

A Comparison of the Ion-Molecule Reactions of Group 11[†] Metal Ions with Alcohols

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Abstract: A systematic study of gas-phase reactions of gold cations with alcohols is reported. These reactions are compared with the reactions of silver and copper cations with alcohols. In contrast with previous laser desorption/ionization studies, metal salts and/or metal oxides served as metal ion sources. Hydride abstraction is the dominant reaction of Au⁺ with alcohols. Study of methide and hydroxide abstraction reactions allows estimation of lower limits for Au-CH₃, Cu-CH₃, Au-OH, and Cu-OH bond dissociation energies ($D(\text{Au-CH}_3) > 27.1$ kcal/mol, $D(\text{Cu-CH}_3) > 59$ kcal/mol, $D(\text{Au-OH}) > 62.5$ kcal/mol, and $D(\text{Cu-OH}) > 97.0$ kcal/mol). Other primary reactions of Cu⁺ and Au⁺ include dehydration, with competitive elimination of H₂O and the alkene via β -hydrogen transfer, and dehydrogenation, with elimination of H₂, via α -hydrogen transfer. Direct cationization is also observed. Silver cations mainly undergo cationization. The gas-phase acidity of AuH has been experimentally determined to be $\Delta H_{\text{acid}}(\text{AuH}) = 331 \pm 3$ kcal/mol by using the bracketing technique.

Gas phase metal ion chemistry studies have proliferated during recent years, particularly with the advent of laser desorption/ionization (LD/I) methodologies introduced by Freiser and co-workers.¹ To date, the majority have concentrated on the reactivity of Fe, Co, and Ni and variations in reactivity between other first-row transition metals.² Comparison of reactivity within the same group has been limited by the lack of data for second- and third-row transition metals.³ In group 11, for example, the ion-molecule reactions of Cu⁺ with alcohols,⁴ alkyl chlorides,⁵ esters, and ketones⁶ have been investigated, yet silver and gold ion chemistry virtually has been unstudied. Reports of Au⁺ reactions have been confined to those describing incidental cationization [M + Au⁺] arising from reactions of gold surfaces during secondary ion mass spectrometry (SIMS)⁷ or to observations of similar ion-molecule reactions that occur during spark source mass spectrometry employing gold electrodes.⁸ Cationization from silver surfaces has been observed with SIMS.⁹ Cooks and co-workers have observed silver cationization using laser desorption with a tandem mass spectrometer and metallic silver as a cation source.¹⁰ Silver cationization also was observed by Hercules and co-workers utilizing a laser microprobe mass analyzer instrument (LAMMA) with silver carbonate as a dopant.¹¹

Here we report the first systematic study of the gas-phase reactions of gold cations with alcohols. An estimate of the lower limits of Au-CH₃, Au-OH, Cu-OH, Cu-CH₃, and metal cation-ligand bond dissociation energies has been obtained by Fourier transform mass spectrometry.¹² In addition, the gas-phase acidity of AuH has been experimentally determined by using the bracketing technique and comparative acidity values calculated by using eq 1, where EA(Au) is the electron affinity of gold, IP(H)

$$\Delta H_{\text{acid}}(\text{AuH}) = \text{DH}(\text{Au-H}) + \text{IP}(\text{H}) - \text{EA}(\text{Au}) \quad (1)$$

is the ionization potential of hydrogen, and DH(Au-H) is the homolytic gold-hydrogen bond dissociation energy.

A major limitation of previous LD/I studies was the use of metal rods as ion sources which restricted application to inexpensive and readily available metals (e.g., Fe, Cu, Co, Cr). Because LD/I of metal rods produces primarily singly charged cations, a variety of important ion-molecule reactions are not easily studied by that technique. In contrast, the use of metal oxides and/or metal salts as alternative metal ion sources extends LD/I applications to studies of (1) the effect of metal oxidation state on reactivity, (2) the ion chemistry of metal clusters,¹³ and (3)

the ion chemistry of metal anions (e.g., gas-phase acidity and halide affinities). In the present work, metal oxides (Ag₂O, Cu₂O, Au₂O₃) are used in laser desorption/Fourier transform mass spectrometry (LD/FTMS)¹⁵ studies of Ag, Cu, and Au ion-molecule reactions with alcohols.

Metal cations are formed in various oxidation states from a particular metal salt when using LD/FTMS; for example, the LD positive ion mass spectrum of ferric chloride (FeCl₃) contains Fe⁺, FeCl⁺, and FeCl₂⁺ ions, with iron in three different oxidation states. The effect of oxidation state upon a reaction is exemplified by ion-molecule reactions of Fe⁺, FeCl⁺, and FeCl₂⁺ with *i*-PrOH. Dehydration of *i*-PrOH by M⁺ occurs by competitive elimination

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(2) Works representative of this field are the following: (a) Halle, L. F.; Crowe, W. E.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1984**, *3*, 1694-1706. (b) Peake, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 115-120. (c) Lombarski, M.; Allison, J. *Int. J. Mass Spectrom. Ion Proc.* **1985**, *65*, 31-58. (d) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1985**, *4*, 1048-1053. (e) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912-1922. (f) Fredeen, D. A.; Russell, D. H. *J. Am. Chem. Soc.* **1985**, *107*, 3762-3768.

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(5) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794-3798.

(6) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641-1650.

(7) Steffens, P.; Nichuis, E.; Friese, T.; Greifendorf, P.; Benninghoven, A. "Secondary Ionization Mass Spectrometry, SIMS IV: Proceedings of the Fourth International Conference"; Shimizu, R., Okano, J., Benninghoven, A., Eds.; Springer-Verlag: Berlin, 1984; pp 404-408.

(8) (a) Grady, W. L.; Bursey, M. M. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 247-258. (b) Grady, W. L.; Bursey, M. M. *Ibid.* **1983**, *52*, 259-266.

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(11) Balasnmugam, K.; Dang, T. A.; Day, R. J.; Hercules, D. M. *Anal. Chem.* **1981**, *53*, 2296-2298.

(12) Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413-416.

(13) Metal dimers and trimers have been previously formed by reaction of metal cations with volatile metal carbonyls, followed by collision-induced dissociation (ref 14).

(14) (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 4623-4624. (b) Jacobson, D. B.; Freiser, B. S. *Ibid.* **1984**, *106*, 5351-5352.

(15) In previous FTMS and ICR mass spectrometry, metal cations were produced either by electron impact ionization of volatile organometallic compounds such as metal carbonyls (ref 16) or by laser desorption/ionization of metal rods (ref 1).

(16) Allison, J.; Ridge, D. P. *Organomet. Chem.* **1975**, *99*, C11-C14.

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

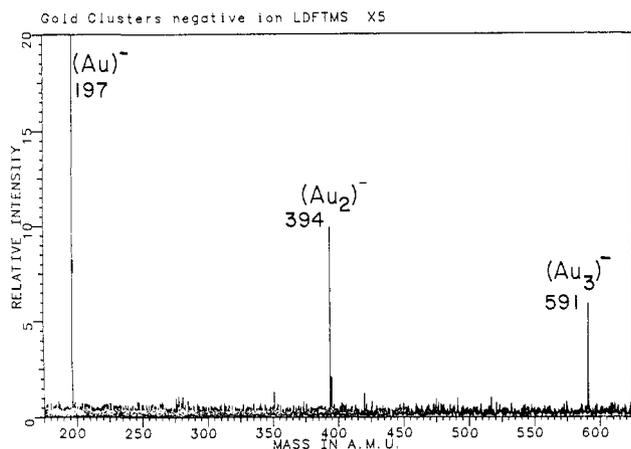
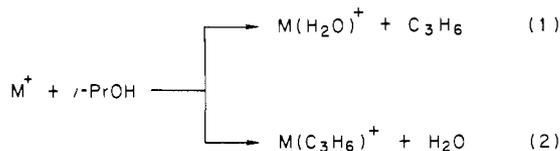


Figure 1. Negative ion LD/FTMS spectrum of gold anion and clusters, $\times 5$.

of water (reaction 1) or propene (reaction 2). For Fe cations, the elimination of H_2O is the dominant reaction (70% $\text{Fe}(\text{C}_3\text{H}_6)^+$:30%



$\text{Fe}(\text{H}_2\text{O})$). The product distribution is reversed for FeCl cations, with propene elimination the dominant reaction (30% $\text{FeCl}(\text{C}_3\text{H}_6)^+$:70% $\text{FeCl}(\text{H}_2\text{O})^+$). Similar results have been reported by Smith and Ridge for electron impact ionization of volatile $\text{FeI}_2(\text{CO})_4$ followed by collision-induced dissociation (CID) to form Fe^+ , FeI^+ , and FeI_2^+ ions.¹⁷

Experimental Section

The operating principles of FTMS are described in detail elsewhere.¹⁸ The LD/FTMS system employs a Tachisto 215G pulsed TEA CO_2 laser coupled with a Nicolet FTMS-1000 mass spectrometer equipped with a 3.0T superconducting magnet.¹⁹ A 5.08 cm cubic analyzer cell made of 80% transmissive etched stainless steel was used. For the measurements reported here, the laser delivered approximately 0.3–0.4 J per 40-ns pulse at 10.6 μm . The laser beam was focussed by a 4-in. focal length zinc selenide lens to a diameter of approximately 1 mm on the stainless steel probe tip. Power density at the probe tip was in the range of 10^8 – 10^9 W/cm^2 . Positive or negative ions were retained in the cell by applying a potential of +1 or -1 V, respectively, to the trap plates. Gaseous neutral pressures of the alcohols were between 4 and 10×10^{-8} torr, as measured with an uncalibrated Granville-Phillips ion gauge.

In a typical experiment sequence, metal ions were formed by triggering the laser with the FTMS filament off. Following the laser pulse (typically a 100-ms delay) all ions except for the metal cation or anion of interest were ejected from the cell by application of two radio frequency sweeps. After a variable reaction delay (from a few milliseconds to several seconds), the ionic products were detected. Ion-molecule reaction pathways were confirmed by ejection of the suspected precursor ion with a radio frequency excitation at the appropriate cyclotron frequency, prior to the reaction delay time.

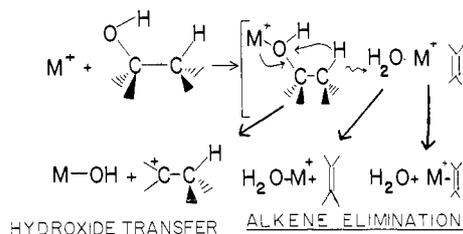
Three sources of gold were investigated. (1) Approximately 1 mg of chloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), obtained from Eastman Kodak, was dissolved in MeOH and transferred to a stainless steel probe tip, and the methanol was evaporated. After 5–10 min oxidation-reduction occurred on the probe tip resulting in metallic gold plating on the surface, covered by a black film (probably stainless steel metals Fe and Cr). (2) Several

(17) Smith, A.; Ridge, D. P. "Reactions of iron in three different oxidation states with organic molecules"; presented at the 32nd Annual Conference on Mass Spectrometry and Allied Topics, May 27–June 1, 1984, San Antonio, TX; pp 221–222.

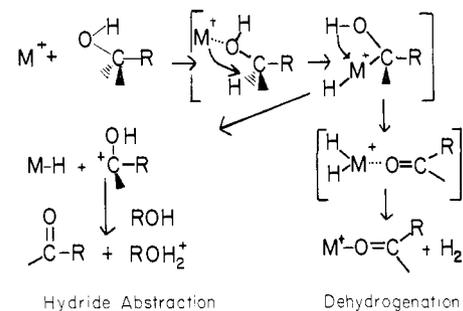
(18) (a) Comisarow, M. B.; Marshall, A. G. *Chem. Phys. Lett.* **1974**, *25*, 282–282. (b) Comisarow, M. B.; Marshall, A. G. *Ibid.* **1974**, *26*, 489–490. (c) Ghaderi, S.; Kulkarni, P. S.; Ledford, E. B., Jr.; Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 428–431. (d) Wilkins, C. L.; Gross, M. L. *Anal. Chem.* **1981**, *53*, 1661A–1676A. (e) Gross, M. L.; Rempel, D. L. *Science* **1984**, *226*, 261–268.

(19) Wilkins, C. L.; Weil, D. A.; Yang, C. L.; Ijames, C. J. *Anal. Chem.* **1985**, *57*, 520–524.

Scheme I



Scheme II



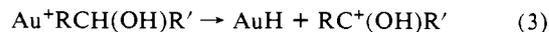
drops of "bright gold", a commercial solution distributed by Duncan Ent. (used to coat infrared light-pipes with Au), were placed on the probe tip. After the mixture was dried for 5–10 min the probe tip was heated to 600 $^\circ\text{C}$, resulting in formation of a gold film. (3) Au_2O_3 (obtained from ICN Pharmaceuticals, K&K Labs) was prepared in the same way as $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$; however, no oxidation-reduction occurred. All three gold sources gave similar ion-molecule reaction results.

The unlabeled alcohols used in this study were purchased from Aldrich, degassed by several freeze-pump-thaw cycles, and used without further purification. No significant impurities appeared in the mass spectra. Labeled ethanol-2,2,2- d_3 (98%) and ethanol- d_1 (99.5%) were obtained from Merck, Sharp and Dohme Isotopes and Aldrich, respectively. Anhydrous hydrogen chloride and hydrogen bromide were purchased from Specialty Gas-Liquid Carbonics and Matheson.

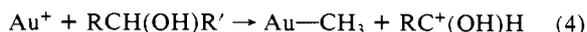
In addition to singly charged metal ions, gold and silver dimer and trimer cations and gold dimer and trimer anions (Figure 1) were formed. No multiply charged Au, Cu, or Ag ions were detected. In contrast with Byrd's statement that metal anions cannot be formed in sufficient quantity with use of the LD/I method for ion-molecule reactions to occur,²⁰ proton-transfer ion-molecule reactions between acids (BH) and gold anions were observed.

Results and Discussion

Au with Alcohol. Table I lists observed ion-molecule reactions of Au^+ , Cu^+ , and Ag^+ with alcohols (reactions A–G for Au^+). The strong Au–H bond (calculated $D(\text{Au}-\text{H}) = 77.5$ kcal/mol)²¹ and large ionization potential of gold, ($\text{IP}(\text{Au}) = 212.7$ kcal/mol)²² make hydride abstraction (reaction 3) the dominant reaction where $\Delta H_{rx1} = -D(\text{Au}-\text{H}) - \text{IP}(\text{Au}) + \text{AP}(\text{RC}^+(\text{OH})\text{R}')$. Au^+ also abstracts methide (reaction 4) and hydroxide (reaction 5), where



$\Delta H_{rx2} = \text{AP}(\text{RC}^+(\text{OH})\text{H}) - \text{IP}(\text{Au}) - D(\text{Au}-\text{CH}_3)$ and $\Delta H_{rx3} = \text{AP}(\text{RC}^+\text{HR}) - \text{IP}(\text{Au}) - D(\text{Au}-\text{OH})$. Assuming that only exothermic ion-molecule reactions occur (ΔH_{rx2} and $\Delta H_{rx3} < 0$),²³



lower limits for $D(\text{Au}-\text{CH}_3)$ and $D(\text{Au}-\text{OH})$ are 27.1 and 62.5 kcal/mol, respectively. These are the first experimental deter-

(20) Byrd, G. D. Ph.D. Thesis, Purdue University, 1982.

(21) Huber, K. P.; Herzberg, G. "Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules"; Van Nostrand-Reinhold: New York, 1979.

(22) Levin, R. D.; Lias, S. G., NSRDS-NBS 71, National Bureau of Standards, Washington, D.C., 1982.

(23) Bohme, D. K. "Interaction Between Ions and Molecules"; Ausloos, P., Ed.; Plenum Press: New York, 1974.

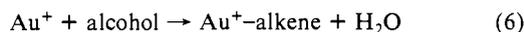
Table I. Primary Ion-Molecule Reaction Products of Group 11 Monocations with Alcohols

| reaction | reaction products | % of products | | | | | | |
|----------|--|-----------------|-----------------|-----------------|----------------|-----------------------------|-----------------------------|----------------|
| | | MeOH | EtOH | <i>n</i> -PrOH | <i>i</i> -PrOH | <i>n</i> -BuOH ^a | <i>i</i> -BuOH ^a | <i>t</i> -BuOH |
| A | AuH + RC ⁺ (OH)R | 85 ^b | 75% | 58 | 39 | 51 | 43 | <i>c</i> |
| B | AuCH ₃ + RCH ⁺ (OH) | | | | 19 | 9 | | 37 |
| C | AuOH + RC ⁺ HR' | | | 5 | 4 | 21 | 26 | 47 |
| D | (Au ⁺ -H ₂ O) + alkene | | | 1 | 10 | 2 | 11 | 5 |
| E | (Au ⁺ -alkene) + H ₂ O | | 25 | 36 | 27 | 3 | 6 | 7 |
| F | (Au ⁺ -ketone) + H ₂ | | | <1 ^d | <1 | 1 ^d | 3 | |
| G | (Au ⁺ -alcohol) | 15 | | <1 | 1 | <1 | <1 | |
| H | CuH + RC ⁺ (OH)R | | | 2 | 4 | <1 | 1 | |
| I | CuCH ₃ + RC ⁺ H(OH) | | | | | | | 5 |
| J | CuOH + RC ⁺ HR' | | | | | <1 | 4 | 4 |
| K | (Cu ⁺ -H ₂ O) + alkene | | | 8 | 9 | 13 | 12 | 19 |
| L | (Cu ⁺ -alkene) + H ₂ O | | | 20 | 21 | 37 | 53 | 64 |
| M | (Cu ⁺ -ketone) + H ₂ | | 75 ^d | 60 ^d | 21 | 34 ^d | | |
| N | (Cu ⁺ -alcohol) | 100 | 25 | 10 | 45 | 16 | 30 | 8 |
| O | (Ag ⁺ -alkene) + H ₂ O | | | | | | | 79 |
| P | (Ag ⁺ -ketone) + H ₂ | | | <2 ^d | 84 | <2 ^d | | |
| Q | (Ag ⁺ -alcohol) | | 100 | 98 | 16 | 98 | | 21 |

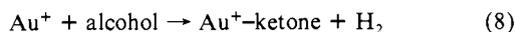
^aThe formation of Au⁺-C₂H₄ and elimination of C₂H₆O was observed for *n*-BuOH and *i*-BuOH, 12% product with *n*-BuOH and 11% product with *i*-BuOH. ^bProduct percentages reported are reproducible to ±15% of the values reported. ^cBlank space indicates the reaction and products were not observed. ^dThe reaction product is (Au⁺-aldehyde) in place of a ketone.

minations of gold bond dissociation energies.

Au cations undergo a number of dissociative attachment reactions with alcohols. Dehydration with competitive elimination of H₂O (reaction 6), or an alkene (reaction 7), occurred with all the alcohols studied except methanol. With use of CD₃CH₂OH



and C₂H₅OD, dehydration was shown to involve β-hydrogen atom transfer followed by elimination of HOD and formation of Au⁺-C₂H₂D₂ or Au⁺-C₂H₄. This mechanism, illustrated in Scheme I, explains how hydroxide abstraction by Au⁺ occurs. A similar mechanism, proposed by Ridge and co-workers, explains how dehydration of alcohols occurs with Fe, Co, and Ni.²⁴ Elimination of H₂O and retention of an alkene, forming Au(alkene)⁺, is the dominant dehydration reaction pathway of all the alcohols but *i*-BuOH. For example, EtOH forms only Au(C₂H₄)⁺. Another dissociative attachment reaction of Au cations with alcohols is dehydrogenation (reaction 8) with elimination of H₂ and retention of a ketone or aldehyde. Dehydrogenation was



observed with *n*-PrOH, *i*-PrOH, *n*-BuOH, and *i*-BuOH, but not with *t*-BuOH. Scheme II illustrates a proposed mechanism for dehydrogenation, involving gold cation insertion into the α-carbon-hydrogen bond followed by an α-hydrogen atom transfer. Scheme II also suggests how hydride abstraction occurs (for example, with EtOD, the hydride abstraction product CH₃CH⁺OD was observed). EtOH does not undergo dehydrogenation as a primary reaction but does as a secondary reaction. With CD₃-CH₂OH and EtOD, dehydrogenation was shown to involve an α-hydrogen atom transfer, followed by elimination of H₂ and HD and formation of Au(CD₂CH₂)(CD₃CHO)⁺ and Au(C₂H₄)-(CH₃CHO)⁺. Staley and Jones proposed dehydrogenation occurred via insertion between the H-OR bond, followed by a hydrogen atom or methyl group transfer and elimination of H₂ or CH₄.⁴ This mechanism is questionable because no CH₄ loss from *t*-BuOH was ever observed in the present experiments with Au⁺, Ag⁺, or Cu⁺ and the mechanism requires the metal cation to break the strongest bond in the alcohol (H-OR).

In contrast with SIMS results reported by Benninghoven,⁷ in LD/I cationization (or direct condensation) (reaction 9) is only a minor reaction pathway.

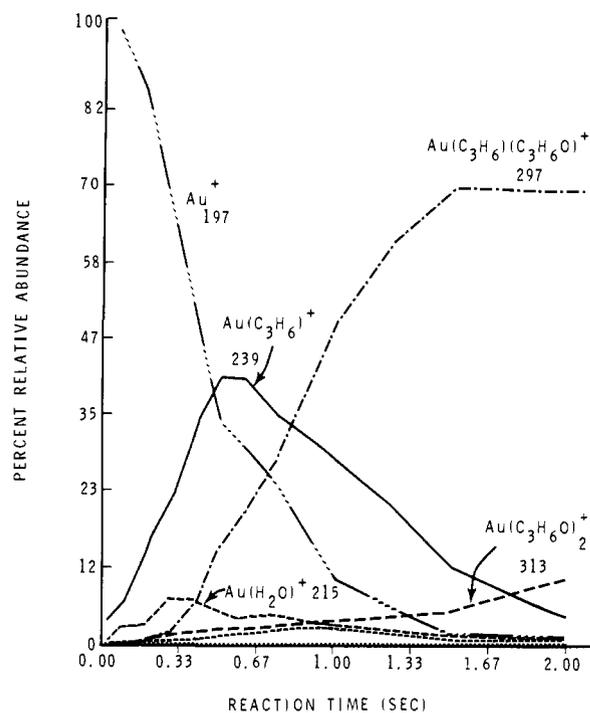
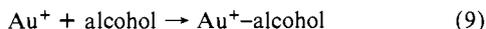
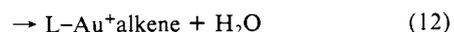


Figure 2. Ion intensities in percent of total ion current of gold cations and ionic reaction products as a function of time, with *i*-PrOH, $P(i\text{-PrOH}) = 6 \times 10^{-8}$ torr.

Transfer of Au⁺ from a ligand to a neutral alcohol (reaction 10) also leads to the formation of Au⁺-alcohol complex. Construction



of an Au⁺ affinity scale similar to the Ag⁺ affinity scale defined by Cooks and co-workers^{10b} is in progress. Other secondary reactions include dehydrogenation (reaction 11), dehydration (reaction 12), and secondary condensation (reaction 13), where L is a ligand such as propene or isopropyl alcohol. Secondary dehydration is observed only when *t*-BuOH reacts with Au-



(C₄H₈)⁺. Dehydrogenation is the dominant secondary reaction

Table II. Neutral Products of Reaction of Au⁺ and Cu⁺ with Alcohols

| compound | assumed neutral products | | estimated minimum dissociation energy, kcal/mol | | |
|--|-------------------------------|---------------------------------------|--|---|--|
| | | | $\Delta H_{\text{diss}}(\text{alcohol})^a$ kcal/mol | Au ⁺ -ligand bond | Cu ⁺ -ligand bond |
| CH ₃ CH ₂ OH | H ₂ O | CH ₂ CH ₂ | 10.9 | $D(\text{Au}^+-\text{CH}_2\text{CH}_2) > 10.9$ | <i>b</i> |
| | H ₂ | C ₂ H ₄ O | 16.5 | | $D(\text{Cu}^+-\text{C}_2\text{H}_4\text{O}) > 16.5$ |
| CH ₃ (CH ₂) ₂ OH | H ₂ O | C ₃ H ₆ | 8.1 | $D(\text{Au}^+-\text{C}_3\text{H}_6), D(\text{Au}^+-\text{H}_2\text{O}) > 8.1$ | $D(\text{Cu}^+-\text{H}_2\text{O}), D(\text{Cu}^+-\text{C}_3\text{H}_6) > 8.1$ |
| | H ₂ | CH ₂ CH ₂ CHO | 15.1 | $D(\text{Au}^+-\text{C}_2\text{H}_5\text{CHO}) > 15.1$ | $D(\text{Cu}^+-\text{C}_2\text{H}_5\text{CHO}) > 15.1$ |
| CH ₃ CH(OH)CH ₃ | H ₂ O | C ₃ H ₆ | 12.3 | $D(\text{Au}^+-\text{H}_2\text{O}), D(\text{Au}^+-\text{C}_3\text{H}_6) < 12.3$ | $D(\text{Cu}^+-\text{H}_2\text{O}), D(\text{Cu}^+-\text{C}_3\text{H}_6) > 12.3$ |
| | H ₂ | C ₃ H ₆ O | 13.2 | $D(\text{Au}^+-\text{C}_3\text{H}_6\text{O}) > 13.2$ | $D(\text{Cu}^+-\text{CH}_3\text{COCH}_3) > 13.2$ |
| CH ₃ (CH ₂) ₃ OH | H ₂ O | 1-C ₄ H ₈ | 7.8 | $D(\text{Au}^+-\text{C}_4\text{H}_8) > 7.8$ | $D(\text{Cu}^+-\text{H}_2\text{O}), D(\text{Cu}^+-1-\text{C}_4\text{H}_8) > 7.8$ |
| | H ₂ | C ₃ H ₇ CHO | 16.6 | $D(\text{Au}^+-1-\text{C}_4\text{H}_8\text{O}) > 16.6$ | $D(\text{Cu}^+-\text{C}_3\text{H}_7\text{CHO}) > 16.6$ |
| (CH ₃) ₂ CHCH ₂ OH | C ₂ H ₄ | C ₂ H ₆ O | 21.9 | $D(\text{Au}^+-\text{C}_2\text{H}_4) > 21.9$ | <i>b</i> |
| | H ₂ O | C ₄ H ₈ | 6.0 | $D(\text{Au}^+-\text{H}_2\text{O}), D(\text{Au}^+-\text{C}_4\text{H}_8) > 6.0$ | $D(\text{Cu}^+-\text{H}_2\text{O}), D(\text{Cu}^+-\text{C}_4\text{H}_8) > 6.0$ |
| | C ₂ H ₄ | C ₂ H ₆ O | 24.2 | $D(\text{Au}^+-\text{C}_2\text{H}_4) > 24.2$ | <i>b</i> |
| (CH ₃) ₃ COH | H ₂ | (CH ₃) ₂ CHCHO | 15.6 | $D(\text{Au}^+-\text{C}_3\text{H}_8\text{O}) > 15.6$ | $D(\text{Cu}^+-\text{C}_3\text{H}_7\text{CHO}) > 15.6$ |
| | H ₂ O | C ₄ H ₈ | 16.0 | $D(\text{Au}^+-\text{H}_2\text{O}), D(\text{Au}^+-\text{C}_4\text{H}_8) > 16.0$ | $D(\text{Cu}^+-\text{H}_2\text{O}), D(\text{Cu}^+-\text{C}_4\text{H}_8) > 16.0$ |

^aThe heat of formation of neutrals taken from one of the following: Rosenstock, H. M.; Drax, L. K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data*, 1977, 6, Supplement No. 1. Benson, S. W. "Thermochemical Kinetics", 2nd ed.; J. Wiley and Sons: New York, 1976. ^bNo product ions were observed for this reaction.

of Au(alkene)⁺ with all the alcohols except *t*-BuOH. A typical plot of ion intensities with time, in this case for Au⁺ with 4.5 × 10⁻⁸ torr of *i*-PrOH, is shown in Figure 2. Dehydration is the major primary reaction, forming both Au(C₃H₆)⁺ and Au(H₂O)⁺. Ligand exchange from Au(H₂O)⁺ is observed. Dehydrogenation of *i*-PrOH by Au(C₃H₆)⁺ to form Au(C₃H₆)(C₃H₆O)⁺ is the major secondary reaction (94% of final product), and condensation forming Au(C₃H₆)(C₃H₈O)⁺ is the other product (6% of final product).

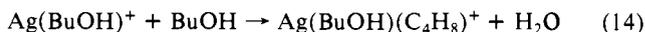
Cu⁺ with Alcohols. Ion-molecule reactions of Cu⁺ with alcohols are also listed in Table I (reactions H-N). In comparison with gold, copper has a lower ionization potential (IP(Cu) = 178.2 kcal/mol)²¹ and only slightly weaker metal-hydrogen bond ($D(\text{Cu}-\text{H}) = 67$ kcal/mol);²² so IP(M) + $D(\text{M}-\text{H})$ for Cu is 245.2 kcal/mol, which is 45 kcal/mol smaller than the values for Au. Hydride abstraction (reaction H) ($\Delta H_{\text{rxn}} = -\text{IP}(\text{Cu}) - D(\text{Cu}-\text{H}) + \text{AP}(\text{RC}^+(\text{OH})\text{R}')$) is endothermic for MeOH and EtOH ($\Delta H_{\text{rxn}} = 15.4$ and 2.7 kcal/mol), and only slightly exothermic for the other alcohols investigated. This explains why hydride abstraction, although observed when exothermic beginning with *n*-PrOH ($\Delta H_{\text{rxn}} = -1.1$ kcal/mol), is not the dominant reaction of Cu⁺ with alcohols. Methide abstraction (reaction I) is found with *t*-BuOH and hydroxide abstraction (reaction J) is observed with the other butyl alcohols. Assuming that only exothermic ion-molecule reactions occur, lower limits for copper-methyl and copper-hydroxide bond dissociation energies [$D(\text{Cu}-\text{CH}_3)$ and $D(\text{Cu}-\text{OH})$] are 59 and 97 kcal/mol, respectively.

The dominant reactions of Cu⁺ are dissociative attachment reactions K-M and direct condensation (reaction N). Dehydrogenation (reaction M) is the dominant reaction of Cu⁺ with EtOH and *n*-PrOH but is not found for *i*-BuOH or *t*-BuOH. Dehydration with retention of H₂O (reaction K) or alkene (reaction L) is the dominant reaction of the butyl alcohols and is also observed with *n*-PrOH and *i*-PrOH. In contrast with Au⁺, condensation reactions (or copper cationization) (reaction N) occur for all the alcohols examined, including EtOH. This may be explained by the difference between Au⁺ and Cu⁺ affinities for hydride, methide, or hydroxide. Copper cations which attach to an alcohol via condensation or ligand exchange do not abstract a hydride, methide, or hydroxide group, and instead a stable Cu⁺-alcohol complex is formed. Au⁺ cations readily abstract hydride, forming AuH and alkyl cations, [M-H]⁺, making Au⁺-alcohol complex formation only a minor reaction pathway.

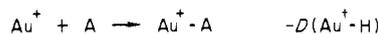
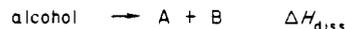
Condensation is the only secondary reaction observed with *i*-PrOH and *i*-BuOH and the dominant reaction with *n*-PrOH and *n*-BuOH. A small amount of secondary dehydrogenation is observed with *n*-BuOH. Both condensation and dehydration with elimination of H₂O secondary reactions occur with *t*-BuOH and Au-L⁺ where L = butene or *t*-BuOH. In contrast with the results of Staley and Jones, no CH₄ elimination is observed with *t*-BuOH.⁴ Furthermore, condensation products were found for all the alcohols. This is clear evidence that such reactions are not ter-

molecular as claimed by Staley and Jones⁴ partially based upon their failure to observe reaction products with the MeOH at 100 times higher pressure (5 × 10⁻⁶ torr) than used in this study.

Reactions of Ag⁺ with Alcohols. Ion-molecule reactions of Ag⁺ with alcohols are listed in Table I (reactions O-Q). In contrast to the rich chemistry found with Cu⁺ and Au⁺, Ag⁺ is very unreactive with many alcohols. Silver has a smaller ionization potential (IP(Ag) = 174.7 kcal/mol)²¹ and weaker metal-hydrogen bond ($D(\text{Ag}-\text{H}) = 55.1$ kcal/mol)²² than gold. Therefore, the calculated IP(M) + $D(\text{M}-\text{H})$ for Ag is 229.8 kcal/mol, 60 kcal/mol smaller than that of Au and 15.4 kcal/mol smaller than that of Cu. Ag cations do not abstract hydride, due to reaction endothermicity. Methide and hydroxide abstractions also do not occur. Ag⁺ does not react with MeOH but does slowly cationize EtOH (observed at reaction delays of ≈ 1 s or more). Silver cationization (reaction A) is the dominant reaction with normal-chain alcohols, *n*-PrOH and *n*-BuOH. In contrast with these alcohols, dehydrogenation (reaction P) is the dominant ion-molecule reaction of Ag⁺ with *i*-PrOH, Ag(C₃H₆O)⁺, while dehydration (reaction O) is the dominant reaction of Ag⁺ with *t*-BuOH, Ag(C₄H₈)⁺. Ligand exchange only occurs between Ag(C₄H₈)⁺ and *t*-BuOH. Condensation is the only other secondary reaction. This conflicts with the Staley and Jones⁴ suggestion that butyl alcohols reacting with Ag⁺ all undergo a second dehydration step after an alcohol molecule is bound to Ag⁺ (reaction 14).



Thermodynamics. Heat of reaction for dissociative attachment reactions 4-6 is determined by the dissociation energy needed to break a neutral alcohol into two fragments, ΔH_{diss} and the Au⁺-ligand bond dissociation energy, $D(\text{Au}^+-\text{A})$. Assuming that only exothermic reactions occur, $\Delta H_{\text{rxn}} < 0$,²³ then $\Delta H_{\text{diss}} - D-$



(Au⁺-A) < 0 and $D(\text{Au}^+-\text{A}) > \Delta H_{\text{diss}}$, yielding lower limits for Au⁺-ligand bond dissociation energies. Table II lists the heat of dissociation values for conversion of the alcohols studied into the assumed neutral products. Additionally, observed Au⁺-ligand ions and estimated minimum dissociation energies are listed (e.g., $D(\text{Au}^+-\text{H}_2\text{O}) > 16.0$, $D(\text{Au}^+-\text{C}_3\text{H}_6) > 12.3$, $D(\text{Au}^+-\text{C}_2\text{H}_4) > 24.2$,²⁵ and $D(\text{Au}^+-\text{C}_4\text{H}_8\text{O}) > 15.8$ kcal/mol). Lower limits for Cu⁺-ligand and Ag⁺-ligand bond dissociation energies [$D(\text{Cu}^+-\text{A})$ and $D(\text{Ag}^+-\text{A})$] also can be obtained from ΔH_{diss} . Table II lists

(25) Preliminary results for the ion-molecule reactions of Au⁺ with 2-butanone and 2-pentanone indicate that $D(\text{Au}^+-\text{C}_3\text{H}_4) > 29.7$ kcal/mol, $D(\text{Au}^+-\text{C}_4\text{H}_8) > 35.7$ kcal/mol, and $D(\text{Au}^+-\text{C}_3\text{H}_6\text{O}) > 22.0$ kcal/mol.

Table III. Experimental Determination of Gas-Phase Acidity of AuH^a

| | $\Delta H_{\text{acid}}(\text{BH})^b$ kcal/mol | proton transfer |
|--|---|--------------------|
| $\text{Au}^- + \text{CF}_3\text{CO}_2\text{H} \rightarrow \text{AuH} + \text{CF}_3\text{CO}_2^-$ | 322.7 | yes |
| $\text{Au}^- + \text{HBr} \rightarrow \text{AuH} + \text{Br}^-$ | 323.6 | yes |
| $\text{Au}^- + \text{Cl}_2\text{HCO}_2\text{H} \rightarrow \text{AuH} + \text{Cl}_2\text{CHCO}_2^-$ | 328.4 | yes |
| $\text{Au}^- + \text{CF}_3\text{COCH}_2\text{COCH}_3 \rightarrow \text{AuH} + \text{CF}_3\text{COCH}^-\text{COCH}_3$ | 328.5 | yes |
| $\text{Au}^- + \text{HCl} \rightarrow \text{AuH} + \text{Cl}^-$ | 333.4 | no |

^a For reactions $\text{Au}^- + \text{BH} \rightarrow \text{AuH} + \text{B}^-$. ^b Gas-phase acidity by values obtained from a compilation by Bartmess (ref 29). Bartmess, J. E. ^c Au⁻ ejection causes disappearance of B⁻ using ejection method of ref 12.

the heats of dissociation values for the copper and silver reactions with alcohols.

Ion-Molecule Reactions of Au⁻. Although there have been numerous studies of gas phase metal ion chemistry in recent years, relatively few have dealt with anions.²⁶ In those studies, metal carbonyl anions (e.g., Fe(CO)₄⁻, Cr(CO)₅⁻, Mn(CO)₅⁻, Co(CO)₄⁻) were formed by electron impact upon volatile metal carbonyls. Cr⁻ has been observed by Freiser and co-workers using collision induced dissociation (CID) to sequentially remove CO molecules from Cr(CO)₅⁻.^{26d} Interpretation of those data is complicated by ion-molecule reactions between metal carbonyl anions and neutral metal carbonyl. Thus, an alternative source of metal anions (not derived from volatile metal carbonyls) is needed. As mentioned earlier, Byrd, using the LD/I method, produced copper anions from copper;²⁰ however, he concluded that the quantity of Cu⁻ was insufficient for ion-molecule reactions to be studied. In contrast, gold anions are formed in high abundance in the present system. Gold anions did not react with the alcohols examined. The gas-phase acidity of AuH, $\Delta H_{\text{acid}}(\text{AuH})$, has been calculated by using eq I (electron affinity, EA(Au) = 53.4 kcal/mol,²⁷ and $\Delta H_f(\text{AuH}) = 70.5$ kcal/mol data²⁸) to be $\Delta H_{\text{acid}}(\text{AuH}) = 329.4$ kcal/mol, which is much lower than the acidity of the alcohols ($\Delta H_{\text{acid}}(\text{MeOH}) = 379.2 \rightarrow \Delta H_{\text{acid}}(t-$

BuOH) = 373.3 kcal/mol)²⁹ studied. Thus, proton transfer from alcohols to Au⁻ is endothermic. Using the bracketing technique, the gas-phase acidity of AuH has been experimentally determined to be between $\Delta H_{\text{acid}}(\text{CF}_3\text{COCH}_2\text{COCH}_3) < \Delta H_{\text{acid}}(\text{AuH}) < \Delta H_{\text{acid}}(\text{HCl})$, 328.5 kcal/mol < $\Delta H_{\text{acid}}(\text{AuH})$ < 333.4 kcal/mol (Table III), thus $\Delta H_{\text{acid}}(\text{AuH}) = 331 \pm 3$ kcal/mol. The experimental and calculated values are nearly identical. Gold-hydrogen bond dissociation energy, $D(\text{Au-H})$, is calculated by using eq II (ionization potential of H, IP(H) = 313.6 kcal/mol)²²

$$D(\text{Au-H}) = \Delta H_{\text{acid}}(\text{AuH}) - \text{IP}(\text{H}) + \text{EA}(\text{Au}) \quad (11)$$

to be $D(\text{Au-H}) = 70.6$ kcal/mol, which is 7 kcal/mol lower than the previously reported value.²¹ Other Au⁻ ion-molecule reaction studies are now in progress in order to determine more Au-X bond dissociation energies experimentally.

Conclusion

The use of metal oxides and/or metal salts has been shown to be an excellent metal ion source for LD/FTMS. Metal cations with specific ligands and selected oxidation states can be formed directly by starting with the proper metal salts or oxides. Metal cation and anion clusters can be formed without using volatile metal carbonyls as precursors. The strong Au-H bond and high ionization potential of Au makes hydride abstraction the dominant reaction of Au⁺ with alcohols. Hydride abstraction is less favored for reactions of Ag⁺ and Cu⁺ with alcohols. Methide and hydroxide abstraction studies allow estimation of lower limits for Au-CH₃, Au-OH, Cu-CH₃, and Cu-OH bond dissociation energies. ($D(\text{Au-CH}_3) > 27.1$ kcal/mol, $D(\text{Au-OH}) > 62.5$ kcal/mol, $D(\text{Cu-CH}_3) > 59$ kcal/mol, and $D(\text{Cu-OH}) > 97.0$ kcal/mol). Dehydration with competitive elimination of H₂O and the alkene involves β -hydrogen atom transfer. Dehydrogenation with elimination of H₂ and production of a ketone or aldehyde involves α -hydrogen atom transfer. The gas-phase acidity of AuH has been determined experimentally to be $\Delta H_{\text{acid}}(\text{AuH}) = 331 \pm 3$ kcal/mol by using the bracketing technique. The experimental and calculated values are nearly identical.

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Registry No. Au⁺, 20681-14-5; Cu⁺, 17493-86-6; Ag⁺, 14701-21-4; MeOH, 67-56-1; EtOH, 64-17-5; *n*-PrOH, 71-23-8; *i*-PrOH, 67-63-0; *n*-BuOH, 71-36-3; *i*-BuOH, 78-83-1; *t*-BuOH, 75-65-0; CD₃CH₂OH, 1759-87-1; C₂H₅OD, 925-93-9; AuH, 13464-75-0.

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