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# Multiphoton Infrared Photoinduced Ion–Molecule Reactions in the Gas Phase

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**Abstract:** In the mature area of condensed-phase photochemistry, a limitless number of examples exist in which a species, activated by 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. This work more than doubles the number of reported examples in the literature, further demonstrating the potential of this new type of photochemistry. A survey is presented involving organometallic ions in which multiphoton infrared absorption is used to create long-lived vibrationally excited ground-state intermediates which exhibit some dramatic changes in reactivity. In two instances, sustained off-resonance (rf) irradiation, or SORI, which also adds energy in small increments, is shown to mimic the infrared results. The five general reaction types demonstrated are (1) deceleration of exothermic reactions; (2) photoinduced secondary fragmentation, whereby an internally excited product ion is generated which can undergo further fragmentation; (3) photoactivated ligand switching; (4) photoinduced isomerization; and (5) photoenhanced hydrogen/deuterium exchange.

## Introduction

The study of gas phase ion photochemistry by Fourier transform mass spectrometry (FTMS) has thus far been largely limited to unimolecular photodissociation[1-13] and, for negative ions, photodetachment[14-16] processes. Compared to the wealth of information on condensed-phase photochemistry, reports of bimolecular photochemistry in the gas phase are rare.[17-21] This is due in part to the long times between collisions in the gas phase, permitting unimolecular dissociation, electron detachment, and radiative relaxation to dominate. Furthermore, even if the activated ion "survives", collisional relaxation, as opposed to reaction, is often the preferred process.

In order that the intermolecular ion–molecule chemistry of a photoactivated reagent ion under the low-pressure conditions used in FTMS (typically $10^{-9}$–$10^{-5}$ Torr) might be observed, the lifetime of the excited intermediate has to be at least on the order of milliseconds and, clearly, the activated ion must exhibit a different reactivity than the thermalized ion. In the most general terms, a photoinduced reaction is identified when irradiation speeds up or slows down a reaction and, most interestingly, when a new reaction channel is observed.

Formation of a long-lived excited intermediate may be accomplished in one of three ways: (1) intersystem crossing to a state spin-forbidden to the ground state; for example, Ridge[22] and others[23,24] have observed unique chemistry arising from metal ions formed in metastable states directly in the ionization process; (2) infrared absorption or internal conversion to a vibrationally excited ground state; of particular relevance are the recent studies by Bowers and co-workers[25] monitoring the chemistry of $NO^+$ in selected vibrational states generated in an FTMS system by multiphoton ionization; and (3) isomerization. In addition, using photon energies below the dissociation energy, and for negative ions below the detachment energy, is clearly helpful in limiting or altogether eliminating photodissociation and photodetachment as competitive pathways. In this last regard, the observation of numerous sequential multiphoton dissociation[1-13] and detachment [6,14-16] processes would seem to provide the perfect ion systems for photoinduced bimolecular chemistry, since these processes necessarily proceed through long-lived excited intermediates. This, however, has not in general been the case for the systems tested so far since, as stated above, collisional deactivation dominates. Thus, although multiphoton photodissociation has been utilized extensively over the past 15 years, particularly by Dunbar and co-workers[9,10] to obtain fundamental information on radiative and collisional relaxation processes involving aromatic radical cations, only one example of a photoinduced reaction was reported prior to 1989.

In that study, Bomse and Beauchamp[17] reported the first example of a photoinduced, or more exactly, photoenhanced, ion–molecule reaction between the proton-bound methanol dimer, $(CH_3OH)_2H^+$, and $H_2O$ to give $(CH_3OH)H^+(H_2O)$ and $CH_3OH$. The reaction rate of this endothermic process was increased by up to 3 orders of magnitude under low-intensity CW infrared laser irradiation.

More recently, our studies of the chemistry and photochemistry of metal-containing ions suggested that these species might be excellent candidates for photoinduced bimolecular reactions for several reasons: (1) Due to the high density of low-lying electronic

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states, these ions tend to absorb broadly in the UV–vis region.[26-29] (2) Several cases have been documented where ions containing excess internal energy upon their birth in exothermic reactions exhibit a different reactivity following collisional deactivation.[30,31] (3) Metal ion centers readily promote isomerization and other chemical transformations.[26,32] Subsequently, three examples of UV–vis photoinduced reactions involving transition metal containing ions have been reported, including photoinduced rhodocenium formation, $Rh(c\text{-}C_5H_5)_2^+$, from the irradiation of $Rh(c\text{-}C_5H_6)^+$ in the presence of cyclopentane;[18] photoinduced isomerization of $Co_2(N)(O)^+$ to $Co_2(NO)^+$, manifesting itself by an increased reactivity with background $O_2$;[19] and most recently, the observation by Pope and Buckner[20] of a photoinduced ligand-switching reaction between $V(C_6H_6)^+$ and $CH_3CN$ to give $V(CH_3CN)^+$. Finally, Smalley and co-workers have reported that irradiation of $Si_n^+$ with 4.0-eV light from a XeCl excimer laser greatly reduces the reactivity of the clusters with ethylene for $n$ = 39, 45, and 48, while the clusters with $n$ = 36, 42, and 51 appear to be even more reactive.[21] Whether this is due to annealing of the clusters (i.e., isomerization) or to simply increasing their temperature is still unclear.[33]

This paper further demonstrates the potential of this new type of photochemistry by presenting several additional examples of photoinduced ion–molecule reactions involving organometallic ions. In each of these cases, multiphoton infrared absorption is used to create long-lived vibrationally excited ground-state intermediates. In two instances, the results are compared to those obtained by using sustained off-resonance (rf) irradiation, or SORI, in the absence of infrared. The SORI technique, recently developed by Jacobson and co-workers,[34] is an alternative way to perform collision-induced dissociation (CID), in which multiple low-energy collisions add internal energy in a stepwise fashion.

## Experimental Section

All experiments were performed on a Nicolet FTMS-2000 spectrometer equipped with a dual cell[35,36] and a 3-T superconducting magnet. The metal ions were generated in a source external to the analyzer side of the instrument by a Nd:YAG laser operated at 1.06 μm.[37] Details of the laser desorption experiments have been described elsewhere.[38]

All chemicals were obtained from commercial sources and used as supplied except that multiple freeze–pump–thaw cycles were used to remove noncondensible gases. Either leak valves or pulsed solenoid valves[39] were used to introduce chemicals into the cell. An uncalibrated ionization gauge was used to monitor the pressure. The ions to be studied were synthesized in the analyzer side by trapping the metal ions with the appropriate reagent gas at $10^{-8}$–$10^{-7}$ Torr for 1–2 s, during which time an argon background pressure of $2 \times 10^{-6}$ Torr was maintained to cool both the metal ions and the product ions. The ions of interest were then isolated by swept double resonance ejection techniques[40] and transferred to the source side, through the conductance limit, by lowering the conductance limit voltage to ground for a period of 100–300 μs. A significant portion of the ion signal is lost (50–80%) because of low transfer efficiency. At this reduced signal level, a noise peak at $m/z$ = 142 is present in most of the spectra recorded. The source and analyzer sides were quenched before and after ion transfer, respectively, to prevent any ions from remaining after each experimental cycle. The transferred ions were then further isolated, if necessary, and trapped on the source side in the presence of a background pressure of a suitable reagent at $4 \times 10^{-8}$ to $1 \times 10^{-7}$ Torr for a specified reaction time. During this time, a Synrad Model 48-2·115W 25-W CW $CO_2$ laser operating at 10.6 μm was pulsed on. A Coherent Model 201 power meter was used to monitor the nominal power of the $CO_2$ laser. The laser beam diameter was about 3 mm measured at the window. The effect of laser irradiation was monitored by comparing the spectra acquired with and without the laser irradiation. A low pressure was maintained during irradiation in order to avoid significantly quenching photoactivated species.

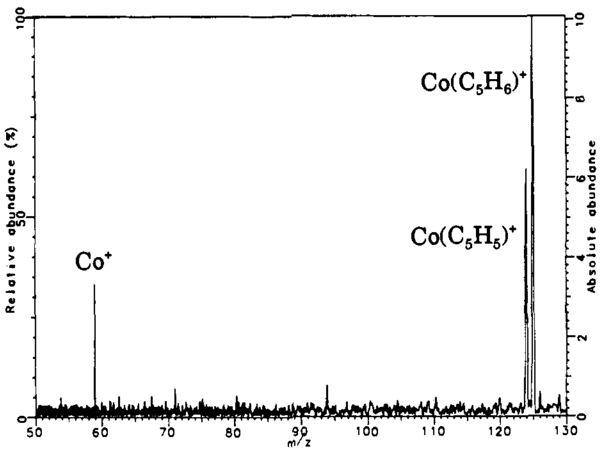


Figure 1. Infrared multiphoton photodissociation of $CoC_5H_6^+$ using 20-W infrared irradiation.

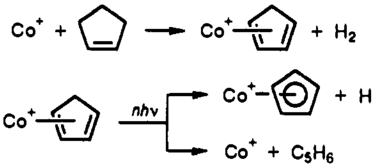
Table I. Branching Ratios (%) for the Infrared-Induced Photodissociation of $CoC_5H_nD_{6-n}^+$ ($n$ = 2–6)

| | $n$ | | | | |
|---|---|---|---|---|---|
| | 6 | 5 | 4 | 3 | 2 |
| $CoC_5H_nD_{6-n}^+ \rightarrow Co^+ + C_5H_nD_{6-n}$ | 30 | 45 | 54 | 80 | >84 |
| $\rightarrow CoC_5H_{n-1}D_{6-n}^+ + H$ | 70 | 55 | 46 | 20 | <16 |

## Results and Discussion

In order to ensure that an ion absorbs at a given wavelength in the infrared, its propensity to undergo multiphoton photodissociation can first be tested. Beauchamp and co-workers have reported on the multiphoton photodissociation of various $CoC_5H_{10}^+$ [13] and $Mn(CO)_nCF_3^-$ ($n$ = 4, 5) isomers.[41] Although the $CO_2$ laser employed in this study emits photons only at 10.6 μm (2.7 kcal/photon), a brief survey in our laboratory indicates that a variety of metal-containing ions will undergo multiphoton photodissociation in this region. Because of the nature of this process, ions with excess internal energy arising, for example, as a result of an exothermic reaction will tend to absorb and photodissociate more readily.[6,14] In fact, it is possible in some cases to take a nonabsorbing ion, collisionally excite it to an energy near or below its dissociation limit, and observe subsequent multiphoton photodissociation. The ions in this study, however, were all irradiated after a collisional cooling period, as discussed in the Experimental Section.

Figure 1 shows that $Co(c\text{-}C_5H_6)^+$, generated by reaction 1,[42] undergoes multiphoton photodissociation to generate two products, as shown in reactions 2 and 3. Isolation of $CoC_5H_5^+$ from reaction 2 followed by laser irradiation yielded no $Co^+$ photoproduct signal, confirming reaction 3. The observation of two photoproducts is unusual[5,11] and indicates either that two ion structures are present



(1)

(2)

(3)

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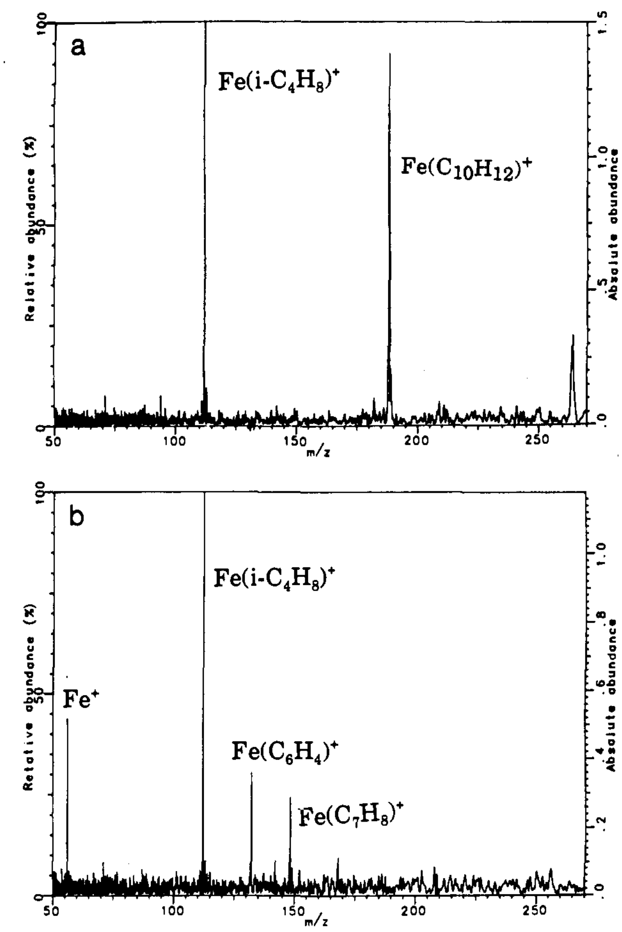


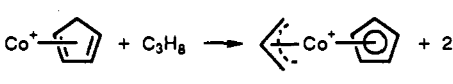
**Figure 2.** (a) Reaction of $CoC_5H_6^+$ with propane, 2 s at 6 × $10^{-8}$ Torr. (b) Same as a except with 20-W infrared irradiation.

or that the two processes have approximately the same activation energies, or both. Interestingly, while the branching ratio for reactions 2 and 3 does not vary significantly with laser power (~15–25 W), a dramatic effect is observed with deuterium substitution. For these studies, $CoC_5H_nD_{6-n}^+$ ($n$ = 2–6) were generated by reacting $CoC_5H_6^+$ with $D_2$ in the analyzer cell. Next the ions were transferred to the source cell, where they were first isolated and then irradiated.

The data in Table I show that (i) process 2 occurs by 100% H loss and (ii) loss of $C_5H_nD_{6-n}$, reaction 3, increases relative to H loss, reaction 2, with increasing deuterium substitution. In an earlier study, the observation that multiphoton infrared dissociation of $(C_2D_5)(C_2H_5)OH^+$ yields exclusively $C_2D_5OHD^+$ was explained by differing activation energies for $\beta$-D or $\beta$-H transfer.[6] In the present case the absence of D loss may be attributed to the zero-point energy difference which makes $D°(Co^+–H)$ about ~0.05 eV lower in energy than $D°(Co^+–D)$.[43] Everything else being equal, with increasing substitution, there are fewer hydrogens available for dissociation and, thus, loss of $C_5H_nD_{6-n}$ becomes more competitive.

These observations further demonstrate that, with CW infrared irradiation, decomposition is favored over further absorption of photons. Finally, in accordance with these conclusions, loss of both H and D is observed during collision-induced dissociation, although substantial isotope effects are still evident (Table II).

**Deceleration of Exothermic Reactions.** In the presence of propane, $Co(c-C_5H_6)^+$ undergoes reaction 4 to generate what is likely to be a cyclopentadienyl–$Co^+$–allyl ion.[30] As shown in Figure 2a,b, this reaction is dramatically slowed by infrared irradiation. Isolation and irradiation of cyclopentadienyl–$Co^+$–allyl ion yielded no photoproducts, eliminating this as a possible reason for the reduced reaction rate. In addition, SORI excitation of $CoC_5H_6^+$ in the absence of light is also observed to slow down reaction 4 significantly. Again, there are two reasonable explanations for these results. First, the reaction is exothermic and will be slower upon "heating" one or both of the reactants; or second, the irradiation has caused a rearrangement of the ion to a less reactive form. Similarly, both of these alternatives have been used to explain the observation that $Si_n^+$ ($n$ = 39, 45) become less reactive following light absorption.[21,33] These possibilities are not easily distinguishable, and further studies are underway.



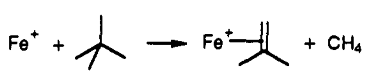
(4)

**Table II.** Branching Ratios (%) for the Collision-Induced Dissociation of $CoC_5H_nD_{6-n}^+$ at 15 eV ($n$ = 0–6)

| | $n$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 6 | 5 | 4 | 3 | 2 | 1 | 0 |
| $CoC_5H_nD_{6-n}^+ \rightarrow Co^+ + C_5H_nD_{6-n}$ | 88 | 87 | 88 | 88 | 87 | 91 | 89 |
| $\rightarrow CoC_5H_{n-1}D_{6-n}^+ + H$ | 12 | 13 | 13 | 9 | 9 | 5 | |
| $\rightarrow CoC_5H_nD_{5-n}^+ + D$ | | | | 3 | 4 | 4 | 11 |

**Photoinduced Secondary Fragmentation.** Just as heating the reactants may slow down an exothermic reaction, it may certainly accelerate (or even open) an endothermic process. In this second example, the energy deposited in the reactant ion is transferred in part to the product ion, causing the product ion to fragment further. The reaction of $Fe(isobutene)^+$ with chlorobenzene may be used to illustrate such a scenario.

$Fe(isobutene)^+$, generated by reaction 5, undergoes a facile reaction with chlorobenzene to give $Fe(2-methyl-1-phenylpropene)^+$,[44] reaction 6 and Figure 3a. The primary product ion reacts further with chlorobenzene to generate $Fe[(C_6H_5)_2C{=}C(CH_3)_2]^+$, which is also seen in the spectrum. Both low-energy collision-induced dissociation and multiphoton photodissociation of the product ion from reaction 6 yield loss of $C_3H_4$ to give $Fe(toluene)^+$, reaction 7. However, carrying out reaction 6 under infrared irradiation, with continuous ejection of the $Fe(2-methyl-1-phenylpropene)^+$ product ion, also leads to formation of $Fe(toluene)^+$, Figure 3b. Thus, the $Fe(isobutene)^+$ reactant absorbs the infrared light prior to its reaction with chlorobenzene, and a sufficient amount of internal energy is carried over to the $Fe(2-methyl-1-phenylpropene)^+$ to cause its further fragmentation. The overall reaction 8 is estimated to be endothermic by about 6 kcal/mol.[45] Also observed in the spectrum in Figure 3b is $Fe^+$,



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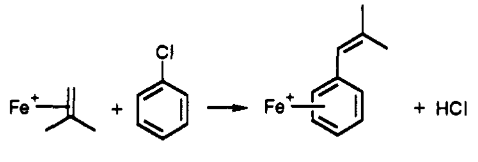

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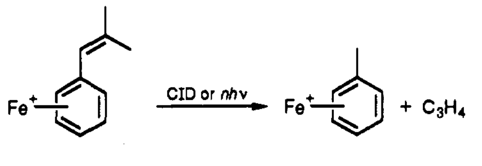

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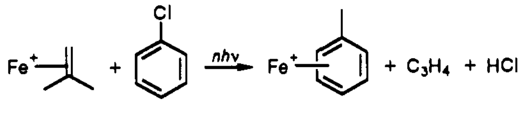

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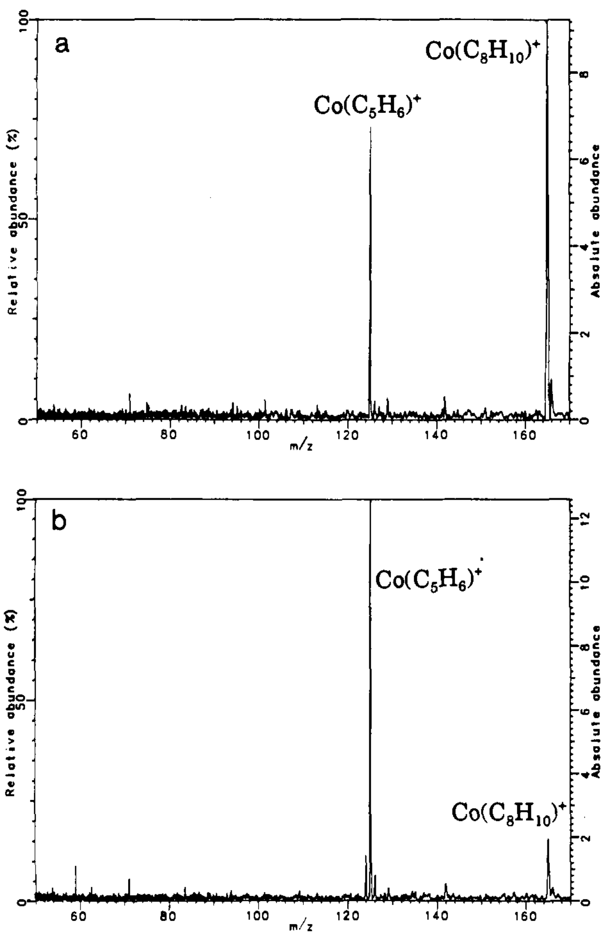


Figure 3. (a) Reaction of Fe(isobutene)$^+$ with chlorobenzene, 1 s at 4 × $10^{-8}$ Torr. (b) Same as a except with 15-W infrared irradiation and continuous ejection of $Fe(C_{10}H_{12})$, $m/z = 188$.

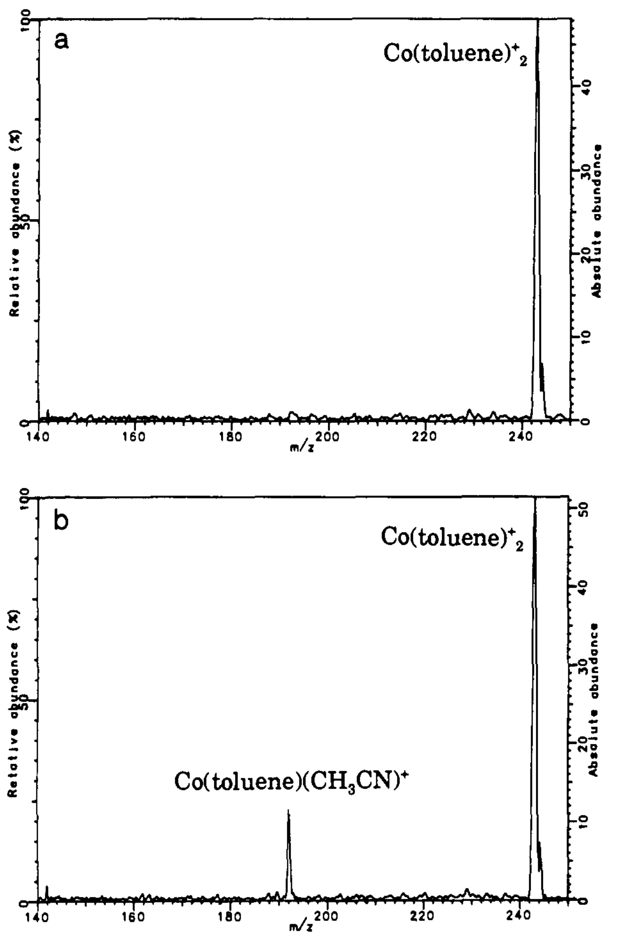
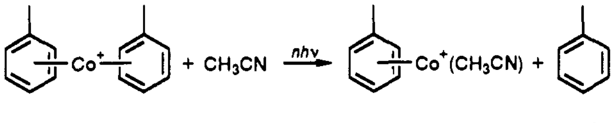


Figure 4. (a) Reaction of $Co(toluene)_2^+$ with $CH_3CN$, 10 s at 1 × $10^{-7}$ Torr. (b) Same as a except with 26-W infrared irradiation and continuous ejection of Co(toluene)$^+$.

produced by multiphoton dissociation of Fe(isobutene)$^+$, and $FeC_6H_4^+$, produced from the subsequent reaction of $Fe^+$ with chlorobenzene.[46] Finally, the photoinduced reaction of Rh(c-$C_5H_6$)$^+$ with cyclopentane to produce rhodocenium, Rh(c-$C_5H_5)_2^+$, reported earlier,[18] is another example of this mechanism in which the internal energy in the reactant ion is carried over to the intermediate product ion, resulting in subsequent dissociation.

**Photoactivated Ligand Switching.** While photoactivated ligand switching has been studied in great detail in the condensed phase, in the gas phase this area has remained virtually unexplored until recently. Pope and Buckner[20] reported that $VC_6H_6^+$ irradiated at 604 nm reacts with $CH_3CN$ to generate $VCH_3CN^+$, a normally endothermic reaction. They explained this process as proceeding through a highly excited $[V(C_6H_6)(CH_3CN)^+]^*$ complex in which the internal energy is equal to the photoexcitation energy plus the energy of coordination of $CH_3CN$ to $[VC_6H_6^+]^*$. The highly excited complex can then partition between benzene loss and $CH_3CN$ loss pathways, the former yielding the ligand-switched product. In the absence of light, the complex only has the coordination energy and, if it is not stabilized, decomposes back to the reactants. This mechanism is analogous to the one proposed by Bomse and Beauchamp[17] to explain the photoinduced reaction between $(CH_3OH)_2H^+$ and $H_2O$, described above. Two additional examples presented here further indicate that this is a general class of photoinduced reactions.

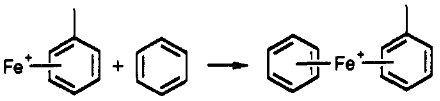
No reaction is observed between $CH_3CN$ and collisionally cooled $Co(toluene)_2^+$ in Figure 4a. Upon intense $CO_2$ laser irradiation, however, reaction 9 is observed, yielding the ligand-



(9)

switched product, Figure 4b. Double-resonance ejection of Co(toluene)$^+$, which could arise from multiphoton photodissociation, had no effect on the reaction, indicating that the product ion is not formed from the condensation reaction of $CH_3CN$ with Co(toluene)$^+$. The reverse of reaction 9 occurs readily in the absence of light, confirming that reaction 9 is endothermic. Thus, the lack of reaction between $Co(toluene)_2^+$ and $CH_3CN$ under thermal conditions is due to thermodynamic, and not kinetic, factors. Similar results were obtained from $Fe(toluene)_2^+$ and $CH_3CN$.

Figure 5a shows that, under thermal conditions, only condensation reaction 10 is observed between Fe(toluene)$^+$ and benzene.



(10)

Performing the same experiment in the presence of light yields the spectrum in Figure 5b, which shows that the intensity of the condensation product signal is greatly reduced and a new ligand-switched product, Fe(benzene)$^+$, is generated. Continuous ejection of the condensation product, Figure 5c, does not eliminate the Fe(benzene)$^+$ product ion. Thus, Fe(toluene)$^+$ undergoes a

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(45) Obtained using $\Delta H_{rxn} \simeq 28$ kcal/mol for $C_6H_5Cl + i\text{-}C_4H_8 \rightarrow C_7H_8 + Cl + C_3H_4$ (Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17*) and assuming that $D°$[Fe(toluene)$^+$] − $D°$[Fe(isobutene)$^+$] is approximately equal to $D°$[Fe(benzene)$^+$] − $D°$[Fe(propene)$^+$] ≃ 22 kcal/mol using $D°$[Fe·(benzene)$^+$] ≃ 55 kcal/mol (ref 27) and $D°$(Fe(propene)$^+$] ≃ 33 kcal/mol (van Koppen, P. A. M.; Jacobson, D. B.; Illies, A.; Bowers, M. T.; Hanratty, M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 1991).

(46) Dietz, T. G.; Chatellier, D. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 4905.

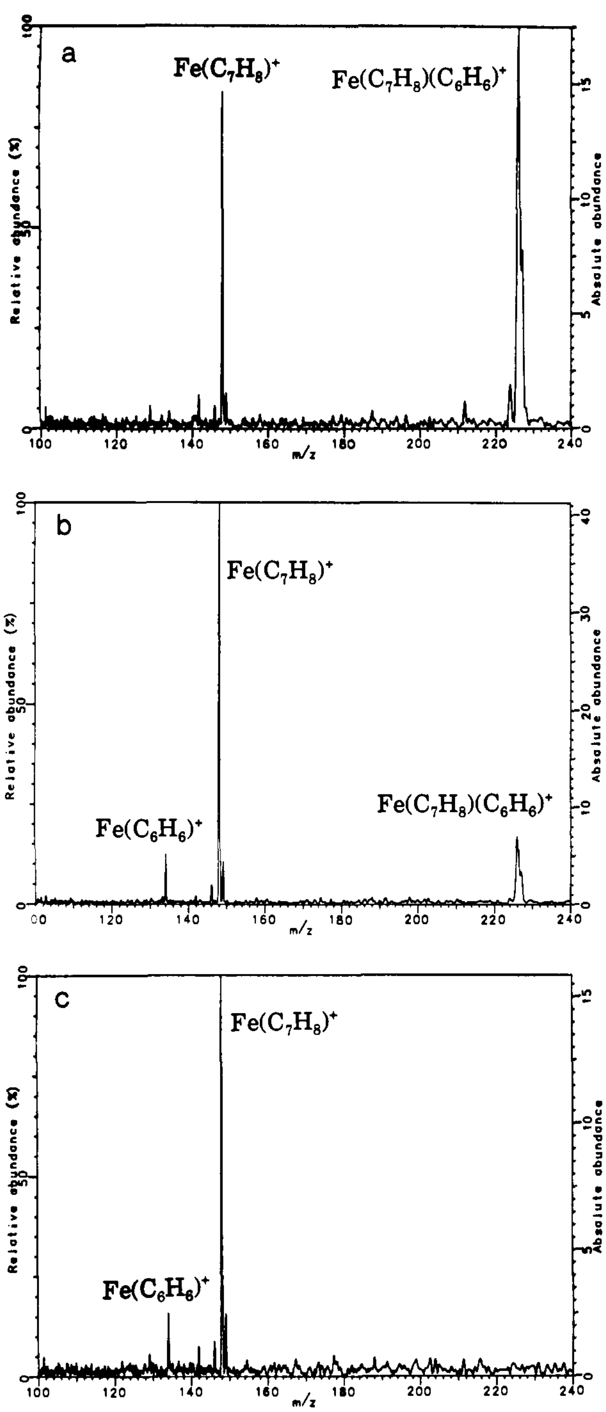
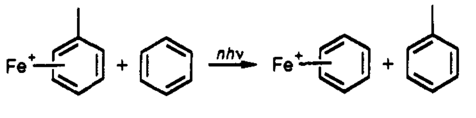


**Figure 5.** (a) Reaction of Fe(toluene)$^+$ with $C_6H_6$, 2 s at 6 × $10^{-8}$ Torr. (b) Same as a except with 26-W infrared irradiation. (c) Same as b except with continuous ejection of Fe(toluene)(benzene)$^+$.

photoactivated ligand-switching reaction (reaction 11) with benzene, proceeding through a highly activated condensation complex intermediate.



(11)

**Photoinduced Rearrangement.** Among the most interesting types of photoinduced reactions will be those involving reactant ion rearrangement, as in the case of $Co_2NO^+$ believed to rearrange from a chemisorbed NO to a molecularly bound NO upon irradiation with visible light.[19] Such cases can arise if the barrier to rearrangement lies below or near the dissociation limit and is especially amenable to infrared excitation.

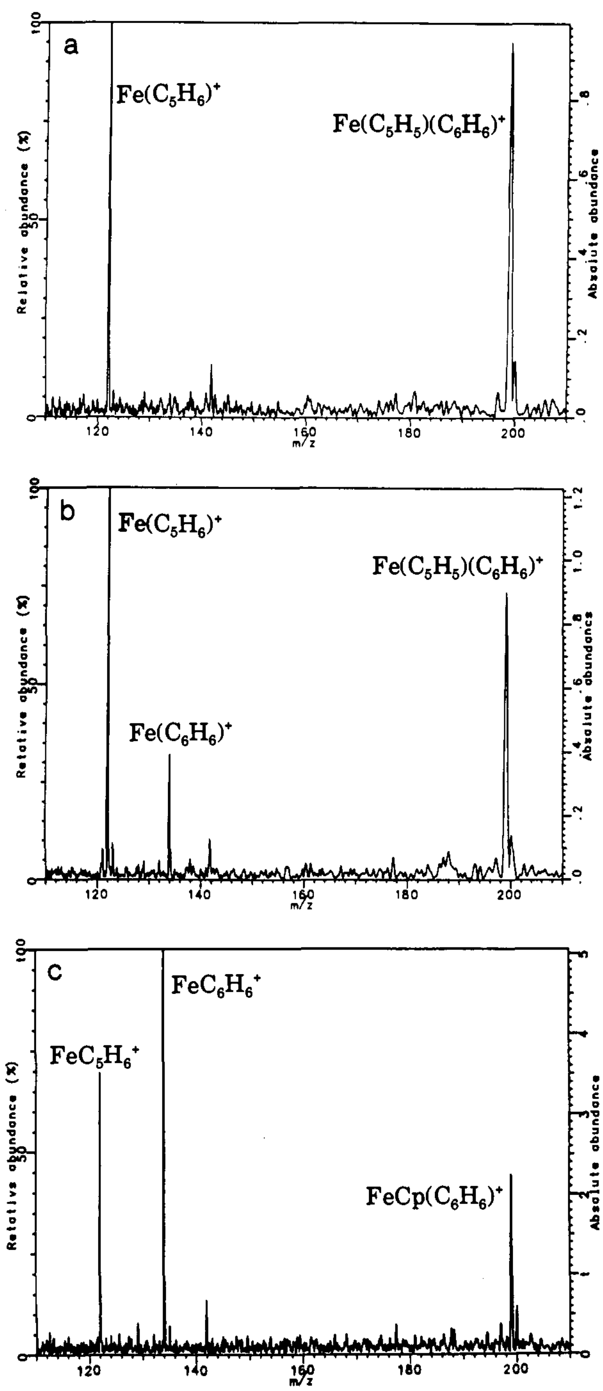
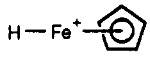


**Figure 6.** (a) Reaction of $FeC_5H_6^+$ with benzene, 1 s at 4 × $10^{-8}$ Torr. (b) Same as a except with 15-W infrared irradiation. (c) SORI on $FeC_5H_6^+$ with a 2-kHz off-center frequency and a 2-s duration while it reacts with benzene. The maximum kinetic energy given is about 7.5 eV in the laboratory frame.

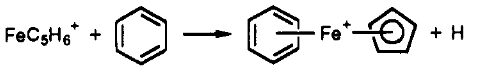
One such interesting case is Fe(c-$C_5H_6$)$^+$ generated from Fe$^+$ and cyclopentene in anology to reaction 1, which has two isomeric forms, I and II.[42,47] As shown by the spectrum in Figure 6a,

I



II

thermalized $FeC_5H_6^+$ reacts readily with benzene to displace one H atom exclusively, as in reaction 12. Upon irradiation, Fe-



(12)

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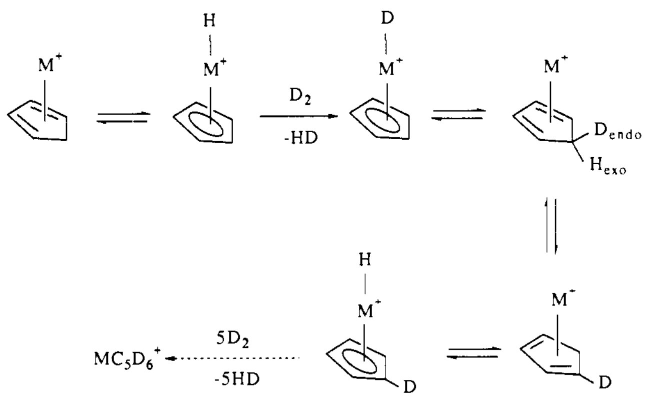
[47] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

**Scheme I**



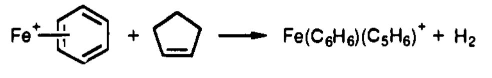
$(C_6H_6)^+$ is generated, apparently from photoactivated ligand-switching reaction 13 (Figure 6b). Multiphoton photodissociation

(13)

of $FeC_5H_6^+$ is also observed to produce $Fe^+$ and $FeC_5H_5^+$ in analogy to reactions 2 and 3 for $CoC_5H_6^+$. Continuous ejection of $Fe^+$ did not eliminate the $FeC_6H_6^+$ signal. In addition, continuous ejection of the product ion from reaction 12, $Fe(C_5H_5)(C_6H_6)^+$, had no effect on the $FeC_6H_6^+$ signal intensity, as would be expected, since $D°(Fe^+–C_5H_5)$ (~88 kcal/mol[30]) > $D°(Fe^+–C_6H_6)$ (~55 kcal/mol[27]).

These results suggest that thermalized $FeC_5H_6^+$ has structure II, in which the H atom can be displaced by benzene as in reaction 12, and that the photoactivated ion has structure I, permitting complete displacement by benzene as in reaction 13. An earlier labeling study also indicated that thermalized $FeC_5H_6^+$ has the hydrido cyclopentadienyl structure II.[42] That the change in reactivity is not simply due to the amount of internal energy in the collision complex was tested by performing CID on $Fe(C_5H_6)(C_6H_6)^+$, which was generated by reactions 14 and 15 and

(14)



(15)

then permitted to undergo thermalizing collisions prior to CID. At the lowest CID energies, loss of H dominates, while at higher energies additional loss of benzene is observed, yielding $FeC_5H_5^+$. Virtually no $FeC_6H_6^+$ is observed over the energy range studied (0–100 eV), thus eliminating a simple explanation based on the amount of internal energy of the excited intermediate. Interestingly, SORI excitation of $FeC_5H_6^+$ in the presence of benzene also yields $FeC_6H_6^+$, Figure 6c, indicating that multistep collisional excitation, like infrared irradiation, is effective in causing the rearrangement. Finally, $CoC_5H_6^+$ reacts with benzene to form $CoC_6H_6^+$ exclusively, suggesting that the cyclopentadiene structure I is the more stable for cobalt, in accordance with an earlier study.[42]

**Photoenhanced H/D Exchange.** As a final example, the effect of infrared irradiation on the H/D exchange of $CoC_5H_6^+$ was studied. In the presence of $D_2$, $CoC_5H_6^+$ is observed to undergo one slow H/D exchange (~1/20 Langevin rate) followed by five considerably slower exchanges.[42] The first exchange is with the hydrogen on the metal in structure II. As shown in Scheme I, in order for subsequent exchanges to occur, structure I must also be accessible where 1,5-sigmatropic shifts are necessary to scramble the hydrogens. The fact that the first exchange is slow and yet faster than subsequent exchanges suggests that there is an energy barrier present involving either the isomerization between structures I and II or the sigmatropic shifts, or both. Cyclopentadiene itself is known to rapidly scramble all of its hydrogens at room temperature despite a 23.6 kcal/mol barrier for the sigmatropic shift.[48,49] As shown in the spectra in Figure 7a, b, infrared irradiation of $CoC_5H_5D^+$ dramatically increases the rate of the additional H/D exchanges, which would be expected from ions which possess internal energy above the barrier for isomerization. Photoenhanced H/D exchange is also observed for $FeC_5H_6^+$ with $D_2$.

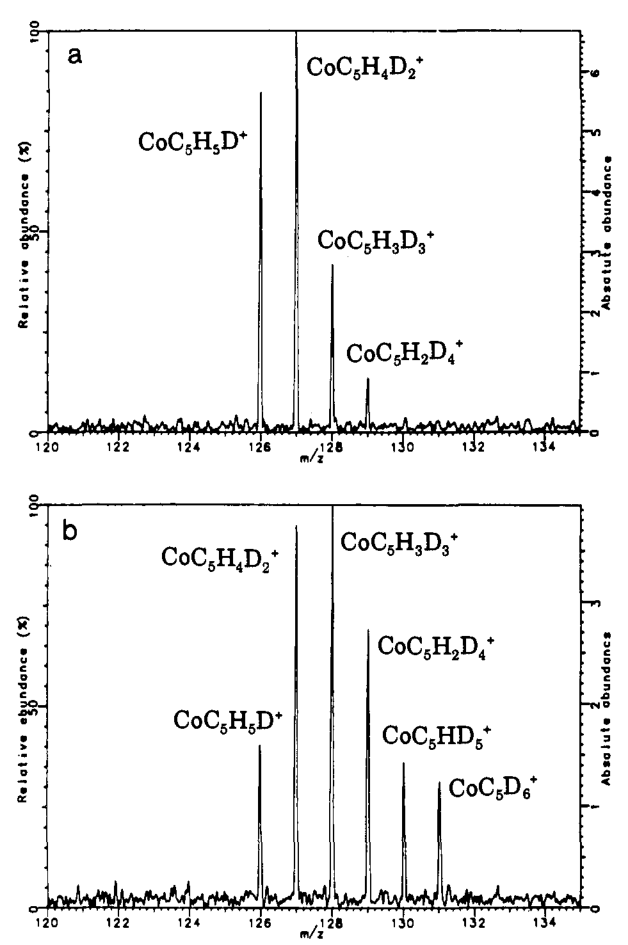


Figure 7. (a) Reaction of $CoC_5H_5D^+$ with $D_2$, 20 s at $1 \times 10^{-7}$ Torr. (b) Same as a except with 15-W infrared irradiation.

## Conclusion

It is evident from this study that, while only five examples of photoinduced ion–molecule reactions studied under FTMS conditions have appeared in the literature to date, a whole new area of photochemistry is on the threshold. In analogy to multiphoton photodissociation, gas-phase ion–molecule photochemistry will permit absorption information on gas-phase ions to be obtained at longer wavelengths than is possible by single-photon photodissociation. In addition, while this study was meant to be a survey, systematic variation of laser power and reactant gas pressure will yield detailed fundamental information complementary to that obtained by multiphoton photodissociation. The use of SORI continues to gain promise as an alternative to infrared irradiation. Finally, the example types described here for positive ions should also apply to negative ions. These experiments are currently underway in our laboratory.

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(49) (a) Roth, W. *Tetrahedron Lett.* **1964**, 1009. (b) Berson, J. H.; Aspelin, G. G. *Tetrahedron* **1964**, *20*, 2697.