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Ambient Preparation and Reactions of Gas Phase Silver Cluster Cations and Anions

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Electrospray ionization of metal salt solutions followed by ambient heating transforms the resulting salt clusters into new species, primarily naked ionic metal clusters. The experiment is done by passing the clusters through a heated coiled loop outside the mass spectrometer which releases the counter-anion while generating the anionic or cationic naked metal cluster. The nature of the anion in the starting salt determines the type of metal cluster observed. For example, silver acetate upon heating generates only positive silver clusters, Ag_n^+ , but silver fluoride generates both positive and negative silver clusters, $\text{Ag}_n^{+/-}$ ($3 < n < 20$). Both unheated and heated metal salt sprays yield ions with characteristic geometric and electronic magic numbers. There is also a strong odd/even effect in the cationic and anionic silver clusters. Thermochemical control is suggested as the basis for favored formation of the observed clusters, with anhydride elimination occurring from the acetates and fluoride elimination from the fluorides to give cationic and anionic clusters, respectively. Data on the intermediates observed as the temperature is ramped support this. The naked metal clusters react with gaseous reagents in the open air, including methyl substituted pyridines, hydrocarbons, common organic solvents, ozone, ethylene, and propylene. Argentation of hydrocarbons, including saturated hydrocarbons, is shown to occur and serves as a useful analytical ionization method. The new cluster formation methodology allows investigation of ligand-metal binding including in reactions of industrial importance, such as olefin epoxidation. These reactions provide insight into the physicochemical properties of silver cluster anions and cations. The potential use of the ion source in ion soft landing is demonstrated by reproducing the mass spectra of salts heated in air using a custom surface science instrument.

1. Introduction

Transition metals exhibit unique physical, optical, and chemical properties both as bulk materials and in the nanoscale. Silver nanomaterials have applications in water purification¹, catalysis², and surface enhanced Raman spectroscopy^{3, 4}, among many others. The properties of atomically precise metal clusters are even more fascinating as the addition or removal of a single atom affects the electronic⁵ and chemical⁶ properties of the cluster. Atomically precise metal clusters can be generated both in solution and in the gas phase. Mass spectrometry (MS) is a critical tool for preparing and understanding the unique properties of metal clusters both in the gas phase^{7, 8} and when deposited onto surfaces.^{2, 9, 10}

The production of gas-phase metal clusters has been demonstrated using a variety of ionization sources, including

magnetron sputtering,¹¹ laser ablation,¹²⁻¹⁵ gas aggregation,^{16, 17} cold reflux discharge¹⁸, pulsed arc cluster ion sources,^{19, 20} and electrospray ionization (ESI).²¹⁻²⁶ These sources produce positive, negative, and neutral clusters over a wide size range with a seemingly unlimited choice of elemental compositions.²⁷ Flow tube reactors^{11, 28, 29} and ion traps^{30, 31} are common ways of studying metal clusters in the gas phase. Small silver clusters ($\text{Ag}_n^{+/-}$, $n < 20$), the topic of interest in this paper, have been studied extensively in the gas phase due to their value in partial oxidation and catalytic reactions.^{6, 23, 24, 28, 32-38}

The silver cluster, Ag_4H^+ has been used to mediate the carbon-carbon coupling of allyl bromide.²³ In the overall reaction, three molecules of allyl bromide are needed to generate $[\text{Ag}(\text{C}_3\text{H}_5)_2]^+$, $[\text{Ag}_3\text{Br}_3]$, and $\text{CH}_2=\text{CHCH}_3$. The product, $[\text{Ag}(\text{C}_3\text{H}_5)_2]^+$ loses C_6H_{10} , most likely 1,5-hexadiene, upon collisional activation, which represents an example of gas

phase carbon-carbon bond coupling.^{39, 40} Silver has long served as a catalyst for the partial oxidation of ethylene to ethylene oxide and Ag_2O^+ has been investigated as a model for silver-mediated olefin epoxidation.³⁷ Roithová and Schröder note clean O-atom transfer reactions with ethylene. Propylene undergoes allylic H-atom abstraction and other oxidation pathways but C-H abstraction from propylene leads to the formation of unwanted byproducts, preventing high selectivity in the formation of propylene oxide.⁴¹

The physical and chemical properties of anionic silver clusters in the gas phase have also garnered attention. Measurements on the binding energies of O_2 and observation of cooperative binding of O_2 to silver cluster anions have been reported.^{32, 33} Recently, Luo et al. noted the enhanced stability of Ag_{13}^- towards etching with O_2 due to a large spin excitation energy.²⁸ The reaction of O_2 with CO in the presence of anionic silver clusters was found to be strongly cluster-size dependent with only Ag_7^- , Ag_9^- , and Ag_{11}^- serving as potential catalytic centers.⁶ Luo et al. found that Ag_8^- reacts with chlorine through a harpoon mechanism³⁵ and reported that silver cluster anions activate C-S bonds in ethanethiol to produce such products as Ag_nSH^- and Ag_nSH_2^- .³⁶

While extensive literature exists on the chemistry of gaseous silver clusters in vacuum, there is also a growing community interested in studying their properties on surfaces. For example, size-selected silver cluster cations with different energies were deposited onto Pt(111) and the surface topography was measured with scanning tunneling microscopy. When the energy was less than 1 eV/atom, it was possible to non-destructively deposit the clusters.⁴² Palmer et al. deposited size-selected silver clusters on graphite as a method for preparing nanostructured surfaces.⁴³ Recently, Ag_3^+ deposited on alumina was found to be a highly selective catalyst for the epoxidation of propylene by O_2 .⁵ Size selected-silver clusters were deposited on passivated carbon in order to understand the discharge process in lithium-oxygen cells. The size of the deposited silver clusters greatly affected the morphology of lithium peroxide, indicating that precise control of sub-nanometer features on a surface might improve battery technology.⁴⁴

In this study, we describe a novel and facile method for the production of naked metal cluster ions by electrospray ionization (ESI) and cluster heating in air. When the appropriate silver salt is subjected to these conditions, it is possible to generate silver cluster cations and anions without use of lasers or collision-induced dissociation (CID). Physicochemical properties are elucidated by subjecting the clusters in the open air to ion/molecule reactions; for example, they can be oxidized in the presence of ozone. The silver clusters can also be used for the analysis of hydrocarbons or to study ligand exchange processes. Finally, it is demonstrated that this ionization source can be coupled to an ion soft landing instrument to perform catalytic studies.

2. Experimental

2.1 Chemicals and Materials

Silver fluoride, silver acetate, silver benzoate, 2-ethylpyridine, 3-ethylpyridine, 4-ethylpyridine, 3,4-lutidine, 2,6-lutidine, 2,5-lutidine, 3,5-lutidine, hexadecane, isocetane, squalane, and ethanol were purchased from Sigma Aldrich, USA. HPLC grade methanol was purchased from Mallinckrodt Baker Inc., Phillipsburg, NJ. Deionized water was provided by a Milli-Q

Integral water purification system (Barnstead Easy Pure II). Deuterated solvents, such as D_2O and CD_3OD were purchased from Cambridge Isotope Laboratories (Tewksbury, MA). Tert-butyl alcohol, 1-propanol, ammonium hydroxide, and pyridine were purchased from Mallinckrodt Chemicals (St. Louis, MI). Isopropyl alcohol, acetic anhydride, and acetone were purchased from Macron (Center Valley, PA). 2,4,6-trimethylpyridine was purchased from Eastman chemical company (Kingsport, TN). All chemicals were used as received without further purification.

2.2 Experimental Methods

A home-built electrosonic spray ionization (ESSI) source was coupled to a heated drying tube as shown in Figure 1.^{45, 46} The heated drying tube is made from 316L stainless steel (AmazonSupply.com, part # S0125028T316SAL 6', O.D. 1/8", I.D. 0.069") and coiled twice to a diameter of 5.5 cm and to a total length of 43 cm. The stainless steel loop was wrapped with heating tape (Omega, part # FGR-030). The ESSI source was typically positioned between 3 mm outside to 3 mm inside the heating loop, the position being chosen such that the maximum ion signal was obtained. Independent positioning of the ESSI sprayer and heating loop was achieved by using two xyz micrometer moving stages (Parker Automation, Rohnert Park, CA). The distance between the heating loop and linear ion trap mass spectrometer (LTQ, Thermo Scientific, San Jose, CA) inlet was typically between 1 to 10 mm. At shorter distances, the ion signal was higher as more of the electrospray plume entered the MS inlet.

In a typical experiment, a metal salt was dissolved in 1:1 methanol:water at a concentration of 1 mM. Spray was initiated using a voltage of +/- 5 kV and N_2 nebulizing gas (105 psi pressure). The electrospray plume entered the heating loop, which was set to 250°C. The temperature was controlled by the voltage supplied using an autotransformer and monitored by a thermocouple. The ions exiting the loop were analyzed by a LTQ mass spectrometer using the following parameters: capillary temperature 200 °C, capillary voltage +/- 140 V, tube lens voltage +/- 240 V, maximum injection time 100 ms, and an average of 3 microscans. Automatic instrument tuning was used to optimize the potential applied to all other lenses. For collision-induced dissociation (CID), normalized collision energies of 25-35% (manufacturer's unit), Mathieu parameter q_z values of 0.25-0.35, and isolation windows were typically 2 m/z units larger than the isotopic distribution (e.g. for Ag_6^+ an isolation window of 14 mass units was used). In certain experiments, high mass accuracy (<5 ppm) was achieved using a hybrid LTQ-Orbitrap mass spectrometer (LTQ-Orbi, Thermo Scientific, San Jose, CA). The mass resolution was set to 30,000 with a typical injection time between 250 ms and 5 s depending on the initial ion intensity. Tandem MS Orbitrap experiments utilized the same conditions as the LTQ.

To perform ion/molecule reactions, the distance between the heating loop and inlet was typically set at 1 cm. Vapors of interest were introduced via a cotton swab held between the heating loop and MS inlet (Figure S1). In order to perform sequential ion/molecule reactions, a short piece of metal tubing (2.5 cm) was placed between the inlet and heating loop (Figure S2). One neutral reagent was introduced into the first gap (between the heating loop and the additional metal tubing) and the second reagent was introduced into the second gap (between the added metal tube and the inlet). In addition, some experiments were performed using ozone which was generated

by low temperature plasma (LTP) (Figure S3). The low temperature plasma source used has been described

previously.^{47, 48} Gases were introduced using Swagelok couplings at a flow rate between 0.5-1 L/min.

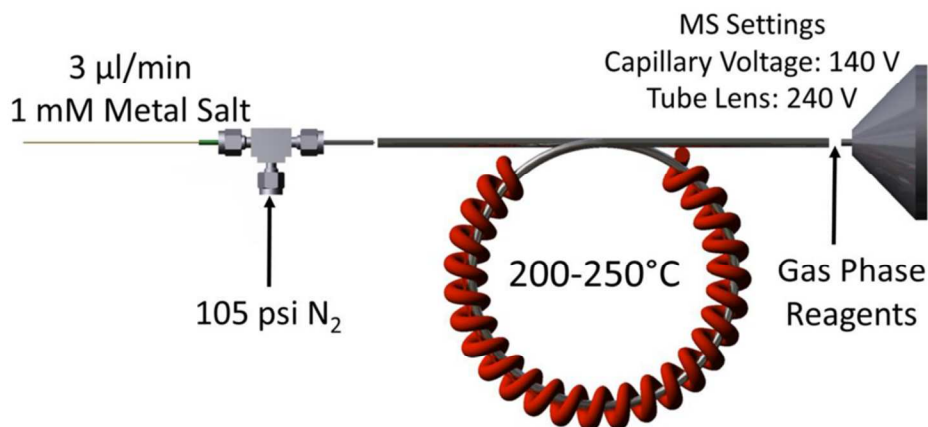


Fig. 1 Apparatus for the production of silver cluster cations and anions

3. Results/Discussion

3.1 Unheated Silver Salts

The electrospray of solutions of metal salts has long been known to produce species of the type $[C_nA_{n-1}]^+$ and $[C_nA_{n+1}]^-$ where C is the cation and A is the anion of the salt.⁴⁹ Consistent with this, the mass spectrum of silver acetate recorded with the heating loop turned off shows the formation of simple salt clusters (Figure 2A). This spectrum is characterized by a weak geometric magic number for $[Ag_5(CH_3COO)_4]^+$ and $[Ag_8(CH_3COO)_7]^+$, the enhanced stability likely being associated with 3x3 and 3x5 units. For smaller clusters (Ag_3 and smaller), some hydration is present. For larger clusters ($[Ag_4(CH_3COO)_3]^+$ and larger), dissociation (by CID) of the mass-selected ion is dominated by the loss of $Ag_2(CH_3COO)_2$ units, which likely occurs in two separate steps.²⁴ Smaller hydrated clusters undergo water loss followed by ejection of $AgCH_3COO$ while the cluster $[Ag_2(CH_3COO)]^+$ undergoes decarboxylation in agreement with observations by O'Hair et al.⁵⁰ Negative ion mode electrospray produces a series of ions $[Ag_{n-1}(CH_3COO)_n]^-$, which do not exhibit any geometric magic numbers (Figure S4A). Dissociation of silver acetate cluster anions is by loss of $Ag(CH_3COO)$. Silver benzoate exhibits similar clustering to that of silver acetate except that the geometric magic numbers are replaced by an abundant ion $[Ag_7(C_7H_6O_2)_6]^+$ (Figure S4 C,E). Silver fluoride exhibits a unique unheated mass spectrum. In the positive ion mode, naked silver cluster cations (e.g. Ag_3^+ , Ag_5^+ , Ag_7^+ , Ag_9^+) along with various oxidized and hydrated cations are observed (Figure S4G). In the negative ion mode, extensive clustering of silver with multiple counter anions is observed (Figure 2C).

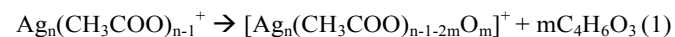
3.2 Heated Silver Salts

The mass spectra of the various silver salts changed significantly when the heating loop was set to 250°C. Regardless of the silver salt chosen, the positive ion mode mass spectra were all essentially identical (Figure 2B, Fig. S4D,H). These spectra are dominated by the naked metal clusters Ag_n^+ and Ag_n^{2+} . All species undergo expected fragmentations (Figure S5.), including the loss of Ag_2 from odd-numbered clusters, coulombic explosion for Ag_{16}^{2+} , and monomer loss from other Ag_n^{2+} ions.⁵¹⁻⁵⁴ The expected odd/even alternation and magic

numbers at Ag_3^+ and Ag_9^+ was also observed.⁵⁵ Thus, the fragmentation behavior of the Ag_n^+ and Ag_n^{2+} ions is the same, regardless of the starting material, viz. silver benzoate or silver acetate. Moreover, during heating there is no evidence for the formation of silver hydride clusters. Interestingly, only silver fluoride has the ability to generate negatively charged clusters, Ag_n^- (Figure 2D). Silver acetate and benzoate do not produce silver cluster anions, but instead produce mainly organic fragments, presumably because of the stability of the organic counter anion (Figure S4B,F). The fragmentation of small silver cluster anions ($n < 12$) matches that reported in the literature (Figure S6).⁵⁶ Larger silver cluster anions typically lose neutral Ag, which has not been reported in literature. For the silver cluster anions, the expected odd/even alternation and magic number at Ag_7^- is observed.²⁸

3.3 Mechanism

The above experiments used heat as well as in-source collisions to transform silver acetate and other silver salts into silver cluster cations and anions. Ready access to these clusters ions facilitated the study of their formation and dissociation as a source of information on their structure and reactivity. Possible intermediates responsible for the formation of silver cluster cations from silver acetate were investigated by monitoring the total ion chromatogram while the temperature of the loop was ramped from room temperature to 250°C over the course of a few minutes (Figure S7). At low temperatures, the salt clusters $[Ag_n(CH_3COO)_{n-1}]^+$ were observed. At intermediate temperatures (100 - 150°C), new species were observed in the MS, including $[Ag_9(CH_3COO)_6O]^+$, $[Ag_8(CH_3COO)_5O]^+$, and $[Ag_7(CH_3COO)_4O]^+$, indicating losses of acetic anhydride ($C_4H_6O_3$), eq.(1). For smaller clusters, an additional water molecule was present on the cluster, as in $[Ag_6(CH_3COO)_3OH_2O]^+$ and $[Ag_5(CH_3COO)_2OH_2O]^+$. This may simply be the result of addition of residual water to coordinatively unsaturated metal complexes by ion/molecule reactions in the ion trap, a known process. An alternative to this pathway, the loss of ethenone (C_2H_2O) followed by water, is considered less likely as discussed in the Supporting Material.



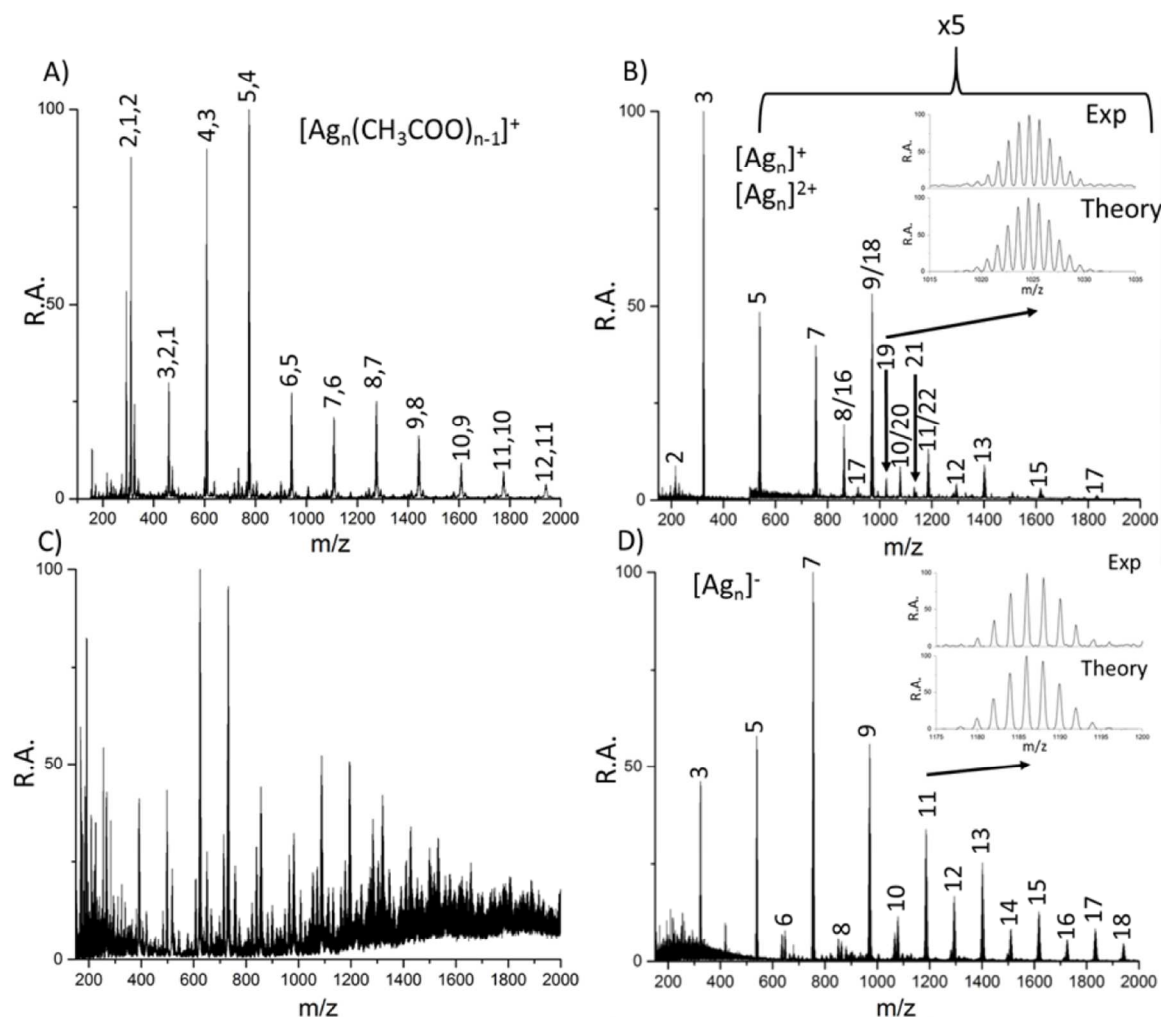


Fig. 2 Positive ion mode mass spectra of A) unheated and B) heated electrosprayed silver acetate. Negative ion mode for C) unheated and D) heated electrosprayed silver fluoride solution. The numbers above each peak in A) indicate the number of silver atoms, ligands, and water molecules present. The numbers above each peak in B) and D) indicate the number of silver atoms.

Thermochemical considerations are useful in deciding on likely decomposition pathways. For example if $n = 3$, then the process shown in (1) forms one molecule acetic anhydride and Ag_3O^+ .⁵⁷ The formation of acetic anhydride is exothermic by -572.5 kJ/mol, which almost 250 kJ/mol more exothermic than the alternative pathway (Supporting Information), suggesting that acetic anhydride formation is the favored pathway leading to oxidized silver cluster cations.

Figure S8 provides a chart of all ions observed in the full scan mass spectra along with their relationships as established by CID experiments for the decomposition of the silver acetate ions in the positive ion mode. All ions observed in the mass spectra can be explained as possible products of equation (1) when water and oxygen are allowed to arrive or leave from the cluster. When the heating experiment is performed at the highest temperatures, the formation of simple silver cluster cations and oxidized silver cluster cations was observed. Once the final temperature was reached and some time had passed, the formation of primarily naked metal clusters was observed.

The thermochemical mechanism for cationic cluster formation extends to other silver salts such as the benzoate,

which is assumed to undergo thermal dissociation by similar routes to give silver cation clusters. A method for the production of Ag_n^+ and $\text{Ag}_{n-1}\text{H}^+$ from cluster ions generated from precursor solutions containing silver nitrate and either glycine or *N,N*-dimethyl glycine has been reported by O'Hair, using ion trap CID.²⁴ The choice of precursor compounds is important in these experiments as it can allow the production of $[\text{C}_{n+1}\text{A}_n]^+$ and $[\text{C}_{n-1}\text{A}_n]^+$ where A is an anion with favorable redox properties. For example, glycine contains both an amine and deprotonated carboxylic group, which appear to meet these redox criteria.²⁴ It should be noted that under the conditions of the O'Hair study, silver acetate did not produce silver cluster cations upon CID.²⁴ The heating loop utilized in our work dissociates clusters to this extent at atmospheric pressure, but the similarities and differences between the ion trap CID and ambient heating experiments are not well understood.⁵⁸

Anionic cluster formation can be considered in a similar vein. The loss of fluorine could be by hydrolysis to give the enthalpically favored HF or in a redox process to give the less favored F_2 . The favored formation of the odd-numbered silver anion clusters (Figure 2D) is simply due to their greater stability than their even-numbered counterparts.²⁸

3.4 Reactivity of Silver Cluster Cations

3.4.1 Alcohol Reactivity

Atmospheric pressure ion/molecule reactions were carried out between organic solvents (ethanol, 1-propanol, isopropyl alcohol, tert-butyl alcohol, acetone, and acetonitrile) and silver cluster cations generated from silver acetate. Typically, an organic solvent of interest was added to a cotton swab and introduced into the region after the heating tube and before the MS inlet (Figure S1). A summary of the reactions can be found in Table S1, Table S2, and Figure S9. Monomeric Ag^+ reacts to form mainly $[\text{AgL}]^+$ and $[\text{AgL}_2]^+$, except in the case of acetonitrile where the only product is $[\text{AgL}_2]^+$. The cluster Ag_3^+ reacts to form $[\text{Ag}_3\text{L}]^+$ and $[\text{Ag}_3\text{L}_2]^+$, except that acetonitrile behaves differently in forming $[\text{Ag}_3\text{L}_2]^+$ and $[\text{Ag}_3\text{L}_3]^+$. This reactivity differs from reported gas phase reactions, where $[\text{AgL}_2]^+$ and $[\text{Ag}_3\text{L}_3]^+$ are the terminal products for all reagents studied except ethanol, which was reported to be unreactive.⁵⁹ The differences in reactivity are not unexpected given that our experiments were performed in air, and the literature data refers to vacuum, and there are also differences in reaction time. The maximum interaction time in our experiments was on the order of a single scan, ca. 0.2–0.5 s, compared to possibly 60 s reported in the literature. The ion/molecule reactions under vacuum do not provide efficient third body stabilization for smaller ions, explaining the difference in reactivity with ethanol.⁵⁹ Tandem mass spectrometry data on the reaction products (e.g. $[\text{Ag}_3\text{L}_2]^+$, Figure S9 A,C,E,F) indicate that the reagents serve as simple ligands. The reaction product, for example $[\text{Ag}_3\text{L}_2]^+$, loses one ligand for each stage of tandem MS to form bare Ag_3^+ . Simple ligation is the main result observed in these reactions. There appears to be relatively good agreement between silver clusters with alcohols obtained under vacuum and in the open air. Due to the inability to mass select the clusters before reaction, it is possible that some of the reaction products form from the larger clusters which react with accompanying losses of Ag_n moieties. The loss of Ag upon ligand addition for even-numbered silver cluster cations is an example of such a reaction that has been previously reported.^{59, 60}

3.4.2 Methyl Substituted Pyridine Reactivity

Atmospheric pressure ion/molecule reactions were carried out between methyl-substituted pyridines and silver cluster cations generated from silver benzoate (Figure S10, Table S3,S4). Ligation of the neutral reagents to the silver cluster was observed with the dominant products being $[\text{AgL}_2]^+$ and $[\text{Ag}_3\text{L}_3]^+$ except in the case of pyridine itself and 2,4,6-trimethylpyridine which also produced species with a smaller number of ligands. The nature of the interaction between Ag_3^+ and the neutral reagent was confirmed by CID (Figure S11) which showed the sequential loss of ligands from the species $[\text{Ag}_3(\text{C}_8\text{H}_{11}\text{N})_3]^+$ and $[\text{Ag}_3(\text{C}_7\text{H}_9\text{N})_3]^+$ generated from 2,4,6-trimethylpyridine and 3,5-lutidine. This confirms that the neutrals are acting as simple ligands on Ag_3^+ .

3.4.3 Ligand Exchange

It is obvious from the previous examples that ligation of Ag_3^+ is easily achieved. A further test was made to determine if the generation of mixed-ligand Ag_3^+ species was possible. A slightly modified version of the apparatus of Figure S1 was used so that multiple neutral reagents could be introduced

separately (Figure S2). The system was tested with three mixtures of ligands: ammonia (from ammonium hydroxide) and acetonitrile, 2,6-lutidine and acetonitrile, and acetone and acetonitrile. For the first set of reagents, ammonia and acetonitrile, a variety of mixed ligand species was observed, including $[\text{Ag}_3+\text{C}_2\text{H}_3\text{N}+\text{NH}_3]^+$, $[\text{Ag}_3+(\text{C}_2\text{H}_3\text{N})_2+\text{NH}_3]^+$, and $[\text{Ag}_3+\text{C}_2\text{H}_3\text{N}+(\text{NH}_3)_2]^+$ as confirmed by MS/MS (Figure S12). 2,6-Lutidine and acetonitrile also generated a mixed ligand species (Figure S13), $[\text{Ag}_3+\text{C}_7\text{H}_9\text{N}+\text{C}_2\text{H}_3\text{N}]^+$; however, this was the only mixed ligand species observed in this case. In addition, $[\text{Ag}_3+(\text{C}_7\text{H}_9\text{N})_2]^+$ and $[\text{Ag}_3+(\text{C}_7\text{H}_9\text{N})_3]^+$ were formed in higher intensity than $[\text{Ag}_3+\text{C}_7\text{H}_9\text{N}+\text{C}_2\text{H}_3\text{N}]^+$, indicating a preference towards binding 2,6-lutidine. To qualitatively test the effect of the sequence used to introduce neutral reagents, acetone and acetonitrile were used. Acetone was allowed to interact first with the cluster spray followed by the acetonitrile and vice versa (Table S5 and Figure S14). When acetone was allowed to react first, it was possible to generate a mixed species as well as species containing either acetone or acetonitrile. This was in stark contrast to the case where acetonitrile was the first reagent as it produced only species with acetonitrile ligands; i.e. ligand displacement did not occur due to stronger binding to this ligand.

3.4.4 Hydrocarbon Reactivity

Silver cationization is known to selectively ionize unsaturated compounds, including polycyclic aromatic hydrocarbons and alkenes.^{61–64} A series of hydrocarbons was analyzed using ambient ion/molecule reactions in the same manner as other neutral reagents (Figure S15). Both cationization by Ag^+ and Ag_3^+ occurred for hexadecane, isocetane, and squalane. Cationization of a pump oil (Ultragrade 19) sample was also demonstrated, but the identity of the silver adducts is unknown. The fact that heat was required to generate the silver cluster spray is advantageous for the analysis of heavy hydrocarbons, which are difficult to vaporize and often have low vapor pressures. The convenient ionization of saturated hydrocarbons in the ambient environment is a potential analytical application of this methodology.

3.4.5 Oxidation

Oxidized silver clusters can serve as model catalysts for partial oxidation reactions, including epoxidation³⁷. Roithová and Schröder produced Ag_2O^+ in vacuum from the dissociation of Ag_2NO_3^+ into NO_2 and Ag_2O^+ . Another possible approach to simple oxides is the direct oxidation of Ag_n^+ clusters, a possibility indicated by the reaction between neutral silver clusters and ozone.⁶⁵ Ionic metal cluster oxidation was achieved by utilizing a low power plasma (LTP) source (Figure 3), which under appropriate conditions serves as a source of ozone.^{47, 66} Silver cluster cations were generated from silver fluoride and allowed to interact with the generated ozone (Figure 3B). A series of oxidized metal clusters was observed which contained multiple oxygen atoms as well as water molecules. The simplest and most notable reaction was the transformation of Ag_3^+ into Ag_3O^+ . It is observed that silver clusters containing at least one oxygen atom can react with water too. It seems that water is only reactive towards already oxidized clusters, since naked silver cluster cations have been reported to be unreactive towards water.⁵⁹ (The water is likely adventitious water in the ambient environment or in the ion trap used for mass analysis.)

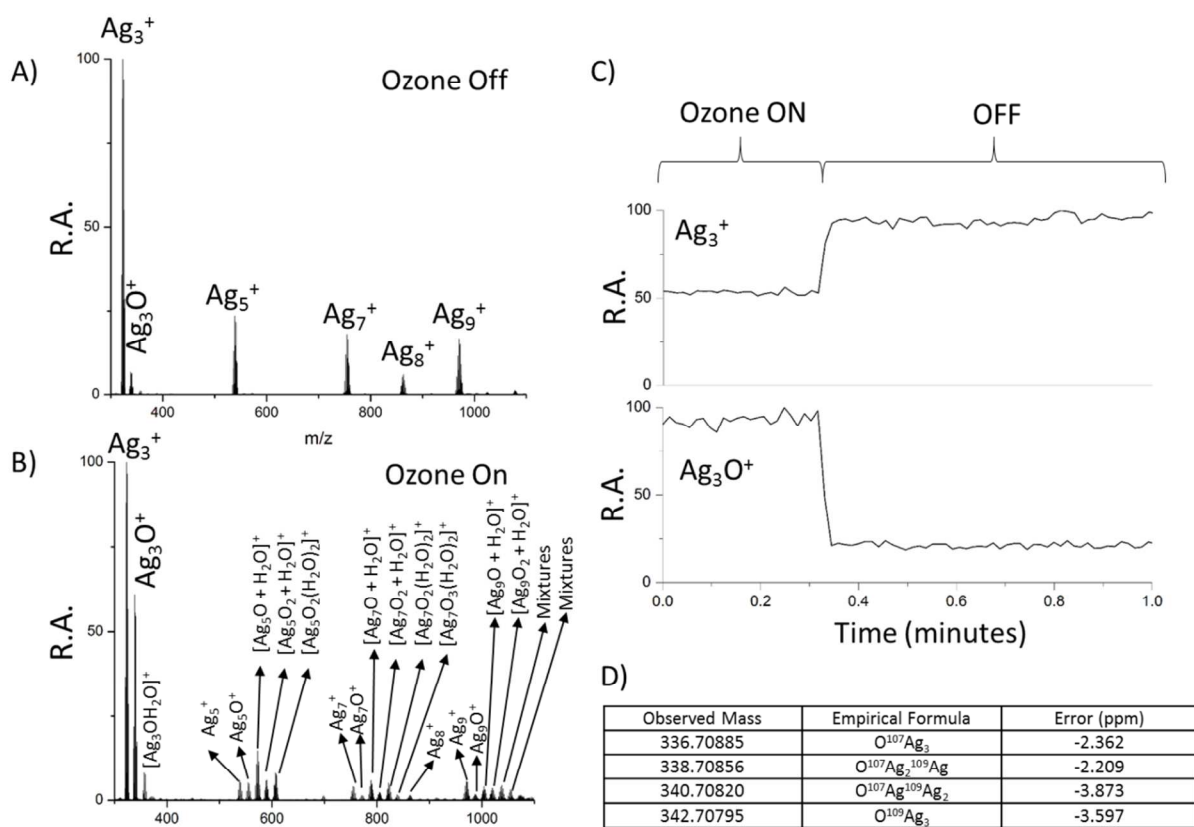


Fig. 3 Mass spectra of silver cluster cations generated from silver fluoride A) without ozone and B) with ozone. C) Shows the selected ion chromatogram of Ag_3^+ (top) and Ag_3O^+ (bottom) in the presence and absence of ozone. D) High mass accuracy measurements confirm the formation of Ag_3O^+ .

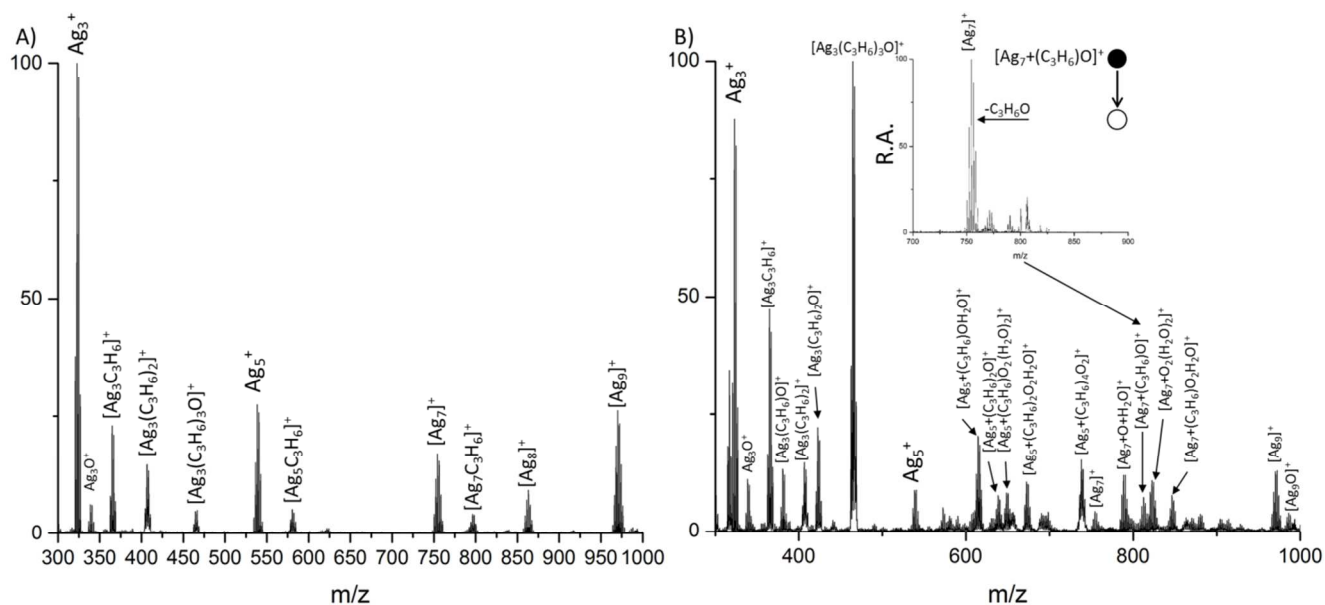


Fig. 4 Reaction of silver cluster cations with A) propylene and B) propylene and ozone

3.4.6 Reactions of Ag_n^+ and oxidized Ag_n^+ with ethylene and propylene

Supported silver trimers have been demonstrated to be catalysts for the direct epoxidation of propylene using gaseous oxygen.² In our study, odd-numbered silver cluster cations interacted with ethylene to produce mono-, bi-, and tri-ligated species (Figure S16A). No ligation was observed for even-numbered clusters, either due to their inertness or to the loss of Ag upon reaction to produce the favored odd-numbered cluster. A small amount of $[\text{Ag}_3(\text{C}_2\text{H}_4)_3\text{O}]^+$ was observed, which presumably arises from reaction with the small amount of Ag_3O^+ present within the spray. With the addition of ozone from the LTP source, the mass spectra change significantly. The intensity of $[\text{Ag}_3(\text{C}_2\text{H}_4)_3\text{O}]^+$ increases dramatically and a species $[\text{Ag}_5(\text{C}_2\text{H}_4)_4\text{O}_2]^+$ is observed (Figure S16B). It is interesting to note that there appears to be a cooperative effect in the binding of ethylene to oxidized clusters as Ag_3^+ binds one or two ethylenes, but it appears that Ag_3O^+ binds only three ethylenes. The same phenomenon occurs for the binding of one, two, or three ethylenes to Ag_5^+ but Ag_5O_2^+ only binds four ethylenes. Cooperative binding has been reported for O_2 and CO with anionic silver clusters, but no such reports exist for cationic silver clusters.^{6, 32} $[\text{Ag}_3(\text{C}_2\text{H}_4)_3\text{O}]^+$ and $[\text{Ag}_5(\text{C}_2\text{H}_4)_4\text{O}_2]^+$ were subjected to CID to identify any potential epoxide products; however, only the products of ligation were observed. The tandem MS of $[\text{Ag}_5(\text{C}_2\text{H}_4)_4\text{O}_2]^+$ (Figure S17) is interesting as the loss of two ethylene molecules is accompanied by the addition of a single water molecule, and the loss of three ethylenes is accompanied by the addition of two water molecules.

Similar experiments were performed with propylene as the reagent gas. In the absence of ozone, propylene exhibits nearly identical reactivity to ethylene (Figure 4). The reactivity of ozone and propylene is similar to ozone and ethylene for the Ag_3^+ cluster but differs for the larger clusters (Figure 4B). A variety of species containing propylene, oxygen, and water are observed for both Ag_5^+ and Ag_7^+ . $[\text{Ag}_7(\text{C}_3\text{H}_6)\text{O}]^+$ is particularly

interesting because it fragments to lose neutral $\text{C}_3\text{H}_6\text{O}$, propylene oxide or a structural isomer.

3.5 Reactivity of Silver Cluster Anions

3.5.1 Formation of $[\text{Ag}_n(\text{OH})]^-$

The reactivity of silver cluster anions generated from silver fluoride was examined. The position of the ESI source relative to the heating tube was altered to form an ambient discharge. Without the discharge, naked metal silver clusters are observed (Figure 5). With the discharge, the even-numbered clusters (especially $n = 6, 8, \text{ and } 10$) gained an OH group to form $[\text{Ag}_n\text{OH}]^-$, possibly due to reaction with hydroxyl radicals created by the discharge.⁶⁷ The amount of $[\text{Ag}_n\text{OH}]^-$ varies with cluster size but generally decreases as n increases. Deuterated 1:1 methanol:water was used as the spray solution in an attempt to identify the source of the OH. The intensity of $[\text{Ag}_n\text{OD}]^-$ was at most 30% of the $[\text{Ag}_n\text{OH}]^-$ intensity, indicating that the source of OH must be from elsewhere, such as atmospheric water.

3.6 Ion Soft Landing

As a proof of principle, the metal cluster ion source was coupled to a homebuilt ion soft landing instrument.^{4, 68} Each of the three silver salts was electrosprayed and similar mass spectra were obtained as previously described (Figure S18). For unheated silver acetate and silver benzoate, the same type of salt clustering was observed as previously seen (Figure 2A). A similar effect was observed for silver fluoride, but the exact number of silver and amount of oxygen or water bound could not be determined with the given instrument resolution. Upon heating, all three salts produced a range of clusters from Ag_3^+ to Ag_{15}^+ without any even-numbered clusters. This set of ions was deposited onto a gold surface and a current of 10 pA could be achieved. Efforts are underway to improve the current of the source so it will be possible to study mass-selected ions on surfaces.

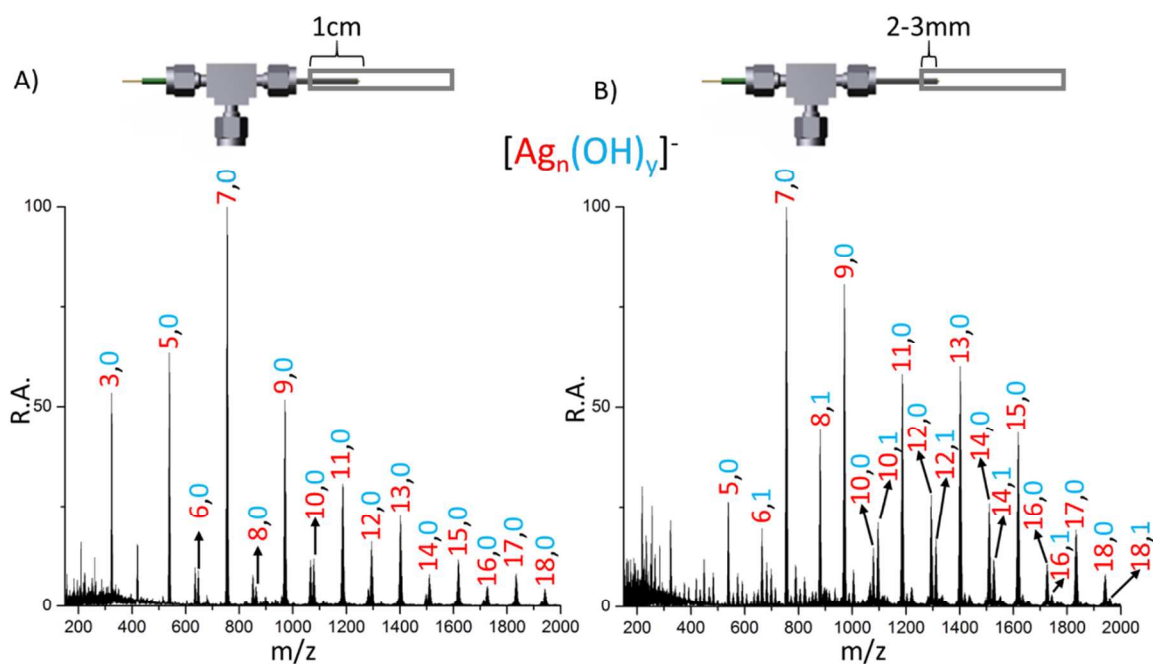


Fig 5. Mass spectra of silver cluster anions with the ESSI sprayer inserted A) 1 cm and B) 2-3 mm inside the heating tube. Red and blue numbers respectively indicate silver atoms and OH molecules.

4. Conclusions

The major significance of this study lies in the development of a simple methodology to produce anionic and cationic metal clusters in the ambient environment. In addition (1) Insights into the mechanisms of formation of the cluster ions was obtained by studying effects of ambient heating and from thermochemical considerations. The formation of a series of odd-numbered silver anions is most remarkable. (2) Ion/molecule reactions at atmospheric pressure revealed a rich chemistry of the silver cluster cations and anions. Examples of this include, ligation, ligand exchange, cationization of alkanes and olefins, and oxidation reactions. Ligand exchange chemistry shows the relative strength of different ligands towards silver cluster cations, which may be of use in choosing ligands for capping atomically precise clusters. (3) The potential analytical utility of the cluster ions was demonstrated by silver cationization of saturated alkanes. (4) The use of ozone to produce oxidized clusters especially Ag_3O^+ was demonstrated; these silver clusters are especially important as partial oxidation catalysts.

In future work, attempts will be made to operate these ambient sources so as to produce a narrower range of cluster ions, to select clusters of a particular size by ion mobility and to explore further the chemistry of such anionic species Ag_n^- and Ag_nOH^- . Extensions of this approach to the generation of cluster ions from other metals will also be attempted. For example, it is already known that Pd_n^+ , Pd_nO_y^+ , and Pd_nO_y^- (where $3 < n < 13$, and $3 < y < 8$) are formed from palladium acetate. The formation of alloy clusters from a mixture of metal salts is also expected to be straightforward. Given the existence of a rationale for the loss of the counterion as a small stable molecule (acetic anhydride in the case of acetates), other counterions will be selected to optimize cluster ion formation. The most interesting aspect of the new capabilities provided will be the investigation of processes of industrial significance using metal clusters and metal oxide clusters, which have some of the structural features believed to be important in full scale heterogeneous catalysis (certain metal cluster sizes and compositions).^{8, 69, 70} The fact that these species can be generated in air compensates to a degree for the fact that they are not atomically precise.

Acknowledgements

Financial support from the Separations and Analysis Program, Office of Basic Energy Sciences, US Department of Energy, DE-FG02-06ER15807 is acknowledged. TP acknowledges DST for funding. DS acknowledges UGC for their research fellowship. Zane Baird is thanked for technical assistance.

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† Electronic Supplementary Information (ESI) available: Additional experimental setups, mass spectra of unheated and heated silver salts, tandem MS of silver cluster cations and anions, mass spectra of silver

cluster cation/anion reactivity, and tabular results of silver cluster reactivity. See DOI: 10.1039/b000000x/

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