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Tracking Reactive Intermediates by FTIR Monitoring of Reactions in Low-Temperature Sublimed Solids: Nitric Oxide Disproportionation Mediated by Ruthenium(II) Carbonyl Porphyrin Ru(TPP)(CO)

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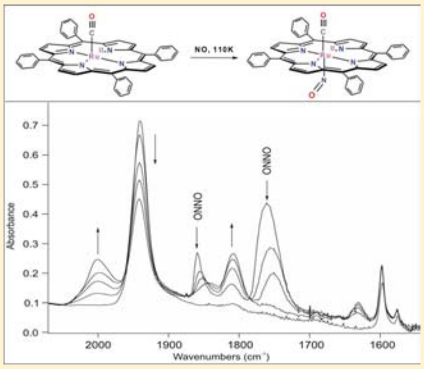
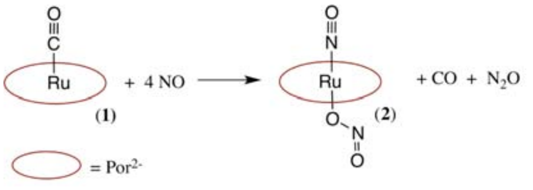
Supporting Information

ABSTRACT: Interaction of NO (^{15}NO) with amorphous layers of Ru(II) carbonyl porphyrin (Ru(TPP)(CO), TPP^{2-} = *meso*-tetraphenylporphyrinato dianion) was monitored by FTIR spectroscopy from 80 K to room temperature. An intermediate spectrally characterized at very low temperatures (110 K) with ν(CO) at 2001 cm^{-1} and ν(NO) at 1810 cm^{-1} (1777 cm^{-1} for ^{15}NO isotopomer) was readily assigned to the mixed carbonyl−nitrosyl complex Ru(TPP)(CO)(NO), which is the logical precursor to CO labilization. Remarkably, Ru(TPP)-mediated disproportionation of NO is seen even at 110 K, an indication of how facile this reaction is. By varying the quantity of supplied NO, it was also demonstrated that the key intermediate responsible for NO disproportionation is the dinitrosyl complex Ru(TPP)(NO)$_2$, supporting the conclusion previously made from solution experiments.



1. INTRODUCTION

Ruthenium(II) carbonyl porphyrin complexes Ru(Por)(CO) (**1**, Por^{2-} = *meso*-tetraphenyl (TPP)-, *meso*-tetra(4-tolyl) (TTP)-, or octaethyl (OEP)- porphyrinato dianions) have been shown to react with NO to give the corresponding *O*-nitrito nitrosyl complexes Ru(Por)(NO)(ONO) (**2**) both in solution[1,2] and in thin porous layers of solid Ru(Por)(CO).[3] Since stoichiometric quantities of nitrous oxide are also formed, this reaction is the result of NO disproportionation mediated by the ruthenium carbonyl porphyrin (e.g., eq 1). Similar reactivity has been seen for the osmium analog[4] and for other metal centers.[5]



(1)

The kinetics of the Ru^{II}(Por)-mediated NO disproportionation were studied in dry, deaerated toluene solution at 298 K using a stopped-flow spectrophotometer. With excess NO two stages were observed, each being first order in [Ru^{II}(Por)] (Por^{2-} = OEP^{2-} or TTP^{2-}):[2] an initial rapid reaction to give an observable intermediate with a rate that was first order in [NO] and a slower transformation to **2** that was second order in [NO]. By probing the reaction at relatively low [NO] (where the second stage was very slow owing to the [NO]^2 dependence) and with modest concentrations of added CO (0.8−2.5 mM), it was possible to show that the first stage leads to reversible formation of a dinitrosyl intermediate (**C**, eq 2) with equilibrium constants (K_2) of 2.0 × 10^5 and 6.3 × 10^4 for Por = TTP and OEP, respectively.[2] The dinitrosyl complex **C** was subsequently characterized by infrared spectroscopy and computation.[6,7]

$$\mathrm{Ru(Por)(CO)} + 2\mathrm{NO} \rightleftharpoons \underset{(\mathbf{C})}{\mathrm{Ru(Por)(NO)_2}} + \mathrm{CO} \tag{2}$$

The proposed pathway to formation of **2** from **1** is illustrated in Scheme 1. The first step would be reversible addition of one NO to give the carbonyl nitrosyl intermediate **A**. Carbon monoxide dissociation from **A** (the steady state concentration of which is first order in [NO] at low [NO]) to give the mononitrosyl species Ru(Por)(NO) (**B**) would be rate limiting under these conditions.[2] Flash photolysis studies have shown that **B** is rapidly trapped by NO to form **C** ($k_C \approx 10^8$ M^{-1} s^{-1}).[8] As a result, in the absence of added CO, reaction of **1** with excess NO to give **C** is first order in [NO].

However, although logic clearly suggests the intermediacy of **A**, this nitrosyl carbonyl complex has not previously been directly observed. Here we use the sublimed layers methodology[9,10] to identify and characterize this species using FTIR

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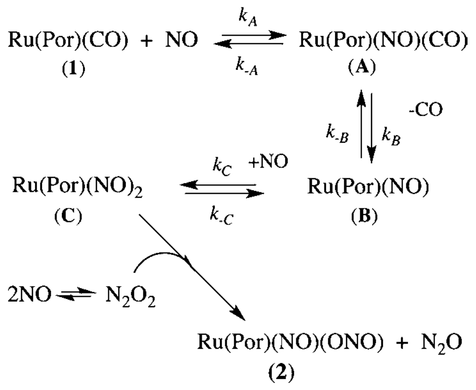
Scheme 1. Proposed Mechanism for Reaction of Excess NO with Ru(Por)(CO) in 298 K Toluene Solution (ref 2)



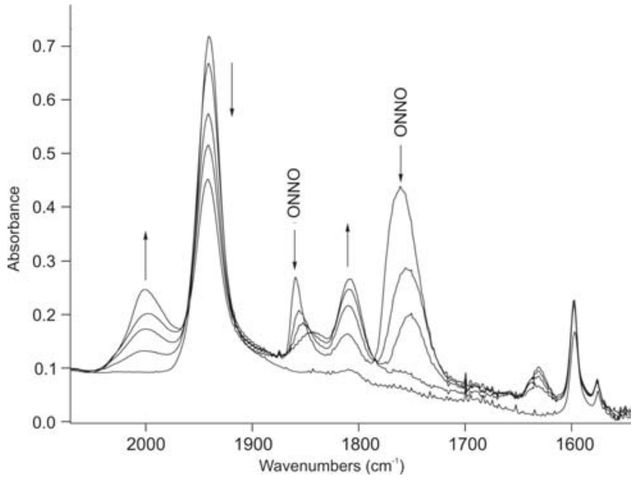


Figure 1. FTIR spectral changes accompanying reaction of NO (4 Torr equivalent) with a sublimed layer of Ru(TPP)(CO) upon warming from 80 to 110 K.

spectroscopy of low-temperature (80−110 K) solids for Por^{2-} = TPP^{2-}. We were also able to demonstrate formation of dinitrosyl complex **C** along the reaction coordinate leading to **2.**

■ EXPERIMENTAL SECTION

Ru(TPP)(CO)·EtOH was purchased from Midcentury Chemicals Inc. (Posen, IL). It was placed in a Knudsen cell and heated to about 470 K under high vacuum ($P = 10^{-5}$ Torr) for about 1 h to eliminate solvated EtOH. Then liquid nitrogen was poured into the cryostat, and sublimation of **1** with an appropriate rate required heating to about 550 K. For obtaining layers with thicknesses convenient for IR spectral studies, sublimation was carried out for about 2 h. For reactions with nitric oxide, NO was fed to the cryostat from a vessel provided with a mercury manometer to measure the quantity of this gas. NO and ^{15}NO (with isotopic enrichment 98.5% purchased from Institute of Isotopes, Republic of Georgia) were purified by passing through a trap containing KOH pellets immersed in an acetone/dry ice slurry to remove higher nitrogen oxides and trace quantities of water. 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 characteristic IR bands of N_2O, N_2O_3, or H_2O, thus indicating the absence of these species. (The absence of N_2O_3 also indicates that no NO_2 impurities were present in the NO introduced to the cryostat.) Infrared spectra were recorded with a Nexus (Thermo Nicolet Corp.) FTIR spectrometer in the range 400−4000 cm^{-1} with a spectral resolution of 2 cm^{-1}.

■ RESULTS AND DISCUSSION

Thin layers of metal tetra-arylporphyrinates obtained by sublimation onto a low-temperature (77 K) surface are amorphous and have high microporosity.[9,10] Thus, the metalloporphyrins in these layers can readily interact with volatile reactants, and adducts thus formed can be studied by IR spectroscopy over a wide temperature range without the interference of solvent absorptions. In this context, it was shown earlier[5] that reaction of excess NO with sublimed layers of Ru(TPP)(CO) (**1**) leads to formation of *O*-nitrito−nitrosyl complex Ru(TPP)(NO)(ONO) (**2**) in analogy to solution experiments.

The IR spectrum of **1** in sublimed layers prepared as described at 80 K displays an intense band at 1944 cm^{-1} that can be attributed to the carbonyl stretch $\nu(CO)$ (Figure 1, initial spectrum). With the cryostat at 80 K, a small amount of NO was introduced; the system was slowly warmed, leading to the spectral changes shown in Figure 1. Introduction of NO led to the appearance of IR bands at ∼1760 and 1860 cm^{-1} representing the asymmetric and symmetric $\nu(NO)$ bands of *cis*-ONNO, which forms spontaneously from NO at low temperature.[11] These bands slowly decreased in intensity as the system was warmed. Simultaneously, the intensity of the $\nu(CO)$ band at 1944 cm^{-1} also decreased, and two new bands of about equal intensity grew in at 2001 and 1810 cm^{-1} (Figure 1). When ^{15}NO was used, the latter band shifted to 1777 cm^{-1} while the position of former slightly shifts to lower frequency to 1999 cm^{-1} (Figure 2), as would be anticipated due to a coupling of the CO and NO stretching vibrations. Analogous experiments using a 1/1 mixture of NO and ^{15}NO are described in the Supporting Information.

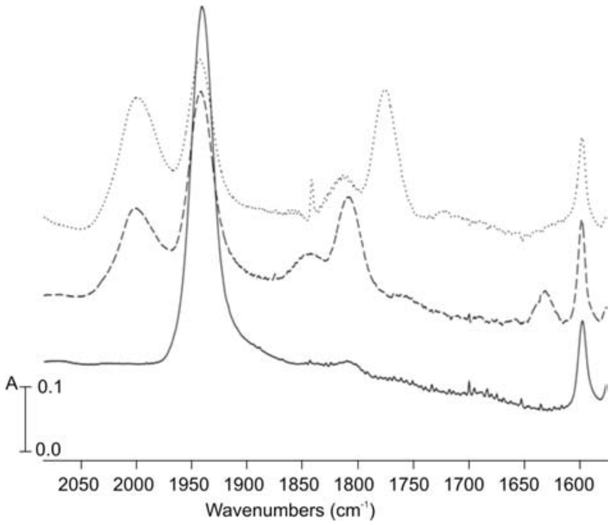


Figure 2. (Solid line) FTIR spectrum at 110 K of a sublimed layer of Ru(TPP)(CO). (Dashed line) Spectrum after introduction of NO (4 Torr equivalent) into a cryostat at 80 K and warming to 110K. (Dotted line) Spectrum resulting from the same procedure performed with ^{15}NO.

These spectral data clearly indicate that the low-temperature reaction of **1** with NO leads to formation of the carbonyl−nitrosyl complex Ru(TPP)(CO)(NO) (**A**, Scheme 1) with the high-frequency band near 2000 cm^{-1} assigned to the carbonyl stretch $\nu(CO)$ and the lower frequency band near 1800 cm^{-1} assigned to the nitrosyl stretch $\nu(NO)$ {$\nu(^{15}NO)$}. As noted in the Introduction, the existence of such a species at the initial stage of reaction was suggested previously[2] but never confirmed.

Spectra shown in Figures 1 and 2 also display weak bands of growing intensities at 1636 and 1845 cm^{-1} that appear at lower frequency (~1600 and 1810 cm^{-1}) in experiments with ^{15}NO isotopomer. The lower frequency band can be assigned as $\nu(NO)$ of the dinitrosyl complex $Ru(TPP)(NO)_2$ (**C**)[6] and the other to $\nu(NO)$ of Ru(TPP)(NO)(ONO) (**2**), the product of eq 1. Thus, it is notable that, even at 110 K, disproportionation apparently is occurring.

The carbonyl−nitrosyl intermediate **A** is thermally unstable and begins to decompose at temperatures above 110 K. Simultaneously, when excess NO is present, the rate of disproportionation is apparently markedly increased, as manifested by the growth of bands at 1845(1810) {ν(NO)}, 1516(1489) {ν(-N═O)}, and 928(908) cm^{-1} {ν(O−N═)} (numbers in parentheses represent data for ^{15}N isotopomer). These new bands indicate formation of the nitrito−nitrosyl complex **2** (Figure 3).[5] Notably, the absorbance at 2220 cm^{-1} (2151 cm^{-1} for reaction with ^{15}NO) also increases. This is evidence for formation of N_2O that is adsorbed in the layer. As the layers are warmed, this absorbance is maintained until ~150 K, but on further warming N_2O passes into the gas phase. This observation unambiguously confirms that the transformations of the ruthenium complexes are due to nitric oxide disproportionation and are not the result of accidental O_2 contamination in the course of experiment. We recognize that such contamination could generate NO_2, and reaction of that species with Ru(TPP)(NO) would also form Ru(TPP)(NO)(ONO), as observed for analogous Fe−porphyrins.[12] In experiments with excess nitric oxide in the form of a 1:1 $NO/^{15}NO$ mixture the *O*-nitrito−nitrosyl complexes with differently labeled nitrogen in nitrito and nitrosyl moieties are formed (Figure 4). In this case, also four bands of equal intensity (not shown) of the differently labeled nitrous oxide grow in spectra at 2220, 2197, 2174, and 2151 cm^{-1} that belong to asymmetrical stretching of $^{14}N_2O$, ^{15}NNO, $N^{15}NO$, and $^{15}N_2O$ correspondingly.[13]

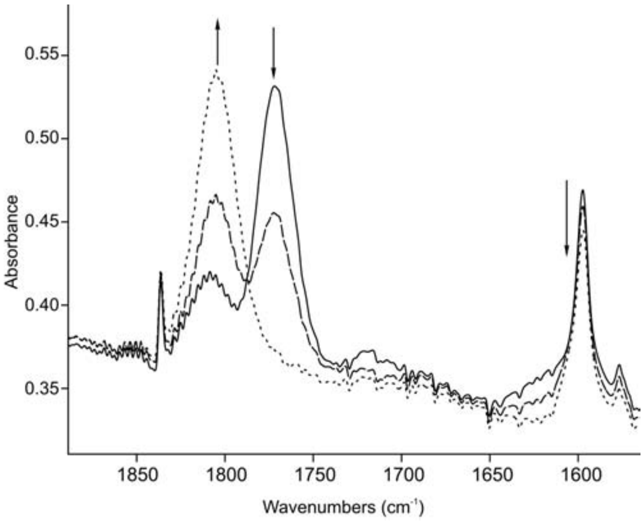


Figure 3. FTIR spectral changes demonstrating decomposition of $Ru(TPP)(CO)(^{15}NO)$ and formation of $Ru(TPP)(^{15}NO)(O^{15}NO)$ upon warming of the layer from 110 to 180 K.

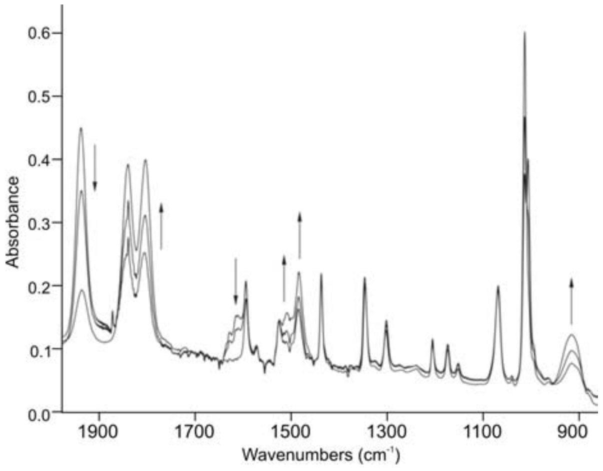


Figure 4. Formation of differently labeled nitrito−nitrosyl complexes Ru(TPP)(NO)(ONO) upon interaction of an equimolar $NO/^{15}NO$ mixture with Ru(TPP)(CO).

Spectra of the various N and ^{15}N species described in this article are summarized in Table 1. Notably, the ν(NO) frequency at 1810 cm^{-1} for the nitrosyl−carbonyl intermediate A is in a range that is often seen for linearly coordinated nitrosyl complexes, which would be certainly unexpected for a compound with formulation Ru^{II}(TPP)(NO)(CO). Linear NO coordination is typical of Ru(III) and Fe(III) complexes where NO coordination leads to charge transfer to the metal center to give (formally) diamagnetic $M^{II}(NO^+)$ species. Such a resonance form would not be expected for A, since charge transfer to the Ru(II) center would be much less favorable. For comparison, the ν(NO) frequencies of 6- and 5-coordinate nitrosyl complexes of ferrous porphyrin complexes Fe^{II}(Por)(L)(NO) and Fe^{II}(Por)(NO) fall in the range 1625−1690 cm^{-1}, and these have Fe−N−O bond angles in the range 137−148°.[14] The IR spectrum of the analogous dinitrosyl species $Ru^{II}(TPP)(NO)_2$ displays only a single ν(NO) at 1642 cm^{-1} in solution, and computational studies suggest that both Ru−N−O angles are in the range of 130°.[7] Given the relatively weak interaction between **1** and NO, there may be some analogy between **A** and the copper nitrosyl complex $[Cu(CH_3NO_2)_5(NO)][PF_6]_2$ reported by Hayton and co-workers,[13] where ν(NO) was found to be 1933 cm^{-1}, even higher

Table 1. Axial Ligands' Vibrational Frequencies in Corresponding Ru(TPP)(L)(L′) Complexes

complexes	ν(CO)	ν(N═O)	ν(—N═O)	ν(O—N═)	*T*, K
Ru(TPP)(CO)	1944				293
$Ru(TPP)(CO)_2$	2009				200
$Ru(TPP)(NO)_2$		1636			293
$Ru(TPP)(^{15}NO)_2$		1607			293
$Ru(TPP)(NO)(^{15}NO)$		1616			293
Ru(TPP)(CO)(NO)	2001	1810			110
$Ru(TPP)(CO)(^{15}NO)$	1999	1777			110
Ru(TPP)(NO)(ONO)		1845	1516	929	293
$Ru(TPP)(^{15}NO)(O^{15}NO)$		1810	1489	908	293

than that of free NO (1875 cm^{-1}), but that the Cu−N−O bond angle was quite acute (121.0°). Given the very weak coordination of the NO in that complex, these workers concluded that the resonance form making the greatest contribution had formulation Cu^{II}(NO).

For **A**, the ν(CO) band appears at higher frequency than that of **1** (Table 1). This suggests that there is some charge transfer from the metal center to the NO, since this would decrease the backbonding from metal d$_{\pi}$ orbitals to the π* orbitals of CO. The effect on ν(CO) is less for **A** than for the dicarbonyl complex Ru(TPP)(CO)$_2$, however (Table 1).

For reaction of NO with Ru(Por)(CO) in hydrocarbon solutions, infrared and optical spectroscopic evidence obtained by stopped-flow techniques demonstrated ambient temperature formation of a reactive intermediate concluded to be the dinitrosyl complex Ru(Por)(NO)$_2$.[2] This conclusion is completely supported by the studies reported here for reaction in the layered solid. At low NO pressure when the quantity of NO has not been enough to effectively promote NO disproportionation, the dashed FTIR spectra demonstrated in Figure 5 was obtained. It contains an intense band at 1636 cm^{-1} that has its analogue at 1642 cm^{-1} in solution and should be unequivocally assigned to dinitrosyl complex Ru(TPP)(NO)$_2$ (**C**). In the solid state, this species is fairly stable at room temperature (RT), in contrast to Fe(TPP)(NO)$_2$, which loses its sixth ligand upon warming to RT both in solution[14] and in amorphous solid.[15] Addition of the new NO portion into the cryostat at room temperature slowly converts dinitrosyl complex into the *O*-nitrito−nitrosyl species **2** (Figure 5, dotted line). This observation is consistent with the conclusion of a kinetic study demonstrating that the dinitrosyl complex Ru(TPP)(NO)$_2$ is the key intermediate responsible for NO disproportionation.[2]

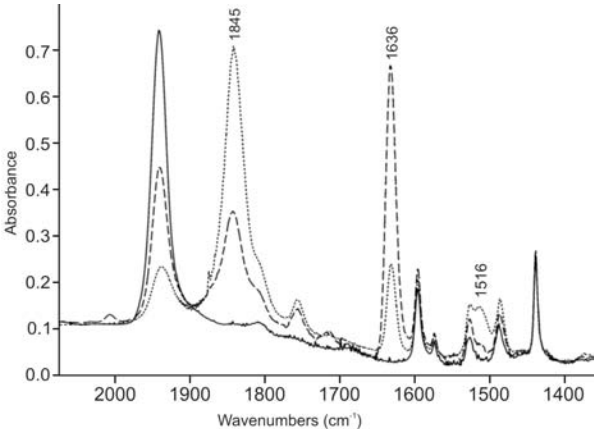


Figure 5. (Solid line) FTIR spectra of layered RuTPP(CO). (Dashed line) After storage under NO (0.7 Torr) overnight. (Dotted line) After additional overnight storage under NO at 4 Torr of NO.

In summary, NO reaction with amorphous layers of Ru(TPP)(CO) (**1**) follows the pattern seen in solution. The dinitrosyl intermediate **C** is formed, and this undergoes further reaction with excess NO to give the nitrosyl nitrito complex **2**. Remarkably, Ru(TPP)-mediated disproportionation of NO is seen even at 110 K, an indication of how facile this reaction is. In the solution-phase study,[2] it was suggested that oxidation of **C** to **2** may occur by O-atom transfer from N$_2$O$_2$ formed by NO dimerization. Since N$_2$O$_2$ formation is favored by low temperature and is seen in the present studies (see above), this pathway would appear to be a reasonable mechanism. Unseen in the earlier solution-phase studies, however, was the mixed carbonyl−nitrosyl complex Ru(TPP)(CO)(NO) (**A**), the logical precursor to CO labilization. Described in the present study is the use of FTIR spectroscopy to probe the transformations following reaction of small quantities of NO with low-temperature sublimed layers of **1** where this unstable intermediate was readily identified and characterized.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

FTIR spectral changes demonstrating low-temperature (80−110K) interaction of equimolar NO/^{15}NO mixture with sublimed layers of Ru(TPP)(CO); comments regarding the equimolar NO/^{15}NO mixture interaction with layered Ru(TPP)(CO). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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