distance dependence in these systems.[2] Figure 2B shows the best plot obtainable from a correction which is based on the continuum model but uses a smaller than computed solvent parameter.[10]

While there are problems remaining with the correction for the reorganization energy, there can be little doubt that the fundamental relationship expressed by eq 4 is a valid one for the case of weak coupling. These results may be regarded as a confirmation of the Dexter mechanism viewing triplet energy transfer as a simultaneous double-electron exchange. In addition, it shows that triplet energy transfer rates may be used to obtain information on electronic coupling in ET and HT. This is valuable because of the low solvent reorganization energy in TT it is much easier to separate contributions from electronic coupling terms from those originating in the Franck–Condon factors.

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(10) The dielectric continuum model[8] characterizes the solvent properties by the difference between the inverse of the high frequency and static dielectric constants of the solvent. Using these values for the solvents used in ET and HT overestimates the reorganization energies and using reasonable donor and acceptor radii gives a value too large by a factor of 2 in the case where the reorganization energy has been determined in an independent way.[1] Therefore we reduced this solvent parameter to a value giving the best correlation with eq 4. Experiments are in progress to derive a more satisfying procedure by determining the distance dependence of the reorganization energy by experiment.

Gas-Phase Photoinduced Reactivity of $RhC_5H_6^+$ with Cyclopentane

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In the mature area of solution-phase photochemistry, a limitless number of examples exist in which a species, activated by the absorption of a photon, undergoes a reaction not observed in its ground state. In contrast, under the conditions used to study gas-phase ion-molecule chemistry at low pressures (10^{-5}–10^{-9} Torr), examples of photoinduced or photoenhanced reactions have been surprisingly sparse. In this environment, the time between reactive collisions is sufficiently long that internal conversion, photodissociation, or radiative and collisional relaxation of photoexcited ions significantly reduce the possibility of photoinduced reactivity.

Only one example of a photoenhanced ion-molecule reaction in this pressure regime has been reported to date.[1] Bomse and Beauchamp observed selective enhancement of k_r by $>10^3$ during an ion cyclotron resonance (ICR) study of the effect of infrared irradiation (10.6 μm) on reaction 1. In this communication, we

$$(CH_3OH)H^+(OH_2) + CH_3OH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (CH_3OH)_2H^+ + H_2O \qquad (1)$$

report a second example of photoinduced reactivity in the ICR pressure regime and the first such example involving an organometallic ion.

All experiments were performed on a Nicolet-FTMS 2000 equipped with dual 4.76-cm cubic cells immersed in a 3 T magnetic field. Rh^+ was generated by direct laser desorption/ionization[2] from a rhodium foil (Alfa) situated in an external ion source.[3] Reagents were introduced through Varian leak valves or General Valve Series 9 pulsed valves.[4] Double resonance techniques[5] were used to isolate ions of interest and confirm parent–photoproduct relationships. Argon was maintained at $\sim 10^{-6}$ Torr to provide collisional thermalization of laser desorbed ions[6] and reaction products. Photochemical studies were performed using the 514.5-nm output of a Spectra-Physics Model 2030 Ar^+ laser operated at 1–3 W.

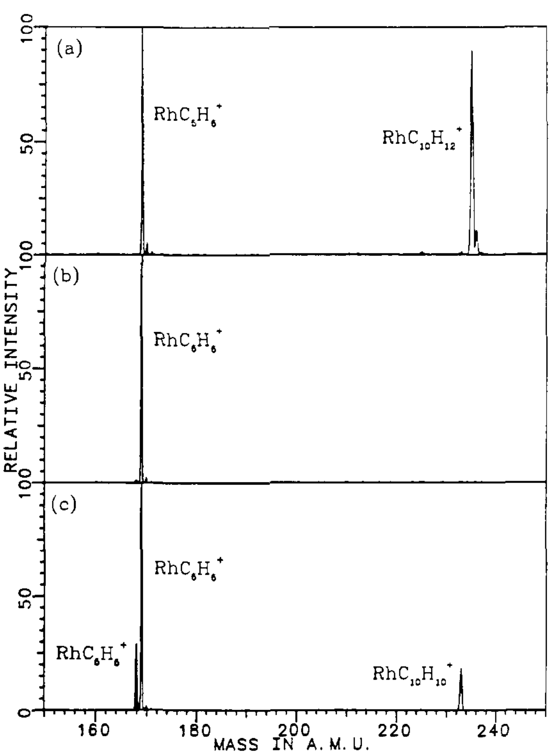

Figure 1. (a) Reaction of $RhC_5H_6^+$ and cyclopentane ($\sim 10^{-7}$ Torr) for 0.75 s with no irradiation, (b) with no irradiation and continuous ejection of $RhC_{10}H_{12}^+$, and (c) with 3-W 514.5-nm irradiation and continuous ejection of $RhC_{10}H_{12}^+$.

$RhC_5H_6^+$ was prepared through reaction of laser-desorbed Rh^+ with cyclopentane.[7] Thermalized $RhC_5H_6^+$ reacts with cyclopentane to produce $RhC_{10}H_{12}^+$, reaction 2. However, photoexcited $RhC_5H_6^+$ reacts with cyclopentane to produce the rhodocenium ion, reaction 3. In addition, irradiation results in photodissociation, reaction 4.[8] The fact that reaction 3 competes favorably with reaction 4 implies that the photodissociation pathway proceeds slowly, either because the photon energy is near the dissociation energy or because multiple photon absorption is

$$RhC_5H_6^+ + c\text{-}C_5H_{10} \rightarrow RhC_{10}H_{12}^+ + 2H_2 \qquad (2)$$

$$RhC_5H_6^+ \xrightarrow{h\nu} [RhC_5H_6^+]^* \xrightarrow{c\text{-}C_5H_{10}} RhC_{10}H_{10}^+ + 3H_2 \qquad (3)$$

$$RhC_5H_6^+ \xrightarrow[-H^\bullet]{h\nu} RhC_5H_5^+ \xrightarrow{h\nu} \text{other photoproducts} \qquad (4)$$

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(8) To confirm that $RhC_5H_5^+$ is produced directly via reaction 4 as opposed to via reaction 3 in competition with $RhC_{10}H_{10}^+$ production, $RhC_5H_6^+$ was also studied using pulsed valve introduction of cyclopentane to ensure that no cyclopentane was present during subsequent isolation and photodissociation.

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required to produce photodissociation at this wavelength.

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

$$\mathrm{RhC_{10}H_{12}^+} + h\nu \rightarrow \mathrm{RhC_{10}H_{10}^+} + \mathrm{H_2} \tag{5}$$

On the time scale of this experiment, no higher order reaction products were observed, eliminating the possibility of $\mathrm{RhC_{10}H_{10}^+}$ production by other photodissociation pathways. Isolated and thermalized $\mathrm{RhC_5H_5^+}$ shows no reaction with cyclopentane, with or without laser irradiation. Finally, the time scale for decomposition of the intermediary complex, $\mathrm{Rh^+(C_5H_6)(C_5H_{10})}$, 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). $\mathrm{FeC_5H_6^+}$ and $\mathrm{CoC_5H_6^+}$ both undergo hydrogen/deuterium exchange with $\mathrm{D_2}$ and react with $\mathrm{NH_3}$ to form metal-amido-cyclopentadienyl ions providing evidence for the existence of two rapidly equilibrating isomers, reaction 6.[9-11] Beauchamp observed a single H/D exchange during reaction of $\mathrm{D_2}$ with $\mathrm{(H)Rh^+(c\text{-}C_5H_5)(CO)}$ generated by protonating $\mathrm{Rh(c\text{-}C_5H_5)(CO)_2}$,[12] but $\mathrm{RhC_5H_6^+}$ is unreactive with $\mathrm{D_2}$ and forms only a condensation product with $\mathrm{NH_3}$ under both light and no-light conditions, perhaps suggesting that this species is frozen in the cyclopentadiene form. However, $\mathrm{RhC_5H_6^+}$ reacts with $\mathrm{C_2D_4}$ 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 $\mathrm{RhC_{10}H_{10}^+}$ when the $\mathrm{RhC_5H_6^+}$ population was made nonthermal, either by omitting collisional cooling of laser-desorbed $\mathrm{Rh^+}$ or by kinetically exciting $\mathrm{RhC_5H_6^+}$ through application of a resonant low power rf signal. In addition, Beauchamp observed $\mathrm{RhC_{10}H_{10}^+}$ production when internally excited $\mathrm{RhC_5H_5D^+}$, generated by reaction of $\mathrm{Rh(c\text{-}C_5H_5)(CO)_2}$ with $\mathrm{D_3^+}$, was allowed to react with cyclopentane.[12]

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

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 $\mathrm{Co_2NO^+}$ with $\mathrm{O_2}$ 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 $\mathrm{Co_2NO^+}$.[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 $\mathrm{Co_2NO^+}$, one which reacts with $\mathrm{^{18}O_2}$ by nitrosyl displacement, reaction 1, and a second which is unreactive with $\mathrm{O_2}$.

$$\mathrm{Co_2NO^+} + \mathrm{^{18}O_2} \rightarrow \mathrm{Co_2{}^{18}O_2^+} + \mathrm{NO} \tag{1}$$

The absence of isotope scrambling in reaction 1 suggests that the reactive form of $\mathrm{Co_2NO^+}$ involves a molecularly chemisorbed nitrosyl ligand. Further studies using $\mathrm{H_2{}^{18}O}$ 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 $\mathrm{O_2}$. 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. $\mathrm{Co_2NO^+}$ was generated in the FTMS-1000 through ion-molecule reactions of laser-desorbed $\mathrm{Co^+}$[6] with $\mathrm{Co(CO)_3NO}$ followed by collision-in-

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