

Reactions of Sputtered Copper Cluster Ions

Royal B. Freas[†] and Joseph E. Campana*

Contribution from the Naval Research Laboratory, Chemistry Division, Washington, D.C. 20375-5000. Received April 1, 1985

Abstract: Gas-phase ion/molecule reaction products of copper cluster ions with isobutane have been characterized by using tandem mass spectrometric techniques. The reaction product ions are formed by the reaction of sputtered metal cluster ions with isobutane in a novel, combination high-pressure/particle-induced emission mass spectrometer ion source. Metal/organic cluster ions of stoichiometry $[\text{Cu}_n(\text{C}_4\text{H}_{10})_m]^+$ ($n = 1, 3, 5$; $m = 1, 2, 3$) were observed. The collision spectra of these species showed fragment ions indicative of metal insertion into C-C and C-H bonds. The new technique presented is amenable to the study of ion/molecule reactions of cluster ions with any volatile reactant species.

Introduction

There is a great deal of interest in studying the reactions of bare transition-metal clusters with organic and inorganic species. Studies of model metal systems enhance our understanding of chemisorption and catalysis on metal surfaces¹ as well as the gas-phase ion chemistry of metal clusters. Several theoretical studies have examined the relationship of cluster size with the properties of bulk materials.^{2,3} Only recently have experiments been performed that provide an empirical understanding of the reactivity of bare-metal clusters. For example, gas-phase chemical reactions of transition-metal clusters, produced by molecular beams, report the chemisorption of hydrogen, hydrocarbons, and other species on iron, nickel, cobalt, niobium, and platinum clusters.⁴⁻⁷ In these beam studies, the reactivity of the metal cluster was found to be dependent on the size of the metal cluster. Recently, the gas-phase reactions of metal carbonyl cluster ions,⁸ metal/oxygen,⁹ and heterogeneous^{10,11} bare-metal cluster ions (produced in a multireaction sequence) have been reported to dehydrogenate alkanes.

The activation of C-C and C-H bonds of hydrocarbons by transition-metal ions has been studied in the gas-phase.¹²⁻¹⁵ The first-row groups 8-10 (group VIII) metal ions (Fe^+ , Co^+ , and Ni^+) react by oxidative addition to alkanes and other organic molecules. The mechanism is by metal insertion into a C-C or a C-H bond followed by a β -hydrogen shift and reductive elimination of hydrogen or an alkane, thus yielding a metal/olefin product ion.¹² These oxidative addition reactions of atomic metal ions are analogous to dissociative chemisorption on bulk metal surfaces¹⁶ and the dehydrogenation of hexanes by platinum clusters.⁶ Tandem mass spectrometric techniques have been used to probe the structures of metal/organic complexes formed by ion/molecule reactions of metal carbonyl ions with alkanes. The characterization of ion/molecule reaction products of metal cluster ions with organics by such mass spectrometric techniques can provide information relating to structure, reactivity, thermochemistry, etc. of the metal/organic cluster ions.^{13,17} These established methods also have been used to study the structure and stability of a variety of cluster ions, inorganic¹⁸ and organic.^{19,20}

We report here the ion/molecule reactions of isobutane with copper cluster ions, sputtered from a metal foil, and the tandem mass spectrometric characterization of the resulting copper/isobutane cluster product ions. To our knowledge, this is the first report on gas-phase interactions between ionic copper species and alkanes. Previous studies of the gas-phase chemistry of atomic copper ions (produced by laser vaporization/ionization techniques) have reported reactions with organic molecules such as alkenes, alcohols, alkyl chlorides, esters, and ketones²¹⁻²⁵

Method

The secondary ion emission of metal cluster ions from metal surfaces is well-known from surface physics.²⁶ We have used this phenomena to

Table I. Observed Product Ions of Copper Cluster Ions with Isobutane^a

| m/z^b | formula | m/z^b | formula |
|------------------|--|------------------|--|
| 119 | $[\text{Cu}(\text{C}_4\text{H}_8)]^+$ | 247 | $[\text{Cu}_3(\text{C}_4\text{H}_{10})]^+$ |
| 121 | $[\text{Cu}(\text{C}_4\text{H}_{10})]^+$ | 305 | $[\text{Cu}_3(\text{C}_4\text{H}_{10})_2]^+$ |
| 179 | $[\text{Cu}(\text{C}_4\text{H}_{10})_2]^+$ | 363 | $[\text{Cu}_3(\text{C}_4\text{H}_{10})_3]^+$ |
| 237 ^c | $[\text{Cu}(\text{C}_4\text{H}_{10})_3]^+$ | 373 ^c | $[\text{Cu}_5(\text{C}_4\text{H}_{10})]^+$ |

^aProduct ions containing even-numbered copper clusters and isobutane were not observed. ^bNominal mass based on the ⁶³Cu isotope. ^cIon abundances were too low to perform collision-induced dissociation experiments.

produce copper cluster ions ($[\text{Cu}_n]^+$; $n = 1-11$) from a copper substrate by bombardment with an energetic (8-10 keV) primary beam of xenon atoms. In our experiment, the metal sputtering occurs within a high-pressure/particle-induced emission ion source (described in detail elsewhere.^{27,28} A gas is admitted to the ion source at pressures of 0.1 to 0.2

- (1) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91-137.
- (2) Sinanoğlu, O. *Chem. Phys. Lett.* **1981**, *81*, 188-190.
- (3) Demuyneck, J.; Rohmer, M. M.; Strich, A.; Veillard A. *J. Chem. Phys.* **1981**, *75*, 3443-3453.
- (4) Riley, S. J.; Parks, E. K.; Pobo, L. G.; Wexler, S. *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 287-289.
- (5) Geusic, M. E.; Morse, M. D.; Smalley, R. E. *J. Chem. Phys.* **1985**, *82*, 590-591.
- (6) Trevor, D. J.; Whetten, R. L.; Cox, D. M.; Kaldor, A. *J. Am. Chem. Soc.* **1985**, *107*, 518-519.
- (7) Whetten, R. L.; Cox, D. M.; Trevor, D. J.; Kaldor, A. *J. Phys. Chem.* **1985**, *89*, 566-569.
- (8) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 825-826.
- (9) Freas, R. B.; Campana, J. E., submitted for publication.
- (10) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 5351-5352.
- (11) Jacobson, D. B.; Freiser, B. S.; *J. Am. Chem. Soc.* **1985**, *107*, 1581-1589.
- (12) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332-1333.
- (13) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129-7131.
- (14) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197-5206.
- (15) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818-1829.
- (16) Tompkins, F. C. "Chemisorption of Gases on Metals"; Academic Press: London, 1978; pp 5-9.
- (17) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912-1922.
- (18) Campana, J. E.; Green, B. N. *J. Am. Chem. Soc.* **1984**, *106*, 531-535.
- (19) Campana, J. E.; Doyle, Jr., R. J. *J. Chem. Soc., Chem. Commun.* **1985**, 45-46.
- (20) Doyle, Jr., R. J.; Campana, J. E. *J. Phys. Chem.*, in press.
- (21) Burnier, R. C.; Byrd, G. D.; Freiser, G. S. *Anal. Chem.* **1980**, *52*, 1641-1650.
- (22) Kappes, M. M.; Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 888-889.
- (23) Jones, R. W.; Staley, R. H. *J. Phys. Chem.* **1982**, *86*, 1669-1674.
- (24) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2296-2300.
- (25) Cassidy, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 1566-1573.
- (26) Blaise, G. In "Materials Characterization Using Ion Beams"; Thomas, J. P., Cachard, A., Eds.; Plenum Press: New York, 1978; pp 166-170.
- (27) Campana, J. E.; Freas, R. B.; *J. Chem. Soc., Chem. Commun.* **1984**, 1414-1415.
- (28) Freas, R. B.; Ross, M. M.; Campana, J. E. *J. Am. Chem. Soc.*, preceding paper in this issue.

* Author to whom correspondence should be addressed. Current address: Environmental Research Center, University of Nevada, Las Vegas, NV 89154.

[†] National Research Council Cooperative Research Associate.

Torr to react with the sputtered metal cluster ions. The ion source temperature was 300 K, and no ionizing electrons were used in these experiments. The cluster product ions were analyzed with a reverse-geometry, double-focusing mass spectrometer²⁹ which was also used for mass-analyzed ion kinetic energy spectrometry measurements. Complementary experiments were performed on a hybrid mass spectrometer,³⁰ wide infra.

Copper foil was cleaned in situ by sputtering until the copper cluster ions were the predominant ion signals observed. The abundances of the copper cluster ion series decreased monotonically with increasing cluster size, and the abundance of the odd-numbered species $[\text{Cu}_{2n+1}]^+$ was greater than the abundance of even-numbered species $[\text{Cu}_{2n}]^+$. These observations of the copper mass spectrum are similar to those of other sputtered metals, and they are well understood from studies in surface physics.

In the presence of hydrocarbon or hydrogen-containing species, cluster ions of stoichiometry $[\text{Cu}_n\text{H}]^+$ often were observed. These protonated clusters were more abundant than the corresponding $[\text{Cu}_{2n}]^+$ species. It should be noted that both copper and hydrogen have an s^1 electronic configuration. Therefore, the $[\text{Cu}_n\text{H}]^+$ species are isosteric with the more abundant $[\text{Cu}_{2n+1}]^+$ clusters. The $[\text{Cu}_{2n+1}\text{H}]^+$ species were not observed.

Upon admission of isobutane into the ion source, several copper/isobutane cluster product ions were observed in the mass spectra. The general stoichiometry of these ions was $[\text{Cu}_n(\text{C}_4\text{H}_{10})_m]^+$, where $n = 1, 3, 5$ and $m = 1-3$. With the exception of $[\text{CuC}_4\text{H}_8]^+$, metal/organic cluster product ions containing isobutane fragments were not observed. Table I lists some of the observed product ions from the reaction of copper cluster ions with isobutane. Cluster product ions of stoichiometry $[\text{Cu}_n(\text{C}_4\text{H}_{10})_m]^+$, where $n = 2, 4$, and >5 , were not observed in any significant abundance. This likely is due to a low abundance of the even-numbered and odd-numbered (>5) precursor metal cluster ions.

Discussion

We address two fundamental questions in this work: (1) Are the observed metal/organic reaction products the result of gas-phase ion/molecule reactions, or are they desorbed or sputtered reaction products of isobutane chemisorbed on the copper surface? (2) What is the structure and bonding in the copper/isobutane cluster ions—are the product ions, $[\text{Cu}_n(\text{C}_4\text{H}_{10})_m]^+$, formed by dissociative chemisorption or by associative physisorption of isobutane on the copper?

A majority of the metal/organic cluster ions observed are a result of gas-phase ion/molecule reactions. The reasons are as follows. Variation of the ion residence time (by varying the ion source repeller voltage) affects the abundances of the product ions in the appropriate manner. That is, longer ion residence times result in increased relative abundances of metal/organic cluster ions containing two or three isobutane molecules and concomitant decreased relative abundances of $[\text{Cu}_n]^+$ and $[\text{Cu}_n\text{C}_4\text{H}_{10}]^+$.

More convincingly, we have produced copper/isobutane cluster ions in a tandem mass spectrometric ion/molecule experiment.³⁰ In this experiment, Cu^+ and $[\text{Cu}_3]^+$ were formed by sputtering copper foil in a conventional fast-atom bombardment ion source. Then, either ion was mass-selected in the first, double-focusing (EB) mass spectrometer. The mass-selected copper ions were reacted at low translational energy (0–10-eV lab) in a reaction region (the first quadrupole, Q1) containing isobutane at a pressure of $\leq 1 \times 10^{-4}$ Torr. The copper/isobutane reaction product ions formed in the reaction region (Q1) were mass analyzed by the second quadrupole mass filter (Q2). The gas-phase reaction product ions observed correspond to $[\text{Cu}_n\text{C}_4\text{H}_{10}]^+$, where $n = 1$ or 3. The results of this experiment indicate that gas-phase ion/molecule reactions of copper cluster ions with organic species are facile.

In light of these findings, it is our contention that the predominant process, if not the sole process, involved in the formation of the metal/organic cluster ions by our method is gas-phase ion/molecule reactions. Furthermore, if isobutane is dissociatively

Table II. Fragment Ions in the CID/MIKES Spectra of Copper/Isobutane Cluster Ions

| parent ion | | daughter ions | | | | |
|------------------|--|---------------|--|-----------------------------------|------------------------------|----|
| <i>m/z</i> | stoichiometry | <i>m/z</i> | stoichiometry | % relative abundance ^a | | |
| 119 | $[\text{Cu}(\text{C}_4\text{H}_8)]^+$ | 117 | $[\text{CuC}_4\text{H}_6]^+$ | 88 | | |
| | | 115 | $[\text{CuC}_4\text{H}_4]^+$ | 12 | | |
| | | 103 | $[\text{CuC}_3\text{H}_4]^+$ | 10 | | |
| | | 63 | Cu^+ | 100 | | |
| | | 121 | $[\text{Cu}(\text{C}_4\text{H}_{10})]^+$ | 119 | $[\text{CuC}_4\text{H}_8]^+$ | 12 |
| | | | | 105 | $[\text{CuC}_3\text{H}_6]^+$ | 12 |
| 78 | $[\text{CuCH}_3]^+$ | | | 2 | | |
| 63 | Cu^+ | | | 100 | | |
| 57 | $[\text{C}_4\text{H}_9]^+$ | | | 3 | | |
| 43 | $[\text{C}_3\text{H}_7]^+$ | | | 1 | | |
| 179 | $[\text{Cu}(\text{C}_4\text{H}_{10})_2]^+$ | 41 | $[\text{C}_3\text{H}_5]^+$ | 1 | | |
| | | 39 | $[\text{C}_3\text{H}_3]^+$ | 1 | | |
| | | 121 | $[\text{CuC}_4\text{H}_{10}]^+$ | 100 | | |
| | | 119 | $[\text{CuC}_4\text{H}_8]^+$ | 6 | | |
| | | 105 | $[\text{CuC}_3\text{H}_6]^+$ | 9 | | |
| | | 91 | $[\text{CuC}_2\text{H}_4]^+$ | <1 | | |
| 247 | $[\text{Cu}_3(\text{C}_4\text{H}_{10})]^+$ | 63 | Cu^+ | 34 | | |
| | | 57 | $[\text{C}_4\text{H}_9]^+$ | 5 | | |
| | | 43 | $[\text{C}_3\text{H}_7]^+$ | <1 | | |
| | | 41 | $[\text{C}_3\text{H}_5]^+$ | <1 | | |
| | | 39 | $[\text{C}_3\text{H}_3]^+$ | <1 | | |
| | | 245 | $[\text{Cu}_3\text{C}_4\text{H}_8]^+$ | <1 | | |
| | | 18 | $[\text{Cu}_3]^+$ | 100 | | |
| | | 184 | $[\text{Cu}_2\text{C}_4\text{H}_{10}]^+$ | 4 | | |
| | | 182 | $[\text{Cu}_2\text{C}_4\text{H}_8]^+$ | 1 | | |
| | | 126 | $[\text{Cu}_2]^+$ | 16 | | |
| | | 121 | $[\text{CuC}_4\text{H}_{10}]^+$ | 1 | | |
| | | 63 | Cu^+ | 1 | | |
| 305 | $[\text{Cu}_3(\text{C}_4\text{H}_{10})_2]^+$ | 247 | $[\text{Cu}_3\text{C}_4\text{H}_{10}]^+$ | 100 | | |
| | | 189 | $[\text{Cu}_3]^+$ | 95 | | |
| | | 184 | $[\text{Cu}_2\text{C}_4\text{H}_{10}]^+$ | 15 | | |
| | | 126 | $[\text{Cu}_2]^+$ | 29 | | |
| | | 121 | $[\text{CuC}_4\text{H}_{10}]^+$ | 2 | | |
| | | 63 | Cu^+ | 2 | | |
| 363 ^b | $[\text{Cu}_3(\text{C}_4\text{H}_{10})_3]^+$ | 305 | $[\text{Cu}_3(\text{C}_4\text{H}_{10})_2]^+$ | 100 | | |

^aThe percent abundances are expressed relative to the most abundant fragment. No correction has been made for unimolecular dissociations. ^bThe low abundance of this species may have precluded the observation of other fragment ions.

chemisorbed upon the copper surface, then sputtering of the surface should yield ions containing isobutane fragments or radicals. In fact, no copper cluster ions containing any alkyl radicals ($\cdot\text{C}_4\text{H}_9$, $\cdot\text{C}_3\text{H}_7$, or $\cdot\text{CH}_3$) were observed. The only ion observed containing a hydrocarbon fragment was the aforementioned $[\text{CuC}_4\text{H}_8]^+$ species. The $[\text{Cu}_n\text{C}_4\text{H}_8]^+$ ($n > 1$) species were not observed in the mass spectra.

The second question also pertains to chemisorption or the nature of the copper cluster/isobutane bond(s). If isobutane is dissociatively chemisorbed on a copper cluster ion, a probe of the structure of $[\text{Cu}_n\text{C}_4\text{H}_{10}]^+$ would show significant interaction between the metal atom(s) and C–C or C–H bonds. If isobutane is physisorbed, one would not expect any significant interaction. To probe the copper/isobutane interaction, we used mass-analyzed ion kinetic energy spectrometry (MIKES).^{31,32} In this method, the metal/organic cluster product ion is mass-selected, and its unimolecular dissociation spectrum or its bimolecular dissociation (collision-induced dissociation, CID) spectrum (helium collision gas) is obtained by ion kinetic energy analysis of the dissociation product ions.

In general, the only unimolecular, or more properly “unicluster”, dissociation product observed in the MIKES spectra of the cluster product ions corresponds to a small loss of isobutane from the cluster ion. In contrast, the fragment ions in the CID/MIKES spectra of several copper/isobutane cluster product ions are more

(29) Morgan, R. P.; Beynon, J. H.; Bateman, R. H.; Green, B. N. *Int. J. Mass Spectrom. Ion Phys.* **1978**, *28*, 171–191.

(30) Freas, R. B.; Missler, S. R.; Campana, J. E.; unpublished work. The hybrid mass spectrometer was a VG Analytical LTD. (Manchester, U.K.) 7070 EQ of geometry EBQQ; E = electrostatic sector, B = magnetic sector, and Q = quadrupole mass filter.

(31) Beynon, J. H.; Cooks, R. G.; Amy, J. W.; Baitinger, W. T.; Ridley, T. V. *Anal. Chem.* **1973**, *45*, 1023A–1031A.

(32) Cooks, R. G., Ed.; “Collision Spectroscopy”; Plenum Press: New York, 1978.

significant and interesting, and they are listed in Table II.

The major CID fragmentations of the metal/organic cluster ions result in the loss of an isobutane molecule, the loss of copper atoms, or the loss of copper/isobutane neutral species. This indicates a fairly weak interaction between copper and isobutane. However, a small amount of the $[\text{Cu}_n\text{CH}_3]^+$, $[\text{Cu}_n\text{C}_3\text{H}_6]^+$, and $[\text{Cu}_n\text{C}_4\text{H}_8]^+$ ($n = 1, 2, 3$) species were observed also in the CID/MIKES spectra as fragment ions, which are indicative of metal insertion reactions.^{13,14,17} It is possible that the $[\text{CuC}_4\text{H}_8]^+$ species (a C-H bond insertion product) observed in the conventional mass spectrum is due to a fast unimolecular dissociation of reactive copper complexes in the ion source. In contrast, the $[\text{CuC}_3\text{H}_6]^+$ and the $[\text{CuCH}_3]^+$ species (C-C bond insertion products) are not observed in the conventional mass spectra. The CID/MIKES spectrum of $[\text{CuC}_4\text{H}_8]^+$ shows fragments that correspond to the loss of H_2 and C_4H_8 as the major fragmentations. This indicates that the C_4H_8 moiety remains intact on the metal center. That is, there is no scrambling of the carbon skeleton and rearrangement of the isobutane to form a bis(ethylene) complex, $[\text{Cu}(\text{C}_2\text{H}_4)_2]^+$. (Bis(olefin) complexes are observed from the reactions of group 8-10 metal ions with linear hydrocarbons.^{14,17}) An interesting daughter ion, $[\text{CuC}_2\text{H}_4]^+$, was observed in the CID/MIKES spectrum of the $[\text{Cu}(\text{C}_4\text{H}_{10})_2]^+$ species. (An analogous daughter ion was observed in the CID/MIKES spectrum of the congener $[\text{Ag}(\text{C}_4\text{H}_{10})_2]^+$). In contrast, $[\text{CuC}_2\text{H}_4]^+$ was not observed in the CID/MIKES spectrum of $[\text{CuC}_4\text{H}_{10}]^+$. Previous work has noted that rearrangement of the isobutane backbone on a metal ion to form a species such as $[\text{CuC}_2\text{H}_4]^+$ is not likely.⁸ Also, the $[\text{CuCH}_3]^+$ fragment was not observed in the CID/MIKES spectrum of $[\text{Cu}(\text{C}_4\text{H}_{10})_2]^+$. We postulate that the $[\text{CuC}_2\text{H}_4]^+$ species from $[\text{Cu}(\text{C}_4\text{H}_{10})_2]^+$ can be explained by the insertion of Cu^+ into a C-C bond of each isobutane, followed by rearrangement to yield the observed product, a metal-ethylene complex.

The reaction product ions containing three copper atoms do not show any evidence of C-C bond insertion. In comparison to earlier work⁹, these results suggest that Cu^+ and $[\text{Cu}_3]^+$ are similar and that they are intermediate between Fe^+ and Cr^+ in their ability to activate C-C and C-H bonds in copper/isobutane complexes. That is, $[\text{CuC}_3\text{H}_6]^+$ or $[\text{CuCH}_3]^+$ are not observed in a CID/MIKES spectrum. (In contrast, the $[\text{Ag}_3\text{C}_4\text{H}_{10}]^+$ ion does yield collision products indicative of C-C bond insertion, for example $[\text{Ag}_3\text{CH}_3]^+$.) The CID/MIKES spectrum of $[\text{Cu}_3\text{C}_4\text{H}_{10}]^+$ yields $[\text{Cu}_3\text{C}_4\text{H}_8]^+$ and $[\text{Cu}_2\text{C}_4\text{H}_8]^+$ fragment ions, indicating the ability of the $[\text{Cu}_3]^+$ cluster to activate C-H bonds. This is analogous to the ability of the trimoiety cluster ions, $[\text{Co}_2\text{CO}]^+$ and $[\text{FeCo}_2]^+$, to dehydrogenate isobutane.^{8,10} This analogy and the simple loss of Cu and Cu_2 from $[\text{Cu}_3(\text{C}_4\text{H}_{10})_m]^+$ ($m = 1, 2$) suggest a localized metal-atom/organic interaction. This may also indicate that $[\text{Cu}_3]^+$ exists in a bent or linear form and not a triangular structure

as suggested by theory,^{33,34} at least for the metal/organic cluster ion.

Conclusions

The sputtered cluster ion technique we have reported here has a number of advantages over some of the beam techniques and the ion cyclotron resonance (ICR) techniques that involve laser vaporization/ionization or decomposition of metal carbonyls to produce metal ions.

The metal/organic cluster ions studied here are inherently ions; therefore they do not need to be ionized as in molecular beam studies⁴⁻⁷ in order to detect the clusters. Consequently, the structures of the cluster product ions are not susceptible to perturbations induced by ionization. In contrast to some of the ICR studies⁸⁻¹¹, our technique produces bare metal cluster ions directly, whereas the ICR technique requires multiple reaction sequences and/or fragmentation of volatile metal carbonyls. The use of laser vaporization/ionization on metal surfaces within the ICR cell produces abundant atomic metal ions, but metal cluster ions are not produced in significant abundance for reaction studies.

A unique feature of the ion source reported here is the ability to study ion/molecule reactions of clusters at pressures (on the order of 0.1 to 1.0 Torr) that permit such processes as collisional stabilization of product ions.²⁸ Kinetic studies of the reactions may be performed by changing parameters such as reactant gas pressures or the ion residence time in the source. Tandem mass spectrometric techniques can be used to study the structures and properties (such as the degree of association and bonding) of cluster ions and their reaction products.

Although we report one reaction system here, the techniques presented are amenable to study the reaction of any volatile reactant species and any sputtered cluster ion from a metal foil, metal oxide, or metal salt. For example, we are investigating reactions of copper, silver, gold, iron, cobalt, nickel, scandium, titanium, and vanadium cluster ions with organic species (alkanes, alcohols, or alkyl halides), inorganic molecules (NH_3 , O_2 , or CO), and organometallic compounds.

Acknowledgment. We acknowledge Stephen R. Missler, U.S. Army Medical Research Institute of Infectious Disease, for assistance in the preliminary study of the Cu^+ and Cu_3^+ reactions in the gas phase with an EBQQ hybrid mass spectrometer. We gratefully acknowledge the Office of Naval Research for supporting this research.

Registry No. Cu, 7440-50-8; isobutane, 75-28-5.

(33) Post, D.; Baerends, E. J. *Chem. Phys. Lett.* **1982**, *86*, 176-180.

(34) Basch, H. *J. Am. Chem. Soc.* **1981**, *103*, 4657-4663. In this paper, the congener of copper, $[\text{Ag}_3]^+$, is predicted to be an equilateral triangle, Ag_3 is bent, and $[\text{Ag}_3]^-$ is linear.