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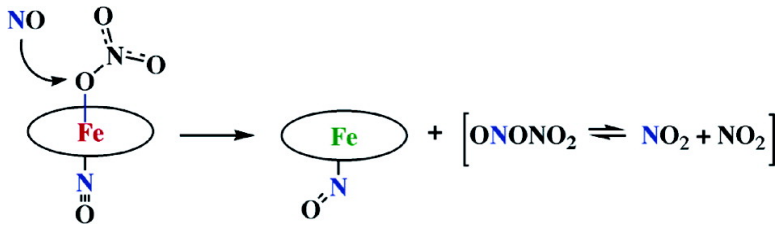

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Reactions of Nitrogen Oxides with Heme Models. Spectral and Kinetic Study of Nitric Oxide Reactions with Solid and Solute $Fe^{III}(TPP)(NO_3)$

Tigran S. Kurtikyan,*[,†,‡] Gurgen M. Gulyan,[†] Garik G. Martirosyan,[†] Mark D. Lim,[§] and Peter C. Ford*[,§]

Contribution from the Research Institute of Applied Chemistry (ARIAC), 375005, Yerevan, Armenia, Molecule Structure Research Centre (MSRC) NAS, 375014, Yerevan, Armenia, and Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106

Received December 24, 2004; E-mail: tkurt@msrc.am; ford@chem.ucsb.edu

Abstract: The reaction(s) of nitric oxide (nitrogen monoxide) gas with sublimed layers containing the nitrato iron(III) complex $Fe^{III}(TPP)(\eta^2\text{-}O_2NO)$ (**1**, TPP = *meso*-tetraphenyl porphyrinate^{2-}) leads to formation of several iron porphyrin species that are ligated by various nitrogen oxides. The eventual products of these low-temperature solid-state reactions are the nitrosyl complex Fe(TPP)(NO), the nitro-nitrosyl complex Fe(TPP)(NO_2)(NO), and **1** itself, and the relative final quantities of these were functions of the NO partial pressure. It is particularly notable that isotope labeling experiments show that the nitrato product is not simply unreacted **1** but is the result of a series of transformations taking place in the layered material. Thus, the nitrato complex formed from solid Fe(TPP)(η^2-O_2NO) maintained under a ^{15}NO atmosphere was found to be the labeled analogue Fe(TPP)(η^2-$O_2{}^{15}NO$). The reactivities of the layered solids are compared to the behaviors of the same species in ambient temperature solutions. To interpret the reactions of the labeled nitrogen oxides, the potential exchange reactions between N_2O_3 and ^{15}NO were examined, and complete isotope scrambling was observed between these species under the reaction conditions ($T = 140$ K). Overall it was concluded from isotope labeling experiments that the sequence of reactions is initiated by reaction of **1** with NO to give the nitrato nitrosyl complex Fe(TPP)(η^1-ONO_2)(NO) (**2**) as an intermediate. This is followed by a reaction in the presence of excess NO that is equivalent to the loss of the nitrate radical $NO_3^{\bullet}$ to give Fe(TPP)(NO) as another transient species. A plausible pathway involving NO attack on the coordinated nitrate of **2** resulting in the release of N_2O_4 concerted with electron transfer to the metal center is proposed.

Introduction

Nitric oxide (NO) has been well-characterized as an important regulatory molecule in mammalian biology. The interaction of NO with ferro- and ferri-*heme* proteins plays a central role in this bioregulatory activity,[1] and the reactions of NO with various iron porphyrin complexes have been investigated as models for these processes.[2] In addition to simple association reactions, NO has been shown to participate in reversible redox reactions involving biologically relevant metal centers. In model reactions it is clear that metal complexes mediate both oxygen atom and electron-transfer processes involving NO and various other nitrogen oxide species (NO_x). Such oxidative processes may not only be significant in the biological chemistry of various NO_x but also have potential in the catalytic oxidations of various organic substrates.[3] It was in these contexts that the present study was initiated, with the goal of elucidating the redox transformations between various NO_x complexes of the *heme* model compound Fe(TPP) (TPP = *meso*-tetraphenyl porphyrinate^{2-}) using the bidentate nitrato complex Fe(TPP)(η^2-O_2NO) (**1**)[4] as the entry point. This compound can be prepared by reaction of the oxo-bridged $[Fe(TPP)]_2O$ with HNO_3,[4] and it has also been shown to be a product of the NO_2 reactions with Fe(TPP) species both in the solid state and in solutions.[5,6]

The present investigations were carried out both in solution and in sublimed layers of the iron porphyrin complex using infrared and electronic spectroscopic probes of the transformations. The low-temperature spectral investigations of the sublimed layers provide the opportunity to observe the stepwise reactions that lead to the formation of the final products and to

[†] Research Institute of Applied Chemistry.
[‡] Molecule Structure Research Centre NAS.
[§] University of California.

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characterize the intermediates that define these transformations. The solution studies offer the opportunity to evaluate whether such reactions follow analogous pathways in fluid media and to observe the dynamics of these processes.

Experimental Section

Preparation of Fe(TPP)(η^2-O_2NO) Sublimates. Fe(II) porphyrinates are very sensitive to oxygen and readily transform to Fe(III) derivatives. For this reason, the more stable Fe(TPP)$(B)_2$ complexes with nitrogen bases (B is pyridine or piperidine) were used as parent compounds. These were synthesized by a known procedure.[7] The low-temperature sublimate was prepared[8] by placing an Fe(TPP)$(B)_2$ sample in a Knudsen cell and heating to about 470 K under high vacuum ($P = 3 \times 10^{-5}$ Torr). Evacuation for 3 h resulted in the complete elimination of the coordinated axial ligands B, as monitored by measurement of the pressure at the outlet of the cryostat. Liquid nitrogen was then poured into the cryostat, and the Knudsen cell was heated to 520 K, at which temperature sublimation of Fe(TPP) onto the KBr and CaF_2 substrate occurred. In the latter case, CaF_2 plates were also used as the optical windows of the cryostat.[9,10] The M(TPP) layers obtained in this manner by sublimation onto a low-temperature (77 K) surface are spongelike and have high microporosity.[11] Potential reactants easily diffuse across these layers, and adducts thus formed can be studied spectroscopically without solvent interference.

Sublimation was typically carried out over periods of 0.1−2.0 h to build up layers of thickness convenient for UV−visible and IR spectral studies. The Fe(TPP) sublimed layer was heated to room temperature under dynamic vacuum, and then NO_2 gas was introduced. As shown previously,[5] this procedure leads to the formation of a very clean spectrum of the bidentate nitrato complex **1**. These layers were then cooled with liquid nitrogen, and NO was fed to the cryostat from a vessel provided with a mercury manometer to measure the pressure of NO. The layers were warmed to specified temperatures controlled by thermocouple, and FTIR or electronic absorption spectra were measured.

Labeled and Unlabeled Nitric Oxide. NO gas was purified by passage through KOH pellets and a cold trap (dry ice/acetone) to remove higher nitrogen oxides and trace quantities of water. The purity was checked by IR measurements of the layer obtained by slow deposition of NO on the cooled substrate of the optical cryostat (80 K), which did not show the characteristic IR bands of N_2O, N_2O_3, or H_2O, thus indicating the absence of these species. (Freezing the purified NO with the liquid nitrogen on the wall of the glass storage bulb serves as a rapid procedure for checking purity, since in the presence of NO_2, this solid takes on the bluish color from the trace N_2O_3.) ^{15}NO with 98.5% enrichment was purchased from the Institute of Isotopes, Republic of Georgia, and was purified by the same procedures. NO_2 ($^{15}NO_2$), obtained by oxidation of NO (^{15}NO) with excess of pure dioxygen, was dried over P_2O_5 and then was purified by fractional distillation until a pure white solid was obtained.

Solution Studies. Solid Fe(TPP)(η^2-O_2NO) (**1**) was prepared following a published procedure[4] and was stored in an inert atmosphere glovebox. Solutions were prepared in the glovebox using distilled and deoxygenated solvents and then loaded into gastight syringes for transfer to the reaction cells. NO was purified, measured, and transferred quantitatively using vacuum line techniques directly into an airtight flask that included a 1.0-cm quartz cuvette for monitoring reactions via changes in their UV−visible spectra. A typical reaction would be initiated by injection of the porphyrin solution into this reaction vessel, shaken vigorously to provide gas/solution equilibration, and then mounting the cuvette in the spectrophotometer. The electronic spectra were acquired at 10-s intervals for the initial 200 s and at longer time increments afterward.

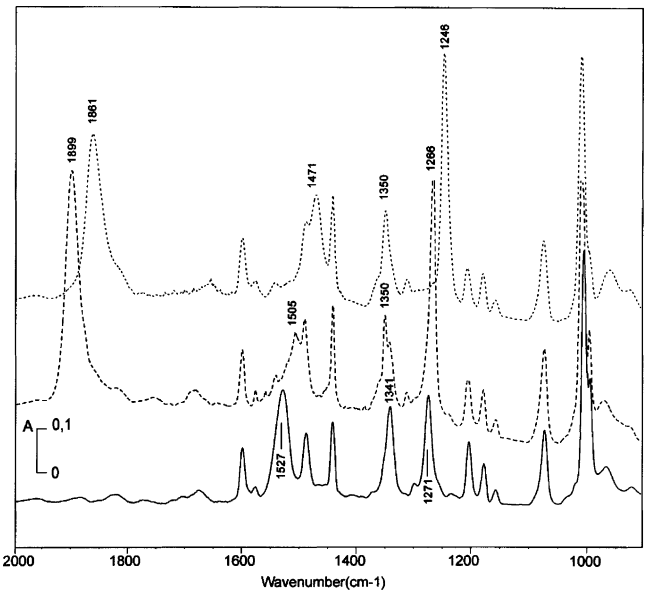

Figure 1. Low-temperature (80 K) FTIR spectra of (a) a thin film of Fe(TPP)(η^2-O_2NO) (solid line), (b) after supplying 10 Torr NO to cryostat at 80 K followed by warming to 140 K, pumping briefly to remove excess NO and recooling to 80 K (dashed line), (c) the same after interaction of ^{15}NO with Fe(TPP)(η^2-$O_2{}^{15}NO$) (dotted line).

Infrared spectra of reacting solutions were recorded using rapid mixing techniques with a custom-made instrument. Two gastight syringes were connected via PEEK tubing to a mixing block that preceded the entrance to a 0.5-mm CaF_2 IR cell. Before use, the apparatus was evacuated overnight under vacuum. Purified NO was transferred using vacuum line techniques into a sealed glass flask and brought into the glovebox where degassed CH_2Cl_2 was injected into the NO-containing flask. The equilibrated solution was then loaded directly into one of the gastight syringes. The second syringe was filled with a CH_2Cl_2 solution of **1**. A mechanical device was used to engage the two syringes simultaneously, causing the solutions to mix and flow to an IR cell mounted in an FTIR spectrometer. The first acquisition was taken while the syringe driver was running, and spectra were acquired after this was disengaged and the exit valve was closed.

Instrumentation. FTIR spectra of porphyrin sublimates were obtained on Nicolet Nexus FTIR and Specord M-80 spectrometers, and electronic spectra were recorded on a Specord M-40 spectrophotometer. Solution kinetics studies were carried out on an HP 8452 diode array spectrophotometer or on a modernized BioRad model FTS-Pro FTIR spectrophotometer.

Results and Discussion

Formation of Fe(TPP)(η^1-ONO_2)(NO) (2) in Low-Temperature Films. The nitrato nitrosyl complex **2** represents the only characterized example of a six-coordinate nitrato ferro or ferri-porphyrinato complex. This was described several years ago in a preliminary communication[12] and is described in greater detail here. Figure 1 presents the FTIR spectra of the product

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Table 1. IR Spectral Data of Nitrosyl and Nitrate Groups for Fe(TPP)(ONO_2)(NO) in cm^{-1}

Fe(TPP)(ONO_2)(NO)	Fe(TPP)(ONO_2)(^{15}NO)	Fe(TPP)($O^{15}NO_2$)(NO)	Fe(TPP)($O^{15}NO_2$)(^{15}NO)	assignment
1899 s	1862 s	1900 s	1863 s	ν(N═O)
1505 m	1505 m	1472 m	1472 m	$\nu_a(NO_2)$
1265 s	1265 s	1246 s	1246 s	$\nu_s(NO_2)$
969 w	969 w	954 w	954 w	ν(N−O)
605 vw	602 vw	605 vw	602 vw	δ(Fe−N−O)
548 vw	542 vw	548 vw	542 vw	ν[Fe−N(NO)]

obtained after exposing a low-temperature (80 K) layer of solid Fe(TPP)(η^2-O_2NO) to NO gas, warming to 140 K, pumping out the excess NO, and then recooling. The transformation is characterized by appearance of new bands at 1899 s, 1506 m, 1265 s, and 969 w cm^{-1} and disappearance of bands at 1528 and 1273 cm^{-1} attributed to bidentate-coordinated nitrate. Additionally, a porphyrin band at 1341 cm^{-1} is shifted to 1350 cm^{-1}, while new weak bands at 605, 548, and 464 cm^{-1} appear at low frequency (Supporting Information Figure S1). The intensities of the new bands correlate during their growth (Supporting Information Figure S2) and can be confidently assigned to the formation of **2** as depicted in eq 1.

$$\underset{(\mathbf{1})}{\text{Fe(TPP)}(\eta^2\text{-O}_2\text{NO})} + \text{NO} \rightleftharpoons \underset{(\mathbf{2})}{\text{Fe(TPP)}(\eta^1\text{-ONO}_2)(\text{NO})} \quad (1)$$

When the same procedure is carried out with the isotopically labeled materials ^{15}NO and Fe(TPP)(η^2-$O_2{}^{15}$NO), the new bands appear at the shifted frequencies 1863 s, 1472 m, 1246 s, 954 w, 602 vw, and 542 vw cm^{-1} (Figure 1, dotted line), but others at 1350 and 464 cm^{-1} are not affected by the isotope labeling. If instead the reaction is between ^{15}NO gas and unlabeled **1**, the product spectrum displays bands at 1862 s, 1505 m, 1265 s, 969 w, 602 vw, and 542 vw cm^{-1} (Supporting Information Figure S3), that is, only the new bands at 1862, 602, and 542 cm^{-1} are shifted relative to the product bands seen in the reaction between unlabeled NO and **1** shown in Figure 1. When this procedure was performed with unlabeled NO and Fe(TPP)($O_2{}^{15}$NO), the IR spectrum displayed bands at 1900 s, 1472 m, 1246 s, 954w, 605 vw, and 548 vw cm^{-1} (Supporting Information Figure S3) where only those at 1900, 605, and 548 cm^{-1} are unchanged relative to the unlabeled reaction. Spectral data obtained for these systems are summarized in Table 1. These results indicate that, in the 80−140 K temperature interval, the only observable reaction proceeding in the layer is addition of NO to Fe(TPP)(η^2-O_2NO) (**1**) to give the six-coordinate complex Fe(TPP)(η^1-ONO_2)(NO) (**2**).

The electronic absorption spectra recorded under identical conditions and using CaF_2 optics as used to record the FTIR spectra with the same sample also demonstrated formation of the new complex. The Soret band of **1** in the 80 K thin film appears at 423 nm, about 10 nm red-shifted from that seen in the ambient temperature solution spectrum of **1**, but the Q-bands at 511 and 572 nm are close to the reported solution values.[4,13] Upon addition of NO gas, the optical spectrum (Figure 2, dashed line) is significantly changed. The Soret and Q-bands of the new species are shifted to higher wavelengths (436, 547 and 582 nm) as illustrated in Figure 2 (solid line). Notably, this spectrum is similar to that of other hexacoordinate Fe^{III}

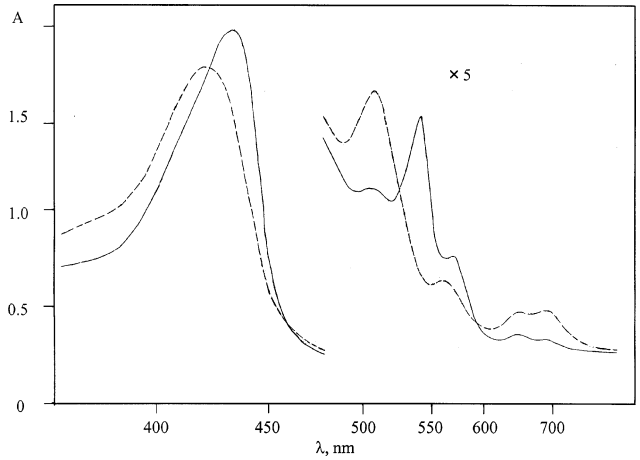

Figure 2. (a) Low-temperature (80 K) UV−visible spectrum of a sublimed layer of Fe(TPP)(η^2-O_2NO) (dashed line). (b) Optical spectrum after exposing **1** to NO (5 Torr at 77 K warming to 140 K and recooling (solid line).

porphyrin complexes of mixed nitrogen oxides. For example, the electronic spectrum of the nitro nitrosyl complex Fe(TPP)-(NO_2)(NO) (**3**) in chloroform solution displays a spectrum with maxima at 433, 545, and 577 nm.[14]

The bidentate nitrate ligand of Fe(TPP)(η^2-O_2NO) (**1**) has been shown to be bound in a slightly asymmetric mode with a large out-of-plane displacement (0.6 Å) of the d^5 high-spin Fe-(III) center toward the lone axial ligand.[4] For this structure, the η^2-nitrate ligand would be expected to show three IR-active stretching modes, a high-frequency ν(N═O) stretch for the uncoordinated oxygen, and symmetric and asymmetric stretching modes for the coordinated NO_2 fragment. Two bands of compatible intensity seen for **1** at 1530 and 1275 cm^{-1} in Nujol mull[4] and in sublimed layers[5] were assigned, respectively, to ν(N═O) and to the asymmetric mode of the coordinated NO_2 fragment.[15] The low-intensity, but isotopically sensitive, FTIR band near 965 cm^{-1} (Figure S3) can plausibly be assigned to the symmetric stretching mode of the NO_2 fragment of **1**.[15]

Adding NO to samples of **1** shifts the high-frequency vibrations of coordinated nitrate to lower frequencies with a change in the relative intensities, the higher energy band diminishing and the lower energy band becoming much stronger. Additionally there is enhancement and shift of the weak symmetric stretching mode of the NO_2 fragment. These changes can be interpreted in terms of the bidentate-to-monodentate transition of the nitrate coordination illustrated by Scheme 1. The highest-frequency nitrato band at 1505 cm^{-1} now represents $\nu_a(NO_2)$, while that at ∼1260 cm^{-1} is assigned to $\nu_s(NO_2)$. For comparison, the IR spectrum of the monodentate nitrato complex Fe(OEP)(η^1-ONO_2) (OEP = octaethylporphyrinato^{2-}) displays

(13) The UV−vis spectrum of the film sample dissolved in CH_2Cl_2 is quite similar to reported solution data;[4] hence the red shift of Soret band is evidently a solid-state effect.

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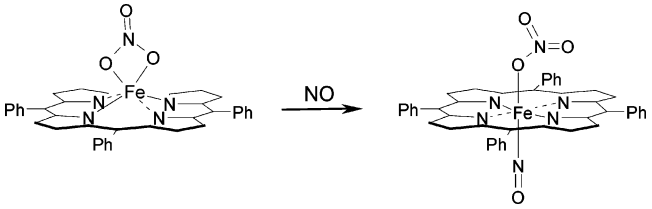
Scheme 1. Schematic Representation of the Reaction between Fe(TPP)(NO_3) and NO



a coordinated nitrate band at 1515 cm^{-1} (KBr pellet).[16] Closer disposition of the high-frequency bands is one criterion of monodentate coordination in nitrate complexes.[15] The band at ~970 cm^{-1} can be assigned to the N−O vibration for the coordinated oxygen.

The low-frequency weak bands at 605 (602) and 548 (542) cm^{-1} sensitive to NO labeling should be assigned to metal-nitrosyl vibrations. The former was tentatively assigned to δ(Fe−N−O), while the latter to ν(Fe−N) by analogy with Fe(III)(tropocoronand)(nitrosyl) complex,[17] in which deformation Fe−N−O mode of linearly bound NO is disposed at higher frequencies and revealed smaller isotopic shift than Fe−N stretching.

Additional information regarding the nature of **2** can be drawn from porphyrin vibrational modes that reveal systematic changes depending on the spin and oxidation states of axial complexes of Fe(TPP).[18] The band in vicinity of 1350 cm^{-1} representing a porphyrin core mode ($\nu(C_a-C_m)$ mixed with some $\nu(C_m-$phenyl)) lies at higher frequencies in low-spin complexes. Similarly, a low-energy porphyrin core deformation mode occurs in the range 450 cm^{-1}. For the high-spin η^2-nitrato complex **1**, these bands lie at 1341 and 436 cm^{-1}. Upon coordination of NO, they shift to 1350 and 464 cm^{-1} (see Figures 1 and S1), indicating a change to the low-spin state. This result is consistent with other low-spin, six-coordinate ferri-heme nitrosyl complexes[19] and supports the conclusion that, under these conditions, NO reacts with Fe(TPP)(η^2-O_2NO) to give Fe(TPP)(η^1-ONO_2)(NO). While this bidentate-to-monodentate transition may alleviate nonbonded repulsions between nitrate oxygens and porphyrin nitrogens, it is likely to involve relatively moderate energy expenditures given the existence of monodentate and bidentate binding, respectively, in Fe(OEP)(ONO_2) and Fe(TPP)(O_2NO), which differ only in the nature of the peripheral substituents. To our knowledge, the only other six-coordinate nitrato Fe(P) complex known is an aqua complex (Fe(P)(η^1-ONO_2)(H_2O)) (P not identified) reported in a review by Wyllie and Scheidt.[19]

Notably, ambient temperature solution studies described below also indicate the formation of **2** as an intermediate in the reaction of **1** with NO, although the former is unstable toward decay to other products. This behavior is in contrast to the greater stability of the analogous ruthenium complex Ru(TTP)(ONO_2)(NO) (TTP = *meso*-tetra(4-tolyl)porphyrinate dianion), which was first prepared by the solution reaction of Ru(TTP)(NO)Cl with $AgNO_3$[20] and subsequently by the reaction of Ru(TTP)(CO) with NO_2/N_2O_4.[21]

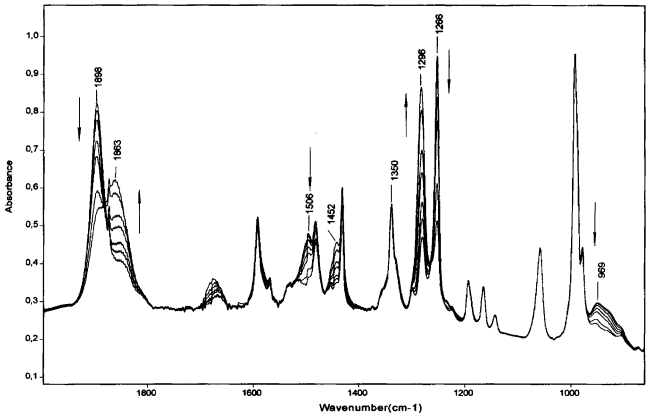


Figure 3. Formation of nitro nitrosyl complex Fe(TPP)(NO_2)(NO) from nitrato nitrosyl complex Fe(TPP)(η^1-ONO_2)(NO) during the course of warming the sublimed layers from 145 to 180 K in the presence of NO (4 Torr).

Low-Temperature Reactions of Fe(TPP)(ONO_2)(NO) with NO. Transformations of solid Fe(TPP)(O_2NO) in thin films under a NO atmosphere can be divided into three temperature-dependent processes. At very low temperatures (80−140 K), the only process is the formation of nitrato nitrosyl complex **2**. Raising the temperature into the 140−200 K range leads to the further reaction of NO with this species, as illustrated in Figure 3. Warming of the layered material, in which **2** has been formed, leads to gradual intensity decreases in its characteristic bands at 1899, 1506 1266, and 969 cm^{-1}, while new bands at 1863, 1452, and 1296 cm^{-1} gain intensity. The latter indicate the formation of the well-known nitro nitrosyl complex Fe(TPP)(NO_2)(NO) (**3**).[6,14]

Further warming to room temperature is accompanied with partial reformation of the nitrato complex **1** and the appearance of the iron(II) nitrosyl complex Fe(TPP)(NO) (**4**). At this stage, the reactions are sensitive to the partial pressure of NO, and depending on P_{NO}, different relative quantities of **1**, **3**, and **4** are formed. At relatively high P_{NO} (a few decades of Torr), **3** is the main species seen in the solid layer, while at lower P_{NO} (a few Torr) all three are present in comparable amounts. Continuous evacuation to remove the headspace gases shifts the product mixture from Fe(TPP)(NO_2)(NO) to give increased yields of Fe(TPP)(O_2NO) and Fe(TPP)(NO).[6]

Scheme 2 offers several scenarios as starting points for discussing the reactions following exposing sublimed layers of Fe(TPP)(O_2NO) to NO gas. In each case, the first stage is formation of the nitrato nitrosyl complex **2** as evidenced from the low-temperature solid-state FTIR and by rapidly mixing UV−visible measurements in solution (see below). Three different pathways may be considered in evaluating the second stage of the reaction leading to Fe(TPP)(NO_2)(NO). Scenario (i) suggests that this is initiated by β-bond cleavage of NO_2 from **2** to give an oxo nitrosyl complex Fe^{IV}(TPP)(O)(NO), scenario (ii) involves oxygen atom abstraction from the coordinated nitrato ligand by excess NO to give directly a species of the same stoichiometry (but perhaps a linkage isomer) as **3** and NO_2, and scenario (iii) would be initiated by dissociation of an $^{\bullet}NO_3$ radical (perhaps assisted by reaction with NO) to give directly **4**, which is then rapidly oxidized to **3** by reaction with the NO_2 resulting from reaction of NO_3 with NO.[25]

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Scheme 2. Pathways for the Reactions of Fe(TPP)η^2-O_2NO) with Excess NO

$$Fe(TPP)(\eta^2\text{-}O_2NO) + NO \rightleftharpoons Fe(TPP)(\eta^1\text{-}ONO_2)(NO)$$

Scenario i (β–bond cleavage)

$$Fe^{III}(TPP)(ONO_2)(NO) \rightleftharpoons (Fe^{IV}{=}O)(TPP)(NO) + NO_2$$

$$(Fe^{IV}{=}O)(TPP)(NO) + NO \longrightarrow Fe^{II}(TPP)(ONO)(NO) \rightleftharpoons Fe^{III}(TPP)(NO_2)(NO)$$

Scenario ii (Oxo-transfer from coordinated nitrate to free nitric oxide)

$$Fe^{III}(TPP)(ONO_2)(NO) + NO \longrightarrow Fe^{III}(TPP)(ONO)(NO) + NO_2$$

$$Fe^{III}(TPP)(ONO)(NO) \rightleftharpoons Fe^{III}(TPP)(NO_2)(NO)$$

Scenario iii (elimination of nitrate radical)

$$Fe^{III}(TPP)(ONO_2)(NO) \rightleftharpoons Fe^{II}(TPP)(NO) + {}^{\cdot}NO_3$$

$${}^{\cdot}NO_3 + NO \rightleftharpoons 2NO_2$$

$$Fe^{II}(TPP)(NO) + NO_2 \longrightarrow Fe^{III}(TPP)(NO_2)(NO)$$

IR measurements with isotopically labeled NO were used to lend insight into differentiating these pathways, with particular focus on the early stages before subsequent reactions lead to isotopic scrambling. For example, reaction of Fe(TPP)(O_2NO) with excess ^{15}NO (system **A**) leads first to the formation of Fe(TPP)(ONO_2)(^{15}NO), and different products are predicted for the subsequent reactions according to the three scenarios. Scenario (i) should give Fe(TPP)($^{15}NO_2$)(^{15}NO), scenario (ii) should give Fe(TPP)(NO_2)(^{15}NO), and scenario (iii) should give a mixture of Fe(TPP)($^{15}NO_2$)(^{15}NO) and Fe(TPP)(NO_2)(^{15}NO). Since all three are accompanied by formation of 1 mol of NO_2, which in excess NO will give dinitrogen trioxide (N_2O_3), the appearance of the latter in the low-temperature spectrum would also be expected.

The results were as follows: Figure 4 (bottom) displays the FTIR spectral changes observed when excess ^{15}NO was added to Fe(TPP)(O_2NO) (system **A**) to give Fe(TPP)(ONO_2)(^{15}NO), and then the mixture was gradually warmed. The further reaction of Fe(TPP)(ONO_2)(^{15}NO) is manifested by diminishing intensities of bands at 1860 (not shown), 1506, and 1266 cm^{-1} accompanied with the appearance of new bands at ∼1830 (not shown), 1452, 1422, 1295, and 1273 cm^{-1}. The new bands at 1830, 1452, and 1295 cm^{-1} belong to the ν(^{15}NO), ν_a(NO_2), and ν_s(NO_2) absorptions of Fe(TPP)(NO_2)(^{15}NO), while those at 1422 and 1273 cm^{-1} can be assigned to $^{15}NO_2$ stretches of the doubly labeled complex Fe(TPP)($^{15}NO_2$)(^{15}NO). In the latter case, unambiguous assignment of the band at 1273 cm^{-1} is complicated, since (^{15}N)$_2O_3$ also shows absorptions in the same region. IR bands at 1830, 1546, and 1277 cm^{-1} are reported for solid (^{15}N)$_2O_3$.[22] The growth of the weak band at ∼1550 cm^{-1} confirms formation of (^{15}N)$_2O_3$. These coincidences do not challenge the formation of Fe(TPP)($^{15}NO_2$)(^{15}NO) at this stage, since the band at 1422 cm^{-1} appears in a region relatively free of interference from the spectra of other NO_x species and of porphyrin itself. However, the bands at 1273 cm^{-1} (Figure 4, bottom) and in the vicinity of 1830 cm^{-1} may represent the overlapping absorptions characteristic of Fe(TPP)($^{15}NO_2$)(^{15}NO) and (^{15}N)$_2O_3$.

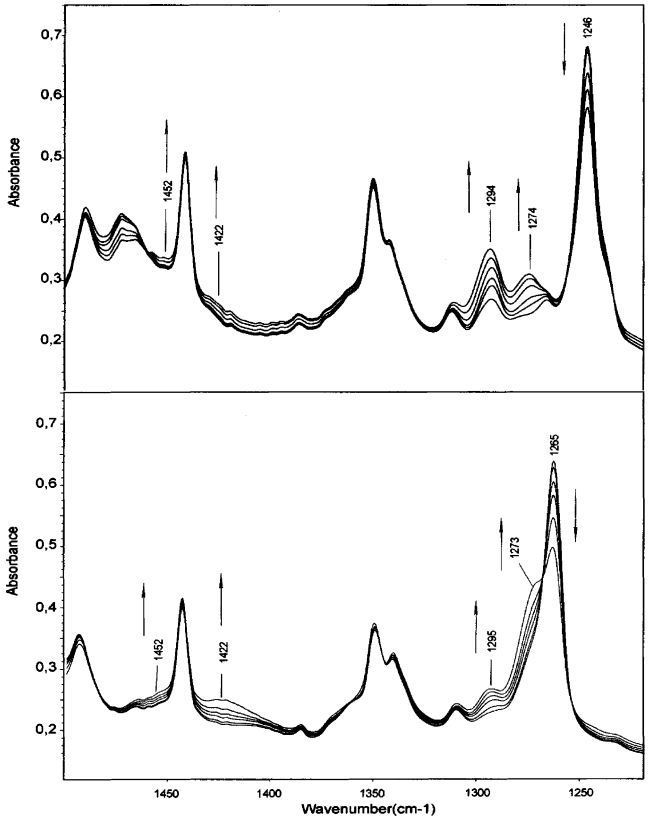


Figure 4. Isotope effects on FTIR spectra changes during the course of warming sublimed layers from 145 to 170 K in the presence of nitric oxide (4 Torr). Bottom: ^{15}NO + Fe(TPP)(NO_3) (system **A**). Top: NO + Fe(TPP)($^{15}NO_3$) (system **B**).

Analogous data for addition of NO to Fe(TPP)($O_2{}^{15}$NO) (system **B**) to give initially Fe(TPP)($O^{15}NO_2$)(NO) are displayed in Figure 4 (top). The same analysis shows the disappearance of the latter to be accompanied by growth of bands at 1860 (not shown), 1452, 1422, 1296, and 1275 cm^{-1}. This can be interpreted in terms of the initial formation of two isotopomers: Fe(TPP)(NO_2)(NO) (bands at 1860, 1452, and 1296 cm^{-1}) and Fe(TPP)($^{15}NO_2$)(NO) (bands at 1860, 1422, and 1275 cm^{-1}). Simultaneously, a weak band in the vicinity of 1590 cm^{-1} appears (due to N_2O_3) and enhances the intensity of the porphyrin band disposed in this region. Other bands characteristic of solid N_2O_3 appear at 1863 and 1297 cm^{-1},[22] and they overlap with bands assigned to Fe(TPP)(NO_2)(NO).

Interpretation of Isotope Studies of the Low-Temperature Reaction of 2 with NO. To a first approximation, these data appear to be consistent with scenario (iii) and not with (i) or (ii). For example, scenario (i) predicts that system **A** would give Fe(TPP)($^{15}NO_2$)(^{15}NO) and singularly labeled dinitrogen trioxide ($O^{15}NNO_2$) and system **B** to give Fe(TPP)(NO_2)(NO) and $ON^{15}NO_2$.[23] In contrast, system **A** gave Fe(TPP)(NO_2)(^{15}NO), Fe(TPP)($^{15}NO_2$)(^{15}NO), and (^{15}N)$_2O_3$ while system **B** gave Fe(TPP)(NO_2)(NO), Fe(TPP)($^{15}NO_2$)(NO), and N_2O_3. Additionally, no new IR bands were found in the region where ferryl ν(Fe═O) stretches are usually disposed (750−860 cm^{-1}).[24]

(22)) Hisatsune, I. C.; Devlin, J. P.; Wada, Y. *J. Chem. Phys.* **1960**, *30*, 714−719.

(23) Here we consider only the more stable N−N bonded form of N_2O_3.

(24) Nakamoto, K. *J. Mol. Struct.* **1997**, *408/409*, 11−16.

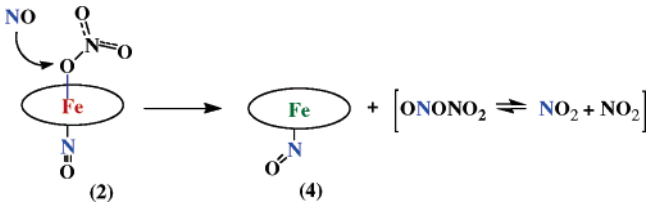
The situation is more ambiguous with regard to scenario (ii), which predicts system **A** formation of $(^{15}N)_2O_3$ and Fe(TPP)-$(NO_2)(^{15}NO)$ (after isomerization of the initially formed nitrito complex) and system **B** formation of Fe(TPP)$(^{15}NO_2)$(NO) and N_2O_3. For each set of reaction conditions, products not predicted by scenario (ii) were formed, Fe(TPP)$(^{15}NO_2)(^{15}NO)$ in system **A** and Fe(TPP)$(NO_2)(^{15}NO)$ in system **B**.

As outlined in greater detail in Supporting Information Scheme S1, scenario iii predicts the formation of Fe(TPP)-$(^{15}NO_2)(^{15}NO)$, Fe(TPP)$(NO_2)(^{15}NO)$, and both doubly and singly labeled dinitrogen trioxide for the conditions of system **A**, and Fe(TPP)$(^{15}NO_2)$(NO), Fe(TPP)(NO_2)(NO), and both singly labeled and unlabeled dinitrogen trioxide for the conditions of system **B**. The experimental results obtained are in agreement with scenario iii with the exception that only one type of dinitrogen trioxide was observed under each set of conditions, namely $(^{15}N)_2O_3$ for system **A** and N_2O_3 for system **B**. A possible explanation of this inconsistency would be isotopic scrambling of the monolabeled species $O^{15}NNO_2$ and $ON^{15}NO_2$ by reaction with the excess nitric oxide present (^{15}NO in system **A** and NO in system **B**). This would give dinitrogen trioxide with the same nitrogen labeling as the added nitric oxide (^{15}NO and NO, respectively). This process should be facilitated by the formation of dinitrogen trioxide species isomers at very low temperatures.[26] Consistent with this point of view is the absence of published data describing the mixed isotope species as $O^{15}NNO_2$ or $ON^{15}NO_2$.

The possible exchange reaction between NO and N_2O_3 was examined under closely related experimental conditions using amorphous Ni(TPP) layers as adsorbent.[27] Partly oxidized NO was deposited on the Ni(TPP) layer at 80 K and warmed to 120 K, and then the system was evacuated to expel any free NO and then cooled back to 80 K. This procedure led to the formation of N_2O_3 which was manifested by IR bands at 1842, 1593, and 1292 cm^{-1} and a small amount of N_2O_4 in the layer with weak IR bands at 1734 and 1254 cm^{-1}.[22] ^{15}NO was then introduced into the cryostat, and the FTIR spectra of this system were measured at various temperatures upon slow warming. This procedure showed that isotope exchange reaction occurs at temperatures as low as 140 K. Thus, under the experimental conditions used in the NO reaction with **2** to give **3**, the suggested isotopic exchange reaction should indeed lead to formation of dinitrogen trioxide species dominated by the isotopic composition of the excess nitric oxide.

Hence, of the three scenarios described by Scheme 2, the most plausible appears to be scenario iii, which is represented as initiating by elimination of a $^{\bullet}NO_3$ radical (however, see the discussion below). Beside the experimental results given above, there is additional, indirect evidence consistent with this scenario. During the course of the reaction of Fe(TPP)(ONO_2)-(NO) (**2**) with NO to give Fe(TPP)(NO_2)(NO) (**3**), a weak band in the vicinity of 1675 cm^{-1} initially grows and then diminishes in intensity (Figure 3). This can be interpreted in terms of formation and decay of Fe(TPP)(NO) (**4**) as an intermediate resulting from $^{\bullet}NO_3$ elimination.

Scheme 3



The fundamental problem with scenario iii is that the $^{\bullet}NO_3$ radical is a high energy species,[28] and although its formation from **2** should be facilitated by the high thermodynamic stability of **4**, the first step in this sequence would appear to be substantially uphill. However, an alternative step by which the loss of an $^{\bullet}NO_3$ equivalent might be effected would be the direct reaction of the excess NO with the coordinated nitrate ligand. In effect, this is equivalent to the reductive nitrosation of a coordinated ligand identified recently with a copper(II) complex[29] in the context that the coordinated anion is nitrosated concomitant with the reduction of the metal center (in this case the reduced metal species is **4**) as illustrated in eq 2. With X^- = nitrate and L_mM^{n+} = Fe(TPP)(NO), the concerted transfer of a NO_3 equivalent to NO to give some form of N_2O_4 and the very stable **4** as intermediates would give the same product distributions as scenario iii while avoiding the formation of the very high energy nitrate radical.

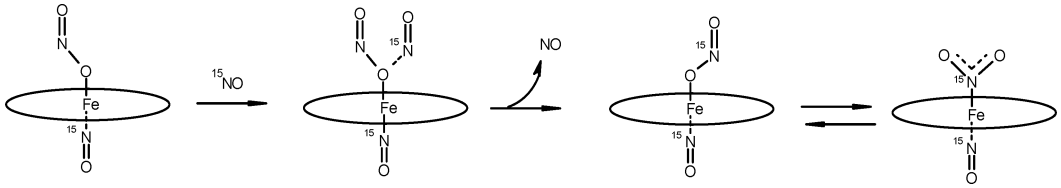
$$[L_mM{-}X{:}]^{n+} + NO \rightarrow [L_mM]^{n+} + X{-}NO \qquad (2)$$

Hence, we believe that the most plausible mechanism for formation of Fe(TPP)(NO_2)(NO) (**3**) from **2** involves the pathway represented in Scheme 3. Reaction of NO_2 with the nitrosyl complex **4** would rapidly give **3**.[6] Notably, the reaction of NO with coordinated nitrate to give an $ONONO_2$ species is the microscopic reversal of a likely first step in the formation of Ru(TTP)(ONO_2)(NO) by the reaction of N_2O_4 with Ru(TTP)-(CO).[21]

Higher Temperature Reactions of Fe(TPP)(NO_x) Films with NO. For system **A**, further warming of the layer does not significantly change the intensity of the 1296 cm^{-1} band of Fe-(TPP)$(NO_2)(^{15}NO)$, but the $\nu_s(^{15}NO_2)$ and $\nu_a(^{15}NO_2)$ bands (1275 and 1422 cm^{-1}, respectively) corresponding to the fully labeled nitro nitrosyl complex Fe(TPP)$(^{15}NO_2)(^{15}NO)$ grow more intense. An analogous pattern is observed for system **B** (excess NO) where the intensity of the $\nu_s(^{15}NO_2)$ band for Fe(TPP)-$(^{15}NO_2)$(NO) (1275 cm^{-1}) grows only to a certain level while intensities of the $\nu_s(NO_2)$ and $\nu_a(NO_2)$ bands of Fe(TPP)(NO_2)-(NO) (1296 and 1452 cm^{-1}, respectively) continue to increase. At the end of this stage of reaction, the layers consist mostly of Fe(TPP)$(^{15}NO_2)(^{15}NO)$ and Fe(TPP)(NO_2)(NO) for experiments with excess ^{15}NO and NO, correspondingly. This process can be rationalized according to the hypothetical pathway presented in Scheme 4. Other mechanisms involving oxidation of coordinated NO by NO_2, decomposition of a putative dinitro

(25) Wayne, R. P., et al. *Atmos. Environ.* **1991**, *25A*, 1−203.
(26) Fateley, W. G.; Bent, H. A.; Crawford, B. *J. Chem. Phys.* **1959**, *31*, 204−217.
(27) (a) At low temperatures, sublimed layers of Ni(TPP) react with neither NO nor NO_2, while at room temperature NO_2 oxidizes porphyrin ring with formation of $Ni(TPP)^{\bullet+}(NO_2)^-$ ion pair.[26b] (b) Martirosyan, G. G.; Kurtikyan, T. S. *Zh. Prikl. Khim.* (Russ.) **1998**, *71*, 1595−1598.
(28) (a) The electron affinity of the NO_3 radical has been reported[27b] to be 375 kJ mol^{-1}. (b) Lias, S. G.; Barmes, J. E.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17* (Suppl. 1), 1−86 as summarized on p 43 in Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper-Collins College Publishers: New York, 1993.
(29) (a) Tsuge, K.; DeRosa, F.; Lim, M. D.; Ford, P. C. *J. Am. Chem. Soc.* **2004**, *126*, 6564−6565. (b) Ford, P. C.; Fernandez, B. O.; Lim, M. D. *Chem. Rev.*, published online Feb 18, 2005. http://dx.doi.org/10.1021/CR0307289.

Scheme 4. Possible Mechanism of Isotope Exchange for $Fe(TPP)(NO_2)(^{15}NO) + {}^{15}NO$



complex, and re-formation of isotopically exchanged **3** cannot be ruled out. Isotope mixing could also occur just by ligand exchange.

In contrast to the well-defined temperature interval that divides formation of the nitrato nitrosyl complex **2** from the subsequent transformation of **2** to the nitro nitrosyl complex **3**, there are no clear temperature boundaries between the latter processes and subsequent steps in these solid films leading to the partial formation of $Fe(TPP)(NO_3)$ and Fe(TPP)(NO). In the presence of NO, all three species, namely, **1**, **3**, and **4**, are formed in the layer in relative quantities depending on P_{NO}. Exhaustive evacuation of NO from the cryostat depleted **3** and increased quantities of **1** and **3**.

Isotopic experiments with systems **A** and **B** help elucidate reformation of $Fe(TPP)(O_2NO)$ during this stage (Figure 5). The bands that appear at 1245 cm^{-1} in system **A** and at 1265 cm^{-1} in system **B** can be assigned, respectively, to formation of $Fe(TPP)(^{15}NO)(O^{15}NO_2)$ and $Fe(TPP)(ONO_2)(NO)$. Further warming of the layer is accompanied by decreases of these bands and increased intensities of new ones at 1253 and 1273 cm^{-1} corresponding to the appearance of $Fe(TPP)(^{15}NO_3)$ and $Fe(TPP)(NO_3)$. The well-defined isosbestic points seen in Figure 5 indicate that these spectral changes are coupled to the transformation of $Fe(TPP)(O^{15}NO_2)(^{15}NO)$ to $Fe(TPP)(^{15}NO_3)$ (in **A**) and $Fe(TPP)(ONO_2)(NO)$ to $Fe(TPP)(NO_3)$ (in **B**). Oddly, under these conditions, the processes described before appear to be reversed; that is, **3** is oxidized to the nitrato analogue **2**, which loses NO to regenerate **1**.

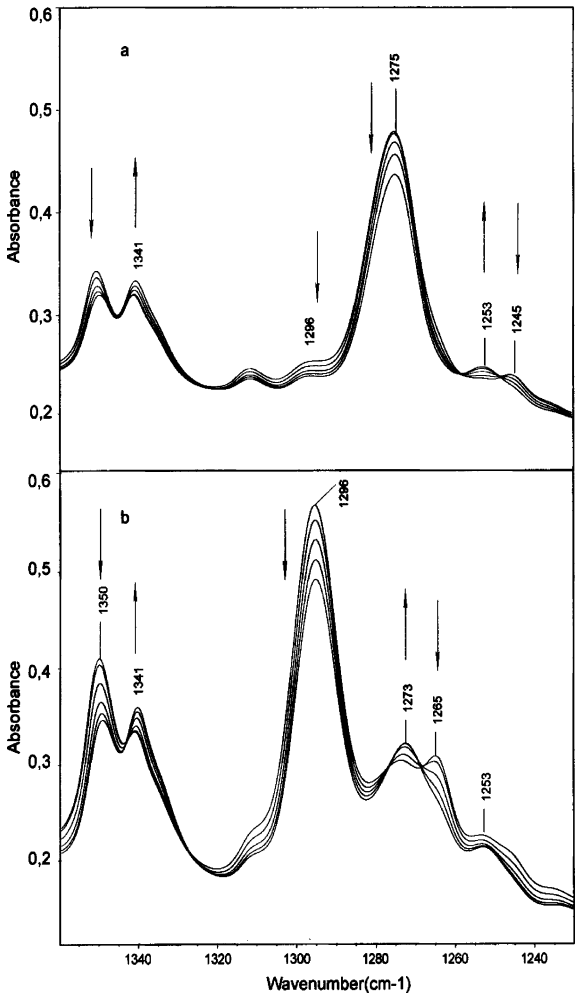


Figure 5. FTIR spectra changes resulting from warming sublimed layers from 200 to 240 K in the presence of nitric oxide (4 Torr). Bottom: $^{15}NO + Fe(TPP)(NO_3)$ (system **A**). Top: $NO + Fe(TPP)(^{15}NO_3)$ (system **B**).

A plausible pathway for the oxidation of the coordinated nitro ligand would involve linkage isomerization of **3** to the nitrito analogue Fe(TPP)(ONO)(NO) (**5**) prior to oxygen transfer from one of the NO_x species present, probably NO_2. There is only moderate spectral data regarding **5**, which was recently observed by irradiation of a KBr pellet containing $Fe(TPP)(NO_2)(NO)$ at low-temperature conditions.[30] In difference spectra, isotope-sensitive bands at 1507 and 934 cm^{-1} were assigned to ν(N=O) and ν(N−O) of coordinated nitrito ligand in six-coordinate nitrito nitrosyl complex Fe(TPP)(ONO)(NO). Similar isotope-sensitive bands at 1528 and 908 cm^{-1} were recorded in the course of low-temperature studies of the reaction between small quantities of NO_2 with sublimed layers of Fe(TPP) and were assigned to the same stretching modes as those in five-coordinate nitrito complex Fe(TPP)(ONO).[31] Close examination of the spectra presented in Figure 3 shows that the broad band in the vicinity of 970 cm^{-1} has a low frequency shoulder, suggesting the presence of an additional weak band with a maximum in the vicinity of 940 cm^{-1}. We believe that this isotope-sensitive band belongs to **5**, although bands in the vicinity of 1900 and 1500 cm^{-1} are obscured by those of $Fe(TPP)(ONO_2)(NO)$ (**2**).

Solution-Phase Reactivity Studies at Ambient Temperature. We have also briefly investigated the solution-phase reactions of $Fe(TPP)(O_2NO)$ (**1**) with NO at ambient temperature, and these gave spectral changes consistent with the chemical processes found in the solid films. The transformations after rapidly mixing solutions of **1** in toluene or dichloromethane and NO were followed by UV−vis and IR spectral measurements. Similar spectral changes were seen in both solvents. Figure 6 displays the changes in the electronic spectrum featuring the disappearance of **1** (λ_{Soret} = 414 nm, λ_Q = 510 nm) and the generation of a species with an electronic spectrum similar to that of $Fe(TPP)(NO_2)(NO)$ (**3**) (λ_{Soret} = 432 nm). Over a period of minutes the solution underwent further spectral changes to give a λ_{Soret} value at 406 nm, consistent with the formation of Fe(TPP)(NO) (**4**). No simple [NO] and $[N_2O_3]$

(30) Lee, J.; Kovalevsky, A. Y.; Novozhilova, I.; Bagley, K.; Coppens, P.; Richter-Addo, G. B. *J. Am. Chem. Soc.* **2004**, *126*, 7180−7181.
(31) Kurtikyan, T. S.; Gulyan, G. M.; Ford, P. C. *Book of Abstracts*; XVI All-Russian Symposium on Modern Chemical Physics, Tuapse, Russia, Sept. 20−Oct. 1, 2004; p 179.

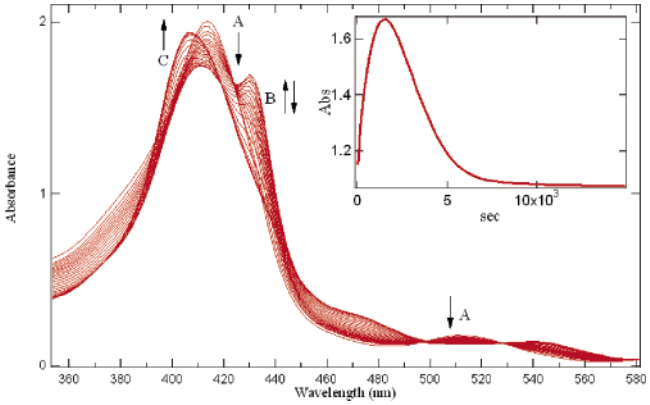


Figure 6. UV−vis absorption spectra recorded every 80.3 s after introduction of 1.6 mM NO to toluene solution containing 20 μM **1** (A, λ_{Soret} = 414 nm, λ_{Qband} = 510 nm). This is interpreted in terms of the conversion of Fe(TPP)(O_2NO) to a new species (B, λ_{Soret} = 432 nm), probably Fe(TPP)(NO_2)(NO), followed by subsequent reaction to give Fe(TPP)(NO) (C, λ_{Soret} = 406 nm). Inset: time dependence of the absorbance changes at 432 nm (B).

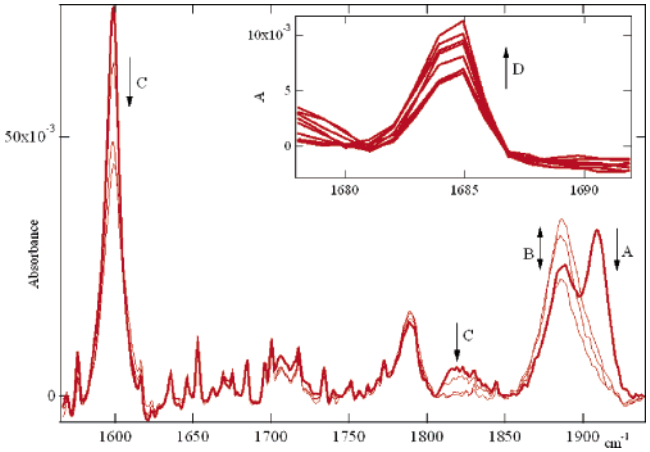


Figure 7. IR spectral changes (degassed 0.5-mm CaF_2 cell) after rapid mixing (deadtime ~1 s) of dichloromethane solutions containing 30 μM Fe(TPP)(NO_3) and 4.7 mM NO. The initial spectrum is taken during continuous flow through the cell, and the following spectra were accumulated approximately 1, 2, and 4 min after the flow was stopped. The quick formation and transformation of Fe(TPP)(ONO_2)(NO) (A, ν_{NO} = 1909 cm^{-1}) was followed by the formation and decay of Fe(TPP)(NO_2)(NO) (B, ν_{NO} = 1886 cm^{-1}). N_2O_3 was also observed to decrease (C, ν_{NO} = 1830 cm^{-1}, ν_{NO2} = 1600 cm^{-1}). Inset: Eventual formation of Fe(TPP)(NO) (D, ν_{NO} = 1684 cm^{-1}), initial spectrum taken 4 min after stopping the flow with the following spectra taken every 10 min.

dependencies on the rates of reaction were apparent, but it was noted that the presence of N_2O_3 stabilized **3**.

Addition of PPh_3 (as an N_2O_3 sink) to the reaction mixture, or scrupulous purification of NO prior to mixing, led to faster transformation of **3** to **1**.

A custom-made rapid flow apparatus was used in conjunction with IR measurements to help reveal the identity of the intermediates. As shown in Figure 7, rapid mixing of dichloromethane solutions of NO and Fe(TPP)(O_2NO) led to the formation of a species that displayed IR band maxima at 1909 and 1886 cm^{-1}. At longer times, the band at 1909 cm^{-1} was found to decay, leaving the species with a band at 1886 cm^{-1} as the dominant product. On the basis of the analogous reactions in the solid state, the band centered at 1909 cm^{-1} was assigned as the ν(NO) of Fe(TPP)(ONO_2)(NO) (**2**). Rapid mixing of dichloromethane solutions of isotopically labeled $^{15}N^{18}O$ and Fe(TPP)(O_2NO) resulted in formation of a product with a band

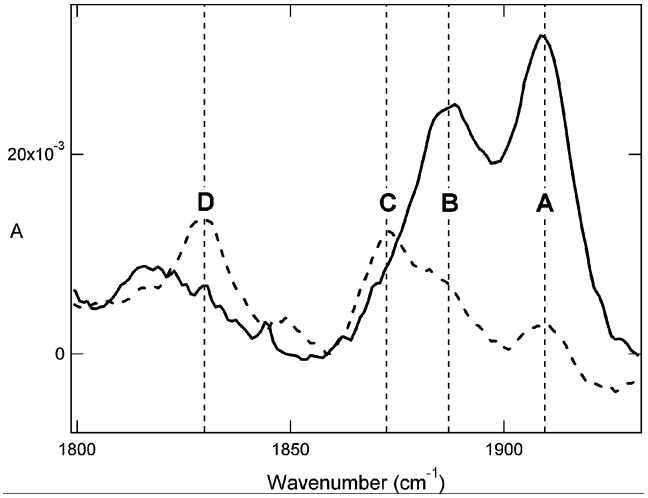


Figure 8. Infrared spectral changes (degassed 0.5-mm CaF_2 cell) during the rapid mixing (deadtime ~1 s) of 30 μM Fe(TPP)(NO_3) with either 4.7 mM $^{14}N^{16}O$ (dark, solid line) or 4.7 mM $^{15}N^{18}O$ (light, dashed) in dichloromethane. Reaction with $^{14}N^{16}O$ resulted in the formation of two new species with absorption peaks matching the ν_{NO} characterized for Fe(TPP)(ONO_2)(NO) (A, ν_{NO} = 1909 cm^{-1}) and Fe(TPP)(NO_2)(NO) (B, ν_{NO} = 1885 cm^{-1}). Reaction with $^{15}N^{18}O$ resulted in spectra that were interpreted as a mixture of Fe(TPP)(ONO_2)($^{14}N^{16}O$) (A, ν_{NO} = 1909 cm^{-1}), Fe(TPP)(NO_2)($^{14}N^{16}O$) (B, ν_{NO} = 1885 cm^{-1}), Fe(TPP)(ONO_2)($^{15}N^{16}O$) (C, ν_{NO} = 1873 cm^{-1}), and Fe(TPP)(ONO_2)($^{15}N^{18}O$) (D, ν_{NO} = 1829 cm^{-1}).

at 1829 cm^{-1} (Figure 8). This is in agreement with the formation of Fe(TPP)(ONO_2)($^{15}N^{18}O$) and the assignment of the isotope-sensitive absorption bands at 1909 and 1829 cm^{-1} as the nitrosyl stretch(es) of the nitrato nitrosyl complex **2**. The other species formed under these conditions (ν(NO) = 1886 cm^{-1})[14] has been characterized as Fe(TPP)(NO_2)(NO). Unfortunately, the bands expected for coordinated NO_2 or ONO (1200−1550 cm^{-1}) were obscured by solvent overtones. At longer times, the absorption bands characteristic of N_2O_3 (ν(NO) = 1830 cm^{-1}, $\nu(NO_2)$ = 1600 cm^{-1})[22] decreased simultaneous with the growth of a new band at 1684 cm^{-1} characteristic of the ν(NO) of Fe(TPP)(NO).

Summary

We have described here redox transformations of NO_x ligands coordinated to the heme model Fe(TPP) in the solid state as layered films and in aprotic media. The entry point to these investigations was the η^2-nitrato complex Fe(TPP)(η^2-O_2NO) (**1**), which undergoes a rapid NO addition step to form Fe(TPP)-(η^1-ONO_2)(NO) (**2**) (Scheme 1). In the presence of excess NO, the latter species undergoes further reaction in a process that would appear to be the result of a "simple" oxygen atom transfer from **2** to give the nitro nitrosyl complex Fe(TPP)(NO_2)(NO) (**3**). However, reactivity studies in low-temperature films using IR detection and isotope labeling techniques argue against this transformation occurring by oxygen atom transfer from the η^1-coordinated nitrate of **2** to NO to give (initially) the nitrito nitrosyl complex Fe(TPP)(ONO)(NO) (**5**) and NO_2 (scenario ii of Scheme 2). Similar arguments based on these data can be mounted against a mechanism proceeding via β-bond cleavage of the FeO−N bond of the coordinated nitrate of **2** to give a ferryl complex and NO_2 (scenario i). Neither of these scenarios can explain the isotopic distributions of products when the reactions are initiated with labeled NO or labeled **2**, unless there is significant isotopic exchange between the coordinated nitro group and the free NO.

A third pathway (scenario iii) involves Fe−O bond homolysis of **2** to give Fe(TPP)(NO) (**4**) and the $^{\bullet}NO_3$ radical, followed by rapid trapping of this radical by excess NO to give N_2O_4, which then reacts with **4** to give **3**. While this would indeed explain the product isotopic distributions given the demonstrated exchange between N_2O_3 and NO under these conditions, the high energy of the $^{\bullet}NO_3$ radical would make the first step in scenario iii highly endoergic. A more palatable alternative giving the same isotopic distributions is represented above in Scheme 3. In this model, loss of the $^{\bullet}NO_3$ radical is effected by attack of NO at the oxygen of the coordinated nitrate concerted with electron transfer to the metal center, leading to rapid dissociation of the transient N_2O_4 ligand and the formation of **4**. An analogy can be drawn between this pathway and the recently documented reductive nitrosylation of a copper(II)-coordinated amine that has been suggested to occur via such an inner sphere electron transfer process.[29]

It is notable that the various scenarios for NO interaction with the nitrato complex **1** lead to the intermediacy of highly reactive species such as NO_2, N_2O_3, and N_2O_4 that contribute to oxidative and nitrosative stress and can be damaging to cellular species.[32] Hence, the present study shows that under certain conditions, the nitrate ion, usually considered relatively innocuous in mammalian systems, can be activated by NO and hemes to form other reactive NO_x intermediates.

Acknowledgment. Financial support from CRDF (Grant No. AC2-2520-TB-03), the U.S. Department of Energy (DE-FG02-04ER15506), and a Visiting Scholarship for T.S.K. at UCSB from Petroleum Research Fund is gratefully acknowledged.

Supporting Information Available: Scheme S1 showing transition of Fe(TPP)(ONO_2)(NO) to Fe(TPP)(NO_2)(NO) by mechanism of NO_3 radical elimination for mixed isotope species. Complete citations for refs 3d and 25. Figure S1 demonstrating IR spectra in the range 600−400 cm^{-1} of thin layers containing Fe(TPP)(O_2NO) and Fe(TPP)(ONO_2)(NO), Figure S2 showing spectral changes describing formation of (NO)Fe(TPP)($O^{15}NO_2$) in the course of Fe(TPP)($O_2{}^{15}NO$) interaction with NO, and Figure S3 showing FTIR spectra of Fe(TPP)(ONO_2)(^{15}NO) and Fe(TPP)($O^{15}NO_2$)(NO) isotopomers. This material is available free of charge via the Internet at http://pubs.acs.org.

JA042237R

(32) Kirsch, M.; Korth, H.-G.; Sustmann, R.; de Groot, H. *Biol. Chem.* **2002**, *383*, 389−399.