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Reactions of Metal Ions and Their Clusters in the Gas Phase Using Laser Ionization - Fourier Transform Mass Spectrometry

Progress Report

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Abstract

This report will focus on seven areas we have made substantial new progress in over the past several months: (1) Gas-Phase Reactions of $\text{Fe}(\text{Benzyne})^+$ with Simple Alkyl Halides; (2) Photodissociation and Collision-Induced Dissociation of Molecular Ions From Methylphenol and Chloromethylphenol; (3) Isotopomer Differentiation Using Metal Ion Chemical Ionization Reagents; (4) Multiple Excitation Collisional Activation (MECA) in Fourier Transform Mass Spectrometry; (5) Chemistry of Fe^+ -Arene Ions with Halobenzenes; (6) Gas-Phase Photodissociation Study of $\text{Ag}(\text{Benzene})^+$ and $\text{Ag}(\text{Toluene})^+$; and (7) Reactivity of Ti^{2+} and V^{2+} with Small Alkanes.

I. Gas-Phase Reactions of $\text{Fe}(\text{Benzyne})^+$ with Simple Alkyl Halides

The Fourier transform ion cyclotron resonance mass spectrometer FT-ICR-MS has been shown to be a superb "beaker" for the synthesis, manipulation, and storage of ions in the gas phase, where one may observe the chemical reactivity of such species in the ultimate non-polar medium. Increasingly, the chemistry of transition metal ions in this environment has proved to be rich, with studies revealing intrinsic physical and chemical properties of these species. In particular, several research groups have worked on the characterization of Fe^+ with a variety of organic compounds. Allison and Ridge, for example, looked at the reactions of Fe^+ with alkyl halides. Subsequently, Ridge and co-workers studied the reactions of Fe^+ with aryl halides, and discovered an interesting polymerization reaction

between Fe^+ and chlorobenzene initiated by the formation of $\text{Fe}(\text{benzyne})^+$. They also reported a lower limit for $\Delta H_f(\text{C}_6\text{H}_4)$. Bjarnason and Taylor also studied Fe^+ with halobenzenes and documented the aforementioned polymerization reaction. Huang and Freiser studied the reactions of $\text{Fe}(\text{Benzyne})^+$ with small alkanes, alkenes and cycloalkenes, as well as the reactions of $\text{Fe}(\text{alkenes})^+$ with chlorobenzene. The metal-ligand bond energy, $D^\circ(\text{Fe}^+-\text{C}_6\text{H}_4) = 81 \pm 10$ kcal/mol, was bracketed by ion-molecule reactions, collision-induced dissociation (CID), and photodissociation studies.

As an extension of our work on $\text{M}(\text{benzyne})^+$ complexes ($\text{M}=\text{Fe}$, Fe_2 , Sc), the primary and secondary reactions of $\text{Fe}(\text{benzyne})^+$ with CH_3F and the small alkyl halides, $\text{C}_n\text{H}_{2n+1}\text{X}$ ($n=1-3$; $\text{X}=\text{Cl}$, Br , I) were investigated. Reaction mechanisms were postulated based on the product ion structures which were determined by ion-molecule reactions and collision-induced dissociation. In general, the reactions were observed to proceed by an initial C-X, C-C, or C-H insertion. If β -hydrogens were present on the alkyl moiety, subsequent β -H transfer and elimination of HX was observed. Secondary reactions generally involved dehydrohalogenation and halogen abstraction. One of the most interesting reactions was with CH_3I . Following C-I insertion, transfer of the CH_3 group to the benzyne ligand results in an $\text{Fe}(\text{I})(\text{tolyl})^+$ intermediate which competitively eliminates either FeI to generate C_7H_7^+ or $\text{I}^\cdot$ to generate FeC_7H_7^+ . Ion-molecule reactions indicate that the C_7H_7^+ species has the benzyl structure. Additionally, CID and ion-molecule reactions suggest

that FeC_7H_7^+ has an o-tolyl iron structure. The o-tolyl iron species was observed to exhibit chemistry uniquely different than its benzyl and tropylium isomers. For larger alkyl halides, the analogous reactions are not observed due to the availability of β -hydrogens which undergo facile transfer and elimination of HX as described above. Finally, thermochemical implications from these results were obtained.

II. Photodissociation and Collision-Induced Dissociation of Molecular Ions from Methylphenol and Chloromethylphenol

The photodissociation of aromatic ions has been the focus of several mass spectral investigations. In particular, Dunbar and coworkers have extensively studied the photodissociation of the molecular ions of various mono- and disubstituted benzenes using ion cyclotron resonance mass spectrometry. In general, the photodissociation spectra of these species have two absorption maxima. The first, which occurs in the 270 - 320 nm region, appears to involve a $\pi \rightarrow \pi^*$ transition and correlates well with the UV absorption spectrum of the neutral. The second absorption, a $\pi \rightarrow \pi$ transition, is found around 400 - 600 nm. This transition often corresponds to the third or fourth ionization potential observed in photoelectron spectroscopy (PES) studies. In some cases, isomeric ions can be distinguished based on the position and intensity of these bands.

During a photodissociation study in our laboratory of aromatic $\text{C}_7\text{H}_7\text{O}^+$ isomers, the molecular ions of the precursor compounds were observed to readily photodissociate. Since these

ions often generated $C_7H_7O^+$ as a photoproduct at wavelengths where $C_7H_7O^+$ photodissociation was being monitored, it was necessary to study the photodissociation of the molecular ions in detail.

The photodissociation spectra of these ions were also found to contain both UV and visible absorption maxima. The positions of these bands correlate well with solution electronic absorption spectra and photoelectron spectra, respectively, suggesting that photodissociating populations of the molecular ions have not rearranged. The molecular ion of benzyl alcohol can be readily distinguished from the isomeric 2- and 4- methylphenol ions on the basis of the position and intensity of the photodissociation bands, as well as on the identity of the photoproduct. The para-chlorophenol isomers, 4-chloro-2-methylphenol and 4-chloro-3-methylphenol, cannot be distinguished by their photodissociation spectra. Minor differences exist between these spectra and that of the ortho-chlorophenol isomer 2-chloro-5-methylphenol, suggesting that the relative positions of the chloro and hydroxy groups may have a greater effect on photodissociation than the position of the methyl group. For comparison, low-energy collision-induced dissociation using FTMS was also performed on the compounds involved in this study. Some interesting differences were observed which we believe is due to the mode of excitation.

III. Isotopomer Differentiation Using Metal Ion Chemical Ionization Reagents

Catalytic hydrogenation of perdeuterated aromatic species generate selectively deuterated hydrocarbon species. Detailed structural characterizations of these selectively deuterated end products hold the key to understanding the stereochemistry involved in the hydrogenation process. Proton NMR may be employed in limited cases where the sample consists predominantly of one component as a result of high regioselectivity and stereoselectivity during the hydrogenation. Even in these simple cases, however, high resolution NMR instruments are needed to acquire spectra with enough useful structural information, and the interpretation can require computer simulations. The task becomes prohibitive for slightly more complicated mixtures of end products. Our goal was to demonstrate that transition metal ion chemical ionization, used in conjunction with FTMS, holds promise as a simple, qualitative and potentially quantitative solution to this problem. This goal was achieved, as discussed below.

The analysis of isotopomers (molecules of a particular compound having the same number of isotopes in different configurations) is based on the intrinsic regioselectivity and stereoselectivity involved in the gas-phase dehydrogenation of cyclic hydrocarbons by transition metal ions. This may be illustrated in a simple reaction of a metal ion, M^+ , with cyclohexane to generate $M(\text{benzene})^+$. Assuming the absence of

hydrogen scrambling during dehydrogenation, this process is

regiospecific in that the six hydrogen atoms eliminated come from the six individual CH_2 units. It may also be stereospecific if the six hydrogen atoms eliminated come from the same side of the plane of the ring structure. The stereospecificity could conceivably be created by the constraint of the ring structure since, once dehydrogenation is initiated via initial M^+ insertion into a C-H bond on either side of the cyclic plane, metal ion migration to the opposite side might not occur. In fact this idea proved very successful.

The isotopolog distribution could be obtained by generating the pseudomolecular ions, ML^+ (M = transition metal; L = cyclic hydrocarbon). A particular isotopolog could then be isolated followed by collision-induced dissociation resulting in dehydrogenation. The dehydrogenation process proved to be regio- and stereoselective permitting information to be obtained on the isotopomer composition within the particular isotopolog. The samples analyzed were the end products from the metal-catalyzed hydrogenation of perdeuterated naphthalene and benzene. We were able to determine which hetero- and homogeneous catalysts were stereoselective. The isotope effects observed in the dehydrogenation reactions are still under investigation.

IV. Multiple Excitation Collisional Activation (MECA) in Fourier Transform Mass Spectrometry

McLafferty and coworkers have recently demonstrated that multiple excitation of a single ion population is capable of dramatic improvements in sensitivity. This focused our attention

on the high potential that this technique affords for the solution of a number of interesting problems in the use of FTMS. In the area of collisional activation, for example, the well known difficulty of fragmenting high molecular weight ions, common to all mass spectrometric techniques including traditional FTMS single excitation methods, should yield to multiple excitation collisional activation (MECA). Specifically, the greater internal energy required by high mass ions to achieve fragmentation should be attainable in this fashion. In addition, broadband multiple excitation can provide a new and more effective method for synthesizing specific cluster ions in situ.

Thus, multiple excitation collisional activation (MECA) was examined using FTMS. In analogy to the multiple excitation detection schemes, MECA is a process in which ions are translationally excited to larger orbits by applying an rf signal over the desired mass range. Next, collisional cooling of the ions collapses them spatially back to the center of the cell, where the process can be repeated. Two examples of the utility of MECA were examined. The first involved a novel way of growing cluster ions by sequential ion-molecule reactions followed by MECA. The second used MECA to increase the energy deposition in a stable and difficult to fragment ion, thereby inducing fragmentation. We believe that these results are positive enough to suggest that MECA will become an important and commonly used method for FTMS.

V. Chemistry of Fe^+ -Arene Ions with Halobenzenes

Gas-phase monatomic transition metal cations are unique in their abilities to activate a variety of chemical species, most notably highly stable small hydrocarbons via oxidative insertion into C-C and C-H bonds. A natural extension of bare transition metal ion chemistry is to study transition metal complex ions having a limited number of ligands. For example, a species such as ML^+ with a low formal oxidation state on the metal is highly coordinatively unsaturated and, like the bare metal ion, may insert oxidatively into an X-Y bond. The two σ -bonded moieties resulting from such an oxidative insertion, -X and -Y, are usually highly reactive in nature and may interact with the nearby L ligand. This opens up reaction pathways not associated with bare transition metal ions. The overall reaction process may be viewed as the metal acting as a reaction-initiating center to induce structure modifications to its ligand. Chemistry emerging from such studies has proven to be both interesting and diversified, depending on the specific ML^+ studied and the neutral reactants involved. Results from such studies could also suggest synthetic pathways of tailor-designing complex ions of desired structures starting with an easily available ionic species.

As a continuation of this work, the gas-phase ion chemistry between a series of $\text{Fe}(\text{arene})^+$ ions and halobenzene and dihalobenzene species was studied. Fe^+ in the arene complex, once again, was found to act as a reaction-initiating center to insert oxidatively into the phenyl-X bond ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The

arene ligand then underwent migratory insertion into the Fe^+ -phenyl σ bond. Subsequent hydrogen abstraction from the organic moiety and HX elimination generated $\text{Fe}(\text{biphenyl})^+$ ions. This reaction cycle could be repeated up to five times to give $\text{Fe}(\text{polyphenyl})^+$. In contrast, $\text{Fe}(\text{fluorobenzene})^+$ shows no reactivity with chlorobenzene, while CH_3 groups on the arene ligand sterically hinder the migratory insertion into the Fe^+ -phenyl bond. Nevertheless, this system holds promise for the development of gas-phase polymerization schemes.

VI. Gas-Phase Photodissociation Study of $\text{Ag}(\text{Benzene})^+$ and $\text{Ag}(\text{Toluene})^+$

The gas-phase chemistry of transition metal ions with small hydrocarbons has been the focus of intense investigation over the past ten years. Of the arsenal of mass spectrometric techniques which are being applied to this important problem, photodissociation is among the most promising, providing spectroscopic, dynamic, structural, and thermochemical information on metal ion complexes and cluster ions. In particular, photodissociation studies on a variety of $\text{M}(\text{benzene})^+$ (M =transition metal) species have been reported focussing primarily on obtaining quantitative metal ion binding energies. Most of these transition metal ion complexes have a high density of low lying excited states in the bond enthalpy region which allow the ions to readily absorb photons at this energy and dissociate. Thus, photodissociation thresholds for these systems via reaction 1 have directly yielded M^+ -ligand bond energy values in good agreement with limits obtained from ion-molecule

reactions and competitive collision-induced dissociation (CID) experiments, and with theoretically calculated values.

Recently, Duncan and co-workers reported a novel dissociative charge transfer pathway for $\text{Ag}(\text{benzene})^+$ and $\text{Ag}(\text{toluene})^+$ in which arene radical cation was the only photofragment observed reaction 2. Their results, obtained using a supersonic expansion ion source with a reflectron time-of-flight (TOF) mass spectrometer, were intriguing since such a charge transfer process had not been observed in the earlier photodissociation studies of metal ion-benzene complexes conducted in our laboratory using ion cyclotron resonance (ICR) methods. The observation of a 100% yield of C_6H_6^+ via reaction 2 for $\text{Ag}(\text{C}_6\text{H}_6)^+$ was reasonably explained since the charge transfer state is, presumably, the only excited electronic state at low energy and involves a weak interaction of the delocalized benzene cation with Ag. Nevertheless, we expected that some internal conversion might be observed to form Ag^+ . Furthermore, the upper limit for the bond energy calculated from the observed threshold, $D^\circ(\text{Ag}^+-\text{C}_6\text{H}_6) \leq 30$ kcal/mol, was uncharacteristically low for a transition metal ion-benzene complex, which is generally about 50 kcal/mol and higher. This prompted us to explore the process under the longer time scales (msec to sec versus μsec for (TOF) accessible through Fourier transform ion cyclotron resonance (FTICR) mass spectrometry. Interestingly, our results on

$\text{Ag}(\text{benzene})^+$ and $\text{Ag}(\text{toluene})^+$ have proven to be significantly different from those obtained from the TOF experiments. This study has drawn the attention of at least 3 other groups who have applied their techniques to the problem.

VII. Reactivity of Ti^{2+} and V^{2+} with Small Alkanes

Transition metal organometallic chemistry in the gas phase has been mostly restricted to singly charged positive ion studies. The primary reason for the lack of experimental data on multiply charged transition metal ions in the gas phase is the difficulty in generating these ions. However, in solution there is a higher stability and hence a greater prevalence of multiply charged transition metal ions. Therefore, the preparation of gas phase ions such as $\text{M}^{n+}(\text{H}_2\text{O})_m$ should be possible by transfer from solution to the gas phase. In fact, recent mass spectrometric methods, such as fast atom bombardment (FAB), thermospray, electrohydrodynamic ionization (EHI) and electrospray have been used to generate and study doubly charged ion-ligand species. Of these ionization methods, electrospray has been the most efficient in producing multiply charged transition metal ions. By interfacing an electrospray ion source to a quadrupole mass spectrometer, Kebarle and coworkers observed a variety of triply charged ions of the form $\text{M}(\text{L})_n^{3+}$ for $\text{M} = \text{Y}, \text{La}, \text{etc.}$ They also reported the ligand binding energies of $\text{M}(\text{L})_n^{2+}$ for $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ and $\text{L} = \text{H}_2\text{O}, \text{NH}_3, \text{DMSO}, \text{etc.}$ The authors attribute the stability of the ions to the delocalization of the charge onto the ligands, even though the it originates from the metal.

Laser desorption has been successful in generating bare doubly charged metal ions and several recent studies over the past decade have demonstrated their fascinating properties. The first reports came from the laboratory of Jim Weisshaar, where Ti^{2+} was accidentally laser desorbed into the reaction chamber of a fast flow reactor. The reactions with small alkanes ($\text{C}_1 - \text{C}_3$) yielded interesting reaction products, contrary to the belief that these species would react primarily via charge transfer, since the second ionization energy of the metal is higher than the first ionization energy of these organic molecules. We have reported on the reactions of Nb^{2+} , Ta^{2+} , Zr^{2+} , LaFe^{2+} , La^{2+} , Y^{2+} and Sc^{2+} with small linear alkanes. The dimer LaFe^{2+} was generated by first laser desorbing La^{2+} and then allowing it to react with $\text{Fe}(\text{CO})_5$ to form $\text{LaFe}(\text{CO})_n^{2+}$. Collision-induced dissociation (CID) of these ions resulted in the loss of CO to form LaFe^{2+} .

A survey of gas-phase ion photochemistry revealed that in some cases the singly charged ion is bound more strongly to the ligand than the doubly charged analogue. These findings spawned a detailed theoretical treatment by Bauschlicher and coworkers, in an effort to explain the bonding. One outcome of our studies was the unexpected displacement of alkenes by alkanes in the reactions of $\text{M}(\text{alkene})^{2+}$ for $\text{M} = \text{La}$ and Y , which demonstrated that in some cases the alkane is bound more strongly than the alkene. This past year we investigated the reactivity of V^{2+} and Ti^{2+} with small alkanes, with a view to evaluating the periodic trends of the Groups 4 and 5 early transition metal ions. The

behavior of Ti^{2+} was also compared with the reactivities observed by Tonkyn and Weisshaar, using the flowing afterglow technique. The results obtained from this work have provided more evidence for a simple curve-crossing potential energy model.

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