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O Atom Transfer from Nitric Oxide Catalyzed by Fe(TPP)

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Abstract: The reaction of NO-Fe(TPP) with low pressures of NO gas proceeds through three distinct transformations, the first of which we suggest is the formation of an N−N-coupled, $(NO)_2$ adduct intermediate. The subsequent formation of $NO(NO_2)Fe(TPP)$, which under these conditions readily loses NO, suggests that it is formed by addition of free NO_2 to the starting nitrosyl. A mechanism is proposed which implies that the addition of a competitive O atom acceptor would lead to catalytic production of N_2O. In agreement with the proposed mechanism, the formation of N_2O is decoupled from the formation of the nitrite by using PPh_3 as the competitive acceptor. The mechanism of O atom transfer was examined by cross-labeling experiments, which show that both O atoms in the intermediate are equivalent, even under catalytic conditions. The formation of an intermediate was confirmed by IR spectroscopy of the heterogeneous reaction of an NO-Fe(TPP) film with gaseous NO, in which transient, isotope-sensitive ν(NO) bands are seen prior to $NO(NO_2)Fe(TPP)$ formation. Mixed $^{14}N/^{15}N$ label experiments demonstrate coupling between the two bound nitrosyls in the transient species.

Introduction

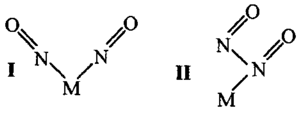
The identification of the physiological activity of nitric oxide has generated much interest in the chemistry of metal nitrosyls, both as models of metalloprotein reactivity and as possible pharmaceutical delivery systems.[1,2] Though it has been studied for many years, the chemistry of metal-coordinated nitrosyls is complex and still not fully understood.[3−6] For example, many metal−nitrosyl complexes undergo further reaction with excess NO, ultimately forming N_2O and a metal−nitrite complex as shown in eq 1. Examples of such reactivity are known for nitrosyl complexes of Co,[7,8] Fe,[9−12] Ru,[13,14] Mn,[15] Cu,[16,17] Rh,[18] and Ir.[19]

$$3NO \xrightarrow{+\,M} N_2O + M{-}NO_2 \tag{1}$$

Several distinct steps must occur during this metal-assisted disproportionation reaction. First, an N−N coupling must occur to form the precursor to N_2O. Such reactivity mimics that of the Cu-based nitrous oxide reductases (NoR) which transform NO into N_2O with the concurrent formation of water, eq 2.[20]

$$2NO \xrightarrow{Cu-NoR} N_2O + H_2O \tag{2}$$

Various Cu complex models for NoR active sites reductively disproportionate NO by eq 1.[16,17] Work by Tolman and co-workers with Cu tris(pyrazolyl)borate complexes has pointed to a mononuclear coupling of nitrosyls, postulating either a dinitrosyl (**I**) or a hyponitrous form (**II**) as the N_2O-forming intermediate.[21] We have postulated an Fe-bound hyponitrous intermediate similar to **II** in our investigations of the electrocatalytic reduction of NO by myoglobin.[22] Others have suggested similar N−N-coupled intermediates for heme-based NoR enzymes.[23,24]



A second requirement in eq 1 is the loss of an O atom from the N−N-coupled intermediate, ultimately yielding gaseous N_2O

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and a metal nitrite. Several mechanisms have been suggested, such as O atom transfer from a coordinated N_2O_2 to a second metal nitrosyl.[5,8] In a series of papers, Ford and co-workers studied the NO disproportionation reaction catalyzed by Ru-(TPP).[25] Kinetic evidence identified an intermediate, suggested as a dinitrosyl adduct, which subsequently reacted with two additional NO molecules to yield a nitrosyl/nitrito adduct and N_2O. Unexpectedly, recent reports from the same laboratory suggest that Fe(TPP) does not undergo the same reaction, but does form a *trans*-dinitrosyl species at low temperature.[26,27] In our hands, the disproportionation reaction proceeds as previously reported by Yoshimura and others.[9,10]

In this report we give evidence of an N−N-coupled intermediate, generated from reaction of NO-Fe(TPP) with NO, that is capable of O atom transfer reactions which are uncoupled from nitrite formation. This reactivity is demonstrated in catalytic production of N_2O in the presence of suitable O atom acceptors. Isotopic labeling experiments under catalytic conditions were undertaken to probe the nature of the O atom transfer reaction, and rapid infrared spectroscopic studies are used to characterize a possible N−N-coupled intermediate.

Experimental Section

Abbreviations. TPP, 5,10,15,20-Tetraphenyl-21*H*,23*H*-porphine; Fe(TPP)Cl, 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine iron(III) chloride; NO-Fe(TPP), nitrosyl iron tetraphenyl porphine; PPh_3, triphenyl phosphine; $OPPh_3$, triphenyl phosphine oxide.

General Procedures. All experiments were conducted under strict anaerobic conditions by using standard Schlenk techniques. Toluene was distilled from calcium oxide and degassed by freeze−pump−thaw methods. Fe(TPP)Cl was purchased from Porphyrin Products. PPh_3 and $OPPh_3$ were obtained from Aldrich. Sodium nitrite-*15N* was purchased from Cambridge Isotope Laboratories. Nitric oxide obtained from Air Gas was used for most experiments, but further purification was necessary. To trap out NO_x impurities, the gas was bubbled through a 1 M NaOH solution; to trap out N_2O and H_2O contaminants in the NO reactant gas, the gas was passed through a U-tube immersed in acetone/dry ice or liquid N_2 before being exposed to the reaction mix. Trace amounts of N_2O remained and were measured at the start of each experiment quantifying N_2O production. [^{15}N]Nitric oxide was generated from L-ascorbic acid and sodium nitrite-*15N* and purified by the same procedure. All other chemicals were reagent grade and used without further purification.

The electronic spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. Infrared spectra quantifying gaseous N_2O production were measured on a Nicolet 410 Impact spectrophotometer; solid-state spectra were obtained with a ReactIR (Applied System) surface probe, as will be described. The head gas samples from isotopic labeling experiments were separated with a PLOT GC column (fused silica 50 m × 0.32 mm, Al_2O_3, KCl coating) and analyzed by a Micromass Autospec mass spectrometer. Data were acquired in EI mode, and fragmentation was reported as the percentage of N_2O (44) peak.

The reaction of NO-Fe(TPP) with NO is inhibited by solvent contamination (e.g., water, methanol) in the starting material or reactant gas, and care was taken in the purification and thorough drying of the complexes. Several methods were used to synthesize the starting NO-Fe(TPP):

(i) Reductive Nitrosylation.[28] Fe(TPP)Cl was dissolved in toluene (20% v/v methanol) in a round-bottom flask and degassed by the freeze−pump−thaw method. Purified nitric oxide was transferred into the flask, and the solution was stirred vigorously overnight before evaporation under vacuum. The resulting solid was washed with degassed methanol several times.

(ii) Hydroxylamine Reduction.[29] Fe(TPP)Cl was dissolved in toluene in a round-bottom flask and degassed. After hydroxylamine hydrochloride was dissolved in methanol, sodium methoxide in methanol was added. The white precipitate formed was discarded after the product solution was passed through the filter paper. The resulting solution was added to the Fe(TPP)Cl solution and stirred overnight. A large portion of methanol was added to precipitate the red-brown solid. This solid was washed with methanol several times and dried under vacuum.

(iii) Zinc Amalgam Reduction.[3] Fe(TPP)Cl was dissolved in toluene and extensively degassed by the freeze−pump−thaw method. The toluene used was commercial grade and not dried. After addition of zinc amalgam powder, the solution was frozen in liquid nitrogen and evacuated. Nitric oxide was introduced via a vacuum adapter. The solution was then warmed to room temperature and stirred overnight. The powder was filtered anaerobically, and the resulting solution could be used directly or evaporated under vacuum and redissolved in dry solvents if necessary.

^{15}NO-Fe(TPP) was made from Fe(TPP)Cl and sodium nitrite-*15N* in the presence of PPh_3.[30] Fe(TPP)Cl (79.3 mg, 0.11 mmol) and PPh_3 (29.2 mg, 0.11 mmol) were dissolved in chloroform (5 mL). Sodium nitrite-*15N* (11.4 mg, 0.16 mmol) in methanol (5 mL) was added, and the solution was stirred overnight. After removal of the solvent, the red-brown solid was redissolved in chloroform and passed down a neutral alumina column (Fisher, grade I).

Reaction of NO-Fe(TPP) with NO. In a typical kinetic run, a 3-mL sample of 0.1 mM NO-Fe(TPP) in toluene or chloroform was placed in a homemade airtight quartz cuvette with a vacuum stopcock. After the cell was evacuated, nitric oxide was introduced via a vacuum line, and the pressure was measured with a mercury manometer. The cell was pressurized with nitrogen, and the reaction was followed by the UV−vis spectra.

A series of experiments were run in the presence of PPh_3 and monitored by ^{31}P NMR of the reaction mix in NMR tubes with Schlenk adapters. The amount of $OPPh_3$ produced was calculated from the integrals for PPh_3 (−3 ppm) and $OPPh_3$ (30 ppm).

To correlate the formation of N_2O with changes in the solution-based Fe species, the solution-phase UV−vis spectra and the gas-phase IR spectra of the headgas were measured concurrently as the reaction proceeded. A special apparatus was used, consisting of a quartz UV−vis cell connected via a Schlenk adapter to an airtight CaF_2 IR cell; the details of this hybrid cell have been described in the literature.[23] The absorbance spectra of solutions of NO−Fe(TPP) were unchanged after several weeks of storage in this cell. The relative increase in concentration of N_2O in the headgas during a reaction was determined by integrating the IR absorbance from 2120 to 2280 cm^{-1}.[31]

IR Characterization of Reaction Intermediates. An in situ two-reflection ATR probe was used to obtain sequential IR spectra of solid NO-Fe(TPP) films exposed to NO gas. A homemade glass adapter with a rubber O-ring screw top, two gas inlets, and one septum can be fit on the probe to form a small gastight chamber. The chamber was evacuated for 10 min before each set of experiments and pressurized with pure nitrogen gas. A 20-μL solution of NO-Fe(TPP) in toluene or THF was transferred to the probe surface (diamond or silicon) via a gastight syringe. A stream of nitrogen was passed over the probe until the NO-Fe(TPP) solution dried to a film.

Traces of protic solvents affected the obtained spectra and inhibited further reactivity of the NO-Fe(TPP). These observations were verified by use of wet solvents during the deposition. To remove trace water in solution, after evaporation of a thin Fe(TPP)(NO) film on the IR probe,

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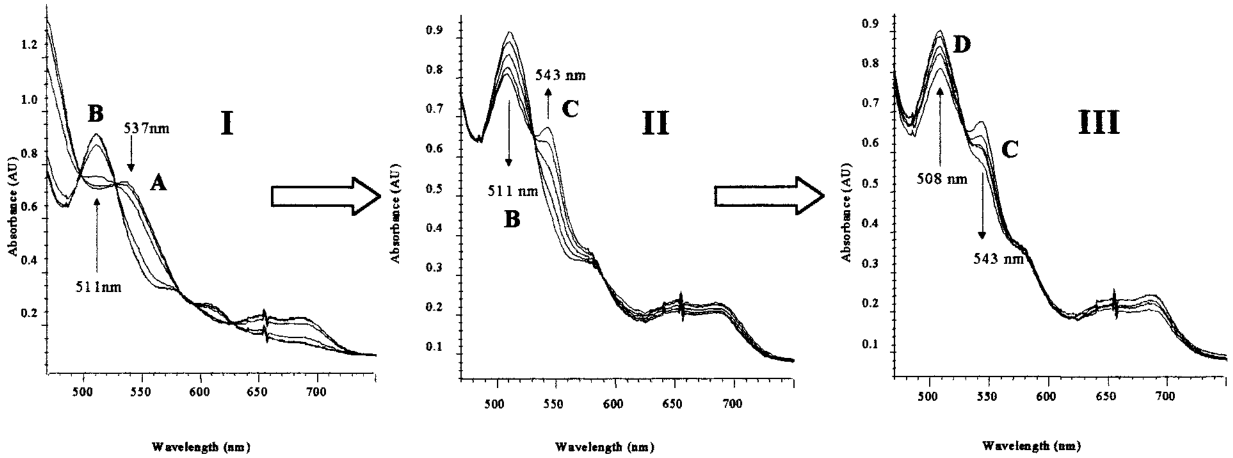

Figure 1. Sequential changes in the absorbance spectra of a 0.07 mM solution of NO-Fe(TPP) under 60 mmHg NO: (I) over 2 min, (II) from 2 to 5 min, and (III) from 5 to 30 min.

pure acetone was cast on the top and re-evaporated with a stream of nitrogen gas. The drying can be followed by IR spectra, as the NO stretch frequency shifts from 1677 to 1697 cm^{-1}. After drying, the system was evacuated, purified nitric oxide was introduced via the Schlenk line, and the pressure was controlled by a manometer. The system was pressurized with nitrogen while the IR spectra were obtained. For mixed-labeling experiments, ^{15}NO gas (ca. 95%) was used, as described above.

Mass Spectroscopy of Labeled N$_2$O. In a typical labeling experiment, ^{15}NO-Fe(TPP) (30.7 mg, 0.044 mmol) and PPh$_3$ (0.6128 g, 2.3 mmol) were dissolved with 5 mL of chloroform in a 250-mL Schlenk flask. Natural abundance nitric oxide was introduced via the vacuum line. The solution was cooled with liquid nitrogen for 10 min and warmed to room temperature. Afterward, the solution was pressurized with He and stirred for 3 h. Next, 0.2-mL aliquots of head gas were analyzed by GC/MS. The absolute abundance of ^{15}NO (*m/z* 31) was corrected by subtracting the contribution from the natural abundance of NO (*m/z* 30), which is about 0.38%. The ratio between ^{15}NO (*m/z* 31) and ^{14,15}N$_2$O (*m/z* 45) thus obtained was used to determine which nitrogen atom was labeled, since only ^{14}N^{15}NO isomer could produce a ^{15}NO fragment.[32]

Results and Discussion

Reaction of NO with NO−Fe(TPP) Like many metal−nitrosyl complexes, NO-Fe(TPP) is not stable in the presence of excess NO gas, forming nitrite adducts.[9,10] Using low NO and NO-Fe(TPP) concentrations, three distinguishable transformations are seen over time in the absorbance spectra, Figure 1. The sequential spectra show clear isosbestic points, suggesting a clean conversion between the four species: the initial complex, NO-Fe(TPP) (**A**), and species **B**, **C**, and **D**. The spectra of **C** and **D** match those of the known compounds, *trans*-Fe(TPP)(NO$_2$)(NO) and Fe(TPP)(NO$_2$), respectively.[9,10,33−34] Figure 2 shows the time course of the reaction at 545 nm which illustrates the rates of the three transformations.

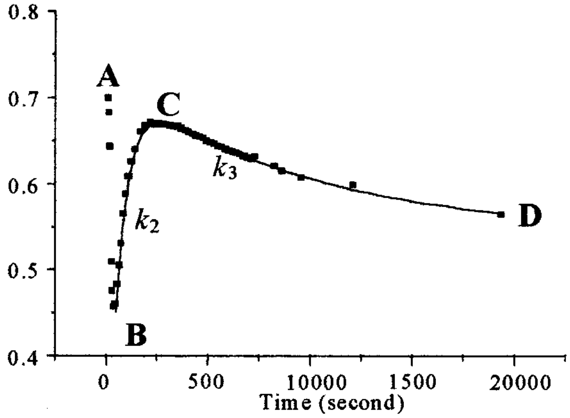

Figure 2. Changes in the absorbance at 545 nm of a 0.07 mM solution of NO-Fe(TPP) under 60 mmHg NO, as in Figure 1. Under these conditions, the apparent rate constant of k_2 is 2.7×10^{-3} s^{-1} and k_3 is 1.0×10^{-4} s^{-1}.

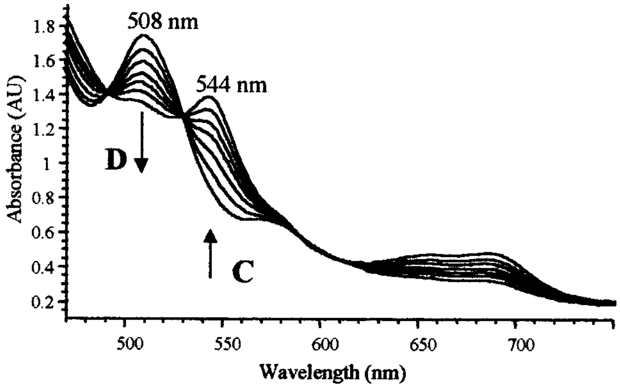

Figure 3. Formation of **D** from **C** upon evacuation of NO headgas. Initial spectra of **C** were generated from a solution 0.15 mM NO-Fe-(TPP) exposed to 10 psi of NO for 30 min. Absorbance spectra were taken at 30 s intervals.

The transformation of **C** to **D** is reversible and is demonstrated in Figure 3. At higher NO concentrations (>100 mmHg), compound **A** is transformed directly to **C**, without buildup of intermediate **B** (Supporting Information). Compound **C** thus formed may be converted to **D** upon evacuating NO from the headgas. Likewise, solutions of **D** will convert to **C** upon exposure to NO gas. Under most conditions used in this work, the endpoint of the reaction is a mixture of products **C** and **D** depending on the [NO]-to-[NO-Fe(TPP)] ratio.

The initial transformation of **A** to **B** is reversible as well, as illustrated in Figure 4; the spectral changes initiated by exposure of NO-Fe(TPP) to NO can be reversed by evacuating the NO from the reaction vessel within the first few minutes. The species **B**, which precedes the formation of the nitrite adducts, is likely the precursor to the formation of N$_2$O. To our knowledge, this is the first clear identification of an intermediate that precedes

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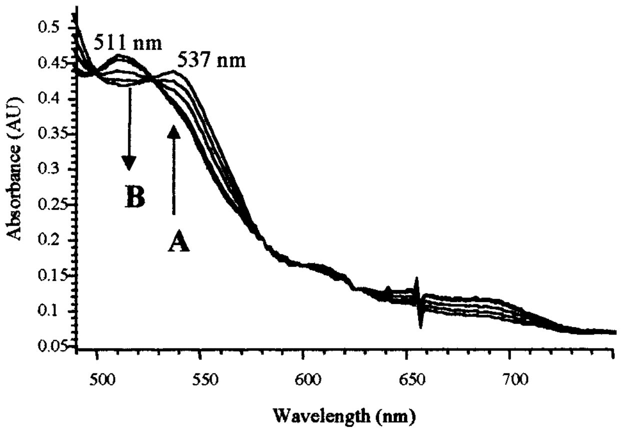


Figure 4. Formation of **A** from **B** upon evacuation of NO headgas. Initial spectra of **B** were generated from a solution 0.05 mM NO-Fe-(TPP) under 60 mmHg of NO for 2 min. Absorbance spectra were taken at 30 s intervals.

nitrite formation. A similar intermediate was previously seen to be formed from reaction of **A** with low pressures of NO but was reported to be in equilibrium with **C**, which at that time was thought to be a trans-dinitrosyl.[35] Physical characterization of this species identifies it as the mononitrite **D**, which has absorbance spectra very similar to those of **B**, Table 1.

The short-lived species **B** irreversibly converts to **C** within minutes. Thus, species **C** must be the initial nitrite adduct formed, as it is unstable with regard to loss of NO under the conditions in which it is formed. From these observations, a tentative mechanism can be proposed for these transformations. The starting nitrosyl **A** reacts with free NO to form an N−N-coupled intermediate, corresponding to **B**, eq 3. The N_2O_2−Fe adduct then transfers an O atom to free NO in solution, releasing the gases N_2O and NO_2, eq 4. The unligated Fe(TPP) thus formed may then react with NO in solution to re-form the starting nitrosyl complex **A**, eq 5, while the NO_2 released can react with **A** directly to give the initially formed nitrite complex **C**, eq 6. Under these conditions, loss of NO from **C** gives the mononitrite adduct **D**, eq 7. In support of this mechanism, both N_2O and NO_2 gases were recently detected during metal-assisted NO disproportionation catalyzed by a binuclear Fe complex.[1]

$$\text{NO-Fe(TPP)} + \text{NO} \rightleftarrows \text{N}_2\text{O}_2\text{-Fe(TPP)} \qquad (3)$$

$$\text{N}_2\text{O}_2\text{-Fe(TPP)} + \text{NO} \rightarrow \text{Fe(TPP)} + \text{N}_2\text{O} + \text{NO}_2 \qquad (4)$$

$$\text{Fe(TPP)} + \text{NO} \rightarrow \text{NO-Fe(TPP)} \qquad (5)$$

$$\text{NO-Fe(TPP)} + \text{NO}_2 \rightarrow \text{(NO)(NO}_2\text{)Fe(TPP)} \qquad (6)$$

$$\text{(NO)(NO}_2\text{)Fe(TPP)} \rightleftarrows \text{(NO}_2\text{)Fe(TPP)} + \text{NO} \qquad (7)$$

Catalytic O Atom Transfers. In the proposed mechanism, free NO acts as an O atom acceptor, forming NO_2 which subsequently reacts with the starting NO-Fe(TPP). If another O atom acceptor were available, the reactions described by eqs 6 and 7 would be suppressed, and the formation of N_2O would become catalytic, Scheme 1. The catalytic efficiency would depend on the relative rates of reaction of **B** with free NO and with the O atom acceptor.

Table 1. Energies for Electronic Absorbance Maxima in the Q-Band Region of Fe(TPP) Ligand Adducts[a]

species	Q-band maxima (nm)
(NO)Fe(TPP), **A**	537, 610
(N_2O_2)Fe(TPP), **B**	511, 575(sh), 653(br), 685(br)
NO(NO_2)Fe(TPP),[b] **C**	545, 577(sh)
(NO_2)Fe(TPP),[c] **D**	508, 570(sh), 687(br)

[a] Spectra were obtained in toluene, under conditions of turnover as in Figure 1. (sh) shoulder, (br) broad. [b] Reference 9. [c] Reference 33.

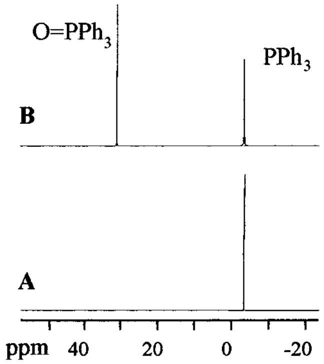
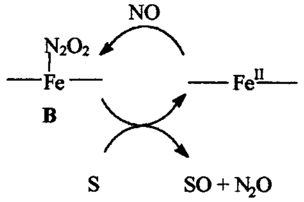


Figure 5. (A) ^{31}P NMR spectrum of 0.01 M PPh_3 in chloroform after exposure to 2 psi NO gas for 3 h. (B) Same conditions with 1 mM NO-Fe(TPP).

Scheme 1



We tested this hypothesis by using PPh_3 as a competitive O atom acceptor, eq 8. Addition of a 100-fold excess of PPh_3 to a 0.1 mM solution of NO-Fe(TPP) under 2 psi NO for 3 h resulted in the formation of over 60% of the PPh_3 to $OPPh_3$ by ^{31}P NMR, Figure 5. The headgas was analyzed by GC/MS, and a strong signal was seen at *m/z* 44, corresponding to N_2O. Under identical conditions in the absence of NO-Fe(TPP), less than 1% $OPPh_3$ was produced, as compared with experiments done in the presence of the metal complex.

$$\text{PPh}_3 \xrightarrow[\text{excess NO}]{\text{NO-Fe(TPP)}} \text{O=PPh}_3 \qquad (8)$$

To correlate the transformations of the Fe complexes with the formation of N_2O, we utilized a cell designed for concurrent determination of UV/vis spectra and IR analysis of the headgas above the reaction.[23] Integration of the absorbance peaks of N_2O in the IR between 2260 and 2160 cm^{-1} was used to quantify its increase in the headgas and plotted on the same time course as the changes in Soret absorbances of NO-Fe(TPP) (407 nm) and Fe(TPP)(NO_2)(NO) (433 nm), Figure 6. The results show that NO-Fe(TPP) is the major species in solution during catalytic N_2O formation and that the catalysis precedes the formation of the nitrite complexes **C** and **D**. In fact, the addition of PPh_3 to the reaction mixture simply delays the formation of **C**; the lag time before the conversion is dependent on the relative concentrations of PPh_3 and NO. For example, 10-fold excess of PPh_3 under 40 mmHg delays the conversion by ca. 3 h, and a 100-fold excess results in a lag time of over 16 h before a

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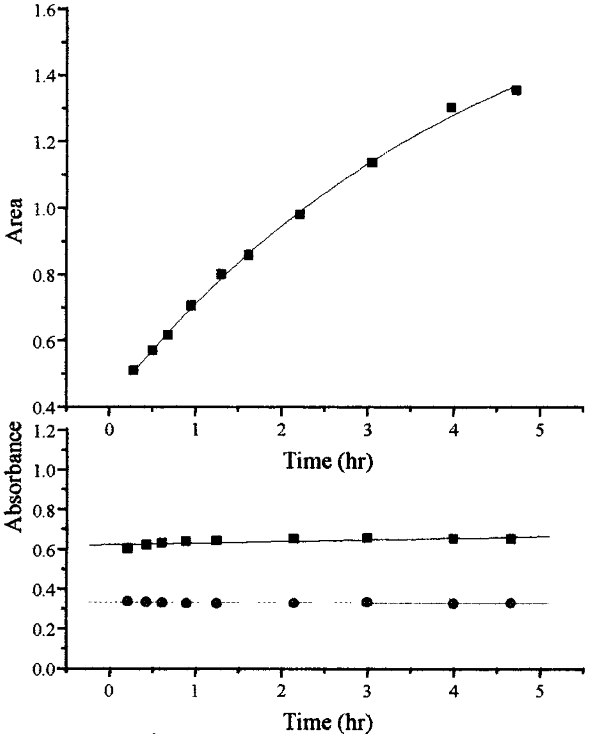

Figure 6. Concurrent measurement of N_2O in the headgas and absorbance changes in a solution of 0.05 mM NO-Fe(TPP) and 1 mM PPh_3 during reaction under 40 mmHg NO. Upper graph, the IR absorbance of N_2O in headgas (area); lower graph, absorbance changes at 407 nm (solid line) corresponding to the Soret band of **A**, NO-Fe-(TPP), and at 433 nm (dotted line) corresponding to the Soret band of **C**, (NO_2)NO-Fe(TPP).

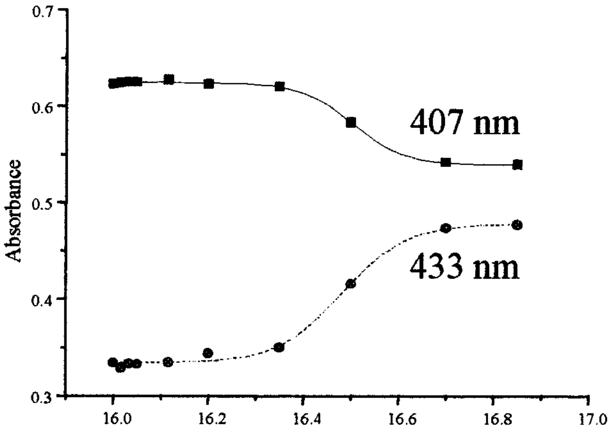

Figure 7. In a continuation of the experiment described in Figure 6 after 16 h, the absorbance at 407 nm (solid line) corresponding to the Soret band of **A**, NO-Fe(TPP), and at 433 nm (dotted line) corresponding to the Soret band of **C**, (NO_2)NO-Fe(TPP).

comparatively rapid formation of the nitrite adducts occurs, Figure 7. Interpreted in terms of our proposed mechanism, the competitive O atom acceptor PPh_3 decouples N_2O formation from that of the nitrite adducts.

Nitrite adducts of Fe^{III} porphyrinates are well known to be unstable to nitrite disproportionation, generating ferrous nitrosyls and apparently nitrate in a stoichiometric reaction.[33] Likewise, it is known that **D** can act as an O atom donor to PPh_3 under certain conditions, eq 9, again in a stoichiometric reaction.[30] The nitrite adducts, **C** and **D**, were tested for their reaction with PPh_3; under the conditions given, the reaction of **C** is negligible, and the reaction of **D** given by eq 9 is ca. 2 orders of magnitude slower than those described by eqs 3−8; sample data are given in the Supporting Information.

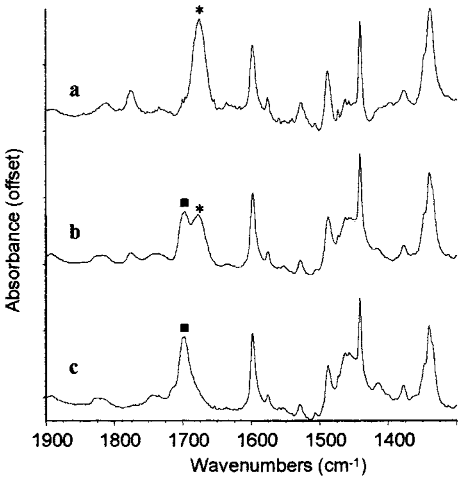

Figure 8. ATR−IR spectra of conversion of the ν(NO) band of an NO-Fe(TPP) film from 1677 (*) to 1697 cm^{-1}(■), (a) as first observed from wet solvent and (b) and (c) taken as the film was dried under an N_2 stream over 1 h.

$$(NO_2)Fe(TPP) + PPh_3 \rightarrow (NO)Fe(TPP) + OPPh_3 \quad (9)$$

Protic Inhibition. The reaction of **A** with NO is inhibited by protic solvents such as water or methanol. Under the same conditions, there is no reaction of **A** in wet chloroform with exogenous NO, but the addition of trace O_2 rapidly produces spectral changes characteristic of mixtures of ferric porphyrins. interaction of water and **A** is evidenced by subtle changes in the electronic absorbance spectra; the band at 536 nm sharpens and shifts to 539 nm upon addition of approximately stoichiometric H_2O to a dry chloroform solution (shown in Supporting Information). The effect is more apparent in the IR spectra of a film of NO-Fe(TPP), shown in Figure 8, where the ν(NO) stretch increases from 1677 to 1697 cm^{-1} during exhaustive evacuation. We, and others, have also observed the protic contaminant shifting of ν(NO) of NO-Fe(TPP) in chloroform solution and in KBr pellets, where mild heating under a vacuum returns the peak frequency to the "dry" value.[36]

The source of the spectral shift is most likely hydrogen-bonding between the nitrosyl and the protic impurity. A recent crystallographic determination of nitrosyl myoglobin shows a strong hydrogen-bonding interaction between the nitrosyl N atom and the distal histidine.[37] We have recently shown that the one-electron-reduced form of nitrosyl myoglobin is protonated at the nitrogen, forming an unusual HNO adduct.[38] Much evidence suggests that the reactivity of a metal nitrosyl with NO, eq 1, depends on the anionic character of the coordinated nitrosyl ligand. For example, the NO disproportionation reactivity of an Fe(topocorand) complex is shut down by nitration of the ligand, which significantly decreases the electron density at the Fe center.[11]

Mass Spectroscopy of Mixed-Labeled N_2O. No buildup of **B** occurs under catalytic conditions; thus, the following irreversible reaction must be fast enough to limit its concentration. This is consistent with the supposition that species **B** is itself the O

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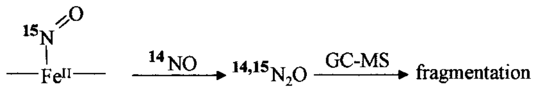
(36) Scheidt, W. R.; Wyllie, G. R. A. Personal communication.

(37) Bruker, E. A.; Olson, J. S.; Ikeda-Saito, M.; Phillips, G. N., Jr. *Proteins: Struct., Funct. Genet.* **1998**, *30*, 352−356.

(38) Lin, R.; Farmer, P. J. *J. Am. Chem. Soc.* **2000**, *122*, 2393−2394.

Scheme 2



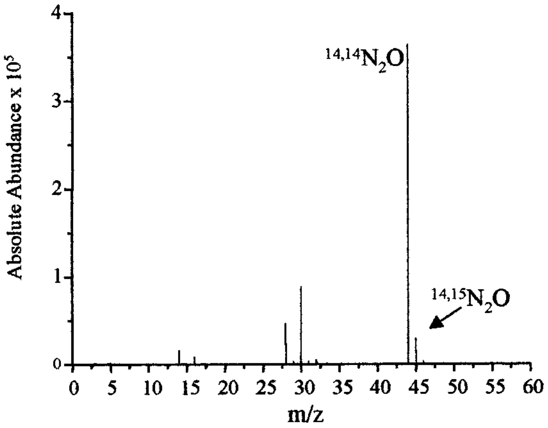


Figure 9. Mass spectrum of N_2O fraction of headgas above the reaction of ^{15}NO-Fe(TPP) with natural abundance NO. Peaks at 45 ($^{14,15}N_2O$) and 31 (^{15}NO) were used to calculate the abundance of $^{14}N^{15}$NO.

atom donor preceding irreversible N_2O formation. To look more closely at this O atom transfer mechanism, labeled ^{15}NO-Fe-(TPP) (ca. 98%) was reacted with excess natural abundance ^{14}NO under catalytic conditions, and the N_2O produced was characterized by GC/MS, Scheme 2.

When ionized in a mass spectrometer, N_2O fragments to yield both N_2^+ and NO^+ fragments in addition to the mother ion N_2O^+. The ratio of the corresponding ions can be used to identify the position of ^{15}N label in mixed-label N_2O.[32] For example, if the terminal N in N_2O is labeled, then only the N_2^+ fragment will have the label, as depicted in eq 10.

$$\text{*NNO} \xrightarrow{\text{ionization}} \text{*NNO}^+ + \text{*NN}^+ + \text{NO}^+ \qquad (10)$$

To determine which O atom is lost in the formation of N_2O, the ratio of $^{15}NO^+$ (m/z 31) to $^{14,15}N_2O$ (m/z 45) from the mixed label experiments were compared to the ratio of NO^+ (m/z 30) to N_2O (m/z 44) for natural abundance N_2O. Because of the ongoing catalytic turnover, only the label-containing peaks at m/z 31 and 45 would correspond to the N_2O formed during an initial turnover from the labeled ^{15}NO-Fe(TPP) precursor.

Three limiting scenarios are possible: (i) equal ratios if the O atom lost is from ^{14}NO; (ii) the ratio of 31/45 should approach zero if the O atom lost is from ^{15}NO; and (iii) if both O atoms are lost equally, or if the label is exchanged with the exogenous NO, the ratio of 31/45 from mixed label N_2O will be about one-half of that of 30/44 from natural abundance N_2O.

The results of a series of experiments are most consistent with the last scenario; i.e., that about one-half of the NO^+ fragments from the mixed label N_2O intermediate are labeled. A typical run is given in Figure 9 (further data are given in the Supporting Information). Likewise, the height of the small peak at m/z 46, corresponding to doubly labeled $^{15}N_2O$, is close to that statistically expected for complete label exchange with the NO headgas.

These experiments show that both the initial Fe-bound NO and exogenous NO are equally active as O atom donors in these experiments. Either the exchange reaction of eq 3 predominates, even under conditions that maximize the rate of O atom transfer by eq 8, or the two nitrosyls are indistinguishable in the precursor complex. Ready exchange of exogenous NO with metal nitrosyls has been previously seen for non-porphyrin Mn and Cu nitrosyl adducts[15,17] and is apparent in the ATR−IR experiments described below.

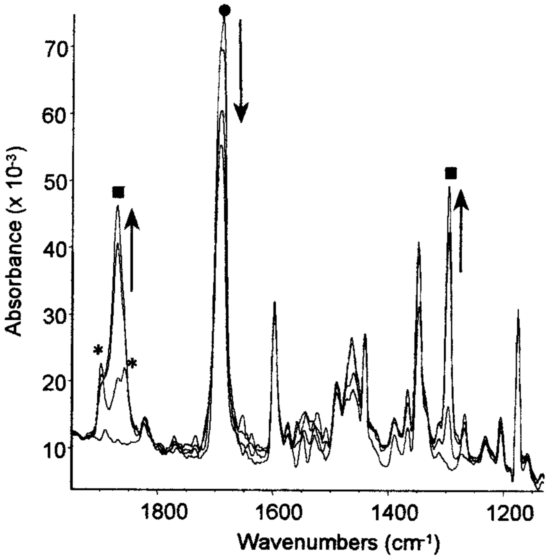


Figure 10. Sequential ATR−IR spectra of a film of NO-Fe(TPP) film taken before exposure and 5, 30, and 60 s after exposure to a stream of purified NO. Absorbances marked are due to the ν(NO) of **A**, NO-Fe(TPP) (●); intermediate **B**, assigned as $(NO)_2$-Fe(TPP) (*); and **C**, (NO_2)NO-Fe(TPP) (■). Experimental details are as given in the text.

Solid-State IR Characterization. Proof of the formation and structure of an N−N-coupled precursor may be obtained from the IR spectra, from the number and stretching frequencies of bands assignable to N−O bonds of a transient species. Several examples of possible N−N-bound species, such as the neutral $(NO)_2$ dimer and the radical anion $N_2O_2^-$, have recently been characterized by IR in matrix isolation.[39,40]

In our hands, the progression of the reaction was difficult to observe by using standard solution IR cells because of the low solubility of NO-Fe(TPP) and masking absorbances of solvents in the region of interest. As an alternative, a solution of NO-Fe(TPP) was evaporated onto the surface of a reflectance IR probe, and the reaction was initiated by exposing the dry film to purified NO gas. The reaction between the dry NO-Fe(TPP) film and gaseous NO occurs rapidly, and conditions were manipulated in order to obtain multiple sequential spectra within the first minute of exposure.

A typical series of spectra of a NO-Fe(TPP) film before and during the reaction with NO is shown in Figure 10. Upon exposure to NO, the band at 1697 cm^{-1} assigned to the ν(NO) of NO-Fe(TPP) decreases rapidly, and several new isotope-sensitive bands grow in. Two of these bands, at 1873 and 1299 cm^{-1}, are identical to those of independently synthesized and characterized Fe(TPP)(NO_2)(NO).[9,10,32] Several other isotope-sensitive, transient bands were seen in various experiments. But of these, only the two high-energy bands (1898 and 1858 cm^{-1}) were consistently formed in the first seconds of reaction during the loss of **A** and subsequently decreased during the formation of **C**, Figure 11.[41]

The use of ^{15}NO gas during the reaction yields corresponding peaks ca. 30 cm^{-1} lower in frequency, a shift somewhat smaller

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(39) Krim, L.; Lacome, N. *J. Phys. Chem. A* **1998**, *102*, 2289.
(40) Andrews, L.; Zhou, M. *J. Chem. Phys.* **1999**, *111*, 6036.

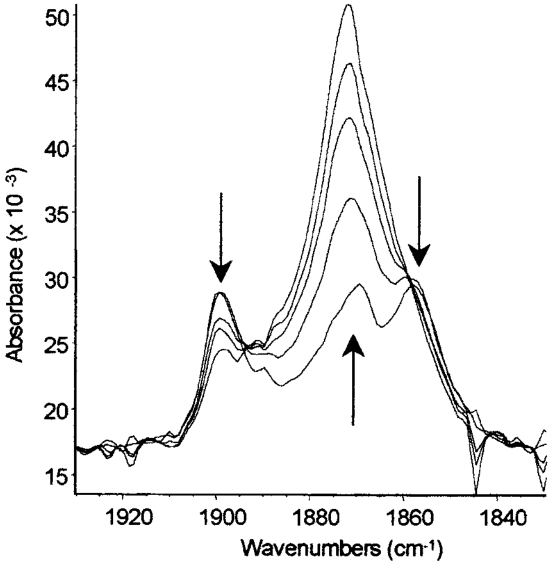


Figure 11. Sequential ATR−IR spectra of the NO region of a film of NO-Fe(TPP) film obtained within the first minute of exposure to a stream of purified NO.

Table 2. Energies, in cm^{-1}, for ν(NO) bands of Fe(TPP) Ligand Adducts

species	^{14}NO	^{14}NO/^{15}NO	^{15}NO
(NO)Fe(TPP), **A**[a]	1697		1669
(NO)$_2$Fe(TPP), **B**[a]	1898, 1856	1888, 1846 plus others	1867, 1823
NO(NO$_2$)Fe(TPP),[a] **C**	1872, 1299		1836, 1280
cis-(NO)$_2$ in Ar[b]	1863, 1776	1850, 1757	1831, 1745

[a] Spectra were obtained by heterogeneous reaction as described in the text. [b] Reference 39.

than that observed in the ultimate product of the reaction, **C**, Table 2.[42] The exchange of the ^{14}NO and ^{15}NO in the starting complex **A** is also apparent in these experiments, though the rate of exchange is not noticeably faster than the production of **C**. Assignment of the transient species to a dinitrosyl species is supported by bands at intermediate energies in mixed ^{14}NO/^{15}NO experiments, as compared to those of ^{14}NO/^{14}NO and ^{15}NO/^{15}NO species, Figure 12.

The presence of unique absorbances for the mixed-label species is indicative of coupling between two nitrosyls, though not conclusive proof of N−N coupling. The bands are broad and overlap those of the product. Also, self-ordering of the Fe(TPP) on the surface of the probe may affect the intensities and positions of observed IR modes by orienting the bound nitrosyls relative to the reflectance, as has been seen for (NO)$_2$ dimers adsorbed on Ag(1,1,1).[43] Further spectroscopic experiments are underway to better characterize the structure of this precursor.

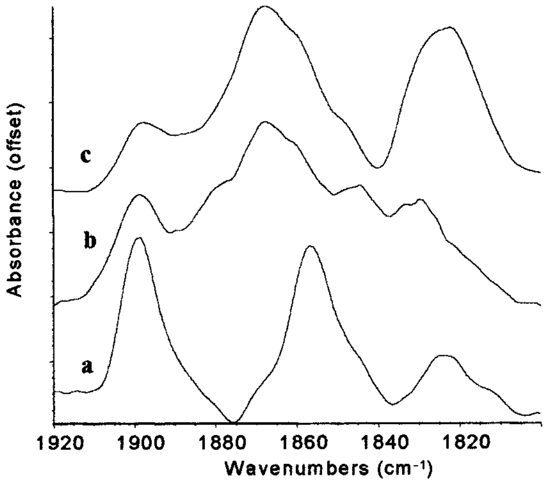
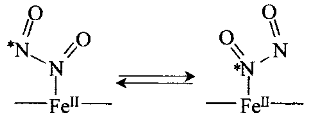


Figure 12. ATR−IR difference spectra of films of ^{14}NO-Fe(TPP) after ca. 10 s exposure to (a) natural abundance NO (>99% ^{14}NO), (b) ^{14}NO/^{15}NO (ca. 50/50), and (c) ^{15}NO (ca. 95%). To emphasize the transient peaks, a normalized product spectrum obtained after ca. 2 min has been subtracted. The band at 1820 cm^{-1} is present in initial spectra.

Scheme 3



The Nature of the N−N-Coupled Intermediate. The absorbance spectrum of intermediate **B** resembles that of a low-spin ferric porphyrin, with distinctive broad bands in the region between 600 and 700 nm. We originally postulated an oxidation of the metal center after N−N coupling, as theoretical calculations suggest that the (NO)$_2$ dimer has an electron affinity on the order of 30 kcal/mol.[44] But the ν(NO) peak frequencies of the intermediate are in the region of neutral or cationic NO metal adducts, inconsistent with reduction of the ligand.

The ν(NO) bands observed in the ATR-IR spectra of the intermediate are distinct from those previously suggested to be of trans-dinitrosyl adducts of Fe(II) porphyrins.[27,28b] We formulate the intermediate as an upright, asymmetrically bound cis-(NO)$_2$ adduct, Scheme 3. The formation of the N−N bond removes two ligand-based electrons from N−O antibonding orbitals, resulting in the observed upfield shift in ν(NO). The bands are at higher frequency than comparable absorbances in the low-temperature spectra of cis-(NO)$_2$, perhaps indicative of σ-bonding interactions with the metal. Such an N$_2$O$_2$ adduct may be susceptible to a fluxional shift between coordination by the two N atoms, Scheme 3, or may undergo NO exchange by eq 3. Both pathways are in accordance with equivalence of N atom positions in the mass spectroscopic experiments and the exchange evident over time in the ATR−IR spectra.

It is interesting to note the parallel between solution and surface chemistry of NO, as similar intermediates have been postulated as forming on metal surfaces. Weakly adsorbed (NO)$_2$ dimers have been characterized at low temperatures on noble metals (Ag, Cu) and metal oxide (Mo, Cr) surfaces under conditions which result in the reductive formation of N$_2$O from NO.[43,45,46] In all cases, the apparent role of metal coordination is to provide a nucleation site for the catenation of NO.

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[41] Free NO, with a ν(NO) ca. 1850 cm^{-1}, should not be seen in the ATR experiment unless it is absorbed onto the surface. Several control experiments under identical NO flow conditions but in the absence of NO-Fe(TPP) show no equivalent peaks ca. 1898 and 1856 cm^{-1}. For instance, an Fe(TPP)Cl film was reacted under these conditions, and only a strong ν(NO) of the known NO-Fe(TPP)Cl was observed at 1882 cm^{-1} (Supporting Information). In the course of this work, we ran over a dozen experiments with NO-Fe(TPP) films that did show these transient peaks under an NO stream.

[42] The peak assignments in Table 2 were determined by difference spectra of the normalized product and intermediate spectras (Supporting Information).

[43] (a) Brown, W. A.; Gardner, P.; Jigato, M. P.; King, D. A. *J. Chem. Phys.* **1995**, *102*, 7277−7280. (b) Brown, W. A.; Gardner, P.; Jigato, M. P.; King, D. A. *J. Chem. Phys.* **1995**, *102*, 7277−7280.

[44] (a) Snis, A.; Panas, I. *Surf. Sci.* **1998**, *412*, 477−488. (b) Snis, A.; Panas, I.; *Chem. Phys.* **1997**, *221*, 1. (c) Snis, A.; Panas, I. *J. Chem. Phys.* **1999**, *110*, 10345.

Conclusions

We have identified an intermediate in the reaction of NO-Fe(TPP) with low concentrations of NO gas, which precedes formation of the nitrite adducts of the Fe complex. We suggest the intermediate to be due to N−N coupling between NO and the metal-bound nitrosyl. The subsequent formation of NO-(NO_2)Fe(TPP) under such conditions that it readily loses NO suggests that it is formed by addition of free NO_2 to the starting nitrosyl and that free NO acts as the O atom acceptor during the formation of N_2O. The addition of the competitive O atom acceptor, PPh_3, leads to catalytic production of N_2O, which was observed and quantified. In agreement with the proposed mechanism, the formation of N_2O is decoupled from the formation of the nitrite adducts under these catalytic conditions. The mechanism of O atom transfer was examined by cross-labeling experiments, which show that both O atoms in the intermediate are equivalent, even under catalytic conditions. The formation of an intermediate was confirmed by IR spectroscopy of the heterogeneous reaction of an NO-Fe(TPP) film with gaseous NO. The disproportionation reaction is rapid under these conditions, but transient isotope-sensitive NO bands are seen, assignable to a precursor to the O atom transfer. Mixed ^{14}N/ ^{15}N label experiments demonstrate coupling between the two bound nitrosyls in the transient species, which may be indicative of N−N bond formation.

Acknowledgment. We thank Dr. John Greaves for valued discussions and mass spectroscopic analysis, Professor Frank Feher for use of a Fischer Porter tube, and Professors Larry Overman and Bill Evans for use of their ReactIR spectrometers. Special thanks are extended to Professor Bill Trogler for the use of a hybrid solution UV−vis/gas-phase IR cell, used extensively in this work. This research was supported by the National Science Foundation (CHE-9702332) and the Petroleum Research Fund, administered by the American Chemical Society (PRF-31804-G3).

Supporting Information Available: Absorbance spectra of the reaction of NO-Fe(TPP) under high [NO], the reactions of $(NO)(NO_2)$Fe(TPP) and (NO_2)Fe(TPP) with PPh_3 as followed by absorbance, a UV−vis spectrum of wet and dry NO-Fe-(TPP), a table of the ion abundances obtained from mixed labeled N_2O with explanation of the data analysis, ATR−IR spectra of the reaction of NO(g) with an Fe(TPP)Cl film, and difference ATR−IR spectra obtained from experiments run under ^{14}NO, ^{15}NO, and ^{14}NO/ ^{15}NO mixtures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(45) (a) Kugler, E. L.; Kokes, R.; Gryder, J. W. *J. Catal.* **1975**, *35*, 142−151. (b) Kugler, E. L. Gryder, J. W. *J. Catal.* **1975**, *36*, 152−158.

(46) (a) Queeney, K. T.; Pang, S.; Friend, C. M. *J. Chem. Phys.* **1998**, *109*, 8058−8061. (b) Queeney, K. T.; Friend, C. M. *J. Phys. Chem. B* **1998**, *102*, 9251−9257.