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Fourier transform mass spectrometry (FTMS) has been employed to study the gas-phase production, dissociation, and reactivity of several transition metal cluster systems. In particular, the production of molybdenum oxide cluster ions by secondary ion mass spectrometry (SIMS) and laser vaporization (LV) have been compared. In addition, silver and copper cluster ions have been produced and the reactivities of M_x^+, x = 1-5, with a variety of small molecules have been probed. Unusual size-related cluster ion reactions have been observed in these studies.

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Gas-Phase Transition Metal Cluster Chemistry Using Fourier Transform Mass Spectrometry

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* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

Enclosure (1)

b. **Published Papers in Refereed Journals**

"Production and Fragmentation of Molybdenum Oxide Ions," Carolyn J. Cassady, David A. Weil, and Stephen W. McElvany, *J. Chem. Phys.*, **96**, 691 (1992).

"Gas-Phase Reactions of Silver Cluster Ions Produced by Fast Atom Bombardment," Paul Sharpe and Carolyn J. Cassady, *Chem. Phys. Lett.*, in press (April or May 1992).

e. **Technical Reports:**

Technical Report No. 1: "Production and Fragmentation of Molybdenum Oxide Ions," Carolyn J. Cassady, David A. Weil, and Stephen W. McElvany, March 26, 1992.

Technical Report No. 2: "Gas-Phase Reactions of Silver Cluster Ions Produced by Fast Atom Bombardment," Paul Sharpe and Carolyn J. Cassady, March 26, 1992.

Part II

a. PRINCIPAL INVESTIGATOR: Carolyn J. Cassady

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d. DESCRIPTION OF PROJECT:

An investigation of the gas-phase chemistry of transition metal cluster ions, M_x^+, and metal oxide cluster ions, $M_xO_y^+$, is underway. These ions are produced, their reactivities and dissociations studied, and the product ions detected using Fourier transform ion cyclotron resonance mass spectrometry (FTMS). Cluster ions are generated by bombardment of metal foils, metal oxides, and metal salts with a beam of heavy atoms (secondary ion mass spectrometry or SIMS) in a region external to the FTMS cell. The emphasis is placed on developing methods for cluster ion production and on understanding the mechanisms of cluster ion formation. In addition, the reactivities of size-selected clusters ions with small molecules are probed. Initial studies have focused on transition metals of importance to materials science and catalysis--such as molybdenum and silver. Reactions have involved small molecules such as deuterium, oxygen, water, and small hydrocarbons. Efforts are made to correlate structure and reactivity. The overall goal of this research is to increase the understanding of cluster chemistry in the gas-phase and apply this knowledge to condensed-phase chemistry.

e. SIGNIFICANT RESULTS:

Production and fragmentation of molybdenum oxide ions have been studied by FTMS. Secondary ion mass spectrometry (SIMS) of molybdenum dioxide and trioxide yielded pure metal clusters and ions with few oxygens, in contrast to laser vaporization which produces highly oxygenated species. This suggests that direct emission is an important mechanism in laser vaporization of metal oxides, while the SIMS results are consistent with ion formation by recombination reactions. Laser vaporization studies employed both pulsed CO_2 and Nd:YAG lasers. The spectra obtained were similar; however, differences in $(MoO_3)_n^+$, n = 1-3, production with the two lasers may be related to sample absorption at the CO_2 wavelength of 10.6 microns. The MoO_3 unit is also prominent in both anion formation and collision-induced dissociation (CID), suggesting that it may be significant in $Mo_xO_y^{+/-}$ structures.

Cluster ion production and reactivity studies have also focused on the group 11 atoms silver and copper. SIMS of silver and copper powder and foil produced high mass M_x^+, but in low abundance. SIMS on silver and copper halides, however, yielded abundant M_x^+, x = 1-9, which could be easily studied. For both metals, odd atom clusters, M_x^+, = 1, 3, 5, are produced in abundance. Collision-induced dissociation studies also suggest that the x = 3 and 5 clusters have very stable structures, while the x = 2 and 4 clusters readily dissociate to produce odd atom cluster ions. These pronounced size-related effects are present in reactivity studies involving C_1-C_4 alkanes, alkenes, and alcohols. Ag_3^+, Ag_5^+, Cu_3^+, and Cu_5^+ react very slowly via only condensation to form species such as $Ag_3L_3^+$ (L = intact alkane, alkene, or alcohol). Ag^+ is also generally unreactive, except for condensation and dehydrogenation, while Cu^+ both dehydrates and dehydrogenates alcohols. Ag_2^+ and Cu_2^+ react via displacement of Ag and Cu, respectively, forming AgL^+ and CuL^+. These metal atom displacement reactions for species such as propanol, butanol, propene, butene, benzene, and acetone indicate that $D(M^+-L) > D(M^+-M)$, M = Ag and Cu. Ag_4^+ and Cu_4^+ also undergo metal atom displacement, producing Ag_3L^+ and Cu_3L^+. This is additional evidence of the enhanced stability of Ag_3^+ and Cu_3^+, and suggests that Ag_4^+ and Cu_4^+, may have structures involving a M_3^+ unit with one weakly bound metal atom. Further studies are underway to probe these unusual size-related reactivity effects of Ag_x^+ and Cu_x^+ with a variety of other molecules.

g. PERSONNEL PARTICIPATING IN THE RESEARCH:

Principal Investigator: Carolyn J. Cassady
Post-Doctoral Associate: Paul Sharpe (partially funded by the grant)
Graduate Student: Sebastian Farrell

h. JOURNAL ARTICLES EMANATING FROM THE GRANT:

"Production and Fragmentation of Molybdenum Oxide Ions," Carolyn J. Cassady, David A. Weil, and Stephen W. McElvany, *J. Chem. Phys.*, **96**, 691 (1992).

"Gas-Phase Reactions of Silver Cluster Ions Produced by Fast Atom Bombardment," Paul Sharpe and Carolyn J. Cassady, *Chem. Phys. Lett.*, in press (April or May 1992).

"Gas-Phase Reactions of Copper and Silver Cluster Ions with Small Hydrocarbons and Alcohols," Paul Sharpe and Carolyn J. Cassady, manuscript in preparation for submission to *Organometallics*.