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-OCH$_3$	0.71	0.89	1.33
o-OCH$_3$	0.75	0.99	*b*
p-CH$_3$	0.76	1.01	1.42
m-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 Fe$^{\mathrm{III}}$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; Fe(TPP)ClO$_4$, 57715-43-2; Fe(TPP)SO$_4$, 76282-26-3; Fe(TPP)NO$_3$, 76282-27-4; Fe(TPP)N$_3$, 51455-98-2; Fe(TPP)NCS, 25482-29-5; Fe(TPP)OPh, 76282-28-5; Fe(TPP)-p-CH$_3$C$_6$H$_4$SO$_3$, 76282-29-6; 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; Fe(OEP)ClO$_4$, 50540-30-2; 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; $[\mathrm{FeTPP}(p\text{-OCH}_3)]_2\mathrm{O}$, 37191-17-6; $[\mathrm{FeTPP}(o\text{-OCH}_3)]_2\mathrm{O}$, 37191-16-5; $[\mathrm{FeTPP}(p\text{-CH}_3)]_2\mathrm{O}$, 110080-08-3; $[\mathrm{FeTPP}(m\text{-CH}_3)]_2\mathrm{O}$, 51799-86-1; $[\mathrm{FeTPP}]_2\mathrm{O}$, 34830-12-1; $[\mathrm{FeTPP}(p\text{-Cl})]_2\mathrm{O}$, 37191-15-4.

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High-Pressure Reactions of Small Covalent Molecules. 12. Interaction of PF$_3$ and SF$_6$

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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-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 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: PF$_5$ (36 mg,

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Table I. SF_6 and PF_3 Reaction Parameters[a]

pressure, atm	temp, °C	conversion, %[b]	products
1600	335		no reaction
2700	284		no reaction
1800	387	60	SF_6, PF_3, PF_3, SPF_3
2800	366	29	SF_6, PF_3, PF_5, SPF_3
3600	379	42	SF_6, PF_3, PF_5, SPF_3
233	424	42	SF_6, PF_3, PF_5, SPF_3
20	500	74	SF_6, PF_3, PF_5, SPF_3
300	500	100	SF_6, PF_5, S
1333	541	100	SF_6, PF_5, SF_4
567	580	91	SF_6, PF_5, SF_4

[a] Approximately equimolar amounts of each reactant were employed for a total of 1.0–2.0 mmol of reactants. [b] Yield on the basis of the amount of PF_5 formed.

0.29 mmol), SPF_3 (11 mg, 0.10 mmol), SF_6 (51 mg, 0.35 mmol), and PF_3 (8.8 mg, 0.10 mmol).[2-5]

Additional experiments were carried out to define the reaction parameters up to 600 °C (3000 atm). Selected results are summarized in Table I.

Reaction of SF_6 and S. Sulfur hexafluoride (121 mg, 0.83 mmol) and sulfur (0.3 mg) were sealed in a gold tube. The tube was heated at 538 °C (2000 atm) for 24 h. The tube was opened; SF_6 (80 mg, 0.55 mmol), SF_4 (44 mg, 0.41 mmol), and sulfur (9 mg) were recovered.[6-7] No reaction took place at 426 °C (2.33 atm).

Reaction of SF_4 and PF_3. Sulfur tetrafluoride (45 mg, 0.41 mmol) and phosphorus trifluoride (53 mg, 0.60 mmol) were sealed in a gold tube and heated at 324 °C (2133 atm) for 24 h. Upon opening of the ampule, the only volatile substance was PF_5 (68 mg, 0.54 mmol).

Reaction of PF_3 and S. Phosphorus trifluoride (45 mg, 0.53 mmol) and sulfur (30 mg) were sealed in a gold tube and heated at 120 °C (133 atm) for 24 h. Phosphorus trifluoride (8.8 mg, 0.10 mmol) and SPF_3 (52 mg, 0.43 mmol) were recovered.

Results and Discussion

Thermodynamic calculations using standard-state data indicate that sulfur hexafluoride should react with phosphorus trifluoride to form PF_5 and SPF_3, S, SF_2, or SF_4 depending on the availability of phosphorus trifluoride.[8] However, no reaction is observed at 20-atm pressure until the reaction is heated above 400 °C. Reaction does occur at lower temperatures when the pressure is increased; however, the best conversions to PF_5 occur at high temperatures.[9]

The observed products are best explained by the reaction sequence (1)–(5).

$$SF_6(g) + PF_3(g) \rightarrow SF_4(g) + PF_5(g) \tag{1}$$

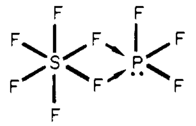
$$SF_4(g) + PF_3(g) \rightarrow SF_2(g) + PF_5(g) \tag{2}$$

$$SF_2(g) + PF_3(g) \rightarrow {}^1/_8S_8(s) + PF_5(g) \tag{3}$$

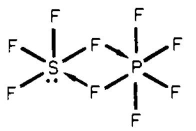
$${}^1/_8S_8(s) + PF_3(g) \rightarrow SPF_3(g) \tag{4}$$

$${}^1/_8S_8(s) + 2SF_6(g) \rightarrow 3SF_4(g) \tag{5}$$

The first step (eq 1) can be postulated as the linking of SF_6 and PF_6 to form a coordinated intermediate:



A bridged structure would be reasonable on the basis of the large number of known substances with fluorine bridges. This intermediate is isomeric with the known complex formed between SF_4 and PF_5



which is believed to have the structure SF_3^+,PF_6^- with enough distortion to have S–F–P bridges.[10-12] Average bond energies for the fluorine linkages of PF_5 (111 kcal/mol), PF_3 (121 kcal/mol), SF_6 (78 kcal/mol), and SF_4 (78 kcal/mol) support the transfer of fluorine from sulfur to phosphorus.[8,13] The bond formation energy for the attachment of a fluorine atom to PF_3 is about 119 kcal,[14] and the first dissociation energy for SF_6 is about 91 kcal.[15] The transfer of a fluorine from SF_6 to PF_3 to form PF_4 and SF_5 is therefore thermodynamically reasonable. These substances can then react further to form the observed products.

Sulfur tetrafluoride is a well-known fluorinating agent. Steps 2 and 3 have not been verified; however, the sum of these steps readily occurs (eq 6). The interaction between sulfur

$$SF_4(g) + 2PF_3(g) \rightarrow {}^1/_8S_8(s) + 2PF_5(g) \tag{6}$$

and phosphorus trifluoride takes place at conditions as low as 120 °C (133 atm).

At the highest temperatures (greater than 500 °C and 500 atm) sulfur tetrafluoride is recovered when phosphorus trifluoride is not available to react with the excess sulfur. The direct reaction of SF_6 with sulfur occurs at 538 °C (500 atm) but not at 426 °C (2133 atm). At lower conditions no SF_4 is recovered since PF_3 reacts very quickly with it to form PF_5 and sulfur. Sulfur is recovered when PF_3 is not available to react, and SPF_3 forms when it is available.

Thermodynamic calculations for reactions 4 and 5 are interesting: when ΔG is plotted as a function of temperature at about 250 °C, the reactions have the same free energy (approximately −12 kcal) and at 500 °C the SF_6 reaction is about 20 kcal more negative.[13] This implies that reaction 7

$$SPF_3(g) + 2SF_6(g) \rightarrow 3SF_4(g) + PF_3(g) \tag{7}$$

should occur; however, this set of products has not been observed. Phosphorus pentafluoride has been recovered from this interaction as well as sulfur (eq 8).

$$SPF_3(g) + SF_6(g) \rightarrow SF_4(g) + PF_5(g) + {}^1/_8S_8(g) \tag{8}$$

Acknowledgment. We are indebted to Bill W. Callaway and Susan Wilburn for technical assistance. The support of the Energy Resources Center of The University of Oklahoma for portions of this work is gratefully acknowledged.

Registry No. PF_3, 7783-55-3; SF_6, 2551-62-4; S_8, 10544-50-0; SF_4, 7783-60-0; PF_5, 7647-19-0; SPF_3, 2404-52-6.

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