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Reactivity of the Iron Porphyrin Fe(TPP)(NO) with Excess NO. Formation of Fe(TPP)(NO)(NO_2) Occurs via Reaction with Trace NO_2

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Nitrosyl complexes of iron(II) and iron(III) porphyrins play key roles in biological chemistry ranging from the activation of *s*-guanylyl cyclase by nitric oxide to the preservation of meat by sodium nitrite.[1] Thus, it is important to understand the chemical properties of such complexes, including further reactions with NO and other nitrogen oxides. The original goal of this study was to elucidate the dynamics of the reported[2−4] reaction of the nitrosyl complex Fe(TPP)(NO) (**1**) ($TPPH_2$ = *meso*-tetraphenylporphine) with NO to give the nitrosyl nitro species Fe(TPP)(NO)(NO_2) (**2**) for comparison to the stopped flow kinetics investigation of analogous ruthenium complexes.[5] However, this work has uncovered surprisingly different reactivity patterns for Fe(II) compared to Ru(II); **1** apparently does not react with NO to give **2** in room temperature toluene or chloroform over the course of hours. Instead, NO_2, a common impurity in NO sources, is shown to be the likely reactant responsible for formation of **2** from **1** under most conditions.

Figure 1 shows the UV−vis and IR spectra of a chloroform solution of **1** (∼1.7 mM, 0.5 mL) in a 1.0 mm CaF_2 IR cell. The electronic spectrum displays characteristic porphyrin Q-band peaks at 538 nm ($\epsilon = 8700\ M^{-1}\ cm^{-1}$) and 606 nm (2800),[6] and the IR spectrum shows the nitrosyl stretch ν_{NO} at 1682 cm^{-1} (800). Exposure of this solution to excess NO (7 mM) scrupulously scrubbed of other nitrogen oxides[7] led to no change in the electronic or IR spectra over several hours. *Thus, there appears to have been no reaction of **1** with NO under these conditions* (eq 1).[8] Furthermore, the IR spectrum demonstrated that N_2O (2221 cm^{-1}, $\epsilon = 910\ M^{-1}\ cm^{-1}$ in $CHCl_3$) was not formed in detectable concentrations (Figure 1b, inset). After 3 days, the IR spectrum revealed some N_2O (∼6 μM), but the yield was <1% assuming the stoichiometry $\mathbf{1} + 3NO \rightarrow \mathbf{2} + N_2O$.

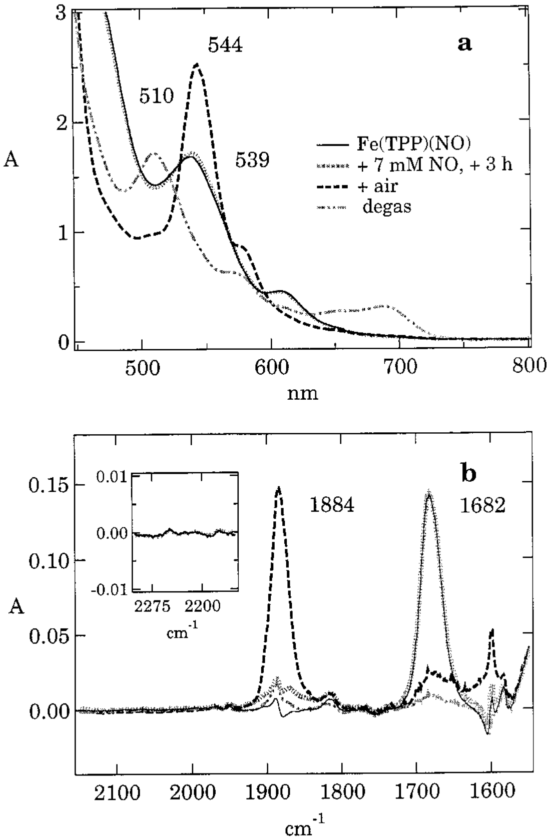

Figure 1. (a) UV−vis and (b) IR spectra of Fe(TPP)(NO) in $CHCl_3$ (1 mm CaF_2): under Ar (solid line); after 3 h in the presence of 7 mM NO, before (gray dotted) and after (dashed) addition of 150 μL of air; same sample after dilution in $CHCl_3$, degassing, and reconcentration (gray dot−dash). Inset shows absence of N_2O after 3 h exposure of **1** to NO (7 mM). The broad absorption at 1876 cm^{-1}, obscured by imperfect solvent subtraction, is due to solution NO (∼20 $M^{-1}\ cm^{-1}$).

$$\text{Fe(TPP)(NO)} + \text{NO} \rightarrow \text{no observable reaction at room temperature} \quad (1)$$

This (lack of) reactivity contrasts sharply with the behavior of similar Ru(II) complexes Ru(P)(CO) (PH_2 = various porphyrins), which react readily with NO to give the nitrosyl nitrito species Ru(P)(NO)(ONO).[9] Stopped-flow kinetics studies indicate the dinitrosyl Ru(P)$(NO)_2$ to be an intermediate, which reacts with an additional 2 equiv of NO via third-order kinetics to give Ru(P)(NO)(ONO) plus N_2O.[5]

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[7] NO was purified by being passed through an Ascarite scrubber and then through an activated silica (80−100 mesh) packed column (5 ft, $^{3}/_{8}$ in stainless steel tubing coil) at −78 °C. The latter procedure removed N_2O and any residual NO_2 and N_2O_3. Warning: at −78 °C, considerable NO absorbs in the column and precaution should be taken for the controlled NO release when the system warms to room temperature. Solutions were prepared and transferred to cells with gastight syringes inside an inert atmosphere "drybox". Materials in contact with NO solutions (septa, stopcocks, and plungers) were deaerated by storage in the drybox for at least 18 h prior to solution exposure.

[8] (a) There have been reports that **1** reacts with excess NO to give Fe(TPP)$(NO)_2$. This was first described by Wayland and Olson,[8b] who presented evidence that low-*T* toluene solutions of **1** under NO demonstrate reversible changes in the EPR and optical spectra consistent with the formation of the dinitrosyl. NMR experiments in this laboratory are in agreement with the observation that such a species may be formed at low temperature but not at ambient temperature. It is also notable that there were no indications in Wayland's spectra that **1** reacts further with NO to give **2** at room or lower *T*. (b) Wayland, B. B.; Olson, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 6037−6041.

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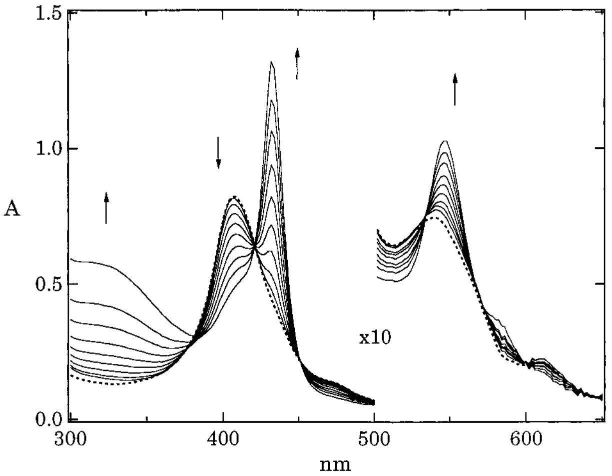
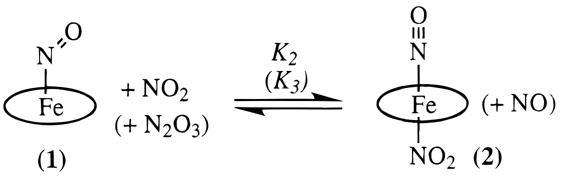


Figure 2. Formation of **2** from **1** in toluene at 22 ± 1 °C, obtained by addition of air (5, 10, 15, 20, 30, 40, 50, 100 μL) to a 117 mL cell containing **1** (8 μM) in toluene (25 mL), with NO (500 Torr, 8 mM). The initial spectrum of **1** in the absence of NO is shown as a dotted line. The spectrum of **1** in the presence of 8 mM NO, the first solid line, is nearly the same, with subsequent spectra representing addition of air.

It is difficult to reconcile the present results with reports that **1** reacts under these conditions to give **2**, unless the previous observations were due to trace higher nitrogen oxides in the NO gas streams of (Scheme 1). This hypothesis was tested by adding air (~150 μL, 2.6 μmol of O_2) directly to the NO/Fe(TPP)(NO) solution described above. The resulting UV−visible and IR spectra are identical to those reported for **2** (Figure 2).[2,4] NO autoxidation in aprotic solvents gives NO_2,[10] and this reacts with excess NO to give N_2O_3, so it is the equilibrium mixture of these species ($K_1 = [N_2O_3]/[NO][NO_2]$) to which the oxidation of **1** is attributed. Preliminary stopped-flow kinetics studies show the reaction of **1** with N_2O_3 to have a second-order rate constant $>10^6$ M^{-1} s^{-1} (Scheme 1).

The equilibrium constant K_3 was evaluated from the spectral changes as microliter aliquots of air were introduced into a dilute solution of **1** ([Fe] = 8 μM) in toluene ([NO] = 8 mM) (Figure 1). Stepwise addition of O_2 led to decreased absorbance in the Soret band region at 406 nm due to **1** and increases at 432 nm due to **2** as well as increased absorbance at 306 nm indicating the buildup of N_2O_3 ($\epsilon = 2 \times 10^3$ M^{-1} cm^{-1}).[11] The spectral changes at 432 nm and calculated $[N_2O_3]$ values were used to determine $K_3 = 160 \pm 20$ according to Hoshino's method[12] (Supporting Information, Figure S-1). One can also estimate the K_2 for the reaction of NO_2 with **1** from the relationship $K_2 = K_1K_3$. If one assumes K_1 in toluene to be similar to that reported in acetonitrile (6.7×10^3 M^{-1}),[13] then K_2 is $\sim 1.1 \times 10^6$ M^{-1} in toluene.

Scheme 1



Further manipulations of **2** demonstrated that this easily undergoes dissociation of NO. For example, the solution of **2** for which the optical and IR spectra displayed in Figure 1 were recorded was removed from the IR cell, diluted under Ar with $CHCl_3$, and then evaporated in vacuo back to the original volume. The IR spectrum of the resulting solution (Figure 1b) shows no ν_{NO} band, and the Q-band spectrum (Figure 1a) displays features (510 nm ($\epsilon \sim 10^4$ M^{-1} cm^{-1}), 576 (3.5×10^3, sh), 650 (1.7×10^3), and 688 (2×10^3)) characteristic of an $Fe^{III}(TPP)(X)$ type complex.[14] Since **2** is re-formed promptly upon reintroduction of NO, we assign this species as $Fe(TPP)(NO_2)$ (**3**), formed by NO dissociation (eq 2).

$$\mathrm{Fe(TPP)(NO)(NO_2)} \rightleftharpoons \underset{\mathbf{3}}{\mathrm{Fe(TPP)(NO_2)}} + \mathrm{NO} \tag{2}$$

Analogous spectral changes were observed upon controlled removal of NO from the headspace of a toluene solution of **2**, NO, and a known amount of NO_2, followed by equilibration. This procedure allowed estimation of K_4 at $(3 \pm 2) \times 10^{-2}$ M^{-1} very similar to the value previously reported for dissociation of NO from $Fe(TpivPP)(NO_2)$ in CH_3CN.[14a]

In summary, Fe(TPP)(NO), unlike Ru(P),[5,9] does not appreciably bind a second NO in room temperature solutions nor does it promote NO disproportionation to give **2**.[15] The latter is formed readily from Fe(TPP)(NO) by reaction with (the much more soluble) NO_2 (N_2O_3) present in many NO gas streams or formed by NO reaction with trace O_2. Thus, unless care is taken, NO_x impurities are likely to play a major role in the observed chemistry of transition metal complexes whenever NO is used in large excess. Qualitatively, NO is more readily dissociated from **2** than is NO_2.

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Supporting Information Available: Supplemental Figure S-1 that demonstrates the determination of K_3. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) It has been suggested[15b] that trace H_2O may interact with **1** to inhibit its reactivity with NO. However, solutions of **1** plus NO prepared in an oven-dried silanized UV/vis cell by vacuum line transfer of toluene from highly activated 3 Å molecular sieves (to minimize such traces) demonstrated no differences in reactivity. (b) Farmer, P. J. Personal communication.