Other effects, exerted by protons in oxidoreductases, concern, e.g., redox potentials,[17] oxidation states,[18] geometries,[19] and coupling to electron-transfer reactions.[20]   Here, the reactions of [Ru-(PPh₃)(S₄)] complexes yield models for H⁺-coupled substitution

reactions. Ligand exchange at transition-metal–sulfur centers is much more complicated than expressed by eq 1 and can involve several protonation and deprotonation steps.

As shown by Scheme I, the protons take over a definite role in the release and coordination of ligands (substrates), which becomes important when L and Z represent *soft* and *hard* substrates, respectively. The state of protonation determines which kind of substrate is bound.

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Instability of the Nitrite/Iron(III) Porphyrinate System

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Reactions of (porphinato)iron(III) complexes (porphyrin = H₂TPP, H₂TTP, and H₂OEP) with nitrite ion have been investigated by means of attempted product isolation, UV–visible spectroscopy, solution IR and EPR spectroscopy, and a study of the time dependence of the reaction system. All observations are consistent with an instability of this system that leads not to coordinated nitrite species but rather to the production of iron nitrosyl complexes. These nitrosyl species appear to be formed by single oxygen atom transfer from a coordinated nitrite ion to an uncoordinated nitrite ion.

Hemoprotein reactions of nitrite ion are widespread. Assimilatory nitrite reductases catalyze the six-electron reduction of nitrite ion to ammonia,[1] while the dissimilatory nitrite reductases[2] reduce nitrite ion to nitrous oxide, nitric oxide, or dinitrogen. The assimilatory enzymes possess a heme prosthetic group of the isobacteriochlorin type, called siroheme, which serves as the binding and reactive site.[3] Introduction of nitrite to the reduced enzyme results in the rapid formation of a nitrosyl complex of the heme.[4]   The nitrosyl complex is also observed as the steady-state species during enzyme turnover. The dissimilatory nitrite reductases contain four hemes, two of c and two of d₁. Heme d₁ has recently been shown to be a dioxoisobacteriochlorin,[5] and again there is the probable intermediacy of a nitrosyl complex in the catalytic reaction.

The reduction of nitrite to ammonia has been mimicked electrochemically in aqueous solution by utilizing a number of iron or ruthenium complexes, including water-soluble iron porphyrinate complexes.[6]   These systems also suggest the intermediacy of a nitrosyl complex in the reductive pathway. Adler et al.[7] have described reactions of nitrite with hemoproteins that are suggested

as potentially harmful. Finally, nitrite interactions with hemoproteins form seemingly important complexes in meat-curing processes.[8]

Despite the apparent importance of the interaction of nitrite with hemoproteins, there appeared to have been little work done on the interaction of nitrite with iron porphyrinate complexes. Several years ago, we began such an investigation with a primary goal of synthesizing nitrite-coordinated iron porphyrinate complexes. Questions that we wanted to resolve included a determination of stoichiometry, spin state of the species, mode of ligand binding (N- or O-bound; mono- or bidentate), the possible effects of other axial ligands, and the assignment of definitive spectroscopic parameters. Although the formation of such nitrite species should be possible by means of straightforward metathesis processes, we found that iron(III) porphyrinate/nitrite systems do not yield the expected nitrite complexes. Rather, the systems yield nitrosyl complexes under a variety of conditions. Our finding of this apparent instability of the desired nitrite complex seems to be in distinct contrast to a report that appeared while this work was in progress. This paper[9] implies that (porphinato)iron(III) nitrite complexes are relatively stable. While we concur with at least some of the spectroscopic properties reported, which are reasonably interpreted in terms of forming nitrite complexes, we also believe that these complexes undergo subsequent reaction rather quickly.

Our work leads us to conclude that the dominating feature of the porphinatoiron(III)/nitrite system is the loss of an oxygen atom from coordinated nitrite to yield an iron NO complex. These conclusions about this reaction system are derived from product isolation, time-dependent solution EPR and IR spectroscopy, UV–visible spectra and a kinetic analysis of the (porphinato)-iron(III)/nitrite system. We have also briefly explored reactions related to this system. We have examined the reaction of nitrosyliron complexes with excess nitrite ion and finally we have

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examined the stability of nitrosyliron complexes under oxidizing conditions.

Experimental Section

General Data. Dichloromethane was dried by distillation from CaH_2 under argon. Dimethylformamide was dried by vacuum distillation (40 Torr, 65 °C) from CaH_2. All other solvents were dried by distillation from sodium or potassium benzophenone ketyl under argon. All procedures were carried out under argon in Schlenk-type vessels. Nitrite salts of Bu_4N^+,[10] Ph_4P^+, Ph_4As^+, and PPN^+ were prepared by metathesis of the chloride or bromide salt with potassium nitrite in water or water/ethanol[11] and vacuum-dried at the appropriate elevated temperature (44 °C for Bu_4N^+ and 140 °C for the others). These salts were stored and weighed in a Vacuum Atmospheres drybox. Silver nitrite and H_2OEP were purchased from Aldrich Chemical Co. H_2TPP and H_2TTP were prepared by the method of Adler et al.[12] Iron was inserted into the porphyrin ligand by the $FeCl_2/DMF$ method.[13] Published methods were used to prepare perchlorato,[14] nitrato,[15] and nitrosyl[16] complexes of the iron porphyrin species. Iodosobenzene was prepared by the reaction[17] of sodium hydroxide with iodosobenzene diacetate (Aldrich). N,N-Dimethylaniline N-oxide was prepared through oxidation of N,N-dimethylanaline by m-chloroperbenzoic acid.[18] Ultraviolet–visible spectra were taken on a Varian Model DMS-100 spectrometer or a Perkin-Elmer Model Lambda 4C spectrometer. Infrared spectra were obtained with a IBM Model IR/32 Fourier transform infrared spectrometer using either KBr pellets or solutions. EPR spectra were recorded on a Varian E-line Century Series EPR spectrometer.

Solutions for ultraviolet–visible spectroscopic studies (including kinetic studies) were prepared by the following procedure: A solution of the iron porphyrin complex was prepared in a septum-sealed flask. The appropriate volume of this solution was then injected into an argon-flushed, septum-sealed spectrophotometric cell containing a known amount of Ph_4PNO_2. Additional solvent was added (syringe) if necessary. The cell was shaken to insure complete dissolution and mixing and then placed in the spectrometer at ambient temperature (23 °C). Multiple spectroscopic scans were taken over the range 350–600 nm. The largest spectral changes occur at 538 and 508 nm and these were chosen for kinetic studies. Tangents to plots of absorbance vs time were used to generate instantaneous rates.

Solutions for infrared or EPR studies were prepared by dissolution of a mixture of the porphyrin complex and a nitrite salt in a septum-sealed flask. The solution was immediately transferred (syringe) to an infrared cell or quartz EPR tube that had been sealed with a septum and flushed with argon. The cell or tube was then placed in the spectrometer. We noted that solutions of nitrite in dichloromethane are susceptible to "aging". Hence, all work in dichloromethane solution used freshly prepared solutions.[19] Complete experimental details may be seen elsewhere.[20]

(10) Abbreviations used: Bu_4N^+, tetra-n-butylammonium; Ph_4P^+, tetraphenylphosphonium; Ph_4As^+, tetraphenylarsonium; PPN^+, bis(triphenylphosphine)nitrogen(1+); DMF, dimethylformamide; THF, tetrahydrofuran; H_2TPP, tetraphenylporphyrin; H_2TTP, tetratolylporphyrin; H_2OEP, octaethylporphyrin; $H_2TpivPP$, *meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis(o-pivalamidophenyl)porphyrin (picket-fence porphyrin); H_2P, generalized porphyrin; EPR, electron paramagnetic resonance.
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(19) A reviewer has pointed out a recent paper (Fanning, J. C.; Keefer, L. K. *J. Chem. Soc., Chem. Commun.* **1987**, 955) reporting the solvolysis of the PPN^+ salt in dichloromethane. We observed a similar decomposition with the Ph_4P^+ salt, although the process appears slower than that reported for the PPN^+ salt. Aged solutions behave similarly to freshly prepared dichloromethane solutions except for the effects of an apparent decrease in nitrite ion concentrations. However, we emphasize that we observe no solvent-dependent reactions of the nitrite/iron(III) porphyrinate system when the solvents are dry (judged in terms of final products of the reaction). Wet solvents can of course lead to the formation of μ-oxo species. As shown in Table I, initially formed intermediates do show solvent dependence.

Table I. Summary of Electronic Spectra

species	solvent	band maxima, nm	ref
$Fe(TPP)OClO_3$	CH_2Cl_2	399, 517, 570 (sh), 672	this work
$Fe(TPP)OClO_3 +$ NO_2^- (complex 1)	CH_2Cl_2	417, 508, 570 (sh), 650, 687	this work
$[Fe(TPP)(DMF)_2]^+$	DMF	402, 530, 699	this work
$[Fe(TPP)(DMF)_2]^+ +$ NO_2^- (complex 1)	DMF	417, 556, 604, 640	this work
"$Fe(TPP)(NO_2)_2^-$"	CH_2Cl_2	426, 540, 576 (sh), 602 (sh)	9
"$Fe(TPP)(NO_2)_2^-$"	DMF	420, 560, 608 (sh), 690 (sh)	9
$Fe(TPP)NO$	CH_2Cl_2	408, 536, 570 (sh), 606	this work
$[Fe(TPP)(NO)(ONO)]^-$	CH_2Cl_2	430, 540, 565 (sh), 604	this work
$[Fe(TpivPP)(NO_2)_2]^-$	CH_2Cl_2	424, 551, 651	24
$[Fe(TpivPP)(NO_2)_2]^-$	DMF	425, 552	24
$[Fe(TpivPP)(NO_2)_2]^-$	toluene	424, 551	24
$[Fe(TpivPP)(NO_2)(py)]$	CH_2Cl_2	420, 546	a
$Fe(TPP)NO_3$	CH_2Cl_2	412, 513, 574	15

^{a} Nasri, H. Work in progress.

Attempted Metathesis Reactions. A total of 50–250 mg of [Fe(TPP)Cl] or [Fe(OEP)Cl] was stirred with a slight excess (1–3%) of silver nitrite in THF for periods ranging from 3 h to 3 days and at temperatures ranging from ambient to that of the boiling point of THF. Solutions were then filtered to remove the silver chloride precipitate. The porphyrin product(s) was recovered by vacuum evaporation of the solvent or addition of a nonsolvent (hexane, heptane). This procedure was repeated with [Fe(OEP)Cl] in 1,2-dimethoxyethane and ethyl acetate. Chloride, bromide, nitrate, and perchlorate complexes of several iron porphyrin species (H_2TPP, H_2OEP, H_2TTP) were allowed to react with quantities of nitrite ion (as the Bu_4N^+, Ph_4P^+, Ph_4As^+, or PPN^+ salt) ranging from stoichiometric to a 6-fold excess in various solvents (CH_2Cl_2, toluene, THF, DMF, or benzene). Concentrations of the iron porphyrin complex ranged from 0.16 to 14.2 mM. Reaction times ranged from 1 h upward. Products were recovered by solvent evaporation under vacuum or by the addition of a nonsolvent.

Results and Discussion

Attempted metathesis reactions between chloro(porphinato)iron(III) complexes (porph = H_2TPP or H_2OEP) and silver nitrite or perchlorato(porphinato)iron(III) complexes (H_2TPP, H_2OEP, or H_2TTP) and nitrite salts (Ph_4P^+, Bu_4N^+, and PPN^+ cations) resulted only in the isolation of nitrosyl complexes rather than the expected nitrite complexes.[21] The nitrosyl complexes were often accompanied by nitrato complexes, particularly when the nitrite/(porphinato)iron(III) ratio was low. Species identification was primarily done by IR and UV–vis spectroscopy. The formation of nitrosyl complexes occurs in the presence or absence of Lewis bases (pyridine, imidazoles) and was observed over a wide range of solvents and concentrations. No evidence from these reactions (vibrational spectra of solids were especially closely examined) was ever found for the existence of a bona fide nitrite complex.

The electronic spectrum of [Fe(TPP)OClO_3] in dichloromethane [λ_{max} (ϵ): 399 (9.3 × 10^4), 517 (9.7 × 10^3), 570 (sh), 672 nm (2.7 × 10^3)] changes immediately upon addition of nitrite to produce a species with the following spectral characteristics: 417 (1.2 × 10^5), 508 (9.6 × 10^3), 570 (sh), 650 (2.4 × 10^3), 687 nm (2.4 × 10^3). The identical spectrum is produced upon addition of nitrite ion to a dichloromethane solution of [Fe(TPP)NO_3]. In dimethylformamide, the anion (perchlorate or nitrate) is displaced by the solvent producing a [Fe(TPP)(DMF)_2]^+ complex.[14,22] The spectrum of this complex [402 (9.4 × 10^4), 530

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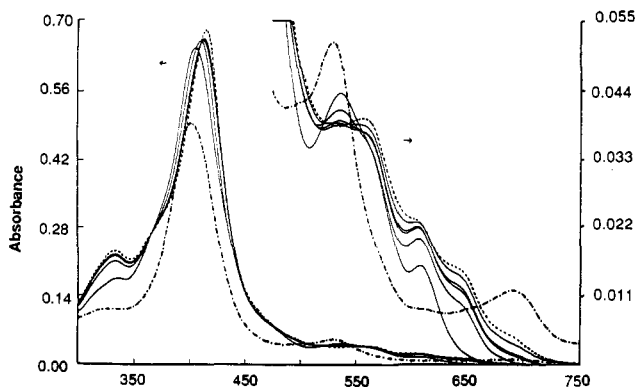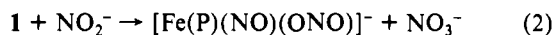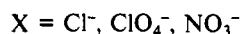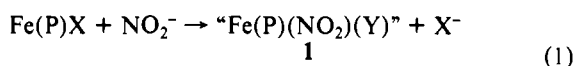
Figure 1. Visible spectra in N,N-dimethylformamide: 5.3 mM [Fe(T-PP)OClO$_3$] (−·−), + 5.46 mM PH$_4$PNO$_2$ (−·). Solid lines show the conversion to the nitrosyl species. Reaction times: 202, 602, 2113, 3222, 6643 s.

Figure 2. Infrared spectrum of the reaction of 13.3 mM [Fe(TPP)O-ClO$_3$] and 30.3 mM Ph$_4$PNO$_2$ in Ch$_2$Cl$_2$ after 16 h. The CH$_2$Cl$_2$ spectrum is overlaid (dashed line). Peaks due to [Fe(TPP)NO], [Fe(T-PP)(NO)(NO$_2$)]$^-$, and unbound nitrate and the shoulder due to perchlorate are labeled.

(1.3 × 10^4), 699 nm (2.3 × 10^3)] changes upon addition of nitrite ion to produce a species with the following spectral features: 417 (1.2 × 10^5), 556 (7.5 × 10^3), 604 (sh), 640 nm (sh). The large spectral changes induced by addition of nitrite to solutions of ferric porphyrin complexes suggest an interaction of these complexes and nitrite ion. The resulting spectra are assigned to a species we call complex 1 and which we interpret as a (porphinato)-iron(III) nitrite complex. The exact nature of this species is not clear. We can not be certain of the stoichiometry (mono or bis), mode of ligation or solvation state of this apparent nitrite species.[23] It is to be noted that the spectra of the species we call complex 1 are similar but not identical with those reported by Fernandes et al.[19] and labeled as bis(nitro) complexes (cf. Table I). More importantly, however, complex 1 is not stable. The electronic spectrum of solutions of complex 1 can be seen to change within minutes of preparation. The reaction proceeds at a moderate rate, requiring several hours to reach completion. The resulting spectrum is that of a nitrosyliron porphyrin complex. Figure I illustrates the spectral changes observed upon addition of nitrite ion to a DMF solution of [Fe(TPP)OClO$_3$] and the subsequent conversion of complex 1 to [Fe(TPP)NO]. We interpret these data in terms of the formation of a nitrite complex that reacts with excess nitrite ion to produce the nitrosyl complex:

$$\text{Fe(P)X + NO}_2^- \rightarrow \text{"Fe(P)(NO}_2\text{)(Y)"} + \text{X}^-$$
$$\mathbf{1}$$

$$\text{X = Cl}^-,\ \text{ClO}_4^-,\ \text{NO}_3^- \tag{1}$$

$$\mathbf{1} + \text{NO}_2^- \rightarrow [\text{Fe(P)(NO)(ONO)}]^- + \text{NO}_3^- \tag{2}$$

There are also indications of further interaction between the nitrosyl complex and excess nitrite ion as shown in eq 2 (vide infra).

This reaction sequence is also supported by other spectroscopic data. First, a dichloromethane solution containing 11.8 mM [Fe(TPP)NO$_3$] and 15.6 mM Ph$_4$PNO$_2$ exhibits a triplet EPR spectrum characteristic of the nitrosyl complex (g = 2.05, a = 17 G)[25] within 30 min of preparation. This EPR signal increases in intensity with time.

Second, the initial infrared spectrum of a dichloromethane solution containing 14.1 mM [Fe(TPP)NO$_3$] and 26.4 mM Ph$_4$PNO$_2$ is notable for the complete absence of an absorbance
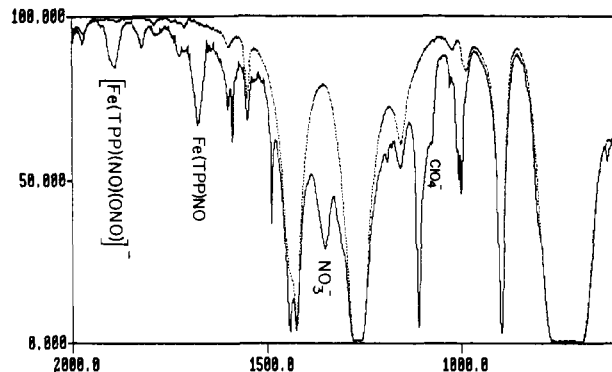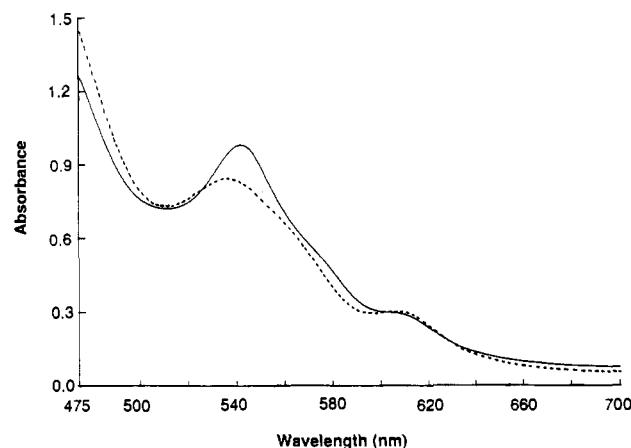

Figure 3. Spectral changes observed upon addition of nitrite to a dichloromethane solution of [Fe(TPP)NO]: (−·) 0.096 mM [Fe(TPP)N-O]; (—) 0.096 mM [Fe(TPP)NO] + 20.0 mM Ph$_4$PNO$_2$.

band due to bound nitrate ion at 1520 cm^{-1} and the presence of an absorbance band at 1340 cm^{-1} due to free nitrate ion. Bands due to ionic nitrite (∼1230 cm^{-1}) can be detected although they are partially obscured by solvent absorption bands. It is possible that additional bands due to bound nitrite are completely hidden by solvent absorbances. Initially, no other new infrared absorbances are observed. Similar spectral changes are observed with [Fe(TPP)OClO$_3$]. However, these IR spectra change with time. A dichloromethane solution containing either 11.8 mM [Fe(TP-P)NO$_3$] or [Fe(TPP)OClO$_3$] and 15.6 mM Ph$_4$PNO$_2$ begins to exhibit the N–O stretch of the nitrosyl complex (1670 cm^{-1})[16] within an hour of preparation (Figure 2). The infrared spectra also indicate the formation of additional nitrate ion (band at 1340 cm^{-1}) in accord with eq 2. As the reaction progresses, a third absorbance band appears at 1891 cm^{-1}. This band is similar to an infrared band produced by reaction of [Fe(TPP)NO] with excess nitric oxide, which has been attributed to either a bis-(nitrosyl) complex[25] or a nitrosyl–nitrogen dioxide complex.[26] However, the reported positions of the infrared absorbance of these species are 1880–1884 cm^{-1} rather than the 1891 cm^{-1} we observe.

The electronic spectrum of this nitrosyl complex (formed in the reaction of ferric porphyrin/nitrite system) is not precisely that of the five-coordinate nitrosyl complex, but is identical with the spectrum obtained from the addition of nitrite ion to a solution of [Fe(TPP)NO]. This, together with the new infrared band, leads us to the conclusion that the product of this series of reactions may be a nitrosyl–nitrito complex: [Fe(TPP)(NO)(ONO)]$^-$, analogous to the [Fe(TPP)(NO)Cl]$^-$ complex reported by Wayland and Olson.[22] The lack of additional splitting in the EPR spectrum is also consistent with the formation of an O-bonded

(22) Bottomley, L. A.; Kadish, K. M. *Inorg. Chem.* **1981**, *20*, 1348.

(23) For simplicity, we call this species (or more probably the several closely related species) complex 1. A summary of spectral characteristics of several species related to complex 1 is given in Table I. The UV–vis spectrum of a bona fide bis(nitro) complex,[24] obtained by use of picket-fence porphyrin strategies, does not match that of complex 1. From the various spectroscopic and reactivity data, the best chemical formula for complex 1 is Fe(P)(NO$_2$)(Y) where Y may either be solvent, O-bonded nitrite, or another anion. For the reacting species, we prefer the formulation involving O-bonded nitrite although we have no direct evidence for this. (See Note Added in Proof.)

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(25) Wayland, B. B.; Olson, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 6037.

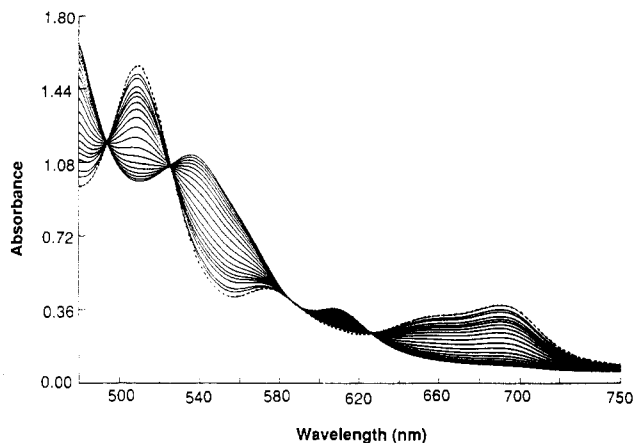(26) Yoshimura, T. *Inorg. Chim. Acta* **1984**, *83*, 17.

Figure 4. Spectral changes observed upon addition of Ph_4PNO_3 (0.442 mM), and trace amounts of Ph_4PNO_2 (<10 μM) to a 0.116 mM CH_2Cl_2 solution of [Fe(TPP)NO]. Spectra were taken every 15 min. Final spectrum is shown as a dashed line.

nitrite adduct. Analogous ruthenium complexes have been characterized.[27] The isolation of a neutral [Fe(TPP)(NO)(NO$_2$)] complex has also been reported.[28] This compound has a visible spectrum different from that of our species. This may be ascribed to an effective change in the oxidation state of the iron.

We have examined the possible existence of the [Fe(TPP)(N-O)(ONO)]$^-$ species by adding nitrite ion directly to solutions of [Fe(TPP)NO]. The resulting spectral changes are shown in Figure 3. Attempts to isolate this species are unsuccessful, yielding only the five-coordinate nitrosyl starting complex. This apparent nitrosyl–nitrito complex has moderate stability. It will decompose if left in solution overnight. The instability of this complex is greatly enhanced by the presence of nitrate ion. If a mixture of nitrate ion *and* nitrite ion are added to a dichloromethane solution of [Fe(TPP)NO], the complex rapidly decomposes, producing the chloro complex, [Fe(TPP)Cl]. It is to be emphasized that both nitrate and nitrite ions must be present. The electronic spectra of [Fe(TPP)NO] is unperturbed by the presence of excess nitrate ion, and no instability is noted under these conditions. However, if trace amounts of nitrite ion are added to a solution containing [Fe(TPP)NO] and excess nitrate ion, the spectrum due to [Fe(TPP)NO] diminishes with the concurrent appearance of the spectrum due to [Fe(TPP)Cl]. The isosbestic behavior of the [Fe(TPP)NO] system in the presence of nitrate and trace nitrite is shown in Figure 4.

The evidence suggests that the initial decomposition reaction of complex 1 involves loss of an oxygen atom to give [Fe(TP-P)(NO)(ONO)]$^-$. We have studied the reaction as a function of time in an attempt to understand the reaction system. Unfortunately, the reaction is complex and presents considerable difficulties for kinetic analysis.[29] Initial reactions involved in the formation of complex 1 intermediates are too rapid for conventional kinetic analysis and were not examined further. Subsequent reactions of complex 1 also present problems since they are multiphasic, consisting of a series of steps, identifiable by shifts in the isosbestic points, which under some conditions are well-defined and under others are rather poorly defined. Initial reaction of complex 1 leads to formation of an intermediate assigned as [Fe(TPP)(NO)(ONO)]$^-$, but further reactions leading to [Fe(TPP)Cl] interfere with the kinetics of this process to a degree that lacks (complete) reproducibility from one solution to another. An additional problem that hampered the study of the initial
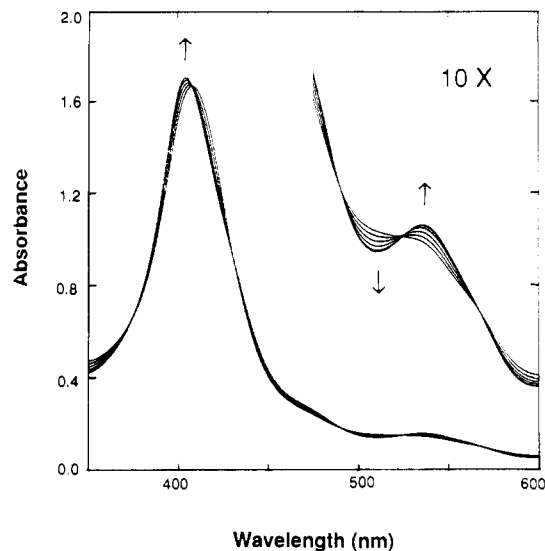

Figure 5. Spectral changes observed in the reaction of 0.0818 mM [Fe(TPP)OClO$_3$] and 2.115 mM Ph$_4$PNO$_2$ in CH$_2$Cl$_2$.

decomposition was limited reproducibility ascribed to trace impurities. For example, in some reaction mixtures, the initial decomposition of complex 1 exhibited a brief induction period, zero order in [complex 1] and [NO$_2^-$] but dependent on the amount of nitrite solution added. Some kinetic information was obtained from the initial rate of decomposition of complex 1 monitored at both 538 and 508 nm (Figure 5). The [complex 1] rate dependence is difficult to ascertain with the small concentration range available. Curvature in plots of absorbance vs time suggest a first-order dependence on complex 1, and this is assumed in the subsequent analysis. The instantaneous rate is dependent on [NO$_2^-$], consistent with the rate law

$$-d[\text{complex 1}]/dt = k[\text{complex 1}][NO_2^-]$$

The mode of reaction in the nitrite/iron(III) porphyrinate system is thus proposed to be single O atom transfer from coordinated nitrite to uncoordinated nitrite:

$$[Fe(P)(NO_2)(ONO)]^- + NO_2^- \rightarrow$$
$$[Fe(P)(NO)(ONO)]^- + NO_3^-$$
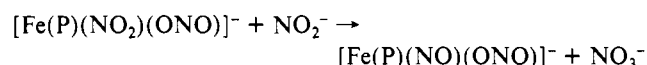
Although to our knowledge iron porphyrinate systems have not been previously documented, single O atom transfer reactions of coordinated nitrite are well-known.[30] A number of these single O atom transfer reactions involve the active participation of nitrocobalt(III) porphyrin species[30,31] that have been used as a catalytic oxidant for alkenes, phosphines, and alcohols with either the known or presumed intermediacy of nitrosyl and nitro complexes. Additionally, the oxidation of nitrite ion by transition-metal nitro complexes is known.[32] Thus, the general chemical processes that are suggested here for the nitrite/iron(III) porphyrinate system are well precedented for related chemical systems.

The catalytic nitro(porphinato)cobalt(III) systems are known to display facile nitro/nitrosyl interconversion. Hence, we have briefly examined the oxidation of nitrosyl(porphyrinato)iron(II) (H$_2$TPP, H$_2$OEP, H$_2$TTP) by controlled reaction with dry dioxygen or single oxygen atom transfer reagents. Solutions of [Fe(TPP)NO] show the largest reactivity toward oxidation with

(27) Carrondo, M. A. A.; Rudolf, P. R.; Shapski, A. C.; Thornback, J. R.; Wilkinson, G. *Inorg. Chim. Acta* **1977**, *24*, L95. Abraham, F.; Nowogrocki, G.; Sueur, S.; Bremard, C. *Acta Crystallogr., Sect. C* **1983**, *C39*, 838.

(28) Settin, M. C.; Fanning, J. C. *Inorg. Chem.* **1988**, *27*, 1431.

(29) Solvent choices are limited by the inadequate range of solubility for some reactants or relatively easy formation of unwanted side products. Nitrite ion slowly decomposes in dichloromethane, the solvent eventually used, and freshly prepared solutions are required.

(30) For a comprehensive bibliography of O atom transfer reactions of transition-metal nitro complexes, see: Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. *Organometallics* **1985**, *4*, 268.

(31) (a) Tovrog, B. S.; Diamond, S. E.; Mares, F.; Szalkiewics, A. *J. Am. Chem. Soc.* **1981**, *103*, 3522. (b) Diamond, S. E.; Mares, F.; Szalkiewics, A.; Muccigrosso, D. A.; Solar, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4266. (c) Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 6616.

(32) (a) Keene, F. R.; Salmon, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2385. (b) Keene, F. R.; Salmon, D. J.; Walsh, J. L.; Abruna, H. D.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1896. (c) Abruna, H. D.; Walsh, J. L.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* **1981**, *20*, 1481.

dioxygen, reacting so rapidly that the electronic spectrum must be obtained under rigorously anaerobic conditions. [Fe(TTP)NO] and [Fe(OEP)NO] are somewhat more resistant to oxidation. When the reaction with dry dioxygen is carried out in sealed reaction vessels, all three porphyrin species yield primarily [Fe-(P)NO$_3$]. Only μ-oxo derivatives are found when the reaction is allowed to proceed in an open vessel. The addition of either a Lewis base (pyridine) or a Lewis acid (BF$_3$·Et$_2$O) significantly increases the stability of the complexes toward dioxygen. Reaction with iodosobenzene was sluggish, and significant amounts of new porphyrinic products were only obtained with excess (20-fold) iodosobenzene. Products in toluene were starting complex, [Fe-(TPP)NO$_3$], and [Fe(TPP)]$_2$O. *N,N*-Dimethylaniline *N*-oxide, a slightly milder oxidant than iodosobenzene, gave no reaction in toluene, dichloromethane, or THF. There was no evidence for the formation of nitrite complexes in any of these sysems.

The conversion of the nitrite complex to a nitrosyl complex is directly analogous to the first step in the catalytic cycle of assimilatory nitrite reductase. Conversions of this type have been observed in other nitrite complexes.[33] Our results suggest that this conversion is an intrinsic property of heme nitrite complexes. If this is the case, such a conversion requires no active participation of an enzyme. The role of the enzyme may be that of control rather than performance in this conversion reaction. Our observation of the instability of the nitrite complex along with the observation of Barley et al.[33] of rapid reduction of ammonia following the reduction of the [Fe(TPP)NO]$^-$ species indicates that the nitrosyl complexes are the most stable complexes in this series. All that is required for the formation of the nitrosyl complex is an accepter for an oxygen atom. Nitrite ion apparently fits this description, although the enzymatic systems may well have other oxygen acceptors available.

As noted earlier, Fernandes et al.[9] have previously reported the preparation of a nitrite complex of (tetraphenylporphyrinato)-iron(III). This report makes no mention of decomposition of the nitrite complex to a nitrosyl derivative, although nitric oxide and nitrosyl complexes were noted in subsequent electrochemical analysis of solutions containing the nitrite complex. The electronic spectrum in DMF of the complex that Fernandes et al. charac-

terize as a bis(nitrite) complex is similar to that of complex 1 we reported (Table I). The spectral characteristics in dichloromethane solution that Fernandes et al.[9] assign to the bis(nitrite) complex are close to those that we have found for the nitrosyl–nitrito complex (Table I). Neither of the two spectra are close to that of a bona fide bis(nitrite) sample prepared with picket-fence porphyrin[24] and whose spectra display almost no solvent dependence (Table I). (It should be noted that picket-fence porphyrin and TPP derivatives have quite similar spectral properties.) We are also intrigued by the report of their difficulties with the formation of the μ-oxo species in dichloromethane but not in DMF. In our hands, the formation of a μ-oxo complex due to residual water was much more facile in DMF than in dichloromethane. Their detection of nitrosyl complexes during cyclic voltametry of solutions containing nitrite and porphyrin may be due to electrochemical reduction of the nitrite complex or to the reaction we have described. The conversion of nitrite complexes to nitrosyl complexes in the presence of excess nitrite presents a caveat for the interpretation of spectra of solutions containing porphyrins and nitrite. Such spectra are likely to be complicated by the production of nitrosyl and/or nitrosyl–nitrite complexes. This is particularly true if the solutions used are not freshly prepared or if the acquisition time of the experimental technique is relative long (such as standard FT-NMR techniques).

Concluding Remarks. Our spectroscopic and kinetic data for the nitrite/(porphinato)iron(III) system are consistent with nitrite ion behaving as a relatively strongly binding ligand toward iron(III) porphyrinates. Nitrite clearly displaces weakly bound ligands such as perchlorate or nitrate. The resulting nitrite complex interacts with excess nitrite ion to produce a nitrosyl complex. The other product of this oxygen atom transfer reactions is most likely nitrate ion. We thus find that the nitrite complex of iron(III) porphyrin has limited stability. The intermolecular reaction that we postulate also suggests appropriate synthetic strategies that could be used to prepare stable nitrite complexes. This question is considered in the following paper.[24]

(33) (a) Godwin, J. B.; Meyer, T. J. *Inorg. Chem.* 1971, *10*, 2150. (b) Murphy, W. R., Jr.; Takeuchi, K. J.; Meyer, T. J. *J. Am. Chem. Soc.* 1982, *104*, 5817. (c) Murphy, W. R., Jr.; Takeuchi, K.; Barley, M. H.; Meyer, T. J. *Inorg. Chem.* 1986, *25*, 1041.

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Use of Protected Binding Sites for Nitrite Binding in Iron(III) Porphyrinates. Crystal Structure of the Bis(nitro)($\alpha,\alpha,\alpha,\alpha$-tetrakis($o$-pivalamidophenyl)porphinato)iron(III) Anion

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The reaction of nitrite ion with iron(III) picket-fence porphyrin species leads to the synthesis of low-spin bis(nitro) complexes. These compounds have been characterized by EPR, IR, UV–vis, and NMR spectroscopy. The crystal structure of one derivative, [K(18-C-6)(H$_2$O)][Fe(NO$_2$)$_2$(TpivPP)], has been determined. The complex has one N-bound nitrite within the ligand-binding pocket of the pickets; the other N-bound nitrite is on the open side of the porphyrin plane but is protected from reaction by the formation of a tight ion pair with the [K(18-C-6)(H$_2$O)]$^+$ cation: there are two K–O(NO$_2$) bonds = 2.9 Å. Equatorial Fe–N bond distances average to 1.992 (1) Å while the axial Fe–N distances average to 1.985 (22) Å. Crystal data: tetragonal system, FeKO$_{15}$N$_{10}$C$_{76}$H$_{90}$, space group $P\bar{4}$, a = 16.691 (6) Å, c = 13.534 (3) Å, Z = 2. A total of 4184 observed data were used in the structure solution and refinement with final values of $R(F_o)$ = 0.069 and $R_w(F_o)$ = 0.066. Ligand-binding studies, followed by NMR or EPR spectroscopy, were performed in an attempt to assign the spin state of the intermediate mono(nitro) complex, which appears to be a high-spin species. Association constants for the formation of mono- and bis(nitrite) complexes are reported; differences as a function of counterion are consistent with significant ion-pairing differences.

In the preceding paper,[1] we described the reactions of the (porphinato)iron(III)/nitrite system that apparently prevented

the isolation of nitro(porphinato)iron(III) complexes. These reactions appear to involve attack on the coordinated nitrite ion to