971**, *54*, 4383.

(27) Zerner, M.; Gouterman, M.; Kobayashi, H. *Theoret. Chim. Acta* **1966**, *6*, 363.

(28) Maltempo, M. M.; Ohlsson, P. I.; Paul, K. G.; Petersson, L.; Ehrenberg, A. *Biochemistry* **1979**, *18*, 2935.

(29) Phillippi, M. A.; Goff, H. M. *J. Am. Chem. Soc.* **1979**, *101*, 7641.

(30) Phillippi, M. A.; Goff, H. M., in preparation.

(31) Fajer, J.; Borg, D. C.; Forman, A.; Dolphin, D.; Felton, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3451.

(32) Schulz, C. E.; Devaney, P. W.; Winkler, H.; Debrunner, P. G.; Doan, N.; Chiang, R.; Rutter, R.; Hager, L. P. *FEBS Lett.* **1979**, *103*, 102.

(33) Kadish, K.; Davis, D. G.; Fuhrhop, J.-H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 1014.

(34) Boggess, R. K.; Hughes, J. W.; Coleman, W. M.; Taylor, L. T. *Inorg. Chim. Acta* **1980**, *38*, 183.

Table III. Half-Wave Oxidation Potentials for the Variously Substituted μ-Oxo Dimers of $[\mathrm{FeTPP(R)}]_2\mathrm{O}^a$

substituent, R	first	second	third
p-$\mathrm{OCH_3}$	0.71	0.89	1.33
o-$\mathrm{OCH_3}$	0.75	0.99	*b*
p-$\mathrm{CH_3}$	0.76	1.01	1.42
m-$\mathrm{CH_3}$	0.80	1.06	1.46
H	0.83	1.09	1.45
p-Cl	1.00	1.19	1.46

^{a} See legend of Table I. ^{b} Poorly resolved wave.

be the case.[15,24] Half-wave potentials must be a function of axial ligand complexation for both oxidized and reduced species. Chloride ion binds to $\mathrm{Fe^{III}}$TPP 10 orders of magnitude more effectively than perchlorate ion.[15] However, the fact that formation constants vary for species in Table I is not proof that porphyrin oxidation is taking place, as differences in potential are determined by a *ratio* of ligand equilibrium constants. Thus, potentials would remain constant if the ratios of anion binding constants for the iron(III) and the oxidized product were invariant. Although the constancy of this ratio cannot be refuted, it would appear fortuitous for anions of diverse charge, structure, and ligand field strength.

Oxidation potentials for natural-derivative iron(III) porphyrin dimethyl ester chloride monomers and μ-oxo-bridged dimers are reported for the first time in Table II. Both natural-derivative monomers and dimers exhibited the expected trend in potentials when considering inductive effects of the 2,4-position substituents, except that iron(III) protoporphyrin IX dimethyl ester was more easily oxidized than the deuteroporphyrin derivative. This anomalous result could well be due to a large resonance effect from the vinyl groups.

The μ-oxo-bridged dimer, $(\mathrm{FeTPP})_2\mathrm{O}$, is known to exhibit three reversible oxidation waves at substantially lower potentials than those for the parent monomer.[35] Phenyl-substituent effects have not been noted previously but would be expected to follow the inductive trends reported for respective monomers. This is indeed the case as is illustrated in Table III. Assignment of formal oxidation states in these species is complicated by the strong antiferromagnetic coupling between iron centers and probable electron delocalization through the μ-oxo bridge. However, proton NMR results reveal considerable π-spin density in the phenyl residues,[29] once again suggesting π-cation radical character.

Although the insensitivity of oxidation potentials for high-spin iron(III) porphyrin complexes was previously alluded to,[13-15] this work represents a systematic attempt to verify and explain the observation. The obvious explanation involving porphyrin-centered oxidation is not proven by cyclic voltammetric measurements alone but is further supported by spectroscopic measurements made on the oxidized products. It should be noted that this result is restricted to iron porphyrins with rather weak-field axial ionic ligands and is not necessarily applicable to hemoproteins such as horseradish peroxidase. Our interpretation does however dictate reexamination of molecular orbital calculations which assign the $d_{x^2-y^2}$ orbital of high-spin iron(III) and high-spin iron(IV) porphyrins as the HOMO and LUMO, respectively.

Acknowledgment is made to donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Support from the National Science Foundation, Grant CHE 79-10305, is also gratefully acknowledged.

Registry No. Fe(TPP)F, 55428-47-2; Fe(TPP)Cl, 16456-81-8; Fe(TPP)Br, 25482-27-3; Fe(TPP)I, 25482-28-4; $\mathrm{Fe(TPP)ClO_4}$, 57715-43-2; $\mathrm{Fe(TPP)SO_4}$, 76282-26-3; $\mathrm{Fe(TPP)NO_3}$, 76282-27-4; $\mathrm{Fe(TPP)N_3}$, 51455-98-2; Fe(TPP)NCS, 25482-29-5; Fe(TPP)OPh, 76282-28-5; Fe(TPP)-p-$\mathrm{CH_3C_6H_4SO_3}$, 76282-29-6; $\mathrm{Fe(TPP)HSO_4}$, 76282-30-9; ZnTPP, 14074-80-7; Mn(TPP)Cl, 32195-55-4; Fe(OEP)F, 41697-91-0; Fe(OEP)Cl, 28755-93-3; Fe(OEP)Br, 41697-92-1; $\mathrm{Fe(OEP)ClO_4}$, 50540-30-2; $\mathrm{Fe(OEP)SO_4}$, 76282-31-0; μ-oxo-bis[2,4-diethyldeuterohemin dimethyl ester], 58280-33-4; μ-oxo-bis[deuterohemin dimethyl ester], 23208-98-2; μ-oxo-bis[2,4-divinyldeuterohemin dimethyl ester], 36655-90-0; μ-oxo-bis[2,4-diacetyldeuterohemin dimethyl ester], 20394-29-0; μ-oxo-bis[2,4-dibromodeuterohemin dimethyl ester], 76282-32-1; 2,4-diethylchlorodeuterohemin dimethyl ester, 14126-91-1; chlorodeuterohemin dimethyl ester, 19442-32-1; 2,4-divinylchlorodeuterohemin dimethyl ester, 15741-03-4; 2,4-diacetylchlorodeuterohemin dimethyl ester, 18040-20-5; 2,4-dibromochlorodeuterohemin dimethyl ester, 15242-34-9; $[\mathrm{FeTPP}(p\text{-}\mathrm{OCH_3})]_2\mathrm{O}$, 37191-17-6; $[\mathrm{FeTPP}(o\text{-}\mathrm{OCH_3})]_2\mathrm{O}$, 37191-16-5; $[\mathrm{FeTPP}(p\text{-}\mathrm{CH_3})]_2\mathrm{O}$, 110080-08-3; $[\mathrm{FeTPP}(m\text{-}\mathrm{CH_3})]_2\mathrm{O}$, 51799-86-1; $[\mathrm{FeTPP}]_2\mathrm{O}$, 34830-12-1; $[\mathrm{FeTPP}(p\text{-}\mathrm{Cl})]_2\mathrm{O}$, 37191-15-4.

---

(35) Kadish, K. M.; Cheng, J. S.; Cohen, I. A.; Summerville, D. *ACS Symp. Ser.* **1977**, *No. 38*, 65.

Contribution from the Department of Chemistry,
The University of Oklahoma, Norman, Oklahoma 73019

High-Pressure Reactions of Small Covalent Molecules. 12. Interaction of PF_3 and SF_6

Arnulf P. Hagen* and Donald L. Terrell

Received July 25, 1980

Sulfur hexafluoride, a normally unreactive substance, has been shown to have an exciting reaction chemistry at increased pressure and temperature.[1] In this study it has been shown to readily oxidize phosphorus trifluoride.

Experimental Section

A borosilicate glass vacuum system with Teflon stopcock keys (Fischer & Porter Co., Warminster, PA) was employed to purify and analyze volatile materials. All apparatus which were employed to manipulate sulfur tetrafluoride were pretreated with trimethylchlorosilane and sulfur tetrafluoride to remove water. Volatile products were identified by infrared spectroscopy and confirmed by Dumas gas-phase molecular weight measurement.

Phosphorus trifluoride (Ozark-Mahoning, Tulsa, OK) was purified by passing the commercial mixture through traps at −96 °C (toluene slush) and −145 °C (pentane/isopentane mixture) into a liquid-nitrogen trap. The material which stopped in the −145 °C trap was employed in this study. Sulfur hexafluoride and sulfur tetrafluoride (Matheson) were used as obtained. Sulfur was recrystallized from carbon disulfide prior to use.

High pressures were generated with a gas pressure booster (High Pressure Equipment Co., Erie, PA) attached to a high-pressure hydrothermal research unit (Model HB-1B-4, Tem-Pres Research, State College, PA). The samples were contained in ampules made from 3 mm diameter thin-walled gold tubing which were placed into a high-pressure reactor (Tem-Pres). Nitrogen gas was used to generate the desired pressure. At the end of a reaction period the reactor was cooled to −196 °C before the pressure was released. The ampule was removed and placed into an opening device attached to the vacuum line.

Infrared spectra were obtained in the 4000–300-$\mathrm{cm^{-1}}$ region with a Beckman Model IR-10 double-beam, grating spectrophotometer. Volatile materials were confined in a 100-mm gas cell fitted with KBr windows sealed with rubber O-rings at reduced pressure.

Reaction of PF_3 and SF_6. Phosphorus trifluoride (42 mg, 0.48 mmol) and $\mathrm{SF_6}$ (65 mg, 0.45 mmol) were condensed into a gold tube at −196 °C. The tube was sealed and held at 387 °C (1800 atm) for 24 h. The gold ampule was opened and an infrared spectrum of the mixture obtained. Standard calibrated infrared spectra were used to obtain the amount of each substance in the mixture: $\mathrm{PF_5}$ (36 mg,

---

(1) Hagen, A. P.; Callaway, B. W. *Inorg. Chem.* **1975**, *14*, 2825

0020-1669/81/1320-1325$01.25/0