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Article

Interaction of Nitrogen Oxides with Sublimed Layers of (*meso*-Tetraphenylporphyrinato)cobalt(II); IR Evidence of Oxo-Transfer from (Nitro)porphyrinatocobalt(III) to Free Nitric Oxide

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Interaction of a low-pressure NO_2 with sublimed layers of (*meso*-tetraphenylporphyrinato)cobalt(II) (Co(TPP)) leads to formation of 5-coordinate nitro complex Co(III)(TPP)(NO_2). Upon exposure of these layers to pyridine vapors, the fast reaction with formation of 6-coordinate nitro-pyridine porphyrins (Py)Co(III)(TPP)(NO_2) occurs. By means of IR spectroscopy and use of nitrogen oxide isotopomers, it is shown that an oxo-transfer reaction occurs from 5-coordinate species to free nitric oxide (NO) while the 6-coordinate complex is rather inert. It is also demonstrated that the stepwise addition of low-pressure NO_2 to nitrosyl complex Co(TPP)(NO) leads to formation of the nitro complex most likely by an exchange reaction.

Introduction

Oxo-transfer reactions from coordinated nitro-groups in transition metal complexes to appropriate oxygen acceptors can serve as important routes for oxidation of various substrates.[1] In those cases in which the nitrosyl complex thus formed is reoxidized by molecular oxygen, these processes may have a catalytic nature. This phenomena is of special interest for metalloporphyrin nitro-complexes because of the biological significance of their reactions with various nitrogen−oxygen species (e.g., NO, NO_2, $OONO^-$, etc.).[2]

In previous investigations,[3] it has been shown that the solution-phase system containing CoTPP, nitrite anion, nitrogen bases, B, and lithium perchlorate catalytically oxidizes a large number of alkenes with molecular oxygen. It was found that, in the absence of the Lewis acid lithium perchlorate, the oxidizing capability was strongly dependent on the Hammett parameters of the nitrogenous Lewis base. This fact prompted us to suggest that the oxo-transfer reactivity occurs preferentially through the pentacoordinate species (nitro)cobalt(III) tetraphenylporphyrin that is generated in solution by addition of lithium perchlorate to (B)-CoTPP(NO_2).

Tetra-arylporphyrins can form microporous “porphyrin sponges”, which allows incorporation of guest molecules with different shapes and sizes.[4a,b] The structure of sublimed layers of metal-*meso*-tetra-phenylporphyrinates is also spongelike.[5a] The amorphous layers of MTPP obtained by sublimation on a low-temperature (77 K) surface have high microporosity. In these layers, potential reagents can easily diffuse across the thickness, and the adducts thus formed can be studied by IR spectroscopy without solvent interference.

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It has previously been shown that sublimed layers of *meso*-tetraphenylporphyrinato-cobalt(II) undergo a series of chemical transformations under low pressures of NO_2.[6a,b] In the first stage, at low NO_2 pressures, the 5-coordinate Co(III)-TPP(NO_2) complex is formed. An increase in the NO_2 pressure and exposure time results in subsequent oxidation with the formation of a π-cation radical Co(III)$TPP^{\bullet +}(NO_2)_2$ ligated with two nitro groups. Further increase in the NO_2 pressure leads to both formation of a dication and nitration of porphyrin ring. It is important to note that this reaction sequence can be interrupted at the stage of the formation of the nitro-complex, which in the solid state is fairly stable at ambient conditions. The isolated nitro-complex can then be tested for its ability to take part in the oxo-transfer reactions with appropriate oxygen acceptors. It is worth noting that thin layers consisting of 5-coordinate nitro-complexes readily form 6-coordinate amino-nitro complexes upon exposure to amine vapors.[6c] Hence, it is possible to carry out a comparative study of the oxo-transfer ability of 5- and 6-coordinate complexes similar to that described for the solution phase. In the present study, we present experimental evidence of this comparison of oxo-transfer in the sublimed porphyrin layers. The 5-coordinate species reveals higher oxo-transfer reactivity than 6-coordinate using the nitric oxide (NO) as an oxygen acceptor.

Experimental Section

CoTPP was synthesized using the literature method.[7] Before the experiment, CoTPP was additionally purified by column chromatography with dry alumina using reagent grade chloroform as an eluent. NO (^{15}NO) 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 low rate deposition of NO on the cooled substrate of an optical cryostat (77 K). The IR spectra did not show the presence of N_2O, N_2O_3, or H_2O. ^{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($^{15}NO_2$) was obtained by oxidation of NO(^{15}NO) with an excess of pure dioxygen. After preliminary drying under P_2O_5, it was purified by fractional distillation using a low-temperature vacuum technique until a pure white solid was obtained.

Sublimed layers of Co(TPP) were obtained on cooled (77 K) KBr support of an optical cryostat according to the published procedure.[5b] This was then heated to 293 K under dynamic vacuum ($P \approx 2 \times 10^{-5}$ mmHg), and NO_2 ($^{15}NO_2$) was introduced into the cryostat. The pressure of NO_2 in the $(1-3) \times 10^{-2}$ mmHg range was monitored by a vacuum gauge. The Co(TPP) layer was exposed to the NO_2 ($^{15}NO_2$) atmosphere for 2−3 min followed by exhaustive evacuation to eliminate the unreacted NO_2. After measuring IR spectra, different pressures of NO were applied to the cryostat from a vessel provided with a mercury manometer (or vacuum gauge for low pressures) to measure the equilibrium pressure of NO. Then the IR spectra of sublimed layers were obtained over time under the exposure to the NO atmosphere on a Specord M-80 and a Perkin-Elmer 1600 FTIR spectrometer.

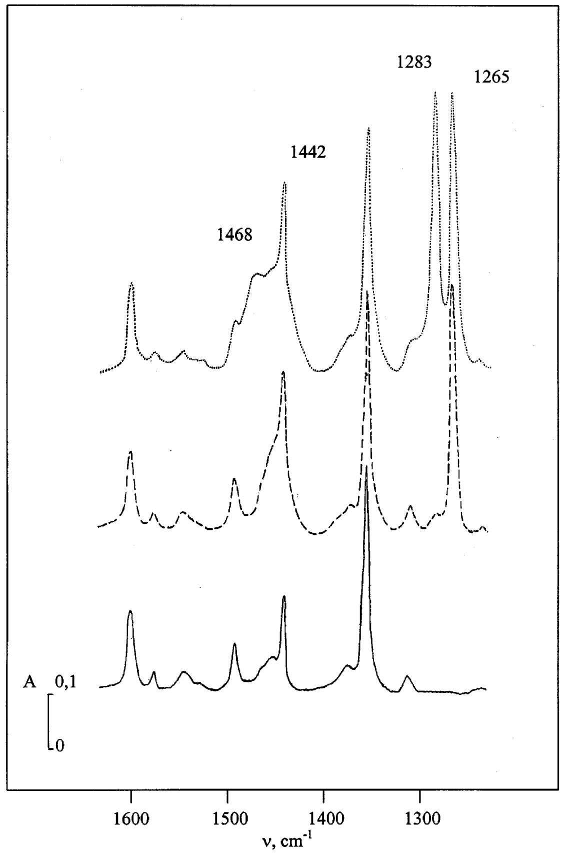

Figure 1. IR spectra of low-temperature Co(TPP) sublimates when heated to 293 K (—) after stepwise exposure in the $^{15}NO_2$ ($\sim 2 \times 10^{-2}$ mmHg, 2 min, - - -) and NO_2 atmosphere ($\sim 3 \times 10^{-2}$ mmHg, 2 min, ···) and exhaustive evacuation after each step.

Results and Discussion

Figure 1 shows the IR spectra of Co(TPP) (—) sublimed films after sequential exposure to low-pressure $^{15}NO_2$ and NO_2. The first procedure leads to the appearance of three new IR bands at ∼1440, 1265, and ∼800 cm^{-1} (Figure 1, - - -). After addition of natural abundance nitrogen dioxide, three other bands at 1468, 1283, and 805 cm^{-1} appear in the spectrum as well (Figure 1, ···). These bands are easy to assign to $\nu_a(NO_2)$, $\nu_s(NO_2)$, and $\delta(NO_2)$[8] of the coordinated nitro-group. The fact that the intense band at 1283 cm^{-1} is isotopically sensitive is very important, since it rules out the possibility of its assignment to the π-cation radical marker band of solid-phase $CoTPP^{\bullet +}$ that lies in the same spectral range.[9] In analogous experiments with ZnTPP,[10] the frequency of the intense new band in this spectral range did not depend on whether NO_2 or $^{15}NO_2$ was used and was assigned with certainty to the π-cation radical marker band. With these small quantities of oxidizing agent, the complex formed is 5-coordinate because of the absence of new bands

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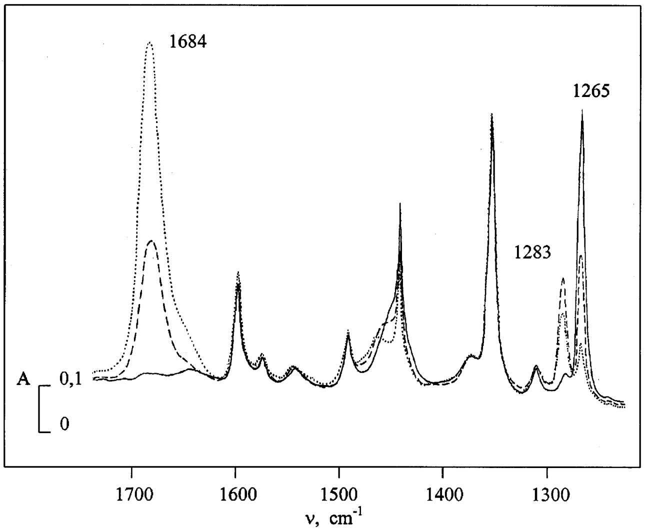

Figure 2. IR spectra of Co(TPP)($^{15}NO_2$) obtained by interaction of $^{15}NO_2$ gas with a sublimed layer of Co(TPP) (—) after exposure under 4 mmHg NO within 20 min (- - -) and overnight (···) ($T = 283$ K).

belonging to the mixed ($^{15}NO_2$)Co(TPP)(NO_2) complex. It can be also concluded that under these experimental conditions the coordinated nitro-group does not undergo a substitution reaction completely different from that of nitrosyl complexes Co(TPP)(NO) (see below).

To confirm that an oxo-transfer reaction between Co(TPP)(NO_2) and NO occurs, it is necessary to use isotopes of nitrogen oxides, since simple ligand substitution leads to formation of the same products as oxo-transfer reaction.

$$\mathrm{Co(TPP)(NO_2) + NO \rightarrow Co(TPP)(NO) + NO_2} \qquad (1)$$

Figure 2 demonstrates the spectral changes caused by exposure of thin films containing Co(TPP)($^{15}NO_2$) to an NO atmosphere. In experiments with excess NO, two new bands appeared in the spectrum at 1684 and 1283 cm^{-1}. These certainly belong to Co(TPP)(NO) and Co(TPP)(NO_2). The formation of these new bands is accompanied by a decrease in the intensity of the band at 1265 cm^{-1} belonging to Co(TPP)($^{15}NO_2$). The intensity of the band at 1283 cm^{-1} of Co(TPP)(NO_2) increased with time until it reached a maximum value before it began to decrease, while the intensity of the nitrosyl stretching band constantly increased. The final spectrum indicates that the sample contained mostly the nitrosyl complex Co(TPP)(NO).

These spectral changes can be interpreted in the following manner. Oxo-transfer from the coordinated nitro-group ($^{15}NO_2$) to NO leads to formation of Co(TPP)(^{15}NO) and oxidation of NO to form uncoordinated NO_2 (eq 2). Since the latter is formed within the layered complex, it is readily coordinated by the free Co(TPP) or substitutes NO in nitrosyl complexes Co(TPP)(NO) (see below) to form Co(TPP)(NO_2) (eq 3). The first of these reactions seems to be very fast. According to Seki et al.,[11] the rate of NO_2 recombination with CoTPP after photodissociation of Co(TPP)(NO_2) in benzene solution is equal to 3.6×10^9 dm^3 mol^{-1} s^{-1}. This process leads to formation of short-lived nitrito-complex Co(TPP)(ONO) with a lifetime of 2.3 ms at room temperature, which undergoes an intramolecular nitrito-nitro linkage isomerization.[11] The solid−gas reaction is also believed to be fast as may be concluded from the conditions of the formation of Co(TPP)(NO_2) (Figure 1).

In the presence of excess NO, the Co(TPP)(^{15}NO) undergoes a ligand exchange (eq 4) so the concentration of Co(TPP)(^{15}NO) in the layer is small. Such exchange for nitrosyl complexes of metalloporphyrins was previously described for iron derivatives[12,13] in solution. According to our measurements in the films of Co(TPP)(NO) obtained by interaction of NO with low-temperature sublimed layers of CoTPP,[14] the exchange reaction in the presence of ^{15}NO atmosphere readily occurs. This process is extremely fast for amorphous layers, in which half of the nitrosyl ligands exchanged under a pressure of 4 mmHg of ^{15}NO within ∼3 min. Because of this exchange, the band belonging to $\nu(^{15}NO)$ has a very low intensity and manifests itself as a low frequency shoulder of the intense ν(NO) band (Figure 2, ···).

$$\mathrm{Co(TPP)(^{15}NO_2) + NO \rightarrow Co(TPP)(^{15}NO) + NO_2} \qquad (2)$$

$$\mathrm{Co(TPP) + NO_2 \rightarrow Co(TPP)(NO_2)} \qquad (3)$$

$$\mathrm{Co(TPP)(^{15}NO) + NO \rightarrow Co(TPP)(NO) + {}^{15}NO} \qquad (4)$$

For reliability of interpretation, it would be desirable, however, to spectrally detect the product of eq 2, i.e., Co(TPP)(^{15}NO). Since the NO exchange reaction (eq 4) is preceded by an oxo-transfer reaction, eq 2, lowering the NO pressure in the gas phase will serve to decrease the quantity of Co(TPP)(NO) formed. Moreover, the use of low NO pressure in the gas phase will lead to lower diffusion rates due to the smaller concentration gradient. It is important if we assume that the ligand exchange reactions in nitrosyl complexes (eq 4) are primarily diffusion controlled, while oxo-transfer reactions that require breaking an N−O covalent bond must be activation controlled. To further decrease the NO diffusion rate, the sample of Co(TPP)($^{15}NO_2$) was annealed (crystallized) by holding it under a vacuum at 323 K for 2−3 h. At these conditions, the NO stretching of Co(TPP)(NO) formed was about 15 cm^{-1} higher than in the amorphous state,[15] the pattern that was also observed for Fe(TPP)(NO).[16] For these layers, more than a 10-fold decrease of the rate of NO/^{15}NO exchange reactions was observed at the same experimental conditions of pressure and temperature. This strategy has led to formation of

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[15] The transfer of the nitrosyl complex from the amorphous to the crystalline state is accompanied with a high-frequency shift of nitrosyl stretching frequency from 1684 to 1699 cm^{-1} (1652 to 1668 cm^{-1} for Co(TPP)(^{15}NO)) due to crystal packing effects.[14] The same pattern is observed for Fe(TPP)(NO).[16]

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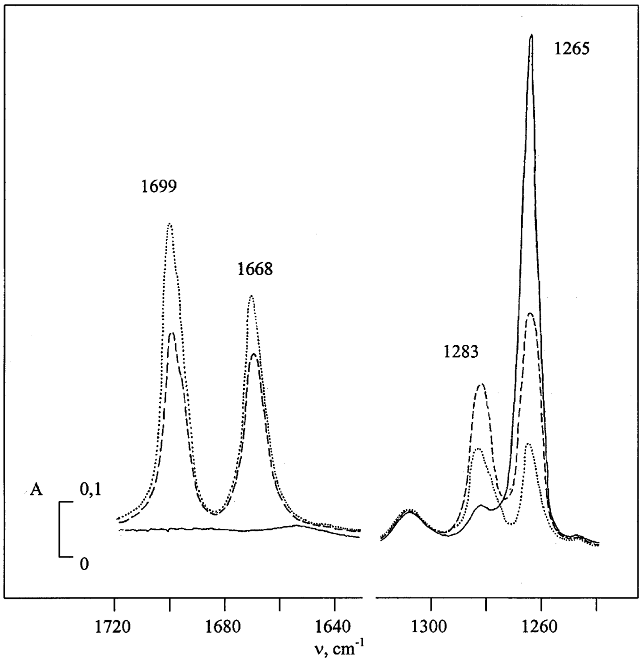

Figure 3. IR spectra of sublimed layer containing $Co(TPP)(^{15}NO_2)$ (—) after exposure under 0.1 mmHg NO at 298 K for 3 h (- - -) and 8 h (···).

samples in which both the 1699 cm^{-1} band of Co(TPP)(NO) and a well-defined nitrosyl stretching band at 1668 cm^{-1} assigned to the $Co(TPP)(^{15}NO)$ complex (Figure 3) are observed. This can serve as clear evidence of the oxo-transfer reaction.

The reactions proceeding in sublimed layers of $Co(TPP)(NO_2)$ in the presence of NO are not limited to those depicted by eqs 2−4. It is seen from Figure 2 that the intensity of the $\nu_s(NO_2)$ band at 1283 cm^{-1} in the sample represented by the dotted line is higher than that of $\nu_s(^{15}NO_2)$. Assuming that the extinction coefficients for $\nu_s(NO_2)$ of two nitro isotopomers are not substantially different, this observation means that the concentration of $Co(TPP)(NO_2)$ in the layer is higher than that of $Co(TPP)(^{15}NO_2)$, although the extraction of the O-atom from both must have the same probability when their concentrations in the layer become equal. This implies that there is an additional pathway for formation of $Co(TPP)(NO_2)$.

Figure 4 shows that in the presence of low-pressure NO_2 the conversion of the nitrosyl complex Co(TPP)(NO) to nitro-complex $Co(TPP)(NO_2)$ occurs. To observe this process, it is necessary to supply into the cryostat small increments[17] of NO_2 followed by exhaustive evacuation of the gas phase after each step. After every NO_2 addition, the intensity of the NO_2 stretching band increases to a certain level, although there is an excess of gas-phase NO_2. These results are easy to interpret if we assume that the substitution reaction given by eq 5 occurs in the sublimed layer.

$$Co(TPP)(NO) + NO_2 \rightarrow Co(TPP)(NO_2) + NO \qquad (5)$$

Substitution of NO by NO_2 leads to elimination of NO, which in its turn will participate in oxo-transfer reactions. When the concentration of NO is low, the rate of reaction 5 is far greater than that of oxo-transfer. At a certain NO concentration in the gas phase, the rates of two competitive reactions will become equal, and this dynamic equilibrium will be maintained until evacuation of the system followed by addition of a new portion of pure NO_2 to the cryostat. High concentrations of NO in the head gas promote the oxo-transfer reaction described in eq 2.

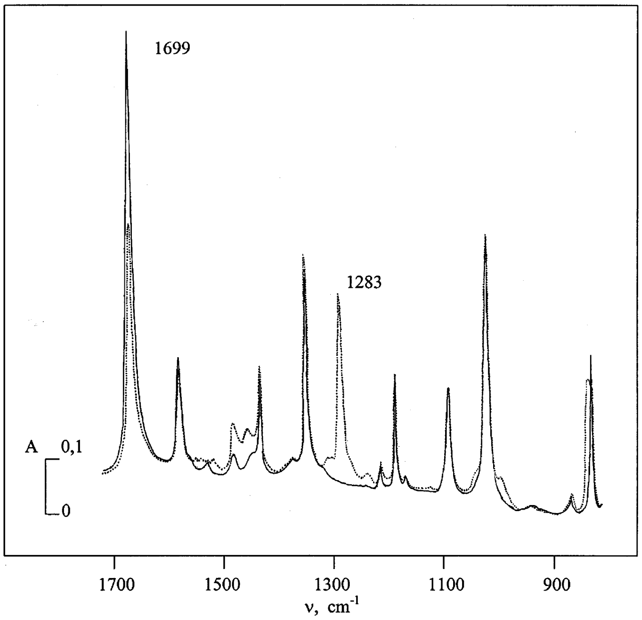

Figure 4. IR spectra of sublimed layer containing crystalline Co(TPP)(NO) (—) after 5 cycles of stepwise addition of NO_2 in to the cryostat followed by exhaustive evacuation (···). The initial pressure of NO_2 in each step was equal to ~0.2 mmHg (T = 298 K). The total time of NO_2 exposure is 6 h.

The results obtained reveal that complex equilibria exist in the systems involving Co(TPP), NO, and NO_2. The same pattern has been observed for Fe(TPP) in solution. In the atmosphere of partially oxidized NO, iron porphyrins form a nitro-nitrosyl complex $FeP(NO)(NO_2)$ that is stable under NO atmosphere and can be spectrally characterized in solution and in the solid state.[18,19] In the absence of NO, this complex dissociates forming Fe(TPP)(NO) and $Fe(TPP)(NO_2)$.[20] The latter is very reactive and easily undergoes transformation to the nitrato complex.[19,20] In contrast, $Co(TPP)(NO_2)$ is fairly stable in solution and in the solid state.[3,6a] It is likely that the ligand exchange reaction given by eq 5 proceeds via formation of a thermally unstable six-coordinate nitro-nitrosyl complex of Co(TPP) similar to iron porphyrins. Low-temperature spectral studies are now in progress to confirm this mechanism.

Exposure of $Co(TPP)(NO_2)$ to pyridine vapors quickly leads to formation of 6-coordinated nitro-amino complex $(Py)Co(TPP)(NO_2)$[6c] as evidenced from the shifting of NO_2

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[17] Low-pressure NO_2 is necessary to prevent further oxidation of $Co(TPP)(NO_2)$.[6b]

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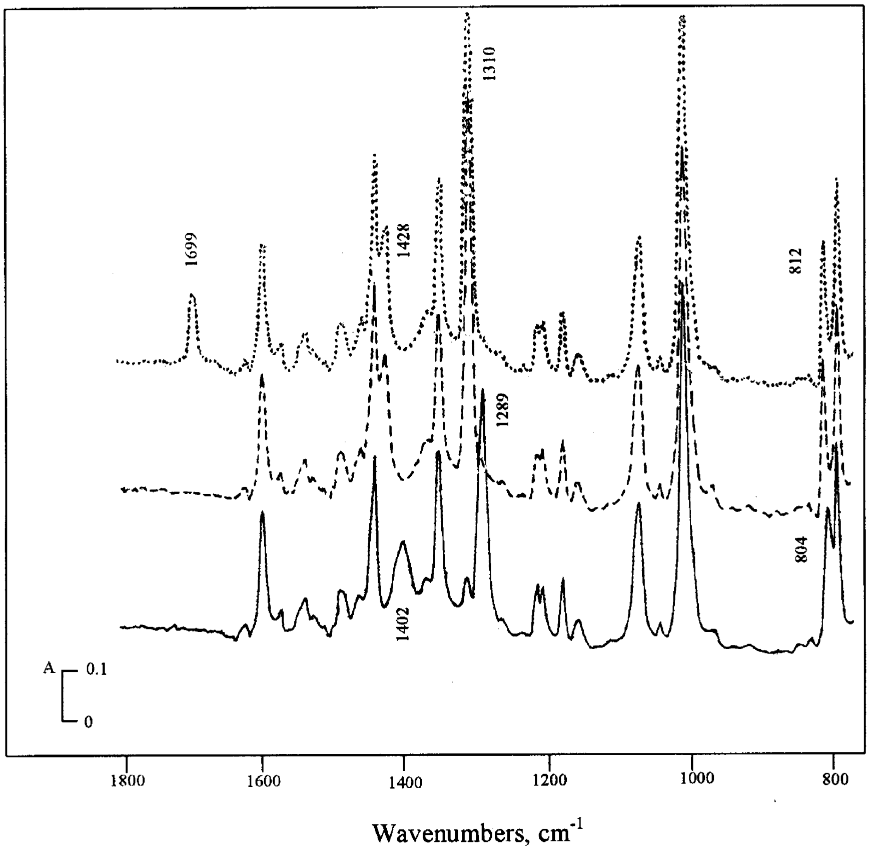

Figure 5. IR spectra of the products formed after introduction of pyridine vapors (10 mmHg, 5 min followed by exhaustive evacuation) on the sublimed layer of Co(TPP)($^{15}NO_2$) (—), Co(TPP)(NO_2) (- - -), and after exposure of layer of (Py)Co(TPP)(NO_2) characterized by the dashed line spectra in the atmosphere of NO (0.1 mmHg) during 16 h (···).

vibrational modes to new values, depicted in Figure 5 (- - -). Experiments with isotopically enriched $^{15}NO_2$ (Figure 5, —) completely confirm its formation. The band frequencies are very close to data measured in a KBr pellet for this complex obtained by the air oxidation of Co(TPP)(NO) in the presence of pyridine.[21] Exposure of these films to NO atmosphere at the same experimental conditions as in the case of Co(TPP)(NO_2) does not lead to noticeable changes in the intensities of NO_2 bands. Their intensities were decreased very slightly (~5%), and a small band at 1699 cm^{-1} attributable to NO-stretching of Co(TPP)(NO) appeared after a long time of exposure (16 h) in the atmosphere of NO (Figure 5, ···).

The results obtained clearly demonstrate the oxo-tranfer ability of the 5-coordinate nitro-complex and show that the 6-coordinate complexes are rather inert. This difference may be the result of the significant difference in electronic structure between the 5- and 6-coordinate species reflected in the larger ONO angle of the 5-coordinate species,[3] but this investigation cannot rule out an oxo-transfer mechanism, in which the vacant site of the metalloporphyrin plays definite role.

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