Multielectron Redox Reactions between Manganese Porphyrins Mediated by Nitrogen Atom Transfer

L. Keith Woo  
*Iowa State University, kwoo@iastate.edu*

James G. Goll  
*Iowa State University*

Follow this and additional works at: [http://lib.dr.iastate.edu/chem_pubs](http://lib.dr.iastate.edu/chem_pubs)

Part of the [Chemistry Commons](http://lib.dr.iastate.edu/chem_pubs)

The complete bibliographic information for this item can be found at [http://lib.dr.iastate.edu/chem_pubs/735](http://lib.dr.iastate.edu/chem_pubs/735). For information on how to cite this item, please visit [http://lib.dr.iastate.edu/howtocite.html](http://lib.dr.iastate.edu/howtocite.html).
Multielectron Redox Reactions between Manganese Porphyrins Mediated by Nitrogen Atom Transfer

Abstract
From the pioneering work of Taube, 1 electron-transfer reactions can be mechanistically categorized into either inner sphere or outer sphere processes. The most well-studied systems in either case typically involve one-electron changes. Redox processes involving transfers of a multiple number of electrons, especially between two metals, are much less prevalent and consequently less well understood. The most extensive studies on multiple electron changes have involved atom transfer processes. These are typically two electron-transfer reactions mediated by either a bridging halogen or a bridging oxo ligand. The consideration of a nitrido ligand as a bridging species in redox reactions has received little attention. In this regard, we initiated studies on the bridging capabilities of the nitrido complexes of metalloporphyrins. We report herein the first example of a reversible net three electron redox process mediated by nitrogen atom transfer.

Disciplines
Chemistry

Comments
duced dissociation (CID)\(^1\) to remove the CO ligands. \(\text{Co}_2\text{NO}^+\) was generated in the FTMS-2000 by electron impact ionization of \(\text{Co}(	ext{CO})_5\text{NO}\) followed by clustering reactions of the ions with the parent neutral and subsequent CID. Swept double resonance techniques\(^2\) were used to isolate the ion of interest. \(\text{Co}(	ext{CO})_5\text{NO}\) was introduced through General Valve Series 9 pulsed valves.\(^3\) Utilizing Varian leak valves, \(\text{O}_2\) was maintained at a relatively low pressure, \(\sim 10^{-7}\) Torr, while argon was maintained at a relatively high pressure, \(\sim 10^{-3}\) Torr, to provide collisional cooling for ion thermalization\(^4\) and to act as a collision gas for CID. The FTMS-1000 has been modified as previously described\(^5\) for photochemical studies using a 2500 W Hg-Xe arc lamp. A Spectra Physics Model 2030 high power Ar\(^+\) laser and a Quanta Ray Nd:YAG laser were used to perform photochemical experiments on the FTMS-2000.

The time between collisions in the low-pressure environment of an FT-ICR-MS dictates that internal conversion, photodissociation, or collisional and radiative relaxation of photoexcited ions can compete favorably with reactive collisions, significantly reducing the possibility of observing a photodissociated ion-molecule reaction pathway under these conditions. However, two examples of such photoenhanced reactivity have been reported.\(^6\)\(^7\) These reactions were driven by the vibrational excitation of the reactant ion arising from photon absorption and internal conversion. Recently, we proposed that an alternative photoinduced reaction mechanism could involve changes in reactivity due to photoisomerization.

In this study we observed the reaction of \(\text{Co}_2\text{NO}^+\) with \(\text{O}_2\) as a function of time with and without irradiation. Figure 1 displays the relative abundances of \(\text{Co}_2\text{NO}^+\) and \(\text{Co}_2\text{O}_2^+\) under these conditions. Jacobson has demonstrated that the populations of the reactant and product ions approach an asymptotic limit with increasing time when no irradiation is present. However, when irradiated with 1064-nm (\(\sim 27\) kcal/mol) photons from a pulsed Nd:YAG laser operated at 10 Hz, the nonreactive isomer is observed to become reactive, presumably because the photoexcited species can access both the reactive and the nonreactive isomers. During the original study, Jacobson determined that \(\sim 55\%\) of the thermally isomerized \(\text{Co}_2\text{NO}^+\) population exists in the reactive form. In this study, the \(\text{Co}_2\text{O}_2^+\) produced during the \(\text{Co}_2\text{NO}^+\) synthesis and isolation period was not ejected from the cell in an effort to prevent inadvertent excitation of \(\text{Co}_2\text{NO}^+\). When the data in Figure 1 are corrected for this initial \(\text{Co}_2\text{O}_2^+\) population, the reactive isomer accounts for \(\sim 65\%\) of the \(\text{Co}_2\text{NO}^+\) present immediately following isolation. Relative abundances in Figure 1 do not sum to 100% due to a small photodissociation contribution not displayed.

Experiments using arc lamp irradiation at \(\sim 35\) kcal/mol resulted in competition between the photoinduced reactivity characterized in Figure 1 and photodissociation, reaction 2. The \(\text{Co}_2\text{NO}^+ + \text{hv} \rightarrow \text{Co}_2^+ + \text{NO} \quad (2)\)

514.5-nm output from the Ar\(^+\) laser produced photodissociation products exclusively. In a continuing series of studies, we are using variable energy light sources in conjunction with this photoinduced reaction to characterize the height of the \(\text{Co}_2\text{NO}^+\) reactive/nonreactive isomerization barrier. In addition, photodissociation threshold studies are underway to determine \(D(\text{Co}_2^+\text{NO})\) for the reactive and nonreactive isomers as well as \(D(\text{Co}_2^+\text{O}_2)\).

The photoisomerization mechanism is supported by recent collisional activation studies performed by Jacobson\(^8\) in which the reactive isomer was permitted to react to completion with \(\text{O}_2\), and the \(\text{Co}_2\text{O}_2^+\) produced was ejected from the cell to isolate the nonreactive isomer of \(\text{Co}_2\text{NO}^+\). Collisional activation of the nonreactive isomer imparts sufficient internal energy to this species to permit it to access the reactive form. This collision-induced isomerization is consistent with our photoinduced reaction mechanism.

The chemistry exhibited by this system may prove to have far reaching ramifications in the study of the reactivity and photodissociation of molecules on metal microsurfaces, particularly concerning the question of molecular vs dissociative chemisorption. The search for additional examples of photoinduced ion-molecule reactions in the gas phase continues in our laboratory.

**Acknowledgment** is made to the Division of Chemical Sciences, Office of Basic Energy Sciences, United States Department of Energy (DE-FG02-87ER13776) for supporting transition-metal ion research and to the National Science Foundation (CHE-8612234) for continued support of FT-ICR-MS instrumentation. J.R.G. gratefully acknowledges the National Science Foundation for predoctoral fellowship support and Lance Safford for many helpful discussions.

### Multielectron Redox Reactions Between Manganese Porphyrins Mediated by Nitrogen Atom Transfer

L. Keith Woo* and James G. Goll

Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received November 2, 1988

From the pioneering work of Taube,\(^1\) electron-transfer reactions can be mechanistically categorized into either inner sphere or outer sphere processes. The most well-studied systems in either case typically involve one-electron changes. Redox processes involving transfers of a multiple number of electrons, especially between two metals, are much less prevalent and consequently less well understood. The most extensive studies on multiple electron changes have involved atom transfer processes.\(^2\) These are typically two electron-transfer reactions mediated by either a bridging halogen,\(^3\)\(^4\) or a bridging oxo\(^5\) ligand. The consideration

---

of a nitrido ligand as a bridging species in redox reactions has received little attention. In this regard, we initiated studies on the bridging capabilities of the nitrido complexes of metalloporphyrins. We report herein the first example of a reversible net electron redox process mediated by nitrogen atom transfer.

Given the stability of µ-nitrido iron porphyrin dimers, it seemed likely that analogous manganese complexes may also exist. When (TTP)Mn=NN=N was treated with Mn(TPP) in toluene under anaerobic conditions, the UV-vis spectrum of the mixture showed only Soret bands at 422 nm (nitrido complex) and 435 nm (MnII complex), indicating that the predominant species in solution are monomeric. Formation of stable µ-nitrido complexes in any appreciable amounts should have resulted in the appearance of a new Soret band. This behavior is in contrast to the oxo chemistry of metalloporphyrins. For example, treating (TTP)-CrO with M(TPP), M = Cr, Fe, results in the formation of µ-oxo dinuclear complexes as shown in eq 1.

\[(TTP)Cr-O + M(TPP) \rightarrow (TTP)Cr-O-M(TPP)\]

M = Cr, Fe

Clearly, nitrido bridged manganese porphyrin complexes are unstable relative to the monomers. Nevertheless, formation of such a species in solution, albeit in undetectable concentrations, could lead to nitrogen atom transfer. In order to examine this possibility, a labeling experiment was performed in which a different porphyrin was used on one of the complexes. Thus, when toluene solutions of (TTP)Mn=NN=N and Mn(OEP) were added together under anaerobic conditions, the UV-vis spectrum of the mixture showed new Soret bands at 404 and 435 nm. This is consistent with the formation of (OEP)Mn=NN=N (404 nm) and Mn(TPP) (435 nm). Independent verification of this was obtained by an NMR study. Under vacuo, toluene-d6 was condensed into an NMR tube containing a 1:1 mixture of solid N=Mn(TTP) and Mn(OEP) at ~78 °C. After flame sealing the tube and warming to ambient temperature, a 300 MHz 1H NMR spectrum was taken. The manganese(V) nitride complexes are diamagnetic and easily detected by NMR. Thus, the appearance of new peaks at δ 10.29 (s, 4 H, meso H), 3.97 (m, 16 H, CH2), and 1.85 (t, 24 H, CH3) indicated the formation of a new nitrido complex, N=Mn(OEP). The complementary experiments, in which solutions of N=Mn(OEP) and Mn(TPP) are combined, result in the formation of N=Mn(TPP) and indicate that this process is reversible. The overall reaction is illustrated in eq 2. This represents the first example of nitrogen atom transfer—a formally a three-electron redox process. The equilibrium constant for this reaction as written in eq 2 was determined by 1H NMR and UV-vis spectroscopy and is 1.7 ± 0.7 at 20.0 ± 0.1 °C.

\[\text{rates for nitrogen atom exchange were measured spectrophotometrically by following absorbance changes at 403 nm using a Cary 17 spectrophotometer equipped with a thermostatted cell holder which was maintained at 20.0 ± 0.1 °C. Treatment of the kinetic data was accomplished with an integrated rate law for reversible reactions derived by King. This analysis utilizes a variable, Δ, which represents the displacement of a reactant’s concentration at a given time, t, from its equilibrium value, t = 0. Hence, reaction 3 is characterized by the integrated rate law

\[\ln \left(\frac{\alpha + \Delta}{\alpha + (1/1)\Delta}\right) = k_1 \alpha t + \text{const} \]

\[\text{(4) Smith, T. P.; Iversen, D. J.; Drogea, M. W.}; \text{Kwan, K. S.}; \text{Tauke, H. Inorg. Chem. 1987, 26, 2852.}

\[\text{(5) Holm, R. H. Chem. Rev. 1987, 87, 140).}


\[\text{(8) Abbreviations: TTP = 5,10,15,20-tetra-p-tolylporphyrinato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion; OEP = 2,3,7,8,12,13,17,18-octacetylporphyrinato dianion.}

\[\text{(9) a)} \text{Hill, C. L.; Hollander, F. J. Am. Chem. Soc. 1982, 104, 7318.}


\[\text{(15) Liston, D. J.; Kennedy, B. J.; Murray, K. S.; West, B. O. Inorg. Chem. 1985, 24, 1561.}

\[\text{(16) Liston, D. J.; West, B. O. Inorg. Chem. 1985, 24, 1568.}

\[\text{Communications to the Editor}

\[\text{Figure 1. Representative plot of } A_{\text{oo}} \text{ versus time used for the determination of } k_1. \text{ [Mn(TTP)]}_0 = 3.39 \times 10^{-5} \text{ M and [Mn(OEP)]}_0 = 3.40 \times 10^{-5} \text{ M. The open circles are experimentally determined data points, and the solid curve was calculated using eq 4.}

\[\text{the kinetic data was accomplished with an integrated rate law for reversible reactions derived by King. This analysis utilizes a variable, } \Delta, \text{ which represents the displacement of a reactant’s concentration at a given time, } t, \text{ from its equilibrium value, } t = 0. \text{ Hence, reaction 3}

\[\text{is characterized by the integrated rate law}

\[\ln \left(\frac{\alpha + \Delta}{\alpha + (1/1)\Delta}\right) = k_1 \alpha t + \text{const} \]

\[\text{(4) Smith, T. P.; Iversen, D. J.; Drogea, M. W.}; \text{Kwan, K. S.}; \text{Tauke, H. Inorg. Chem. 1987, 26, 2852.}

\[\text{(5) Holm, R. H. Chem. Rev. 1987, 87, 140).}


\[\text{(8) Abbreviations: TTP = 5,10,15,20-tetra-p-tolylporphyrinato dianion; TPP = 5,10,15,20-tetraphenylporphyrinato dianion; OEP = 2,3,7,8,12,13,17,18-octacetylporphyrinato dianion.}

\[\text{(9) a)} \text{Hill, C. L.; Hollander, F. J. Am. Chem. Soc. 1982, 104, 7318.}


\[\text{(15) Liston, D. J.; Kennedy, B. J.; Murray, K. S.; West, B. O. Inorg. Chem. 1985, 24, 1561.}

\[\text{(16) Liston, D. J.; West, B. O. Inorg. Chem. 1985, 24, 1568.}
\[ \text{\textcopyright 1989 American Chemical Society} \]