A new source of cold metal cluster ions (both bare and ligated) has been developed and demonstrated. Reactions of transition metal cluster ions formed by this source are then examined using guided ion beam techniques. These techniques allow ionic clusters of variable size and composition to be isolated. Measurement of reaction cross sections and branching ratios characterize the interactions of the clusters with neutral gases. By examining the variation of these quantities with the kinetic energy of the cluster ions, extensive thermochemical data for both ionic and neutral cluster species can be determined. Prototypical data for Fe₇ and Nb₇ have been obtained.
Final Report

Transition Metal Cluster Chemistry

P. B. Armentrout

University of Utah
Salt Lake City, Utah 84112

U. S. Army Research Office
DAAL03-87-K-0122
Statement of Problem Studied

The proposed research was to study the gas phase chemistry and thermodynamics of transition metal clusters using ion beam methods. Mass spectrometric techniques allow ionic clusters of variable size and composition to be isolated. Measurement of reaction cross sections and branching ratios characterize the interactions of the clusters with a variety of neutral gases. By examining the variation of these quantities with the kinetic energy of the cluster ions, extensive thermochemical data for both ionic and neutral cluster species can be determined. These data include metal-metal binding energies and binding energies of inorganic and organic fragments to clusters.

The proposed research was to be broken down into three phases. First, existing equipment and technology would be used to examine cluster chemistry. Second, a new cluster source and apparatus would be developed. This instrument would be capable of generating larger clusters of more metals and examining their chemistry. Finally, this apparatus would be used to greatly extend the scope of the proposed chemical studies. All three phases were successfully completed during the course of the grant.

Summary of Results

A. Transition Metal Cluster Ion Source

Over the past several years, we have spent considerable effort developing a source of ionic metal clusters. This unique source has four important features: 1) the metal cluster ion beam is essentially continuous; 2) cluster ions are thermalized by collisions in a carrier gas flow and then cooled by supersonic expansion; 3) the initial cluster distribution is mass-selected to provide a single cluster ion; and 4) the source appears to be capable of generating cluster ions of most metals. Smalley's group has also...
shown the capability of forming cold metal cluster ions for chemical studies but in a pulsed source. In our source, metal ions are produced by laser vaporization of a metal sample in a configuration similar to that of Smalley using a high repetition rate (8 kHz) Cu-vapor laser. The metal sample can either be in rod form (1/4" diameter) or as a thin sheet (1" diameter disc). The ionized metal vapor is entrained in a continuous flow of He through a 5.7 cm long nozzle (although this length can be varied). Here, a sputtered metal ion is rapidly thermalized and clusters with other metal atoms. Residence times are \( \approx 170 \mu s \) such that particles entering the flow experience \( >10^5 \) collisions with He. The clusters then undergo a mild adiabatic expansion into the initial vacuum chamber. The calculated conditions of the expansion yield a translational temperature of \(<10 \text{ K} \). Cooling is arrested at a skimmer located approximately 2/3 the distance to the mach disk. Sufficient numbers of ions are created to eliminate the need for an external ionizer. Thus, the cluster ions have internal energies which are at least thermal (300 K) and probably colder.

A preliminary version of this source has been described in the literature. We have since increased the differential pumping which enables much higher stagnation pressures. While early results showed rapidly decreasing ion cluster intensities as the size increased, our latest results show that the intensity of the cluster ions is fairly uniform above the dimer. Intensities are usually \( >10^6 \) ions/s, more than enough for our studies. To date, we have made clusters of Fe, Co, V, Nb, Ta, Si, and Al. Our only failure has been C, probably because insufficient numbers of carbon ions are made in the laser vaporization step. Our primary limitation in the size of the cluster we can study is the mass range of the two mass spectrometers (described below), presently about 1000 amu for each.
We have also tested the ability of this source to produce ionic species other than pure metal clusters.4 By introducing O2 to the He flow upstream of the vaporization region, we are able to cleanly convert the bare metal cluster ions to metal cluster oxide ions. The absolute amount of ions does not change appreciably under these conditions. Species like Fe2Oγ+ (γ = 2-5), Fe3Oγ+ (γ = 2-6), Fe4Oγ+ (γ = 4-7) and Fe5Oγ+ (γ = 5-8) can easily be produced. It is clear that larger clusters show more extensive oxygenation, consistent with a preference of iron to retain an oxidation state of between 2 and 3. This indicates that the metal species undergo sufficient collisions with O2 to reach a thermodynamically stable configuration, but not so many that the clustering process is disrupted. Presumably other atomic and molecular species can be attached to the cluster ions in a similar manner.

B. Instrumentation and Experimental Methods

Once formed, the metal cluster ions are studied by using a guided ion beam tandem mass spectrometer built especially for this purpose over the past three years. Our laboratory is a leader in the development and use of this versatile technique for the study of a wide range of chemical phenomena.5 Briefly, our instrument comprises the cluster ion source described above, a magnetic sector mass spectrometer for selection of a particular cluster size, a well-defined zone where reactions occur at variable kinetic energies under single collision conditions, a quadrupole mass filter for product analysis, and a sensitive ion detector which incorporates a 28 kV conversion dynode. The reaction region is surrounded by an octopole ion beam guide, first developed by Teloy and Gerlich.6 This device uses high frequency electric fields to establish a potential well which traps ions radially but does not affect the velocity of the ions along the axis of the trap. Thus, the ions are guided along the instrumental axis, enabling efficient collection of all
products regardless of the reaction dynamics. Use of the octopole also permits very low ion energies (<0.1 eV) to be reached and routine determination of the absolute energy scale by using retarding techniques.\textsuperscript{5,6}

Reactant and product ion intensities are measured as a function of the ion kinetic energy and these are converted to absolute cross sections.\textsuperscript{5} Our absolute cross sections are estimated to have uncertainties of <20\% and that the energy scale uncertainty is <0.05 eV in the laboratory frame.

C. Results for Fe\textsubscript{2}\textsuperscript{+}

A number of our studies so far have concentrated on the reactions of iron clusters. This is motivated by the interest in corrosion, the fact that ionization potentials have been measured for the neutral clusters,\textsuperscript{7} and the fact that reaction studies of the neutrals exist for comparison.\textsuperscript{8,9}

Generally, our cluster studies begin with characterization of the clusters by collision induced dissociation (CID) studies in which the cluster ion is fragmented by collision with a rare gas. This enables a direct measurement of the binding energies of the clusters. Having obtained this critical information, studies involving more reactive gases can then be carried out.

CID of Fe\textsubscript{2}\textsuperscript{+}. A considerable amount of work has been performed on the anionic, neutral, and cationic dimer of iron. Despite this, the bond energy of these species is known only within a 0.5 eV range. Our results for the CID of Fe\textsubscript{2}\textsuperscript{+} by Xe have been recently published.\textsuperscript{10} The threshold for this reaction is found to be 2.72 ± 0.07 eV. Since there should be little internal excitation in the Fe\textsubscript{2}\textsuperscript{+} which would serve to lower the threshold and since we anticipate no activation barriers to the dissociation, this threshold should equal the bond dissociation energy, D\textsuperscript{0}(Fe\textsubscript{2}\textsuperscript{+}) = 2.72 ± 0.07 eV. This value is in good agreement with several less precise literature values. Combined with the known ionization potentials\textsuperscript{7,11} and electron affinities\textsuperscript{12} of Fe and Fe\textsubscript{2},
this bond energy also provides $D_0(\text{Fe}_2) = 1.15 \pm 0.09$ eV and $D_0(\text{Fe}_2^+) = 1.90 \pm 0.09$ eV.

CID of $\text{Fe}_x^+(x = 3-10)$. While a variety of techniques have been used to measure the bond energies of metal dimers (and some trimers), there are few measurements of the bond energies for larger clusters, neutral or ionic. One exception is recent work on cationic aluminum clusters.\textsuperscript{13,14} However, it is straightforward to extend the CID experiment described above to larger clusters. Indeed, the aforementioned bond energies for aluminum cluster ions were measured via CID studies.

We have now studied the CID of iron clusters ranging from the dimer to the decamer. Results for the trimer through decamer have recently been submitted for publication.\textsuperscript{15} In all cases, the lowest energy decomposition channel is always loss of an Fe atom. Our data offer no indication that any molecularly bound neutral products are formed in the dissociation of these cluster ions. Dissociation occurs exclusively by sequential Fe atom loss. This has also been concluded for photodissociation of $\text{Fe}_x^+$ clusters.\textsuperscript{1} This is consistent with the fact that the monomer has a higher ionization potential than any $\text{Fe}_x$ cluster\textsuperscript{7} and also with the weak bond energy of the $\text{Fe}_2$ dimer.\textsuperscript{10}

Table I provides the bond energies measured in this work for the $\text{Fe}_x^+$ clusters. In the case of the trimer and tetramer, these values are determined by the modeling procedure described in the case of the dimer. For larger clusters, it may be important to consider whether the collisionally activated cluster dissociates before it is detected, a timescale of about 10 μs. We have investigated this effect using RRKM calculations in combination with simple models for energy transfer in the cluster-rare gas collision.\textsuperscript{15} Combined with the ionization potentials measured by Rohlfing et al.,\textsuperscript{7} we can also calculate the neutral bond energies for these clusters, Table I. It is
worth noting that the ion and neutral bond energies are similar for clusters larger than the pentamer. Thus, the binding energy appears to be only mildly influenced by the charge above this point. Presumably the ions have slightly stronger bonds due to the ion-induced dipole potential.

<table>
<thead>
<tr>
<th>n</th>
<th>$D^0(\text{Fe}_{n-1}^+-\text{Fe})$</th>
<th>$D^0(\text{Fe}_{n-1}^-\text{Fe})$</th>
<th>n</th>
<th>$D^0(\text{Fe}_{n-1}^+-\text{Fe})$</th>
<th>$D^0(\text{Fe}_{n-1}^-\text{Fe})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2.72</td>
<td>1.12</td>
<td>7</td>
<td>3.26</td>
<td>3.11</td>
</tr>
<tr>
<td>3</td>
<td>1.64</td>
<td>1.79</td>
<td>8</td>
<td>2.74</td>
<td>2.64</td>
</tr>
<tr>
<td>4</td>
<td>1.99</td>
<td>1.94</td>
<td>9</td>
<td>2.88</td>
<td>2.68</td>
</tr>
<tr>
<td>5</td>
<td>2.50</td>
<td>2.05</td>
<td>10</td>
<td>3.10</td>
<td>3.02</td>
</tr>
<tr>
<td>6</td>
<td>3.44</td>
<td>3.39</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\text{Fe}_2^+, \text{Fe}_3^+ + \text{D}_2$. Results for reaction of $\text{Fe}_2^+$ and $\text{Fe}_3^+$ with $\text{D}_2$ have been compared with results for reaction of $\text{Fe}^+$ with $\text{D}_2$ from previous studies in our labs. Results for the monomer ion produced in the cluster source clearly indicate that it is ground state $\text{Fe}^+$. This is one of the first experimental indications that laser vaporization, supersonic expansion sources yield electronically cold species. However, if the length of the condensation region is shortened, then excited monomer ions begin to be produced.

The thresholds for production of $\text{Fe}_x^+\text{-D}$ clearly differ with cluster size and can be analyzed using the same model used previously to interpret the $\text{Fe}^+$ reaction. These thresholds lead to bond energies of $D^0(\text{Fe}_2^+-\text{D}) = 1.5$ eV and $D^0(\text{Fe}_3^+-\text{D}) = 1.8$ eV, which can be compared to $D^0(\text{Fe}^+-\text{D}) = 2.2$ eV. It is interesting that these values are similar to $D^0(\text{Fe}_2^+-\text{Fe})$ and $D^0(\text{Fe}_3^+-\text{Fe})$, Table I. One possible interpretation of this is that the bonding in $\text{Fe}_2^+$ and $\text{Fe}_3^+$ is largely single $\sigma$ bonds, i.e. the d-d interactions are fairly weak. It is also
interesting to note that both the dimer and trimer reaction cross sections have shapes and absolute magnitudes which are comparable to those for Fe*(4F) but dissimilar to those for ground state Fe*(6D). The implication of this result is that the electronic interaction of the dimer and trimer ion with D₂ is quite similar to Fe*(4F) and distinct from Fe*(6D).

\( \text{Fe}_2^+ (x = 2-5) + \text{O}_2 \) We have also obtained detailed results for reaction of molecular oxygen with \( \text{Fe}_2^+ \). We have reported similar results for the reaction of \( \text{Mn}_2^+ \) and \( \text{Co}_2^+ \) with \( \text{O}_2 \). The dimer ion is found to be much more reactive with \( \text{O}_2 \) than the atomic ion. While this enhanced reactivity is partly due to the increase in the number of atoms in this system, it is interesting that the dimer forms \( \text{Fe}_2\text{O}^+ \) with a threshold which is \(-1.3\) eV lower formation of \( \text{FeO}^+ \) in the monomer reaction. Obviously, the dimer ion binds an oxygen atom much more strongly than the monomer ion, a result which is also obtained for Mn and Co. Note that this conclusion differs from that for binding a deuterium atom. This difference is presumably due to the ability of O to form multiple bonds.

As the size of the iron cluster ion increases, the number of products observed in the reaction with \( \text{O}_2 \) also increases substantially. For example, the trimer, tetramer, and pentamer yield 6, 9, and 10 products, respectively. Dominant at low energies are dioxide ions, \( \text{Fe}_2\text{O}_2^+ \) and \( \text{Fe}_3\text{O}_2^+ \), while simple CID products dominate at high energies.

D. Results for \( \text{V}_x^+ \), \( \text{Nb}_x^+ \), and \( \text{Ta}_x^+ \)

CID of \( \text{V}_2^+ \). Results for the CID of \( \text{V}_2^+ \) are similar to that for \( \text{Fe}_2^+ \) and preliminary analysis reveals a bond energy of \( 2.94 \pm 0.2 \) eV. The dissociation behavior of \( \text{V}_3^+ \) is distinct from that of \( \text{Fe}_3^+ \). Again the lowest energy channel is atom loss, with a threshold that gives \( D^0(\text{V}_2^+ - \text{V}) = 2.03 \pm 0.1 \) eV. However, in the Fe system, the Fe⁺ product is formed via loss of a second atom. In the
vanadium system, the comparable process, formation of \( V^+ + V + V \), has a threshold of 4.97 eV (\(-2.03 + 2.94\) eV), well above the observed threshold. Thus, the process observed in this case is formation of \( V^+ + V_2 \). Analysis of the \( V^+ \) cross section yields a threshold of \(2.74 \pm 0.1\) eV. The difference between this threshold and the 4.97 eV atomization threshold is just \( D^o(V_2) = 2.23 \pm 0.2\) eV. This is in reasonable agreement with values from high temperature mass spectrometry studies, \(2.49 \pm 0.13\) and \(2.47 \pm 0.22\) eV.\(^{20}\)

Another way of thinking about these processes is that the difference in the threshold for production of \( V_2^+ + V \) from that of \( V^+ + V_2 \) should be the difference in ionization potentials of \( V \) and \( V_2 \). We find this to be \(0.71 \pm 0.14\) eV. This is in good agreement with direct measurements of the ionization potentials, \( \Delta IP = 0.64 \pm 0.05\) eV.\(^{21}\)

The CID behavior of \( V_4^+ \) is very different from that of \( Fe_4^+ \). Now the lowest energy process forms \( V_2^+ \), at \(2.46 \pm 0.2\) eV, which is only possible if the reaction is symmetric cleavage of the cluster to form \( V_2^+ + V_2 \). Atom loss, \( V_3^+ + V \), cannot occur until \(2.91 \pm 0.15\) eV, but becomes dominant above 4.5 eV. At still higher energies, a second feature in the \( V_2^+ \) cross section beginning about 6 eV is observed. This is due to decomposition of \( V_3^+ \) to form \( V_2^+ + V \). Importantly, the "most probable" process is highly energy dependent, i.e. the relative thermodynamic stability of the dimer and trimer ions is not reflected by the branching ratio at elevated kinetic energies. This has been commented on in a communication which compares the CID behavior of \( Fe_4^+ \) with that of \( Nb_4^+ \) (which behaves the same as \( V_4^+ \)).\(^{22}\)

**CID of \( Nb_2^+ \) and \( Ta_2^+ \).** The behavior of Nb dimer, trimer, and tetramer ions is quite similar to that for the \( V \) system. The major difference is the fact that the bond energies have increased substantially, about a factor of 2. A detailed study of the niobium cluster ions has been submitted for publica-
Similar thermodynamic information can be derived and this is listed in Table II, along with results from preliminary studies of Ta$_2^+$ and Ta$_3^+$.

Table II. Bond Dissociation Energies (eV).

<table>
<thead>
<tr>
<th>Process</th>
<th>$M - V$</th>
<th>$Nb$</th>
<th>$Ta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_2^+$ $\rightarrow$ $M^+ + M$</td>
<td>2.9</td>
<td>6.1</td>
<td>6.4</td>
</tr>
<tr>
<td>$M_3^+$ $\rightarrow$ $M_2^+ + M$</td>
<td>2.0</td>
<td>4.6</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ $M^+ + M_2$</td>
<td>2.7</td>
<td>5.6</td>
</tr>
<tr>
<td>$M_4^+$ $\rightarrow$ $M_3^+ + M$</td>
<td>2.9</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\rightarrow$ $M_2^+ + M_2$</td>
<td>2.5</td>
<td>5.2</td>
</tr>
<tr>
<td>$M_5^+$ $\rightarrow$ $M_4^+ + M$</td>
<td></td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>$M_6^+$ $\rightarrow$ $M_5^+ + M$</td>
<td></td>
<td>5.6</td>
<td></td>
</tr>
</tbody>
</table>

Reactions of Nb$_x^+$. Unlike the reaction of Fe$^+$ with O$_2$, the reaction of Nb$^+$ with O$_2$ is exothermic indicating that $D^0$(Nb$^+$-O) > 5.1 eV. Indeed, from the reaction of Nb$^+$ with CO, we find that $D^0$(Nb$^+$-O) $\approx$ 6 eV and also $D^0$(Nb$^+$-C) $\approx$ 5 eV. Then from analysis of the reaction Nb$_2^+$ + CO $\rightarrow$ NbO + NbC$^+$, we find $D^0$(Nb-O) $\approx$ 8 eV. These niobium-oxide bond energies are much larger than the comparable iron-oxide bond energies. As a consequence, the reactions of niobium cluster ions with O$_2$ have many exothermic channels. The most likely product channel for Nb$_2^+$ is formation of NbO$^+$ + NbO, which is much larger than its iron analogue. This reaction is driven by the formation of two niobium oxygen bonds. Larger niobium ion clusters show similar results, e.g. the trimer ion preferentially forms Nb$_2$O$^+$ + NbO.

In reactions of Nb$_x^+$ with CO, all reactions are endothermic because of the large bond energy of CO, 11.14 eV. This is advantageous, however, since it permits the thermochemistry of niobium oxides and carbides to be measured.
The dominant low energy channel in these reactions is formation of Nb_{x-1}C^+ + NbO (x = 2-4), followed at higher energies by simple CID.

E. Results for Co_2^+: Influence of Internal Energy

CID of Co_2^+. In our studies of Co_2^+, the ions are produced by electron impact ionization and fragmentation of Co_2(CO)_8 in a different apparatus than described above. In order to limit the internal energy, the electron energy is maintained near the appearance potential of this ion, 17.8 eV for Co_2^+. The kinetic energy threshold for collision induced dissociation of Co_2^+, depends strongly on the electron energy (Ee) used to form the dimer ion. A similar effect has been observed for CID of Mn_2^+. This effect is clearly due to the production of internally excited ions which therefore require less kinetic energy to dissociate.

At the lowest Ee which still produces a usable beam of Co_2^+, ~20 eV, the kinetic energy threshold for CID was determined to be 2.57 ± 0.2 eV. This value is a lower limit to the bond dissociation energy of Co_2^+, D°(Co_2^+), since this threshold is the sum of D°(Co_2^+) and the residual internal energy in the dimer ion. Recently, we have studied this same process with Co_2^+ formed in the laser vaporization, supersonic expansion source. Preliminary analysis provides the more definitive bond energy of 2.54 ± 0.1 eV, in good agreement with the result above.

Co_2^+ + O_2. Results for reaction of O_2 with Co_2^+ formed at Ee = 20 eV are similar to that for Fe_2^+, although all reactions are more endothermic. These results agree qualitatively but not quantitatively with FTICR results of Jacobson and Freiser, who observe that reactions 1 and 2,

\[
\begin{align*}
\text{Co}_2^+ + \text{O}_2 & \rightarrow \text{Co}^+ + \text{CoO}_2 & (1) \\
& \rightarrow \text{Co}_2\text{O}^+ + \text{O} & (2)
\end{align*}
\]

are slow, and in roughly a 2 to 1 ratio. Further they interpret their
observation of reaction 2 to indicate that \( D^\circ(\text{Co}_2^+\cdot\text{O}) > D^\circ(\text{O}_2) \). The present results indicate that reaction 2 is at least 10 times slower than reaction 1 and is clearly endothermic, i.e. \( D^\circ(\text{Co}_2^+\cdot\text{O}) < D^\circ(\text{O}_2) = 5.1 \text{ eV} \). The reason for the discrepancy is the effects of internal energy. At the lowest kinetic energies, the cross section for reaction 2 increases by about a factor of 10 in going from reaction of \( \text{Co}_2^+ \) produced at \( \text{E}_e = 20 \text{ eV} \) to \( 25 \text{ eV} \). Reaction 1, on the other hand, is not very sensitive to internal excitation. Thus, the rate of reaction 2 relative to reaction 1 observed in the FTICR studies is due to internal excitation approximately equivalent to ionization at \( \text{E}_e = 24 \text{ eV} \). This demonstrates how pervasive the effects of internal excitation are likely to be in studies of metal cluster ions.

F. REFERENCES


List of Publications

1. Transition Metal Cluster Ion Chemistry

2. A Continuous Source for Production of Cold, Mass-Selected Transition Metal Cluster Ions,

3. Kinetic Energy Dependence of Ion-Molecule Reactions: From Triatomics to Transition Metals,
   P. B. Armentrout, "Structure/Reactivity and Thermochemistry of Ions" P. Ausloos and S. G. Lias, Editors,

4. Collision-Induced Dissociation Processes of Nb4+ and Fe4+:
   Fission vs. Evaporation
   S. K. Loh, Li Lian, David A. Hales, and P. B. Armentrout

5. Collision-Induced Dissociation of Fe2+
   S. K. Loh, Li Lian, David A. Hales, and P. B. Armentrout

6. State-specific Reactions of Fe+(6D, 4F) with O2 and cyclo-C2H4O:
   D0(Fe+-O) and Effects of Collisional Relaxation
Publications (cont’d)

7. Collision-Induced Dissociation of Fe\textsubscript{n+} (n = 2 - 10) with Xe:
   Ionic and Neutral Iron Cluster Binding Energies
   S. K. Loh, David A. Hales, Li Lian, and P. B. Armentrout

8. Collision-Induced Dissociation of Niobium Cluster Ions:
   Transition Metal Cluster Binding Energies
   S. K. Loh, Li Lian, and P. B. Armentrout

Participating Scientific Personnel

Peter B. Armentrout, PI
Steven K. Loh, graduate student, Ph.D. expected Dec. 1988
David A. Hales, graduate student (supported by NSF predoctoral fellowship)
Li Lian, graduate student