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Interaction of gold and silver cluster cations with CH_3Br: thermal and photoinduced reaction pathways

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Abstract. The reactions of free, size selected Au_n^+ (n = 1–3, 5, 7) and Ag_3^+ clusters with CH_3Br as well as the photodissociation of the resulting complexes at 266 nm were studied in a radio frequency ion trap under multiple collision conditions. CH_3Br was found to interact more strongly with the gold clusters than with the silver clusters. All investigated metal clusters exhibited characteristic size dependent adsorbate coverages. Furthermore, the successive loss of methyl radicals was identified as a major thermal reaction channel of the adsorbed CH_3Br molecules. Photodissociation experiments were performed with the product complexes of the trimer clusters and revealed the strongly preferred light-induced fragmentation of $Au_3Br_3^+$ and $Ag_3Br_3^+$, respectively, over any other thermal reaction products. However, whereas in the case of the gold cluster complexes the bare Au_3^+ was exclusively re-formed through laser irradiation, considerable photoinduced metal cluster fragmentation occurred in the case of $Ag_3Br_3^+$.

1 Introduction

Gas-phase studies of free metal clusters provide an ideal means to assess the elementary processes of bond-making and bond-breaking that are potentially involved in reactions catalyzed by metal particles, while avoiding complications due to solvent or substrate effects. Although such investigations might certainly never account for the precise mechanisms operative in applied catalysis, gas-phase studies can provide a conceptual framework and an efficient tool to obtain direct insight into reactivity patterns [1]. Moreover, by increasing the cluster size atom by atom, important knowledge about the transition from the chemistry of single atoms to that of nanoparticles can be achieved [2].

Methyl halogenides have been considered as precursors in a highly selective methanol synthesis via catalytic hydrolysis [3]. In this respect, the reactions of free gold cluster cations with CH_3Cl and H_2O were recently investigated in this laboratory [4]. In the present contribution, these studies were extended to the interaction of small gold and silver cluster cations with CH_3Br. In addition, the light-induced fragmentation of the resulting reaction products was probed employing femtosecond(fs)-laser excitation.

The adsorption and photodissociation of methyl bromide molecules on magnesia supported gold clusters had been recently investigated in this laboratory as well [5,6] and the present study aims to provide data for a direct comparison of the gas-phase and surface results.

The gas phase reactions of the atomic noble metal ions Au^+ and Ag^+ with methyl bromide were studied by various groups before [7–10], but no investigations of the reactions of CH_3Br with Au_n^+ and Ag_n^+ ($n > 1$) cluster cations have been reported so far.

The results presented here reveal a strongly cluster size dependent methyl bromide adsorption coverage and extensive methyl elimination reactions succeeding the molecular CH_3Br adsorption. Most strikingly, a highly selective photodissociation behavior was observed in which preferably the bromine-rich thermal reaction products were depleted through laser irradiation. In the case of Au_3^+ this lead to a light-induced re-formation of the bare gold cluster cation which could further react with residual CH_3Br in the ion trap establishing a photocatalytic methyl radical elimination mechanism.

2 Experiment

The experimental setup employed in the present study consisted of a temperature variable radio frequency (rf) octopole ion trap inserted into a tandem quadrupole mass spectrometer. Details of the experimental technique and the data acquisition method were described previously [11]. Briefly, the gold and silver metal cluster cations were produced by a CORDIS (cold reflex discharge ion source) sputtering cluster source [12]. The thus generated clusters were thermalized at room temperature and mass selected by means of a first quadrupole mass filter. The cluster ion beam of one specific mass was subsequently guided into the octopole ion trap prefilled with about 1 Pa of helium buffer gas and a small, well-defined partial pressure of CH_3Br. The ion trap enclosure was attached to a closed cycle helium cryostat which allowed for temperature adjustment in the range between 20 and 300 K. After

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a chosen reaction time t_R all ions, intermediates and products, were extracted from the ion trap and mass-analyzed by a second quadrupole mass filter.

A commercial amplified Ti:sapphire fs-laser system (Spectra Physics Spitfire) was employed to photoexcite the cluster complexes inside the rf ion trap. In the presented photodissociation experiments the third harmonic (266 nm central wavelength, 80 fs pulsewidth) of the fundamental laser wavelength was employed.

3 Results and discussion

3.1 Thermal reactions of Au_n^+ (n = 1–3, 5, 7) clusters with CH_3Br

The reaction behavior of small cationic gold clusters Au_2^+, Au_3^+, Au_5^+, and Au_7^+ with methyl bromide was investigated experimentally here for the first time. No theoretical studies on the methyl bromide adsorption on free gold atoms or clusters have been reported so far as well. Only for the case of the atomic ion Au^+ the reactions with CH_3Br have been investigated experimentally previously [8–10].

A mass spectrum showing the reaction products of Au^+ with CH_3Br obtained in our ion trap experiment at room temperature is displayed in Figure 1a. Au^+ adsorbed a maximum of two CH_3Br molecules, which however subsequently dissociated on the gold ion under the loss of CH_3 radicals. The resulting product peaks of $Au(CH_3Br)Br^+$ and $AuBr_2^+$ are consequently observed in the mass spectrum in Figure 1a. In addition, two products resulting from an apparent dehydrogenation reaction are detected: $AuC_2H_4(CH_3Br)^+$ and the corresponding methyl elimination product $AuC_2H_4Br^+$.

These results are in very good agreement with the earlier investigations of the gas phase reaction of Au^+ with CH_3Br, in which also the formation of $Au(CH_3Br)_2^+$ and $AuC_2H_4(CH_3Br)^+$ as well as the methyl elimination reactions had been observed [8–10].

Figure 1b displays the reaction products of Au_2^+. The gold dimer is the only cluster size which completely fragmented in the presence of CH_3Br. Furthermore, the formed $Au(CH_3Br)_2^+$ fragment also successively forfeited the CH_3 radicals.

The product mass spectra of Au_3^+ are displayed in Figure 1c and (as a function of the reaction time) in Figures 1f–1j. For the shortest investigated reaction time of 10 ms (Figs. 1c and 1f), the predominant mass peak corresponds to $Au_3(CH_3Br)_3^+$ and additionally only a small $Au_3(CH_3Br)_2Br^+$ signal was observed. The fact that no product complexes with less than the maximum CH_3Br coverage of three molecules were observed even at the shortest reaction time indicates that the adsorption of the first methyl bromide molecule is the rate determining step in the sequential adsorption reaction [13]. At a reaction time of 100 ms (Fig. 1g) the $Au_3(CH_3Br)_2Br^+$ concentration was slightly increased and a small contribution from $Au_3(CH_3Br)Br_2^+$ was observed. The intensities of the methyl elimination products successively increased with reaction time (Figs. 1h–1j) eventually yielding $Au_3Br_3^+$ as major product at $t_R = 5$ s.

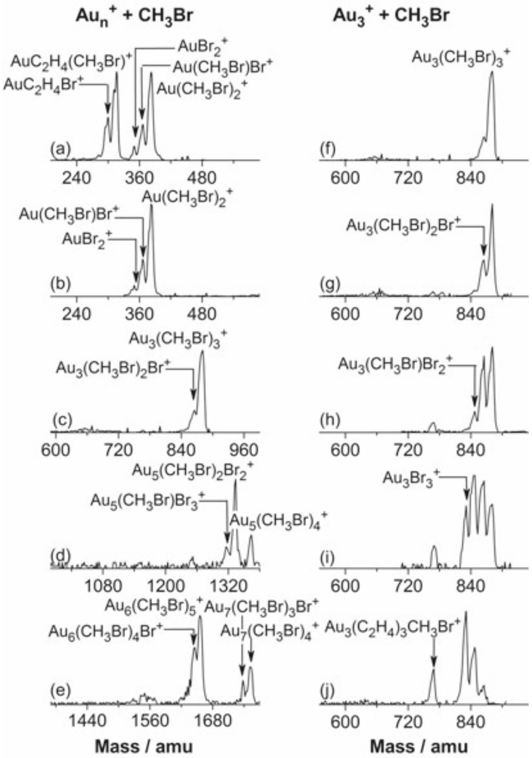

Fig. 1. Product ion mass spectra of the reaction of (a)–(e) Au_n^+ ($n = 1$–3, 5, 7) with CH_3Br ($t_R = 10$ ms), (f)–(j) Au_3^+ with CH_3Br after different reaction times of (f) 10 ms, (g) 100 ms, (h) 500 ms, (i) 1 s, and (j) 5 s (300 K, p(He) = 1 Pa, p(CH_3Br) = 0.1 Pa).

The observation of the adsorption of a maximum of three ligands (CH_3Br or Br) is in accordance with the minimum energy structure of Au_3^+ which is a planar equilateral triangle (D_{3h} symmetry) with three electronically equivalent corners each presenting one adsorption site [14–16]. Since the bromide atom exhibits the largest electronegativity in CH_3Br, it can be assumed that methyl bromide coordinates to the cluster cations through the bromide atom.

In addition to the methyl bromide adsorption and methyl radical elimination product complexes, the emergence of a product peak assigned to $Au_3(C_2H_4)_3CH_3Br^+$ was detected for reaction times longer than 500 ms. A C_2H_4 ligand results apparently from multiple dehydrogenation steps similar to those observed in the case of the reactions of the atomic ion Au^+ (cf. Fig. 1a).

The investigations were extended to Au_5^+ and Au_7^+. The corresponding product mass spectra are depicted in Figures 1d and 1e. In both cases a maximum adsorption of four CH_3Br molecules was observed at room temperature even for longer reaction times (no shown here). A saturation coverage of four ligands is nicely in accordance with the geometry of the Au_5^+ cluster which is an X-shaped configuration (D_{2h} symmetry [17,18]) with four electronically equivalent corner atoms as binding sites. In contrast, Au_7^+ exhibits a hexagon structure [14], which would suggest a

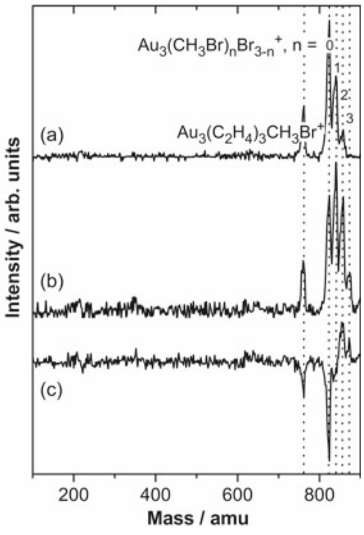

Fig. 2. Photodissociation of $Au_3(CH_3Br)_nBr_{3-n}^+$ (n = 1–3) product complexes. (a) Thermal reaction products of Au_3^+ after 5 s reaction time (300 K, $p(CH_3Br)$ = 0.1 Pa). (b) Product ion mass spectrum obtained under similar reaction conditions after 5 s laser irradiation (266 nm). (c) Difference spectrum (b–a).

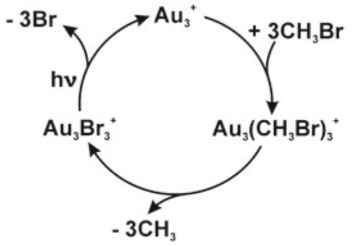

Fig. 3. Proposed mechanism for the photocatalytic methyl elimination reaction.

maximum saturation coverage of six ligands. This indicates that lower reaction temperatures might be required in this case to reach the maximal possible number of ligand molecules [18]. Analogous to Au_3^+, a successive elimination of the CH_3 radical from the adsorbed CH_3Br molecules with increasing reaction time was observed for Au_5^+ and Au_7^+. This methyl elimination was accompanied by the partial fragmentation of the metal cluster for Au_7^+ (see Fig. 1e).

3.2 Photodissociation of $Au_3(CH_3Br)_nBr_{3-n}^+$ (n = 1–3) product complexes

Figure 2a shows again the product mass spectrum obtained after 5 s from the reaction of Au_3^+ with CH_3Br under thermal reaction conditions (300 K). The dominant mass peak corresponds to $Au_3Br_3^+$. In the photodissociation experiments the reaction mixture in the ion trap was irradiated with 266 nm laser pulses at a repetition rate of 1 kHz during the whole reaction time of 5 s. Subsequently, the mass spectrum depicted in Figure 2b was recorded. It can be observed that the relative intensity of the methyl elimination products have changed considerably. Most strikingly, the complex $Au_3(CH_3Br)_3^+$, which is absent in the mass spectrum of Figure 2a, is re-formed during irradiation as can be seen from Figure 2b.

The selective interaction of the laser light with some molecular complexes in the ion trap is even more apparent from the photodissociation difference spectrum shown in Figure 2c which clearly demonstrates the preferred photoinduced depletion of $Au_3Br_3^+$ over all other thermal reaction products. Also the product $Au_3(C_2H_4)_3CH_3Br^+$ and to a small extend $Au_3(CH_3Br)Br_2^+$ are depleted. In contrast, the concentrations of $Au_3(CH_3Br)_2Br^+$ and $Au_3(CH_3Br)_3^+$ increase due to laser irradiation.

These observations in conjunction with the fact that no further fragmentation products are observed in the mass spectra of Figure 2 lead to the conclusion that the preferred light-induced decomposition of $Au_3Br_3^+$ must result in the re-formation of the bare Au_3^+ cluster. The gold trimer cation is in turn able to react again with the residual CH_3Br in the ion trap. As a consequence, the relative concentration of the adsorption products before methyl elimination is increased as observed in the mass spectra of Figure 2b in comparison to Figure 2a. This mechanism is summarized in the photocatalytic reaction cycle displayed in Figure 3 and presents a versatile methyl radical source which might be used in future experiments to methylate coadsorbed ligand molecules.

3.3 Thermal reactions of Ag_3^+ with CH_3Br

Compared to gold, the silver clusters were found to be less reactive toward methyl bromide. Figure 4 displays the product ion mass spectra for the reaction of Ag_3^+ with methyl bromide recorded at a reaction time of 5 s and different reaction temperatures from 300 K to 230 K. At 300 K (Fig. 4a) almost no reaction products were observed. At lower temperatures (Figs. 4b and 4c) the sequential adsorption of CH_3Br molecules was detected. As a consequence of the smaller reactivity of the silver clusters toward CH_3Br compared to gold, the maximum coverage of three CH_3Br was only reached at 230 K (Fig. 4d). Subsequently, similar to the behavior of CH_3Br adsorbed on the gold trimer clusters, the C-Br bond of the adsorbed molecules broke progressively, such that for 5 s reaction time the $Ag_3Br_3^+$ product exhibited the highest intensity in the recorded mass spectrum in Figure 4d. However, no dehydrogenation products were observed in the case of Ag_3^+.

3.4 Photodissociation of $Ag_3(CH_3Br)_nBr_{3-n}^+$ (n = 1–3) product complexes

Also in the case of the silver trimer reactions, the photoinduced dissociation of the reaction products was investigated. Figure 5 shows the photodissociation difference mass spectrum which resulted from the subtraction of the thermal product mass spectrum (5 s reaction time) form the reaction product spectrum obtained with laser irradiation (266 nm, also 5 s reaction time). This difference spectrum clearly shows the preferred chromophoric properties of the product $Ag_3Br_3^+$ compared to all other reaction products. However, the depletion of $Ag_3Br_3^+$ (and to a minor extent of $Ag_3(CH_3Br)Br_2^+$) was accompanied by a considerable metal cluster fragmentation as indicated by the various product peaks at lower masses in Figure 5. This observation is in agreement with previous photodissociation and metastable fragmentation studies on silver bromide cluster cations [19–21].

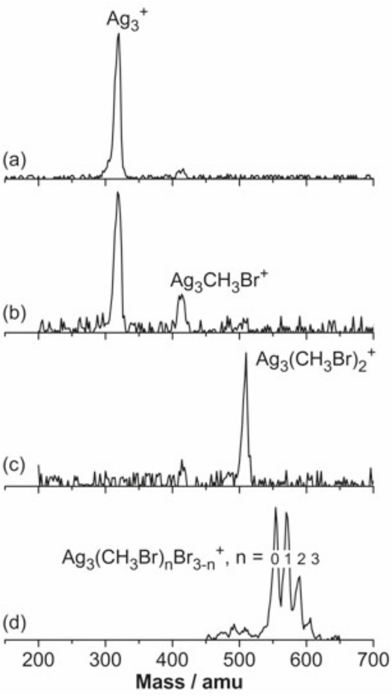

Fig. 4. Product ion mass spectra of the reaction of Ag_3^+ with CH_3Br at various reaction temperatures: (a) 300 K, (b) 250 K, (c) 240 K, and (d) 230 K (p(He) = 1 Pa, $p(CH_3Br)$ = 0.1 Pa, $t_R = 5$ s).

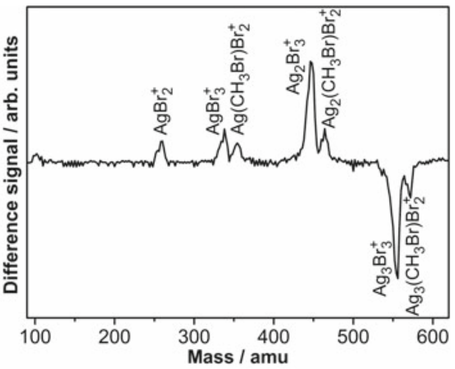

Fig. 5. Photodissociation mass spectrum of the $Ag_3(CH_3Br)_nBr_{3-n}^+$ (n = 1–3) product complexes at a laser wavelength of 266 nm (230 K, t_R = 5 s, $p(CH_3Br)$ = 0.1 Pa).

4 Conclusion

The experiments presented in this contribution showed that Au_n^+ (n = 1–3, 5, 7) and Ag_3^+ react with methyl bromide in an rf octopole ion trap under multiple collision conditions leading to size dependent CH_3Br coverages. Under thermal conditions the successive loss of methyl radicals was identified as major adsorbate reaction channel. Interestingly, these gas phase results, namely that methyl bromide decomposed on small gold clusters, provide an explanation why no molecular CH_3Br desorption was observed in previous temperature programmed desorption experiments of CH_3Br on magnesia supported gold clusters, if the cluster size did not exceed a certain value [5,6].

The photodissociation of the product complexes of the silver and gold trimer clusters in the ion trap revealed a strongly preferred light-induced fragmentation of $Au_3Br_3^+$ and $Ag_3Br_3^+$. In the case of the gold trimer complexes, the metal cluster Au_3^+ was even re-formed without fragmentation, which lead to the formulation of a photocatalytic reaction cycle in which methyl radicals are thermally liberated followed by the light-induced abstraction of the remaining bromine atoms.

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