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

Progress Report

For Period February 1, 1990 - January 31, 1991

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In the past 9 months since submitting my last progress report, we have accomplished a considerable amount of research on a number of fronts. I will briefly summarize some of the highlights here.

Supersonic Cluster Source

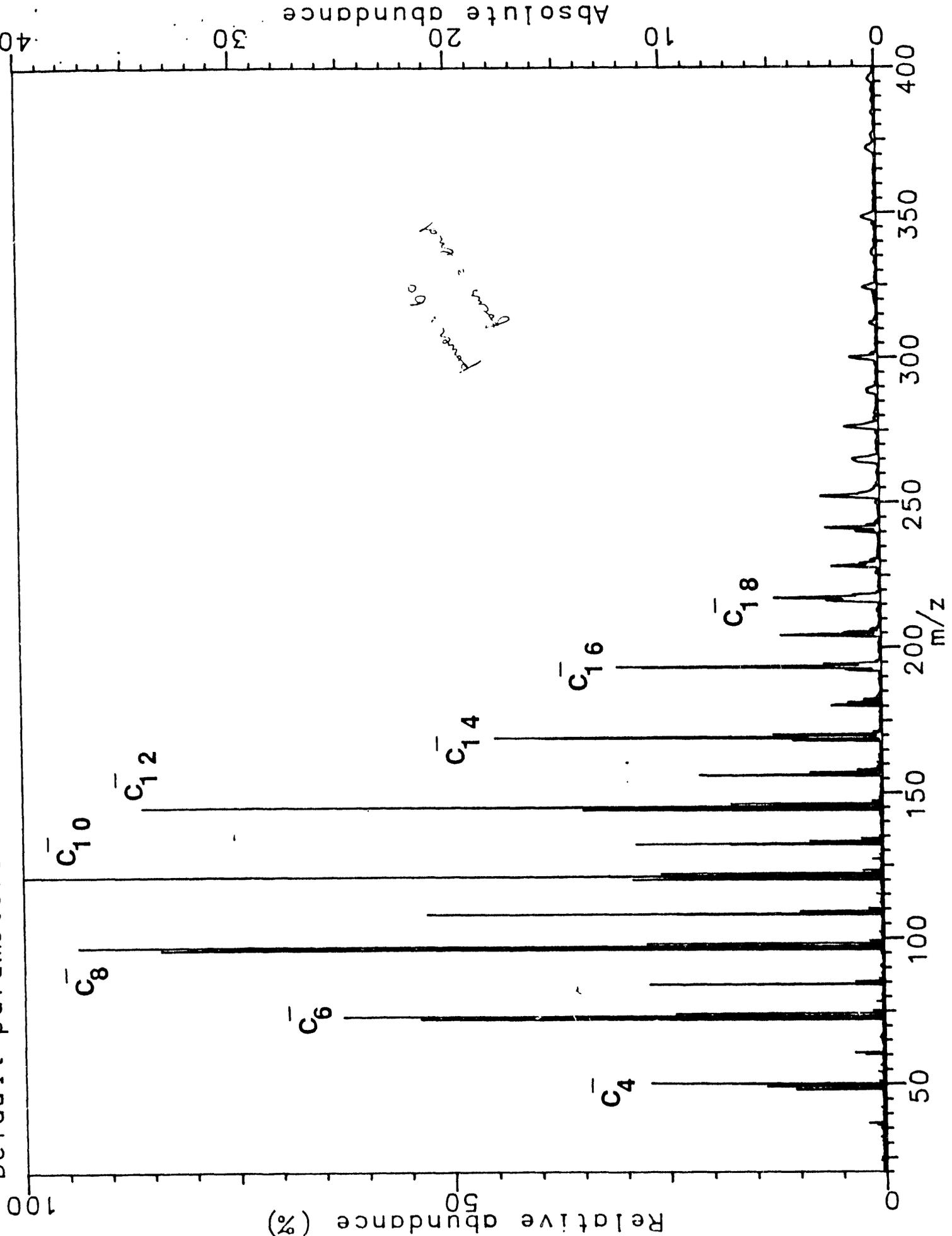
We obtained our first cluster signals from this new source just a few weeks ago. Figure 1 shows the negative ion spectrum generated from a carbon target. Carbon clusters of the form C_N^- are observed at least out to $N = 30$ confirming that cluster formation is occurring in the high pressure "waiting room" of the source. This can be stated unequivocally, since only up to $N = 13$ is observed by direct laser desorption of a carbon target in the absence of supersonic expansion. In fact, two studies on the chemistry and the collision-induced dissociation of C_N^- clusters for $N = 2-13$ have been reported and we are expanding these studies beyond $N = 25$ as our first paper from the source.

While we have not had major success in generating transition metal cluster ions yet, we believe we know what instrumental modifications will be necessary based, once again, on Smalley's work and these improvements should be shortly forthcoming.

Collaborations

As I mentioned in my last progress report, starting about two years ago we began a number of collaborative projects just by coincidence. This trend has certainly continued over this last period. The most profitable and exciting of these collaborations has to be our interactions with the well renowned theoretician Charles Bauschlicher at NASA Ames Laboratory at Moffett Field,

Default parameters



California. Since starting our metal ion work about ten years ago, I have off and on tried to interest theoreticians into "becoming involved", with relatively little success due to the complication of performing the calculations. Such calculations take enormous computing power, the type available at NASA. In addition, of course, it takes a skilled practitioner like Charles Bauschlicher to analyze the quality of the data and provide a meaningful interpretation. Two papers, which have resulted from our collaboration this period, started off with unusual observations in our laboratory. First, in our pioneering studies of the gas-phase chemistry of doubly charged metal ions, Dorothy Hill in my group observed that alkanes can displace alkenes on Sc^{2+} which runs contrary to all previous ligand-exchange studies on singly charged metal ions. Second, Lisa Roth in the group found that the bond energy of Mg^+ to Fe in MgFe^+ was significantly lower than the photodissociation threshold results would indicate. In fact, photodissociation favored formation of Fe^+ and Mg, rather than the thermodynamically preferred pathway of Mg^+ and Fe. Both of these observations have been confirmed by theory providing a basis for a complete understanding of these important fundamental properties.

Choosing a second example from the several available, our collaboration with Professor Graham Cooks at Purdue on the charge transfer reactions of M^{2+} ($\text{M} = \text{Nb}, \text{Ta}, \text{and La}$) with $\text{W}(\text{CO})_6$ has also yielded significant fundamental information. We recently adapted a method originally used in conjunction with conventional ion cyclotron resonance (ICR) instruments for determining the

kinetic energy release resulting from ion-molecule reactions. This new methodology works very well with FTMS. Our first published method involved determining the kinetic energy release in the charge transfer reaction of Nb^{2+} with benzene to form the singly charged ions Nb^+ and benzene^+ . We learned that not all of the energy available from the large exothermicity of this reaction, - 5eV, went into kinetic energy, which arises largely from the coulombic repulsion of the two singly charged products. In fact, in a subsequent study on V^{2+} and Ta^{2+} with benzene, it could be surmised that -3eV of the energy went into generating benzene cation in one of its low lying electronic states. A more detailed approach for obtaining information on the product internal energies is to use what have been termed "thermometer molecules." $\text{W}(\text{CO})_6^+$ is an example of such a molecule utilized extensively in the Cooks' group. Simply explained, since the thermochemistry for sequential loss of CO from $\text{W}(\text{CO})_6^+$ is known precisely, one can determine the internal energy distribution of a newly born $\text{W}(\text{CO})_6^+$ parent ion from the distribution of $\text{W}(\text{CO})_N^+$ ($N = 0-6$) observed. Clearly, the higher the internal energy, the more COs will be lost. Using the methodology developed in our laboratory for measuring kinetic energy release with that of the thermometer molecule $\text{W}(\text{CO})_6$ developed in Cooks' laboratory, we have been able to obtain some of the most detailed information on energy partitioning in ion-molecule reactions to date.

IR Photodissociation

Although Beauchamp recently published two fascinating papers detailing the multiphoton IR photodissociation of a metal ion

containing complex, only one other study (also from Beauchamp's group) has appeared involving Fe^+ -pentene isomers. We have made a good start in greatly expanding the scope of these studies. Currently underway is a systematic investigation of a wide variety of $\text{M}^+-\text{C}_n\text{H}_{2n}$ species with $n = 2-10$ and $\text{M} =$ first and second row transition metal ions. In addition we will shortly apply this methodology to doubly charged ions and metal cluster ions. All indications are that this area will be highly productive.

VI. Publications Acknowledging DOE, 1989 - present

Publications Acknowledging DOE under Contract DE-FG02-87ER13766,
1989-present

1. Gas Phase Reactions of Fe^- and Co^- with Simple Thiols, Sulfides, and Disulfides by Fourier Transform Mass Spectrometry. Sallans, L.; Lane, K.R.; Freiser, B.S. J. Am. Chem. Soc., **1989**, 111, 865-873.
2. A Gas-Phase Photodissociation Study of the Structure and Thermochemistry of FeS_n^+ ($n=1-6$). MacMahon, T.J.; Jackson, T.C.; Freiser, B.S. J. Am. Chem. Soc., **1989**, 111, 421-427.
3. Heterodinuclear Transition Metal Cluster Ions in the Gas Phase. Thermochemistry and Reactivity of NbFe^+ and NbFeL^+ ($L = \text{O}, \text{CO}, \text{H}_2\text{O}$, and Alkenes). Buckner, S.W.; Freiser, B.S. J. Phys. Chem., **1989**, 93, 3667-3673.
4. Combining Lasers with Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: Applications to the Study of Gas Phase Metal Ion Chemistry. Weller, R.R.; MacMahon, T.J.; Freiser, B.S. in "Lasers in Mass Spectrometry", Lubman, D.M. (Editor), invited chapter, in press.
5. Ligand effects on Transition Metal Ion Reactivity: Primary and Secondary Reactions of Co^+ and Ni^+ with Alkenes. Hettich, R.; Freiser, B.S. Organometallics, **1989**, 8, 2447-2453.
6. Kinetic Energy Release in Thermal Ion-Molecule Reactions: The Nb^{2+} -Benzene Charge Transfer Reaction. Buckner, S.W.; Gord, J.R.; Freiser, B.S. J. Chem. Phys., in press.

7. Formation of Primary Amide Complexes of Fe^+ , Co^+ , and Rh^+ in the Gas Phase. Buckner, S.W.; Freiser, B.S. Polyhedron, 1989, 8, 1401-1406.
8. Gas Phase Reactions of Nb^+ and Ta^+ with Alkanes and Alkenes. C-H Bond Activation and Ligand Coupling Mechanisms. Buckner, S.W.; MacMahon, T.J.; Byrd, G.D.; Freiser, B.S. Inorg. Chem., 1989, 28, 3511-3518.
9. Reactions of MCH_3^+ ($\text{M}=\text{Fe}, \text{Co}$) with Nitrogen Containing Species in the Gas Phase. Determination of the Proton Affinity of MCH_2 . Jacobson, D.B.; Gord, J.R.; Freiser, B.S., Organometallics, 1989, 8, 2957-2960.
10. Gas Phase Study of Fe^+ -Benzynes with Alkanes. Huang, Y.; Freiser, B.S., J. Am. Chem. Soc., 1989, 111, 2387-2393.
11. Gas Phase Photoinduced Reactivity of $\text{Rh}^+(\text{c-C}_5\text{H}_6)$ with Cyclopentane. Gord, J.R.; Buckner, S.W.; Freiser, B.S. J. Am. Chem. Soc., 1989, 111, 3753-3754.
12. Gas Phase Ion Chemistry of $\text{Cr}(\eta^6\text{-Arene})(\text{CO})_3$ Complexes by FTMS Techniques. Operti, L.; Vaglio, G.A.; Gord, J.R. Freiser, B.S. Organometallics, in press.
13. Applications of Fourier Transform Ion Cyclotron Resonance Spectrometry to the Study of Transition Metal Containing Ions in the Gas Phase. Freiser, B.S. Chemtracts, 1989, 1, 65-109. (invited).
14. Heteronuclear Diatomic Transition-Metal Cluster Ions in the Gas Phase: Reactions of ScFe^+ with Hydrocarbons. Lech, L.M.; Gord, J.R.; Freiser, B.S. J. Am. Chem. Soc., 1989, 111, 8588-8592.

15. Gas Phase Photoinduced Reactivity of Co_2NO^+ with O_2 Via a Photoisomerization Mechanism. Gord, J.R.; Freiser, B.S. J. Am. Chem. Soc., 1989, 111, 3754-3755.
16. Separation of Experiments in Time and Space Using Dual Cell Fourier Transform Ion Cyclotron Resonance Mass Spectrometry. Gord, J.R.; Freiser, B.S. Anal. Chim. Acta, 1989, 225, 11-24.
17. Thermochemical Properties of Gas-Phase MgOH and MgO Determined by Fourier Transform Mass Spectrometry. Operti, L.; Tews, E.C.; MacMahon, T.J.; Freiser, B.S. J. Am. Chem. Soc., 1989, 111, 9152-9156.
18. Kinetic and Photochemical Studies of FeC_5H_6^+ in the Gas Phase. Huang, Y.; Freiser, B.S. J. Am. Chem. Soc., 1990, 112, 5085-5089.
19. Preparation and Study of Fe_2^+ -Benzyne Ion in the Gas Phase. Huang, Y.; Freiser, B.S. Inorg. Chem., 1990, 29, 1102-1104.
20. Formation of Thermodynamically Stable Dications in the Gas Phase by Thermal Ion-Molecule Reactions: Nb^{2+} with Small Alkanes. Buckner, S.W.; Gord, J.R.; Freiser, B.S. J. Chem. Phys., 1989, 91, 7530-7536.
21. Chemistry of Scandium-Benzyne Ion in the Gas Phase. Huang, Y.; Hill, Y. D.; Freiser, B.S. Inorg. Chem., submitted.
22. Gas-Phase Chemistry Between Fe^+ -Benzyne and Alkenes. Huang, Y.; Freiser, B.S. J. Am. Chem. Soc., 1990, 112, 1682-1685.

23. Study of the Chemistry of Iron-Alkene Cations with Chlorobenzene. Huang, Y.; Freiser, B.S. Inorg. Chem., 1990, 29, 2052-2054.
24. Study of The Gas-Phase Chemistry of Yttrium-Methyl Cation: σ -Bond Metathesis and Migratory Insertion of C=C Bonds into the Y^+ -Methyl Bond. Huang, Y.; Hill, Y.D.; Freiser, B.S., J. Am. Chem. Soc., in press.
25. Methods for Determining Metal-Ligand and Metal-Metal Bond Energies Using FTMS. Freiser, Ben S. "ACS Symposium Series: Bonding Energetics in Organometallic Compounds," Marks, T.J., Ed., American Chemical Society, Washington, D.C. 428, 1990.
26. Collision-Induced Dissociation of Positive and Negative Copper Oxide Cluster Ions Generated by Direct Laser Desorption/Ionization of Copper Oxide. Gord, J.R.; Bemish, R.J.; Freiser, B.S., Int. J. Mass Spectrom. Ion Processes, in press.
27. Comparative Study of Energy Deposition in Gaseous Organic Ions Using Limonene As A Model Compound. Horning, S.R.; Wood, J.M.; Gord, J.R.; Freiser, B.S.; Cooks, R.G., Int. J. Mass Spectrom. Ion Proc., submitted.
28. The Effects of Donor-Acceptor Electronic Interactions of the Rates of Gas-Phase Metallocene Electron-Exchange Reactions; Phelps, D.K.; Gord, J.R.; Freiser, B.S.; Weaver, M.J., J. Phys. Chem., submitted.

29. The Unexpected Displacement of Alkenes by Alkanes in the Reactions of $Y(\text{Alkene})^{2+}$. An Experimental and Theoretical Study. Hill, Y.D.; Freiser, B.S.; Bauschlicher, Jr., C.W., J. Am. Chem. Soc., in press.
30. Refinements of a Seemingly Well-Understood System: The Gas-Phase Chemistry of Fe^+ with n-Pentanenitrile. Eller, K.; Zummack, W.; Schwarz, H.; Roth, L.M.; Freiser, B.S., J. Am. Chem. Soc., submitted.
31. Formation of Thermodynamically Stable Dications in the Gas Phase by Thermal Ion-Molecule Reactions: Zr^{2+} and Ta^{2+} with Small Alkanes. Ranasinghe, Y.; MacMahon, T.J.; Freiser, B.S., J. Phys. Chem., submitted.
32. Kinetic Energy Release in Thermal Ion-Molecule Reactions: The Single Charge-Transfer Reactions of V^{2+} and Ta^{2+} with Benzene. Gord, J.R.; Buckner, S.W.; Freiser, B.S. J. Phys. Chem., submitted.
33. Heteronuclear Diatomic Metal Cluster Ions in the Gas Phase: Theoretical Treatment of MgFe^+ and Study of Its Reactions with Hydrocarbons. Roth, L.M.; Freiser, B.S.; Bauschlicher, C.W.; Partridge, H.; Langhoff, S.R. J. Am. Chem. Soc., submitted.

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