which were suitable for single-crystal X-ray determination. The crystals were separated from the silica gel manually. Yield: ≈70%. Our attempts to obtain the title compound by simply mixing the solutions of starting materials were unsuccessful. However, the compound can be prepared by slow diffusion of reagents through a fritted glass filter (pore size several microns).

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[15] Crystal data for $[\mathrm{Cu_4}(\mu_3\text{-OH})_4][\mathrm{Re_4}(\mu_3\text{-Te})_4(\mathrm{CN})_{12}]$: tetragonal, space group $I4_1/amd$, $Z=4$, $a=10.236(1)$, $c=28.25(1)$ Å, $V=2960(1)$ Å^3, $\rho_{\text{calcd}}=4.240\ \mathrm{g\,cm^{-3}}$, $\mu=23.006\ \mathrm{mm^{-1}}$, 1886 reflections measured, 1082 independent reflections ($R_{\text{int}}=0.0398$), min./max. transitions = 0.815/1.185, 58 parameters, $R(F)=0.0319$ and $wR(F^2)=0.0693$ for 667 reflections having $F_o^2>2\sigma(F_o^2)$, residual electron density 2.23 e Å^{-3}. Data were collected by a standard technique at room temperature on an Enraf-Nonius CAD-4 diffractometer ($\theta_{\max}=30°$), with $\mathrm{Mo_{K\alpha}}$ radiation ($\lambda=0.71069$ Å) and ω scan mode. Data were corrected for absorption with four azimutal scans. The structures were solved by direct methods and refined anisotropically on F^2 for all independent reflections by-full-matrix least-squares method, (SHELX-97).[16] The residual electron density peaks lie very close to heavy atoms and, therefore, do not correspond to any chemically appropriate positions. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408291.

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Reactions of Selected Bismuth Oxide Cluster Cations with Propene**

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Klaus Rademann*

Many chemical and physical properties of metal clusters have been determined over the past few years.[1] One of the main reasons for studying these compounds—in addition to carrying out fundamental research in itself—is the hope of obtaining a deeper insight into the sequence of events involved in catalytic processes.[2] To this end, the reactions of pure metal clusters deposited on surfaces and of free particles in the gas phase were studied.[3] Moreover, a great number of experiments on the formation and stability of metal oxide clusters have been carried out, but very little is known about the reactions themselves.[4] This is all the more astonishing when one considers that metal oxides in particular are widely employed as catalysts in the chemical industry. Bismuth oxide compounds are used, for example, in the oxidation of propene and butene.

We prepared bismuth oxide clusters with a modified gas aggregation source and carried out reactions with them. In order to do this, the pure metal was vaporized directly into a stream of cooled helium, whereupon clusters were formed due to oversaturation. Bismuth oxide clusters were formed by adding oxygen to the bismuth vapor. These were then ionized by using a short-pulse excimer laser (ATL, pulse length 2–4 ns, wave length 248 nm, laser energy 10 mJ) and identified by using a Wiley-McLaren mass spectrometer. The oxidation did not lead to a broad distribution of different mixed oxides, but rather to a cluster series with the general formula $\mathrm{BiO^+(Bi_2O_3)}_n$.[5] The structures of the $\mathrm{Bi_3O_4^+}$ and $\mathrm{Bi_5O_7^+}$ isomers obtained from ab initio geometry optimizations at the MP2 level are shown in Figures 1a–c and 2a, b.[6] Two closed isomers were found for $\mathrm{Bi_3O_4^+}$ (Figures 1a, b). Attempts to formulate structures with terminal O atoms—in as far as any local minima on the potential hypersurface could be found for them—always led to considerably higher energies. The formation of structures with terminal O atoms can thus be excluded under experimental conditions. The open isomer (Figure 1c) is, at 4.6 eV, higher in energy than the isomer in Figure 1a. The ground state in all three structures is a singlet and the corresponding vertical singlet–triplet splittings are 4.6, 3.5, and 1.8 eV. Two isomer types are observed for the closed structures $\mathrm{Bi_3O_4^+}$ and $\mathrm{Bi_5O_7^+}$. In type 1 (Figures 1a and

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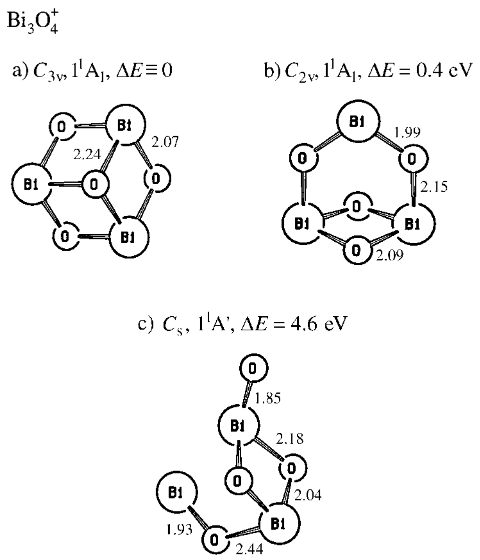

Figure 1. Optimized structures (ORTEP) of $Bi_3O_4^+$ isomers showing the point group, the term symbols, the energy difference ΔE relative to the isomer under a), and the bond lengths [Å].

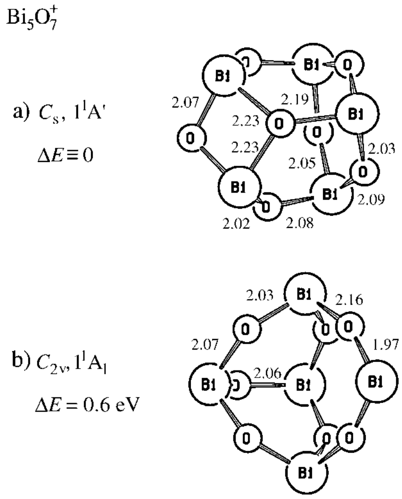

Figure 2. Optimized structures (ORTEP) of the $Bi_5O_7^+$ isomers.

2 a), all Bi atoms have the coordination number 3. In addition, one of the O atoms is also three-coordinate. In contrast, cluster type 2 (Figures 1 b and 2 b) contains a two-coordinate (and therefore coordinatively unsaturated) Bi atom. The three-coordinate O atom in type 1 can be considered as the result of a donor–acceptor bond between Lewis acid and Lewis base centers within the cluster.

In order to carry out further reactions with these oxides, it was necessary to place them in a collision cell, which could be fed with various reaction gases. By operating the cell at low pressure, single collision conditions were imposed on the reactions. Figure 3 a shows the change in the detected bismuth oxide cluster distribution with increasing propene partial pressure in the cell. Even with very low amounts of propene a considerable decrease was observed in the intensity of the oxide peaks. With increasing pressure the intensity of the oxide peaks decreased still further. The change in intensity of the peaks assigned to the pure metal clusters was not significant.

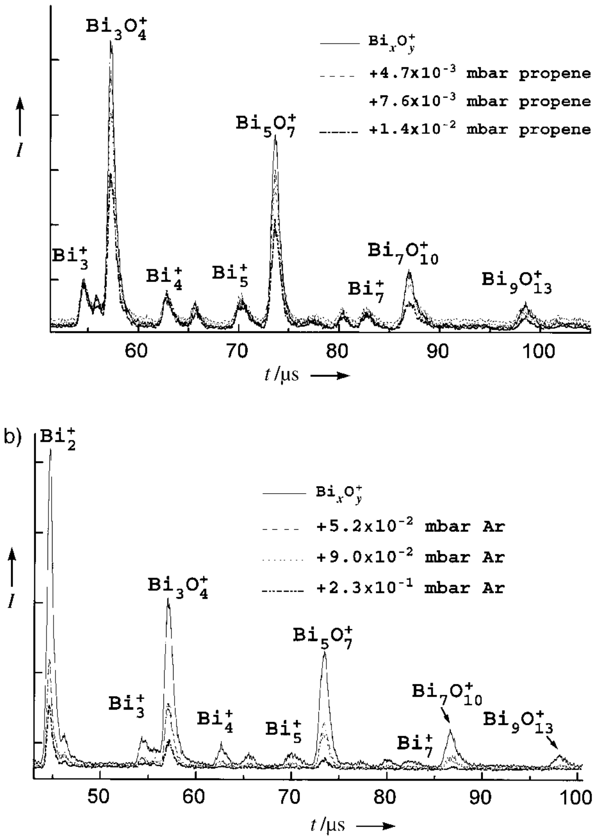

Figure 3. Mass spectra showing the change in intensity distribution of selected bismuth oxide cluster ions and bismuth cluster ions with increasing propene (a) and argon (b) partial pressures. t = time of flight.

These appeared not to react with the propene. The reaction products could not be determined due to the extremely low particle concentration. As the times of interaction were very short and only single collisions occurred, the oxidation of propene leading to CO_2 was rather improbable. In order to be certain that the observed phenomena were not just due to scattering processes, an inert gas (argon) was introduced into the cell. No effect was observed with argon at the same partial pressures used before. A significant change was first observed at higher pressures, but the intensities of all clusters and cluster oxides decreased with increasing argon partial pressure (Figure 3 b). In contrast to the reactions with propene, it is highly probable that this decrease can be attributed to unreactive collisions and scattering processes.

Solid bismuth oxides employed for catalytic purposes are normally used in the form of multicomponent mixtures with other oxides (e.g. $Bi_xMo_yO_z$).[7] Pure bismuth oxide is usually reduced by propene to give elemental bismuth. It was shown, however, that solid bismuth oxide Bi_2O_3 can also be catalytically active under suitable reaction conditions.[8] One of the central questions concerning these oxidations is whether only the terminal oxygen atoms take part in the reaction, or if the bridging oxygen atom also participates. It was assumed that the bridging oxygen atom is not reactive enough to participate in the oxidation process.[9] The minimum requirement on any model substance for bismuth oxide catalysts is clearly that it reacts with propene.

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As the bismuth oxide cluster ions we used have no terminal oxygen atoms, the reactions we carried out show quite clearly that bridging oxygen atoms can indeed participate in oxidation reactions. This is all the more astonishing when one considers that the bismuth oxide clusters detected should be particularly stable compounds due to their "magic" character.[5] In addition, an analysis of the mass spectra indicated—in contrast to what was expected—that no clear size-dependent reactivity could be established for the metal oxides. Even the smallest cluster ions studied behaved similarly to solid bismuth oxide and were reduced by propene. In order to be sure that the reactions did not occur simply due to the higher energy associated with the accelerated and charged particles, the same reactions were performed with neutral bismuth oxide clusters. These experiments also resulted exclusively in a reduction of the oxides. The reduction admittedly first set in at partial propene pressures about one order of magnitude higher in the case of the nonaccelerated uncharged bismuth oxide clusters.[10] The higher energy of the cations thus leads to an increase in the reaction cross-section, but the special selectivity of bismuth oxide clusters is independent of charge and not due to the increased kinetic energy of the cations. As further proof of the special reactivity of the bismuth oxide cluster ions in the oxidation of propene, the reaction introduced here was also carried out with antimony oxide cluster ions. These form stable polyoxides with the general formula $SbO^+(Sb_2O_3)_n$ similar to the bismuth oxide clusters.[11] Here too, experiments were carried out both with propene and argon. In both cases, however, an increase in the partial pressure of the collision gas merely led to a decrease in the intensities of all observed peaks. These results are also a clear indication that the reactivity of the bismuth oxide cluster cations is not due to the fact that they are higher in energy than the solid because of ionization and sublimation.

The work presented here proves for the first time that mass-selected bismuth oxide cluster ions can be reduced by propene in just the same way as solid bismuth oxide. Moreover, it has been shown for the first time that supposedly unreactive bridging oxygen atoms can actively participate in oxidation reactions. Bismuth oxide clusters may possibly provide suitable model systems for bismuth oxide catalyst systems.

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Self-Organization and Formation of Liquid Crystal Phases by Molecular Templates Related to Membrane Components of Archaebacteria**

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Molecular self-assembly and self-organization are becoming increasingly significant for the elucidation of life processes and the generation of new supramolecular structures or ensembles and molecular materials.[1–9] Concomitantly, the most important inspirations for the conceptual development of such structures and materials are those provided by biological cells, which exemplify the assembly of a variety of microstructures of different sizes and functions. Archaebacteria, with their resistance to extreme conditions, are one class of organisms that serve as a rich source of inspiration. This

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