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ScienceDirect
International Journal of Mass Spectrometry 261 (2007) 152–158
www.elsevier.com/locate/ijms

Charge transfer initiated nitroxyl chemistry on free silver clusters $Ag_{2–5}^-$: Size effects and magic complexes

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Received 11 January 2006; received in revised form 20 August 2006; accepted 23 August 2006
Available online 9 October 2006

Abstract

The reactivity of small silver cluster anions $Ag_{2–5}^-$ toward nitric oxide and mixtures of nitric oxide with carbon monoxide is investigated under multi-collision conditions in a radio frequency octopole ion trap at temperatures of 100 and 300 K. A strongly cluster size dependent reaction behavior is observed, where reactive fragmentation dominates for clusters with four or fewer atoms and only Ag_5^- is able to form reaction products without dissociation of the metal cluster. The decisive role of charge transfer in the NO bond breakage, NO oxidation, and the formation of free NO_2^- and $N_2O_4^-$ ions, as well as $N_xO_{(y>x)}$-ligands on the silver clusters is discussed. The mass spectrometric data reveal the particular stability of the reaction products $AgN_2O_4^-$ and Ag_3NO^-. The reaction product mass spectra obtained for Ag_5^- in the presence of NO and CO show the depletion of the $N_xO_{(y>x)}$-ligands on the metal cluster possibly involving the oxidation of CO to CO_2.

Keywords: Ion trap mass spectrometry; Ion catalysis; Silver clusters; Nitric oxide; CO oxidation

1. Introduction

Nitric oxide (NO) plays an important role in many biological and chemical processes. For instance, it is known to be a key physiological regulator in biological processes [1]. At the same time, NO and the higher oxides of nitrogen NO_x are toxic gases liberated during combustion processes in power plants and automobile engines. In atmospheric environment these molecules are very reactive and responsible for the ozone production in urbanities and the generation of acid rain [2]. Modern catalysts, like the three-way catalyst in automotive exhaust converters, aim to eliminate NO_x. During the catalytic process NO is reduced via the catalytically active material and at the same time CO, which is another toxic side product of hydrocarbon combustion, is oxidized:

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \tag{1}$$

This reaction is highly exothermic releasing 343.9 kJ/mol [3]. The most efficient catalyst material known so far is rhodium, but the high cost of this noble metal has stimulated efforts to replace it by a less expensive material. One possible alternative process is the reduction of NO on an alumina supported silver catalyst in the presence of oxygen containing hydrocarbons like ethanol and acetone [4]. Molecular oxygen adsorbed and activated on the catalyst is responsible for this reaction. Both, bulk silver and supported silver catalysts have been characterized with respect to their reactivity toward NO and O_2 [5], the catalytic reaction mechanism itself, however, is still unclear. In particular, the identification of catalytically active sites presents an important issue in catalysis. In this respect studies of small clusters in the gas phase may support the quest for the elementary reaction steps of chemical and catalytic reactions and for the identification of the active sites.

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1387-3806/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.ijms.2006.08.008

Recently, small, size-selected gold clusters were shown to be active catalysts in the CO oxidation reaction by molecular oxygen [6,7]. In a previous study, our group was able to demonstrate that silver cluster anions (Ag_n^-, $n = 7$, 9, 11) do also facilitate this reaction [8,9]. The gas-phase ion trap measurements revealed that a critical cluster size of four silver atoms exists for which a coadsorption of O_2 and CO on Ag_n^- is possible at 100 K. The resulting products $Ag_nCOO_2^-$ are presumed to represent key model systems for the investigation of the catalytic CO oxidation reaction [9]. Interestingly, small palladium clusters deposited on a magnesium oxide surface require a minimum cluster size of five atoms to be catalytically active in the NO + CO reaction [10].

In this contribution we present the first investigation of the reactivity of small free mass-selected silver cluster anions, Ag_n^- ($n = 2$–5), with NO and mixtures of NO with CO. The results reveal the importance of cluster size dependent charge transfer from the metal cluster to the NO ligands with respect to the formation of $Ag_nN_xO_y^-$ ($x < y$) compounds. Furthermore, the influence of the internal degrees of freedom on the stabilization of the energetically excited cluster-adsorbate-complex will be discussed. Finally, the experimental data indicate that Ag_5^- is possibly catalytically active in the reduction of NO in the presence of CO.

2. Experimental

The experimental set-up has been described in detail previously [11,12]. Briefly, silver cluster anions are produced with a sputter cluster source. The experimental procedure for the investigation of metal cluster reactions consists in storing the mass-selected cluster ions in a radio frequency(rf)-octopole ion trap filled with about 1 Pa of helium buffer gas and small partial pressures of reactant gases. These conditions ensure multi-collision reaction dynamics in the low pressure regime of chemical kinetics [13] and provide rapid thermal equilibration [12]. Temperature control inside the trap between 20 and 300 K is achieved with a helium cryostat attached to the trap enclosure. The initial cluster concentration in the ion trap is defined by the space charge limit (about 10^4 ions per mm^3). After a defined reaction time t_R, i.e., a selected storage time of the ions in the rf-trap (a few milliseconds up to several seconds), the product ions are extracted from the trap and mass-analyzed.

The reactivity of Ag_n^- toward NO appeared to be very strong so that only a small partial pressure of the reactive gas compared to the He buffer gas (1%) was introduced into the trap. However, even at the lowest measurable NO pressure, p_{NO}, the bare silver clusters form reaction products very rapidly and after $t_R = 200$ ms no further changes in the product concentrations were observed. Due to these high reaction rates, no reliable reaction kinetics could be recorded with our experimental set-up and instead only product mass spectra were measured for different reaction times. This implies that proposed reaction mechanisms cannot be validated unambiguously, but they relate to the known reaction pathways of NO chemistry. In addition, the nomenclature chosen for the reaction products $Ag_nN_xO_y^-$ is purely stoichiometric, since through mass spectrometry no structural information about the formed complexes can be obtained.

3. Results

Representative product mass spectra for the reactions of Ag_2^-, Ag_3^-, Ag_4^-, and Ag_5^- with NO at a reaction temperature $T = 300$ K and two different reaction times $t_R = 5$ ms and 200 ms are depicted in Fig. 1. No further changes in the product ion distributions are observed at longer reaction times than 200 ms. All initial metal cluster ion signals Ag_n^- (mass peak position marked by rightmost dashed line in each mass spectrum depicted in Fig. 1a–d) almost vanish already after $t_R = 5$ ms. Concurrently, several product peaks appear at lower masses than the initial bare silver clusters. This implies a strong fragmentation of the clusters Ag_n^- as a consequence of the reaction with NO. Interestingly, even for the larger clusters, no NO adsorption reaction sequences (see, e.g., [14–16]) are detected. Only very distinct fragment ion peaks are observed with prominent (magic) product mass signals, like $AgN_2O_4^-$, $Ag_2NO_2^-$, and Ag_3NO^-, similar for all investigated silver cluster anions with larger initial masses (Fig. 1a–d). This might indicate the prevalence of similar major reaction mechanisms for the different cluster sizes and will be detailed further below. Most of the observed product ions do not correspond to simple NO adsorption complexes $Ag_nN_xO_y^-$ with $x = y$, but to oxidation reaction products with $x < y$.

At longer reaction times ($t_R = 200$ ms, $T = 300$ K) in Fig. 1a and b, all products and the initial metal cluster ion signals Ag_2^- and Ag_3^- have completely disappeared except of one single product peak at a mass of 200 amu. This product ion corresponding to the stoichiometry $AgN_2O_4^-$ is the most prominent mass peak for Ag_4^- at $t_R = 200$ ms, too. Besides, a second product, Ag_3NO^-, remains (354 amu, Fig. 1c). $AgN_2O_4^-$ is also present after $t_R = 200$ ms for Ag_5^- together with Ag_3NO^-, which is however now the most abundant product ion at $t_R = 200$ ms (Fig. 1d).

In the case of the silver dimer Ag_2^- (Fig. 1a), charge transfer from the metal cluster to the adsorbate molecules is manifested by the appearance of the products NO_2^- (100 K, 200 ms) and $N_2O_4^-$ (300 K, 5 ms). The presence of these product ions also demonstrates that oxidation of nitric oxide proceeds on the silver clusters. The occurrence of NO adsorbate oxidation is supported by the observation that most reaction products of $Ag_{2–5}^-$ correspond to $Ag_nN_xO_y^-$ complexes with $x < y$ and at maximum $2x = y$.

The reactions of $Ag_{2–5}^-$ were also investigated at a temperature of 100 K. In the case of Ag_2^-, Ag_3^-, and Ag_4^- identical reaction products were observed as at 300 K except for NO_2^-, which was only detected for Ag_2^- at 100 K and long reaction times. For Ag_3^-, though the same product ions appear as at 300 K, the final reaction products are formed a few hundred milliseconds later at 100 K which can be related to the closed shell paired valence electron structure of this ion compared to the open shell clusters Ag_2^- and Ag_4^- [17]. The reaction was however still too fast on the time scale of our instrument for kinetic data to be obtained reliably. For Ag_5^- not only the final product ion distribution at 300 K differs from those of the

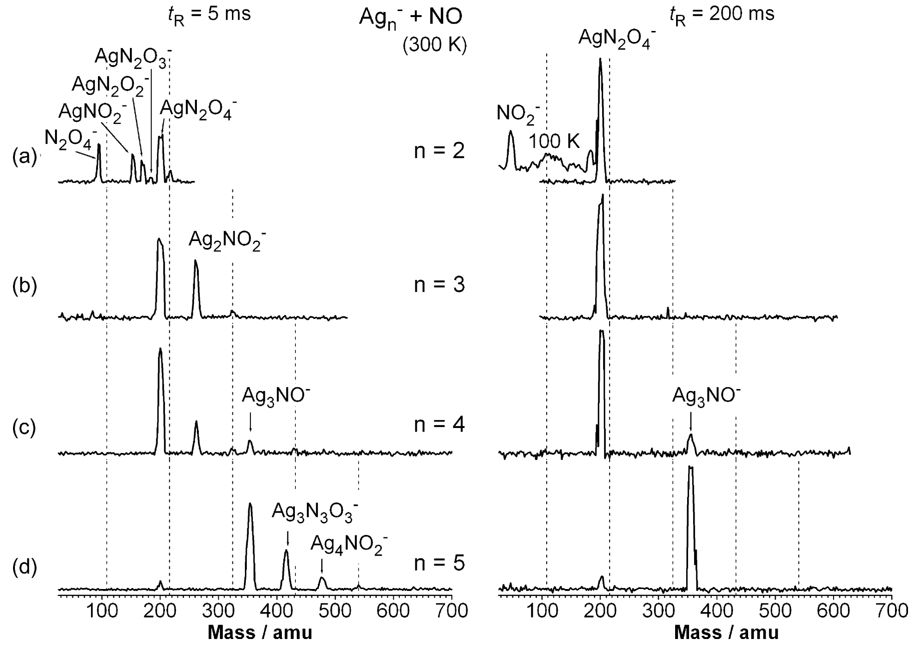

Fig. 1. Product ion mass spectra (ion intensity vs. ion mass) obtained after reaction of mass-selected Ag_n^- with NO in the rf-ion trap for $t_R = 5$ ms (left column) and $t_R = 200$ ms (right column), respectively. Reaction temperature: 300 K; $p_{NO} = 0.01$ Pa; $p_{He} = 1.0$ Pa. The dashed vertical lines indicate the mass positions of bare silver metal clusters Ag_n^-. The rightmost dashed line in each spectrum thus corresponds to the mass of the initial metal cluster: (a) Ag_2^-; (b) Ag_3^-; (c) Ag_4^-; (d) Ag_5^-. The spectrum inserted in (a) (right graph) with a slight ordinate offset shows the detection of NO_2^- at 100 K. Note that in no case adsorption complexes of the initial metal clusters are detected.

smaller clusters (Fig. 1, $t_R = 200$ ms), also the low temperature reaction behavior is in marked difference to that of Ag_2^-, Ag_3^-, and Ag_4^-. In Fig. 2a product ion mass spectra of the low temperature reaction of Ag_5^- with NO at $t_R = 5$ ms and 200 ms are presented. While at 300 K only reactive fragmentation is observed, it is strongly reduced at 100 K, and multiple NO adsorption on Ag_5^- is apparent at this reaction temperature (cf. Fig. 2a). The silver pentamer at 100 K is the first cluster size for which NO adsorption complexes are detected without decomposition of the initial silver cluster itself. Still, minor fragmentation

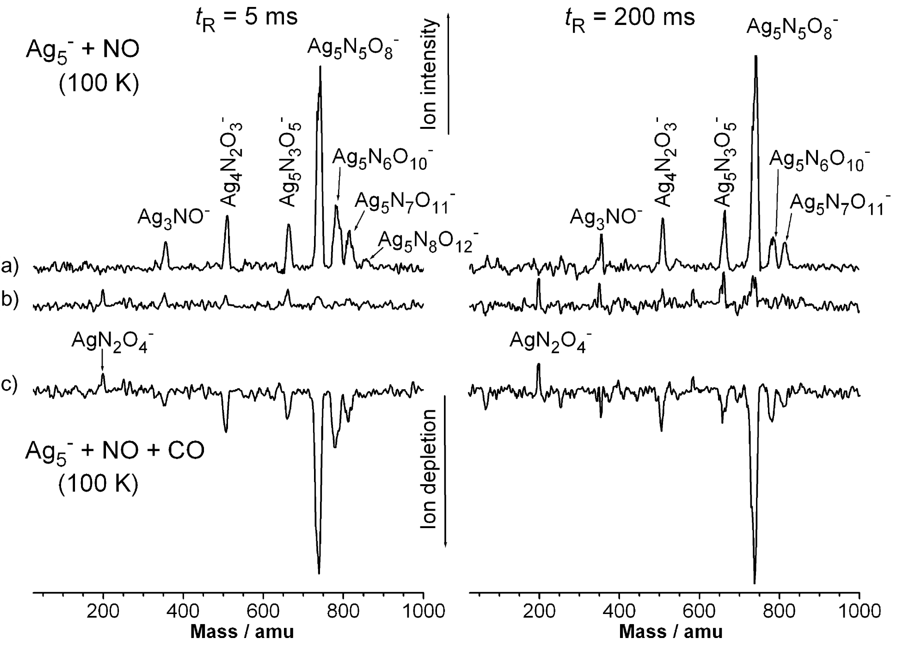

Fig. 2. (a) Product ion mass spectra obtained after reaction of Ag_5^- with NO at 100 K for $t_R = 5$ ms (left mass spectrum) and $t_R = 200$ ms (right mass spectrum). Partial pressures: $p_{NO} = 0.01$ Pa; $p_{He} = 1.0$ Pa. (b) Product ion mass spectra obtained after reaction of Ag_5^- with a mixture of NO and CO under otherwise identical conditions ($p_{CO} = 0.16$ Pa), (c) difference, i.e., reaction depletion mass spectra for the reaction of Ag_5^- with NO and CO at $t_R = 5$ ms (left) and $t_R = 200$ ms (right). The mass spectra for the reaction of Ag_5^- with solely NO (a) have been subtracted from the product mass spectra obtained after reaction of Ag_5^- with a mixture of NO and CO (b).

is observed with Ag_3NO^- being the smallest fragment. Again, just very selected fragments appear, namely only $Ag_4N_2O_3^-$ apart from Ag_3NO^-, indicating major prominent reaction pathways. Also, no $Ag_5N_xO_y^-$ products with $x = y$, i.e., single and multiple NO adsorption without subsequent detectable reaction, are observed. Instead, all products detected, $Ag_5N_3O_5^-$, $Ag_5N_5O_8^-$, $Ag_5N_6O_{10}^-$, $Ag_5N_7O_{11}^-$, and $Ag_5N_8O_{12}^-$, are results of oxidation reactions leading to products $Ag_5N_xO_y^-$ with $x < y$. However, the oxidation is not complete as $2x = y$ is reached in none of these reaction complexes. This fact already indicates that the product complexes observed for Ag_5^- at 100 K might represent intermediates in the reaction mechanisms leading to the final reaction products observed at 300 K ($AgN_2O_4^-$ and Ag_3NO^-, cf. Fig. 1d). The observation of reaction intermediates at low temperatures requires the presence of activated reaction steps, i.e., energy barriers along the reaction paths, in the NO oxidation and the reactive fragmentation reactions [7,12]. These energy barriers might easily be overcome under room temperature conditions, but present an obstacle at cryogenic temperature, enabling the detection of the adsorption complexes, which need thermal activation before further reaction might proceed. On the other hand, no or negligible activation energy barriers are apparently involved in the formation reactions of the observed intermediates in Fig. 2a, because the products are readily formed within a few ms even at 100 K and the ion distribution remains almost unchanged at longer reaction time of 200 ms. Such barrierless reaction steps with increasing reaction rate at decreasing temperature are typical for ion–molecule reactions and are explained within the Lindeman energy transfer model for gas phase association reactions [7,12,13].

In order to study the potential catalytic properties of silver cluster anions toward the NO conversion reaction (1), reactivity studies with well defined reactive gas mixtures of NO and CO were performed. When NO and CO are introduced into the trap, no new reaction products are observed in the mass spectra, but the intensities of the product ions obtained with solely NO change. In the case of Ag_2^-, Ag_3^-, and Ag_4^- only slight changes in the product mass spectra (not shown) compared to Fig. 1a are observed [18]. For Ag_2^-, the observed fragmentation products are reduced in intensity, but $AgN_2O_4^-$ remains the dominant peak and does not change significantly in intensity. Also the apparent charge transfer reaction products NO_2^- and $N_2O_4^-$ are detected in similar abundance. In the case of Ag_3^-, no quantitative nor qualitative changes in the peak intensities are detected. For Ag_4^-, an Ag_3^- fragment is not detected and the $AgN_2O_4^-$ signal is reduced.

The reaction of Ag_5^- with the reactant gas CO in addition to NO in the ion trap leads already at short reaction times to a drastic decrease of the $Ag_5N_xO_y^-$ product peak intensities as well as of the fragment ion peak $Ag_4N_2O_3^-$ compared to the reaction with solely NO. The only product that does experience only minor depletion when carbon monoxide is added, is Ag_3NO^-.

The relative change of the ion signals is clearly visible in Fig. 2b, which displays the difference spectra between the product mass spectra of reaction with both, NO + CO, and NO only. The single newly appearing reaction product and also smallest fragment peak corresponds to $AgN_2O_4^-$, which is the second, less abundant final product of the reactive fragmentation of Ag_5^- at elevated temperature. In addition, clearly, a loss of the total ion signal occurs.

4. Discussion

The following discussion will focus first on potential mechanisms for the observed NO oxidation reactions leading to products $Ag_nN_xO_y^-$ with $x < y$. Second, experimental evidence for the decisive role of charge transfer in the nitroxyl chemistry on the silver cluster anions will be evaluated. The third part of the discussion will be dealing with the prominent (magic) single product peaks $AgN_2O_4^-$ and Ag_3NO^- and their size dependent appearance as final reaction products of the reactive fragmentation of Ag_n^-. Finally, the low temperature chemistry and catalytic activity of Ag_5^-, compared to $Ag_{2\text{–}4}^-$ will be discussed in terms of statistical rate theory.

The observation of the oxidized reaction products $Ag_nN_xO_y^-$ with $x < y$ implies the breaking of the NO bond on the metal cluster. As no monoxide complexes Ag_nO^- are present in the mass spectra, it can be argued that the NO dissociation is facilitated by the adsorption of a second NO molecule and that an intermediate complex Ag_nO–N–O^- is formed subsequently. For the silver dimer Ag_2^-, the complex $AgNO_2^-$ (154 amu) is detected at short reaction time (see Fig. 1a, $t_R = 5$ ms). Apparently, the energy release during the NO dissociation reaction also induces fragmentation of the initial metal cluster Ag_2^-. For Ag_3^-, Ag_2NO_2 is detected at 262 amu (Fig. 1b, $t_R = 5$ ms). $Ag_2NO_2^-$ is also detected in the case of Ag_4^- (Fig. 1c, $t_R = 5$ ms). For Ag_5^-, $Ag_4NO_2^-$ is observed (478 amu, Fig. 1d, $t_R = 5$ ms). The formation of O–N–O ligands after multiple NO adsorption was also observed in the reactions of nickel cluster anions previously [19–22]. The NO dissociation on the metal clusters can be rationalized in terms of frontier orbital considerations: NO has 11 valence electrons and the electronic configuration $2s\sigma_g^2\ 2s\sigma_u^{*2}\ 2p\pi_u^4\ 2p\sigma_g^2\ 2p\pi_g^{*1}$. From a chemical point of view, the binding of NO is unusual since it can act as an electron donor or an electron acceptor, i.e., either donate its $2p\pi_g^*$ electron or accept electron density into the half filled $2p\pi_g^*$ orbital. Theoretical calculations show that in complexes with NO, a charge transfer from silver to the antibonding $2p\pi_g^*$ orbitals of NO takes place, therefore weakening the N=O bond [23]. Coadsorption of a second NO molecule can enhance the $2p\pi_g^*$ charge transfer effect and thus lead to the dissociation of one N=O bond.

A possible driving force for the observed extensive decomposition of the small silver cluster anions in reaction with NO might also be found in the favorable formation of neutral silver or silver oxide cluster fragments. In studies with cationic silver oxide clusters [24,25], e.g., decomposition channels leading to the release of Ag, Ag_2, Ag_2O, and even O atoms could be identified. In the results presented here, however, it turns out to be very difficult to identify the pronounced loss of a particular neutral silver or silver oxide cluster species because of the complete lack of sequential decomposition series in the reaction mass spectra. In addition, intermediate reaction products might immediately react with further NO molecules in the ion trap rendering the assignment of neutral silver or silver oxide cluster fragments involved in the formation of the ionic products highly ambiguous.

On the Ag(1 1 1) surface, the dimerization of NO, i.e., the formation of N_2O_2, could be identified as an initial reaction step after NO adsorption [26]. In Fig. 1a, $AgN_2O_2^-$, an intermediate with similar adsorbate stoichiometry is observed in the reaction of Ag_2^- with NO. $(NO)_2^-$ exists as a free molecule in the gas phase as well and exhibits a relatively high vertical electron detachment energy (VDE) of 2.93 eV [27,28]. The mechanism of the subsequent dissociation of the NO bond on the Ag(1 1 1) surface has also been investigated. Accordingly, the following reaction scheme was formulated [29]

$$2NO \rightarrow (N_2O_2)_{ad} \rightarrow N_2O_{ad} + O_{ad} \qquad (2)$$

where the index 'ad' refers to a species adsorbed on the silver surface. The NO dimerization thus not only leads to a dissociated NO bond but also to the formation of an N_2O molecule, even at low temperature reaction conditions of 90 K [26]. Experiments of NO adsorption on thin MgO films also demonstrate that N_2O is released at low temperatures [30]. Concurrent theoretical calculations emphasize that the presence of excess electrons due to F-centers in the MgO surface promotes N_2O production through charge transfer activation of the N=O bond in the $(N_2O_2^{\delta-})_{ad}$ precursor molecule [30]. Therefore, the release of an N_2O molecule might be assumed in the reactions leading to the formation of $Ag_nN_xO_y^-$ with $x < y$ as well. However, as stated above, no monoxide ions Ag_nO^-, but complexes $Ag_nO–N–O^-$ were detected in the current experiments. This points either toward a very high reaction rate of Ag_nO^- in the subsequent sequential reaction with NO evading its detection under our experimental conditions [31] or toward the involvement of a third NO molecule directly in the oxidation mechanism. The disproportionation of three nitric oxide molecules into N_2O and NO_2 is thermodynamically downhill and releases 104 kJ/mol [3]:

$$3NO \rightarrow N_2O + NO_2 + 104\,\text{kJ/mol} \qquad (3)$$

However, NO gas is kinetically inert, but the metal cluster could indeed effect this transformation of three adsorbed NO molecules.

One of the most interesting features in the mass spectra is the appearance of ions at a lower mass than the silver atom. We assign the peak at 46 amu in the 100 K spectrum displayed as an inset in the right ($t_R = 200$ ms) mass spectrum of Fig. 1a to the species NO_2^- which may be generated by a mechanism on Ag_2^- analogous to the surface reaction (3). NO_2^- could already be detected in previous reactivity studies of Nb_n^- [32] and Ni_n^- [19–22] with NO. The formation of NO_2^- requires a complete electron transfer from Ag_2^- to the product NO_2^-. This electron transfer is however understandable since the electron affinity (EA) of NO_2 formed in analogy to reaction (3) ($EA(NO_2) = 2.273$ eV [33]) is larger than the electron affinity of the silver dimer ($EA(Ag_2) = 1.023$ eV; vertical electron detachment energy $VDE(Ag_2^-) = 1.06$ eV [34]) and also larger than the electron affinity of the second product of reaction (3), N_2O ($EA(N_2O) = 0.22$ eV [35]). The reason, why NO_2^- is not observed at 300 K is yet unclear, but might relate to thermal electron detachment due to the large reaction enthalpy released during its formation. At $t_R = 5$ ms, a product ion of the Ag_2^- reaction is observed at 92 amu corresponding to the mass of $N_2O_4^-$ (Fig. 1a). Dimers and even trimers of NO_2^- were also observed in previous experiments [19–22]. Interestingly, in the case of the silver trimer, tetramer, and pentamer anions (Fig. 1b–d), the products NO_2^- and its dimer $N_2O_4^-$ could not be detected, although the electron detachment energies of Ag_4^- and Ag_5^- are favorable for the electron transfer reaction ($VDE(Ag_3^-) = 2.43$ eV, $VDE(Ag_4^-) = 1.65$ eV, $VDE(Ag_5^-) = 2.11$ eV [34]). The investigation of mass-selected metal clusters in the present study thus provides for the first time clear and direct evidence for this cluster size dependent charge transfer mechanism leading to free NO_2^- and $N_2O_4^-$ formation in the case of the silver dimer. The importance of charge transfer and metal cluster electron affinity to the bonding of NO has also been evidenced in a theoretical contribution on NO adsorption on gold cluster anions [36]. Further experimental evidence for the NO bond activation on free gold clusters is provided by recent gas phase infrared spectroscopic investigations [37].

From Fig. 1a ($t_R = 200$ ms) the cluster size dependent change in the final product of the reaction of Ag_n^- with NO is apparent. $AgN_2O_4^-$, the major end product for $Ag_{2–4}^-$, is clearly a result of a disproportionation analogous to reaction (3). Most likely, it rather has to be denoted $Ag(NO_2)_2^-$. However, the silver atom also exhibits a rather low electron affinity ($EA(Ag) = 1.302$ eV [38]) posing the interesting question of the localization of the electron in this particular stable anionic complex. In contrast, Ag_3NO^- is only appearing as major end product for Ag_5^-. It is however not clear, if the stable complex with the stoichiometry Ag_3NO^- corresponds to a structure with a single NO molecule adsorbed on Ag_3^- or to dissociated N and O bound to the metal cluster. Single NO adsorption on silver atoms and dimers has been observed in matrix isolation experiments at cryogenic temperatures [39]. Combined spectroscopic measurements and density functional calculations show that these complexes include significant charge transfer from the silver, however, not leading to a rupture of the N–O bond under such cryogenic conditions. No single NO adsorption on Ag_3^- is detected and Ag_3NO^- only exhibits small intensities in the reaction of Ag_4^- both for $t_R = 5$ ms and for $t_R = 200$ ms. These observations indicate a fundamentally different mechanism in the reactive fragmentation of Ag_5^- as opposed to $Ag_{2–4}^-$. This might originate in the larger number of internal degrees of freedom of Ag_5^- enabling more efficient internal energy redistribution. Ag_5^- is also the first silver cluster that is observed to adsorb NO without decomposition at 100 K (Fig. 2a), supporting the idea that the adsorption-reaction energy can be efficiently accommodated without fragmentation in the case of the pentamer.

A qualitative interpretation of these experimental findings involves the discussion of the redistribution of the reaction energy. NO is known to adsorb exothermically on silver surfaces, with adsorption energies between 0.47 eV for atop sites and 0.68 eV for three-fold face centered cubic sites [40]. Therefore, in reactions with Ag_n^-, the cluster-adsorbate complex has to accommodate at least the heat of reaction released during NO adsorption. Since the intramolecular vibrational redistribution (IVR) of energy is known to occur very fast already in triatomic noble metal clusters [41,42], the reaction energy will be quickly randomized among the cluster-adsorbate-complex vibrational modes s. Since $s = 3N - 6$ for a non-linear molecule of N atoms, the number of vibrational modes increases linearly with the cluster size. On the other hand, according to statistical rate theory, e.g., RRK-theory [13], the lifetime τ of the energetically excited complex increases non-linearly with s:

$$\tau \sim [E/(E - E_0)]^{s-1} \tag{4}$$

where E is the total internal energy and E_0 the dissociation energy of the respective bond leading to fragmentation of the complex.

The energy available in the critical vibrational mode, which leads to fragmentation and hence also the probability of fragmentation of the complex are reduced with increasing cluster size N. In the case of the reactions of small silver cluster anions with CO and O_2 [9], we could show that co-adsorption of both species on the cluster requires a minimum size of four silver atoms and reactive fragmentation still occurs for Ag_5^- in the presence of both reactants, but is absent for larger cluster sizes. Interestingly, this size dependent transition of the reactive behavior also appears here in the case of reactivity with NO, where cluster fragmentation is strongly diminished for Ag_5^-. This suggests that a main factor which influences the reactivity of gas phase silver clusters is the cluster size.

The investigation of the NO reduction by carbon monoxide (reaction (1)) reveals a distinct size dependence as well. The product signals shown in Fig. 1 are only slightly changed in intensity for Ag_{2-4}^- as a consequence of the addition of carbon monoxide to the ion trap. However, CO is obviously able to undergo a reaction with the N_xO_y entities attached to Ag_5^- at 100 K (cf. Fig. 2b). Recently, we could show that CO does not bind to Ag_5^- and only little reactive fragmentation occurs [9]. However, none of these fragmentation products was observed in the presence of NO and CO. In a study of NO and CO adsorption on the Ag(1 1 1) surface, a NO–CO surface complex was found at low temperature. The NO dimerization leading to N_2O production, which was observed when solely NO was dosed to the surface, was suppressed, if CO was co-adsorbed [26]. This could also explain why the $Ag_5N_xO_y^-$ product peaks disappear in the presence of CO, because the discussed oxidation reaction steps on the cluster as well are assumed to involve NO dimerization. Reactive fragmentation due to the reaction with both, NO and CO, is however also evident as the fragment $AgN_2O_4^-$ is observed which is not a product of the reaction of Ag_5^- with NO only at 100 K (Fig. 2a). It is thus possible that NO is reduced in the presence of CO involving cluster fragmentation. In recent experiments, it was shown that palladium clusters deposited on MgO films show a significant activity for the reduction of NO to N_2 in the presence of CO according to reaction mechanism (1) [10]. The minimum cluster size, which is catalytically active is Pd_5 in this case.

5. Conclusion

Reactive cluster fragmentation is found to be the main reaction channel for the clusters Ag_2^-, Ag_3^-, Ag_4^-, and for Ag_5^- in reaction with NO at 300 K under the multi-collision reaction conditions in the rf ion trap. The mass spectra obtained at longer reaction times reveal the particular stability of the product peak at 200 amu, which is assigned to $AgN_2O_4^-$. A size dependent charge transfer mechanism between the metal clusters, Ag_n^-, and the NO ligands leads to the formation of $Ag_nN_xO_y^-$ $(x < y)$ compounds and of NO_2^-. At low temperatures a non-dissociative reaction pathway opens for Ag_5^- with multiple adsorption of NO molecules onto the cluster, followed by disproportionation reactions analogous to reaction (3), producing product species of the stoichiometry $Ag_5N_xO_y^-$ $(x < y)$.

The reactivity measurements of Ag_n^- in the presence of NO and CO clearly demonstrate that the latter gas strongly reacts with the N_xO_y $(x < y)$ entities adsorbed on Ag_5^- while one stable product of reactive fragmentation, Ag_3NO^-, is only depleted to a minor extent and the other, $AgN_2O_4^-$, is even generated in the course of the reaction with carbon monoxide. These results present a first insight into the reduction of NO in the presence of CO on the small silver clusters.

Acknowledgments

DP thanks the DAAD for a fellowship. SV acknowledges support from the US Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences (contract number W-31-109-ENG-38). Financial support by the Deutsche Forschungsgemeinschaft (SFB 450) is gratefully acknowledged.

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