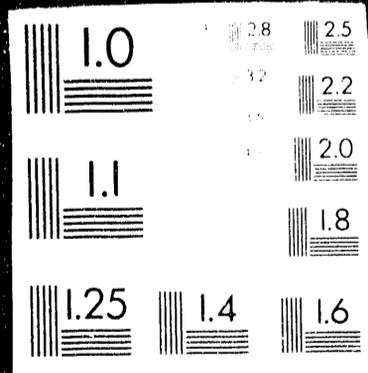


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Reactions of Metal Ions and Their Clusters in the Gas Phase Using
Laser Ionization-Fourier Transform Mass Spectrometry

Progress Report

DOE/ER/13766--10

For Period February 1, 1992 - January 31, 1993

DE93 006505

submitted by

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November 1992

Prepared for

THE U.S. DEPARTMENT OF ENERGY AGREEMENT NO.

DE-FG02-87ER13766

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Abstract

This report will focus on three areas we have made substantial new progress in over the past several months: (1) Infrared multiphoton photoinduced ion-molecule reactions; (2) The use of SF₆ to detect excited state metal ion behavior; and (3) Cluster ion chemistry.

I. Infrared Multiphoton Photoinduced Ion-Molecule Reactions in the Gas Phase

The study of gas-phase ion photochemistry by Fourier transform mass spectrometry (FTMS) has, thus far, been largely limited to unimolecular photodissociation and, for negative ions, photodetachment processes. Compared to the wealth of information on condensed-phase photochemistry, reports of bimolecular photochemistry in the gas phase are rare. 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 to observe the intermolecular ion-molecule chemistry of a photoactivated reagent ion under the low pressure conditions used in the FTMS (typically 10⁻⁹-10⁻⁵ torr), 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 and others 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 coworkers monitoring the chemistry of NO^+ in selected vibrational states generated in an FTMS 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 eliminating altogether, photodissociation and photodetachment as competitive pathways. In this last regard, the observation of numerous sequential multiphoton dissociation and detachment 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 fifteen years, particularly by Dunbar and coworkers 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 reported the first example of a photoinduced, or more exactly photoenhanced, ion-molecule reaction between the proton-bound methanol dimer, $(\text{CH}_3\text{OH})_2\text{H}^+$, and H_2O to give $(\text{CH}_3\text{OH})\text{H}^+(\text{H}_2\text{O})$ and CH_3OH . The reaction rate of this endothermic process was increased by up to three orders of magnitude under low intensity cw infrared laser irradiation.

More recently, our studies on 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 states, these ions tend to absorb broadly in the uv-vis region; (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; and (3) Metal ion centers readily promote isomerization and other chemical transformations. Subsequently, three examples of photoinduced reactions involving transition metal containing ions have been reported using uv-vis light sources, including photoinduced rhodocenium formation, $\text{Rh}(\text{c-C}_5\text{H}_5)_2^+$, from the irradiation of $\text{Rh}(\text{c-C}_5\text{H}_6)^+$ in the presence of cyclopentane, photoinduced isomerization of $\text{Co}_2(\text{N}(\text{O})^+)$ to $\text{Co}_2(\text{NO})^+$ manifesting itself by an increased reactivity with background O_2 and, most recently, the observation by Pope and Buckner of a photoinduced ligand switching reaction between $\text{V}(\text{C}_6\text{H}_6)^+$ and CH_3CN to give $\text{V}(\text{CH}_3\text{CN})^+$. Finally, Smalley and coworkers 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 $n = 39, 45, \text{ and } 48$, while the clusters with $n = 36, 42 \text{ and } 51$ appear to be even more reactive. Whether this is due to annealing of the clusters (i.e., isomerization) or simply increasing their temperature is still unclear.

Our work during this past funding year more than doubled the number of reported examples in the literature, further demonstrating the potential of this new type of photochemistry. Using multiphoton infrared absorption to create long-lived vibrationally excited ground state intermediates, five general reaction types were demonstrated: (1) photoinduced deceleration of exothermic reactions; (2) photoinduced secondary fragmentation whereby an internally excited product ion is generated which can undergo fragmentation; (3) photoactivated ligand switching; (4) photoinduced isomerization; and (5) photoenhanced

hydrogen/deuterium exchange. Ultimately, this new photochemistry will permit absorption information on ions to be obtained in the infrared.

II. The Use of SF₆ to Detect Excited state Metal Ion Behavior

The inertness of SF₆ is well known to be associated with the protective space layer of F atoms surrounding the central S atom, which obstruct the access to the reactive center by an attacking species. Previous gas-phase studies using SF₆ as the reactant gas involved reactants such as He⁺, Ar⁺ and N₂⁺ which have high ionization energies. Our study shows that some transition metal ions, despite their low ionization potentials, can react with SF₆ yielding product distributions much different from those of the reactions studied previously. In fact, the reactivity is a sensitive function of kinetic energy and electronic state configuration, which we are currently investigating. The dual goal of this work is to both understand the unique bonding nature in SF₆ and to try to quantify electronic state distributions in metal ions generated by laser desorption.

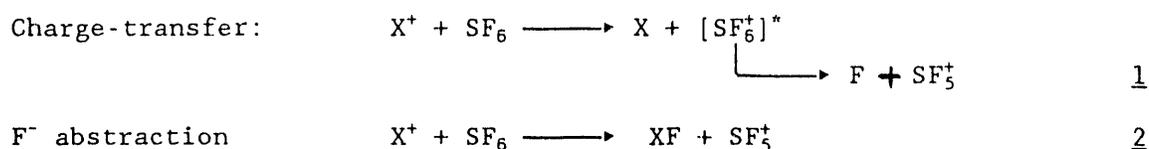
The study of sulphur hexafluoride has been of great interest for several decades. Many of its properties have been investigated with practical applications in mind. Among the most important examples are its applicability for isotope separation by laser irradiation, and its use as a source of F atoms in lasers, as well as in plasma etching processes. For its high chemical stability and excellent insulating properties, it has been widely used in the electrical transmission industry as a highly efficient insulator of high-voltage equipment. In addition, it has also attracted much attention from chemists interested in fundamental questions. For example, SF₆ has been considered as a model representing in many respects the kind of bonding in hypervalent compounds

which exceed the number of valences permitted on the basis of Langmuir-Lewis theory of bonding. Extensive theoretical calculations and experimental research on various aspects of SF_6 , including ionization energies and the electronic structure have been carried out over the past twenty years. Whether the 3d orbitals in the S atom participate in the bonding orbitals is in question, since they are so diffuse that their overlap with the bond orbitals of the fluorides is too small to make a significant contribution to molecular binding. Furthermore, the promotion energy for transferring one s- and one p- electron in the S atom into an empty d orbital is rather high. A number of explanations, based on either valence bond or molecular orbital theory, have proposed to elucidate the bonding nature of this kind of molecule.

Experimental studies aiming to accumulate information about the reactivity of SF_6 with various chemical species should lead to a better understanding of the bonding nature of this molecule. Sulphur hexafluoride, however, is almost inert to both nucleophilic and electrophilic reagents. It is unaffected by aqueous solutions of fused alkali, ammonia, or oxygen. It is attacked readily only by powerful reagents, such as sodium in liquid NH_3 , and strong Lewis acids. It is not surprising, therefore, that most of its reactions which have been well studied occur in the area of gas-phase ion-molecule reactions, where the reactant cations act as the Lewis acids.

The behavior of SF_6 in these reactions can be understood in terms of its structure. The S-F bond energy in SF_6 differs little from that in SF_4 , but the latter is rather reactive while the former is not. Thus, it has been suggested that the inertness of SF_6 must be kinetic rather than thermodynamic. The stability has been considered to be associated with the protective layer of fluorine atoms surrounding the central sulphur atom. In this fully space-filled

molecule, access to the reactive center by an attacking species is obstructed, in contrast to SF₄ (incomplete trigonal-bipyramidal structure) where access is easy. It can be expected that SF₆ will undergo reactions in which S atom is not attacked directly. In previous ion-molecule reaction studies, the reaction mechanisms are either through charge transfer to form an unstable [SF₆⁺]^{*}, followed by fragmentation to SF₅⁺ (1), or through F⁻ abstraction (2). When X has a sufficiently high ionization potential (IP), SF₅⁺ can further fragment to SF₄⁺ and SF₃⁺, as is the case in the He⁺ reaction. In addition, when the energy of the impacting electrons to generate He⁺ is greater, more SF₃⁺ is produced from the reaction.



The reaction heats for the charge-transfer reaction (ΔH_1) and F⁻ abstraction (ΔH_2) are, respectively

$$\Delta H_1 = AP(SF_5^+/SF_6) - IP(X)$$

$$\Delta H_2 = [AP(SF_5^+/SF_6) - D(XF)] - IP(X).$$

For these reactions to take place with observable reaction rates, the ionization potential (IP) of X must be greater than the appearance potential of SF₅⁺ from SF₆, AP(SF₅⁺/SF₆), for reaction 1 or greater than [AP(SF₅⁺/SF₆) - D(XF)] for reaction 2, where D(XF) is the X-F bond energy.

Studies of SF₆ with metal ions could have provided more information. However, prior to our work few such studies had been reported in the literature. Metal species generally have low ionization potentials. Thus, they cannot react

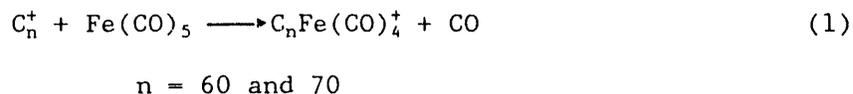
with SF₆ by reaction 1 or 2 exothermically. In 1982, however, we reported that Ti⁺, despite its IP (6.82 eV) being far below the value of AP(SF₅⁺/SF₆)(14.62eV), readily reacted with SF₆ to give a striking product pattern, with SF₃⁺ being the predominant ion, and SF₂⁺ and SF₄⁺ all having significant intensities. This reaction behavior is dramatically different from that reported in the previous studies.

During the last year we began a more in depth investigation of the reactions of SF₆ with a variety of transition metal ions. Our studies showed that for thermalized ions, the early transition metal ions react with SF₆, while the late transition metal ions are inert. However, if the late transition metal ions were kinetically or electronically hot, reactivity was observed. These effects are currently being investigated both to understand the nature of the observed effects and to quantitate the electronic distributions of ions generated by laser desorption. Our initial results indicate that predominantly ground state species are generated which, we believe, may be due to quenching of excited electronic states by collisions with free electrons in the laser generated plasma. In view of the strong current interest in the metal ion community in state-specific ion chemistry, we believe that SF₆ will prove to be an excellent reagent for detecting and quantitating excited metal ion state distributions.

III. Cluster Ion Chemistry

This past year saw the successful implementation of the Smalley compact supersonic cluster source on our FTMS 2000 instrument to generate and study "large" clusters. Due to the timeliness of the topic, we have first applied this source to the generation and study of the carbon clusters, C_n⁺ and C_n⁻(n = 2 - 200), which include the fullerenes. Without a doubt, the most interesting and

intriguing result is the observation that when C_n^+ ions ($n = 52 - 200$) are trapped in the presence of $Fe(CO)_5$, only C_{60}^+ and C_{70}^+ undergo reaction 1 to displace a carbonyl ligand. The remainder of the other clusters are unreactive. It remains a question why this remarkable selectivity occurs especially considering that C_{60}^+ and C_{70}^+ are particularly stable.

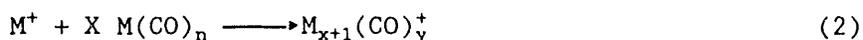


Subsequent reactions with $Fe(CO)_5$ leads to the formation of $C_nFe_4(CO)_x^+$ species. Using the eighteen electron rule, two interesting conclusions are drawn: (1) The C_{60} and C_{70} species act like 2 electron donors as opposed to 5 or 6 electron donors as might be expected. However, this is in accordance with the behavior of C_{60} as a ligand in the few organometallic complexes which have been synthesized. (2) The subsequent reactions of the $C_nFe(CO)_4^+$ species generated in reaction 1 with $Fe(CO)_5$ occur at the metal center and not at different locations on the C_n ligand.

The purpose of this work is to understand the fundamental reactivity of these high profile fullerene compounds and to suggest possible synthetic routes for metallofullerene complexes. For example, we discovered a novel bis-Buckminsterfullerene nickel ion in the gas phase, which has lead us on a search for a stable neutral complex. We are currently in the process of trying to prove the existence of a neutral $Fe(C_{60})_2$ complex which we have synthesized. Finally, a little over a year ago, this work provided the first definitive evidence for the endohedral metal complex proposed by Smalley by clearly demonstrating that the exo-complex has greatly differing properties.

The study of the reactivity of metal cluster ions is still in its infancy. In a sense, the last 10 years we have spent developing the methodology for studying atomic metal ion chemistry, has been in preparation for the investigation of small metal cluster ions. We have done some of the most detailed chemical studies to date on metal dimers and trimers, but clearly larger clusters have interest to a broader range of scientists. These studies can provide information of relevance to surface science and catalysis, as well as materials science.

This past year we began employing two methods for generating intermediate to large clusters. The first method developed in our laboratory to generate dimers and trimers, has now been extended up to M_{10}^+ species and we believe it can be taken further, perhaps up to M_{20}^+ . This method involves the in situ generation of clusters by the general sequential reaction 2.



The product generated in reaction 2 then undergoes collision-induced dissociation to cleave off all of the CO molecules to generate bare M_x^+ . The advantage of this method is that it offers a flexibility for generating mixed clusters by adding more than one volatile metal carbonyl.

The second method which holds the greatest promise involves the Smalley supersonic source. While only small modifications were required to generate good intensities of carbon clusters, we have had difficulty in generating metal clusters. About one month ago, however, by making several subtle and not so subtle modifications, we saw our first clusters with niobium up to Nb_{10}^+ . Interestingly, doping the He expansion gas with O_2 or H_2O lead to the formation of various $Nb_xO_4^+$ species. Thus, I am confident that in the next progress report, I will be able to discuss substantial new and interesting cluster chemistry.

IV. Miscellaneous

In addition to the three topics above, we have continued our studies in a number of other topics including: (1) Obtaining metal-ligand bond energy information from photodissociation thresholds; (2) distinguishing isomeric ion structures by multiphoton infrared photodissociation, collision-induced dissociation and selected ion-molecule reactions; (3) studying the chemistry and photochemistry of doubly charged ions; (4) studying metal ion-benzyne chemistry; and (5) studying methods of distinguishing stereoisomers using metal ion chemical ionization.

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