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Letter

Formation of antimony oxide clusters in a molecular beam

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Abstract

The formation of positively charged antimony oxide clusters has been investigated as a function of oxygen partial pressure. At low oxygen concentration oxide clusters with a large variety of stoichiometries are observed. With increasing oxygen pressure some mass peaks become prominent. The special stability of these antimony oxide clusters can be explained by simple valence bond arguments, all the antimony atoms being in a formal +III and all the oxygen atoms being in a formal −II oxidation state. A further increase in the oxygen partial pressure shifts the distribution to mixed valence oxide clusters with one or more of the antimony atoms in the formal +V oxidation state. According to this model it is possible to predict discrete structures for these clusters. They have no direct Sb–Sb bonds, instead all the Sb-atoms are bridged by O-atoms. Further oxygen can then be added in a terminal position to form the mixed valence oxides. This model is also supported by bulk and gas-phase data of antimony oxides. (Int J Mass Spectrom 177 (1998) L5–L8) © 1998 Elsevier Science B.V.

Keywords: Metal oxides; Clusters; Structure elucidation; Molecular beams

1. Introduction

The key to an understanding of the physical and chemical behavior of metal oxides and metal oxide clusters is their structure. Isolated clusters can be synthesized in a molecular beam and their distribution is easily interrogated by mass spectrometry [1,2]. In these gas-phase experiments direct geometric information is extremely difficult to obtain, because the intensity of the clusters is generally not sufficient for the application of classical structure sensitive methods. Nevertheless, mass spectrometry has turned out to be very informative in this respect, yielding indirect information through pronounced abundance maxima, the so-called magic numbers [3–6]. Here we report on the reaction of positively charged antimony clusters with oxygen, which leads to an unexpected series of stable product molecules. The stability of these cluster ions can be explained by valence bond theory using simple electron counting rules. According to this framework it is possible to predict discrete structures for these clusters.

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2. Experimental

The experimental setup consists of a three stage molecular beam apparatus. Positively charged clusters are produced in a modified pulsed arc cluster ion source (PACIS) [7] and are mass-analyzed in an on axis reflectron arrangement. Pure oxygen as reaction gas is introduced into the expansion channel of the nozzle at different partial pressures or is directly premixed with the seed gas (Helium 6.0). Details of the experimental setup will be presented elsewhere.

3. Results and discussion

Fig. 1 shows a series of mass spectra as a function of oxygen partial pressure. For the sake of clarity only a part of the total mass spectrum is shown. Without additional oxygen the pure antimony clusters are clearly identified [Fig. 1 (a)]. Small side peaks are due to oxygen contamination of the seed gas. At low oxygen partial pressure [Fig. 1 (b) and (c)], clusters with almost any possible combination of oxygen and antimony are formed. At high oxygen content [Fig. 1 (d) and (e)], the pure antimony clusters vanish and several intense peaks are visible, which are supposed to be the most stable product ions. The two most intense peaks are assigned to $Sb_3O_4^+$ and $Sb_5O_7^+$. Given that the most stable oxidation states for antimony and oxygen are +III and −II, we can count the unpaired valence electrons of these species. In the case of $Sb_3O_4^+$ we have eight *p*-electrons for three antimony atoms (three by three minus one for the positive charge) and eight unpaired *p*-electrons for four oxygen atoms. For $Sb_5O_7^+$ we get 14 electrons for five antimony and 14 electrons for seven oxygen atoms. So, in these cases all valences are saturated and all atoms, except the positively charged one, possess a noble gas electron configuration, which is a strong driving force for the formation of heteronuclear covalent bonds. We were able to follow the stable series $SbO^+(Sb_2O_3)_n$ up to $n = 5$. According to the electron counting rule presented above it is not possible for $Sb_4O_x^+$ to form a stable compound, because we get 11 *p* electrons for the antimony atoms. But the Sb_4O_6 molecule is known to be very stable in the vapor and in the bulk phase (Senarmontite), the antimony atoms forming a tetrahedron bridged along the edges by oxygen atoms [8]. Indeed we do observe $Sb_4O_6^+$, which can be explained by the formation of a radical cation. Every antimony atom then employs three p-electrons for the oxygen bonding, which again leads to an even number of bonding electrons. The radical cation can add a further oxygen atom to form $Sb_4O_7^+$, which is also clearly visible from our mass spectra. The series $(Sb_2O_3)_n^+$ and $(Sb_2O_3)_nO^+$ are observed up to $n = 4$. Another possibility for a molecule containing four antimony atoms to form a stable compound with an even number of electrons is to form a doubly charged cluster with 10 antimony and 10 oxygen valence electrons, corresponding to the formula $Sb_4O_5^{++}$, which is observed as a weak shoulder to the right of the $Sb_2O_2^+$-peak in Fig. 1 (d). The low intensity of the peak can be explained by the difficulty of such a small molecule to distribute two positive charges. A more clear signal is seen for $Sb_8O_{11}^{++}$ [Fig. 1 (d)], which appears to the left of the $Sb_4O_6^+$ peak. The same argument applied in the case of $Sb_4O_5^{++}$ is valid for this molecule, except that here there is a better stabilization of the two charges. At increasing oxygen partial pressure further oxidation takes place to form the mixed valence clusters $(Sb^VSb_2^{III}O_5)^+$ and $(Sb_2^VSb^{III}O_6)^+$, which can be explained by the formation of some of the antimony atoms in the +V oxidation state. These mixed valence clusters also appear for the larger clusters in the series $SbO^+(Sb_2O_3)_n$.

The mass spectral data are further supported by experiments in our laboratory, in which antimony oxide clusters are produced by the gas aggregation technique, either by vaporizing antimony and letting it react with pure oxygen or by direct vaporization of solid Sb_2O_3 [9,10]. Similar results have also recently been obtained for the production of antimony and bismuth oxide clusters using a laser vaporization source [11].

According to the framework presented above, which requires that there are no direct Sb–Sb bonds, we are able to propose discrete structures for the observed molecules. Probable structures for selected isomers of the clusters $Sb_3O_4^+$ and $Sb_5O_7^+$ are depicted in Fig. 2, where all antimony atoms are bridged by

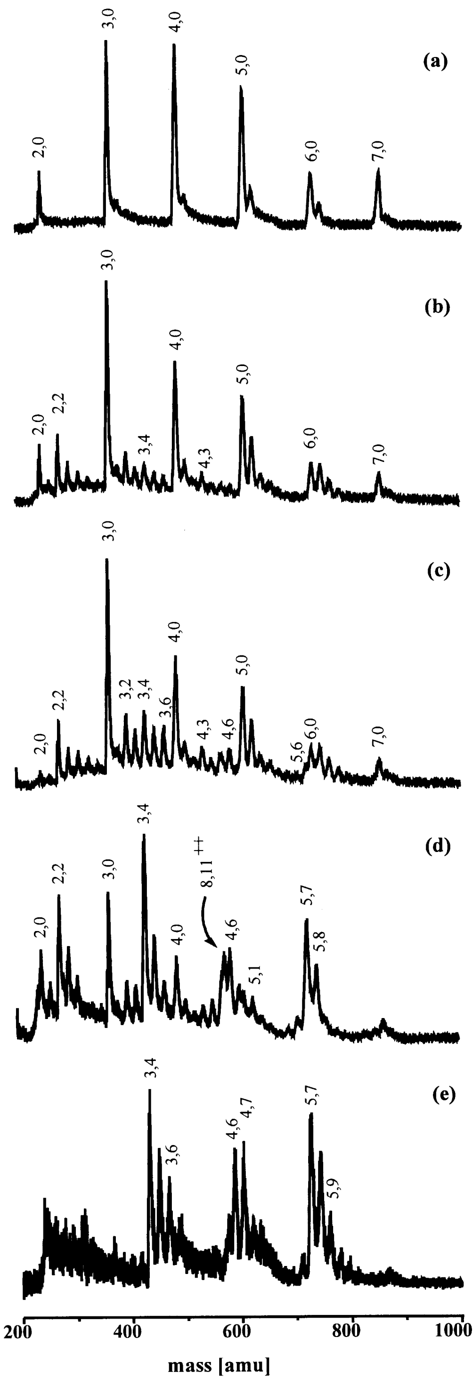

Fig. 1. Mass spectra of antimony oxide clusters produced in an arc discharge cluster ion source at different partial pressures of oxygen: (a) 0, (b) 2.6, (c) 5.3, (d) 20, (e) 40 mbar. Vertical axis displays relative intensity (arb. units). Peak assignment "*x*,*y*" corresponds to the cluster $Sb_xO_y^+$.

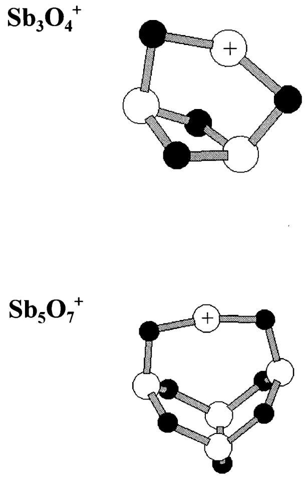

Fig. 2. Proposed structures for selected antimony oxide clusters according to the model developed in the text. Oxygen atoms are represented by filled circles. The + signs indicate the antimony atoms, which carry the positive charge.

oxygen atoms. The mixed valence antimony oxide clusters can then be formed by the addition of a maximum of one terminal oxygen atom per antimony atom in a double bond configuration. Possible structures for $Sb_3O_5^+$ and $Sb_3O_6^+$ are shown in Fig. 3. For each depicted structure geometry optimization has been carried out with the MM+ force field in the

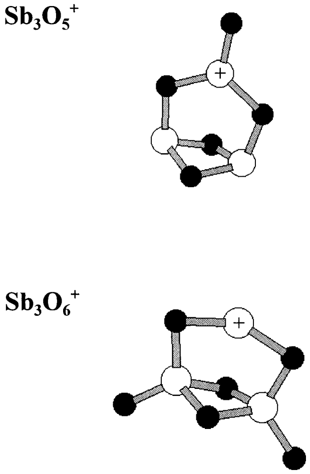

Fig. 3. Proposed structures for selected mixed valence antimony oxide clusters according to the model developed in the text. Oxygen atoms are represented by filled circles. The + signs indicate the antimony atoms, which carry the positive charge.

Hyperchem environment (Hypercube, Inc., Waterloo, Ontario, Canada) [12].

Solid Sb_2O_3 is known to exist in two different modifications, namely Senarmontite and Valentinite [8]. Senarmontite is made up of Sb_4O_6 units, whereas in Valentinite alternate antimony and oxygen atoms are linked into bands. It would be interesting to follow the growth of the above presented cluster ion series $SbO^+(Sb_2O_3)_n$ and $(Sb_2O_3)_n$ to larger clusters to see whether the building blocks of the macroscopic modifications are already found in these small clusters. Sb_2O_4 is known to consist of antimony atoms in the oxidation state $+$III and $+$V, in the gas as well as in the solid phase, which is also observed in our experiment. In particular, these mixed oxides are of special interest for heterogeneous catalytic processes [13].

Acknowledgements

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