required to produce photodissociation at this wavelength.

The mass spectra produced with and without laser irradiation are displayed in Figure 1. $RhC_{10}H_{12}^+$ photodissociates to produce $RhC_{10}H_{10}^+$, reaction 5, so double resonance techniques were employed to ensure that the suspected photoinduced reaction product was not produced via this pathway.

$$RhC_{10}H_{12}^+ + h\nu \rightarrow RhC_{10}H_{10}^+ + H_2 \qquad (5)$$

On the time scale of this experiment, no higher order reaction products were observed, eliminating the possibility of $RhC_{10}H_{10}^+$ production by other photodissociation pathways. Isolated and thermalized $RhC_5H_5^+$ shows no reaction with cyclopentane, with or without laser irradiation. Finally, the time scale for decomposition of the intermediary complex, $Rh^+(C_5H_6)(C_5H_{10})$, is sufficiently short as to prevent any significant photon absorption at these laser powers;[1] however, direct absorption and photodissociation of this complex to produce the suspected photoinduced reaction product, although unlikely, cannot be ruled out entirely. These studies support the photoinduced reaction pathway as described in reaction 3.

Three mechanisms could explain production of the long-lived intermediate necessary to observe photoinduced reactivity: (i) generation of an ion in an electronically excited state which is forbidden to the ground state, formed directly, by intersystem crossing or by some collisional or radiative process involving the initially photoaccessed excited state; (ii) generation of a vibrationally excited ground-state ion by internal conversion; and (iii) generation of a different geometric isomer. Given the high density of low-lying electronic states characteristic of open shell organometallic species, (i) cannot be completely ruled out; however, we believe it is the least likely of the three. Photodissociation of an ion of this size, as observed in reaction 4, typically occurs following internal conversion, consistent with either (ii) or (iii). $FeC_5H_6^+$ and $CoC_5H_6^+$ both undergo hydrogen/deuterium exchange with D_2 and react with NH_3 to form metal-amido-cyclopentadienyl ions providing evidence for the existence of two rapidly equilibrating isomers, reaction 6.[9-11] Beauchamp observed

$$M^+(c\text{-}C_5H_6) \rightleftharpoons (H)M^+(c\text{-}C_5H_5) \\ (M = Co, Fe) \qquad (6)$$

a single H/D exchange during reaction of D_2 with $(H)Rh^+(c\text{-}C_5H_5)(CO)$ generated by protonating $Rh(c\text{-}C_5H_5)(CO)_2$,[12] but $RhC_5H_6^+$ is unreactive with D_2 and forms only a condensation product with NH_3 under both light and no-light conditions, perhaps suggesting that this species is frozen in the cyclopentadiene form. However, $RhC_5H_6^+$ reacts with C_2D_4 to give one H/D exchange indicating that the hydrido-cyclopentadienyl form is either the most stable isomer or, at least, that it is easily accessed during ion excitation.[13] These results do not rule out the photoisomerization mechanism; however, Bomse and Beauchamp invoked mechanism (ii) for reaction 1 based on an RRKM analysis, and it appears to satisfactorily explain our observations. In further support, we observed production of $RhC_{10}H_{10}^+$ when the $RhC_5H_6^+$ population was made nonthermal, either by omitting collisional cooling of laser-desorbed Rh^+ or by kinetically exciting $RhC_5H_6^+$ through application of a resonant low power rf signal. In addition, Beauchamp observed $RhC_{10}H_{10}^+$ production when internally excited $RhC_5H_5D^+$, generated by reaction of $Rh(c\text{-}C_5H_5)(CO)_2$ with D_3^+, was allowed to react with cyclopentane.[12]

Continued study of this system will be aimed at determining the thermochemistry and isomeric forms of the ions involved in reactions 2–5 through photodissociation threshold measurements and labeling experiments. In addition, variable wavelength light sources will be employed to probe the threshold for photoinduced reactivity. Other systems currently under study in this and other laboratories suggest that rich and diverse photoinduced chemistries wait to be uncovered.

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Gas-Phase Photoinduced Reactivity of Co_2NO^+ with O_2 via a Photoisomerization Mechanism

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Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has emerged as an ideal technique for the study of gas-phase ion-molecule chemistry.[1] FT-ICR-MS methodology has recently been applied to investigate the fundamental properties of bare and ligated metal ions as well as metal cluster ions.[2] These studies further our understanding of catalytic processes in the gas phase as well as in condensed phases.

One particularly interesting group of recent studies, conducted by Jacobson and co-workers, involves the gas-phase characteristics of Co_2NO^+.[3] Interest in the surface chemistry and catalytic applications of the nitrosyl ligand makes this work especially significant.[4] During the course of these studies, Jacobson has identified two forms of Co_2NO^+, one which reacts with $^{18}O_2$ by nitrosyl displacement, reaction 1, and a second which is unreactive with O_2.

$$Co_2NO^+ + {}^{18}O_2 \rightarrow Co_2{}^{18}O_2^+ + NO \qquad (1)$$

The absence of isotope scrambling in reaction 1 suggests that the reactive form of Co_2NO^+ involves a molecularly chemisorbed nitrosyl ligand. Further studies using $H_2{}^{18}O$ indicate that the nonreactive form may involve the dissociatively chemisorbed ligand.

In this communication, we demonstrate that the nonreactive isomer can be photoinduced to react with O_2. This experiment constitutes the third example of photoinduced reactivity observed in the low-pressure regime characteristic of an FT-ICR-MS. In addition, this is the first example of such a reaction proceeding by a photoisomerization mechanism, as recently proposed in ref 5.

Experiments were carried out on two instruments, a prototype Nicolet FTMS-1000 equipped with a 5.2-cm cubic cell situated between the poles of a 15 in. Varian electromagnet operated at 0.85 T and a Nicolet FTMS-2000 equipped with dual 4.76-cm cubic cells immersed in a 3 T magnetic field. Co_2NO^+ was generated in the FTMS-1000 through ion-molecule reactions of laser-desorbed Co^+[6] with $Co(CO)_3NO$ followed by collision-in-

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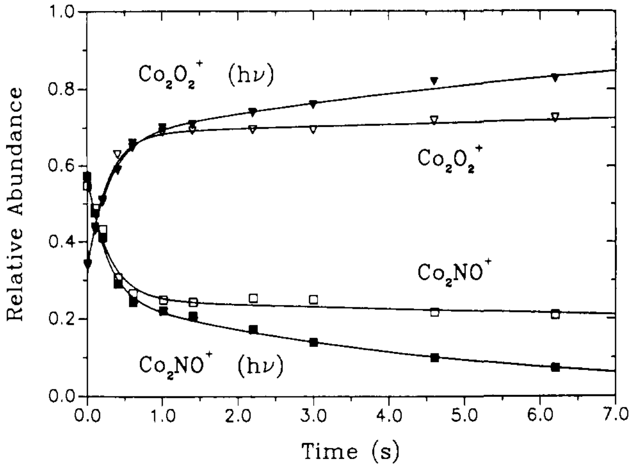

Figure 1. $Co_2NO^+ + O_2 \rightarrow Co_2O_2^+ + NO$ studied as a function of time with and without irradiation. The smooth curves represent optimized biexponential fits to the data.

duced dissociation (CID)[7] to remove the CO ligands. Co_2NO^+ was generated in the FTMS-2000 by electron impact ionization of $Co(CO)_3NO$ followed by clustering reactions of the ions with the parent neutral and subsequent CID. Swept double resonance techniques[8] were used to isolate the ion of interest. $Co(CO)_3NO$ was introduced through General Valve Series 9 pulsed valves.[9] Utilizing Varian leak valves, O_2 was maintained at a relatively low pressure, $\sim 10^{-7}$ Torr, while argon was maintained at a relatively high pressure, $\sim 10^{-5}$ Torr, to provide collisional cooling for ion thermalization[10] and to act as a collision gas for CID. The FTMS-1000 has been modified as previously described[11] 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 photoinduced ion-molecule reaction pathway under these conditions. However, two examples of such photoenhanced reactivity have been reported.[5,12] 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 Co_2NO^+ with O_2 as a function of time with and without irradiation. Figure 1 displays the relative abundances of Co_2NO^+ and $Co_2O_2^+$ 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 thermalized Co_2NO^+ population exists in the reactive form. In this study, the $Co_2O_2^+$ produced during the Co_2NO^+ synthesis and isolation period was not ejected from the cell in an effort to prevent inadvertent excitation of Co_2NO^+. When the data in Figure 1 are corrected for this initial $Co_2O_2^+$ population, the reactive isomer accounts for $\sim$65% of the Co_2NO^+ 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

$$Co_2NO^+ + h\nu \rightarrow Co_2^+ + NO \qquad (2)$$

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 Co_2NO^+ reactive/nonreactive isomerization barrier. In addition, photodissociation threshold studies are underway to determine $D(Co_2^+{-}NO)$ for the reactive and nonreactive isomers as well as $D(Co_2^+{-}O_2)$.

The photoisomerization mechanism is supported by recent collisional activation studies performed by Jacobson[3d] in which the reactive isomer was permitted to react to completion with O_2, and the $Co_2O_2^+$ produced was ejected from the cell to isolate the nonreactive isomer of Co_2NO^+. 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 photoactivation 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.

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Multielectron Redox Reactions between Manganese Porphyrins Mediated by Nitrogen Atom Transfer

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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

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