Angewandte Chemie

Oxygen-Rich Compounds

The Molecules AlO_2, $Al(O_2)_2$, and $Al(O_2)_3$: Experimental and Quantum-Chemical Investigations on the Oxidation of Aluminum Atoms**

*Gregor Stößer and Hansgeorg Schnöckel**

Dedicated to Professor Klaus Krogmann
on the occasion of his 80th birthday

We have already mentioned the significance of peroxo- and hyperoxo complexes with unusual spin states as intermediates in oxidation processes in biology and synthetic chemistry when we reported the oxidation of AlX molecules with O_2 under matrix-isolation conditions.[1][2] The reactions of metal atoms with oxygen discussed herein also prove to be complex, since electrons are taken up stepwise by the O_2 molecules with retention of symmetry and spin rules ($O_2 \rightarrow O_2^{-} \rightarrow O_2^{2-}$). On the preparative scale, this process results exclusively cleavage of the O–O bond and the formation of O^{2-} ions; with metal cations these ions form particularly stable oxides, such as Al_2O_3. To investigate the primary steps of this reaction we have treated aluminum atoms with an increasing excess of O_2 in the matrix-gas argon under matrix-isolation conditions and have obtained the molecules AlO_2 (**1**), $Al(O_2)_2$ (**2**), and $Al(O_2)_3$ (**3**). These result are reported herein, while details of the spectra and the results of quantum-chemical calculations are given in the Supporting Information.

The formation of C_{2v} symmetrical AlO_2 (**1**) in solid argon from aluminum atoms with approximately 0.1 % O_2 has been reported elsewhere.[3]. In our experiments, and in agreement with the literature, we have observed the symmetrical AlO_2 vibration in the IR spectrum at 496 cm^{-1} and measured its $^{16}O/^{18}O$ shifts.[4] A new band at 1070 cm^{-1} is observed at higher O_2 concentrations in argon gas (1–3 %) after reaction of aluminum atoms, again in agreement with the literature.[5] $^{16}O/^{18}O$ substitution experiments indicate that this new band belongs to a species with four equivalent oxygen atoms.[6] As will be shown below, this species is $Al(O_2)_2$ (**2**), which is assigned the structure (D_{2d} symmetry) illustrated in Figure 1. At still higher O_2 concentrations in the matrix and finally in pure solid O_2 a band at 688 cm^{-1} is observed in the IR spectrum. This band shifts to 671 cm^{-1} in $^{18}O_2$ enriched O_2 and occurs at 679 cm^{-1} in the presence of $^{16}O/^{18}O$ species.[7] Since,

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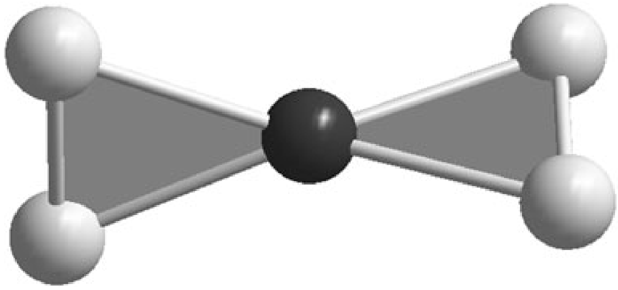

Figure 1. Minimum structure of $Al(O_2)_2$ (**2**) calculated with B3LYP/TZVPP (see Table 1).

under identical conditions, a new band appears at 1065 cm^{-1} in the Raman spectrum,[8] we have assigned these two intense bands as well as a weak signal in the Raman spectrum at 406 cm^{-1} to the molecule $Al(O_2)_3$ (**3**), whose calculated molecular structure (D_3 symmetry)is illustrated in Figure 2.

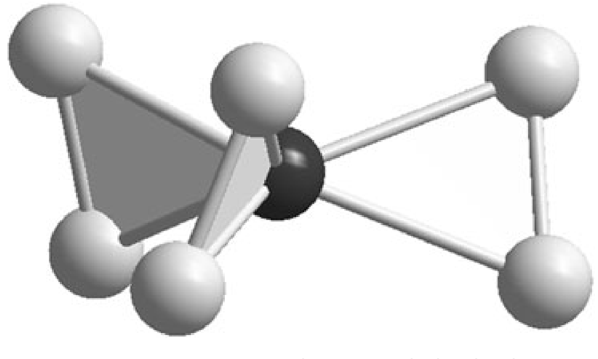

Figure 2. Minimum structure von $Al(O_2)_3$ (**3**) calculated with B3LYP/TZVPP (see Table 1).

To confirm the assignment of the cited vibrational frequencies to molecules **1**, **2**, and **3** extensive quantum-chemical calculations were carried out; these gave the Al–O and O–O distances and force constants listed in Table 1.

Table 1: Distances r [pm] and force constants f [$N\,m^{-1}$] of AlO_2 (**1**), $Al(O_2)_2$ (**2**), and $Al(O_2)_3$ (**3**) calculated with B3LYP/TZVPP.

	r_{Al-O}	r_{O-O}	f_{Al-O_2}	f_{O-O}
1	195	134	210	648
2	175	148	386	473
3	185	136	353	632

The special bond properties in **1**, its stability, and the kinetics of the conversion of its different isomers have been reported in detail recently.[9] We have been able to confirm these results according to which the observed C_{2v} hyperoxide **1** has a stability similar to that of the linear $D_{\infty h}$ isomer. Presumably the energy barrier between the two species is very high so that in our spectra only the somewhat less stable (according to calculation[9]) C_{2v} isomer is observed.[10]

For **2**, the D_{2d} isomer shown in Figure 1 is approximately 55 $kJ\,mol^{-1}$ more stable than a molecule with D_{2h} symmetry. The other isomers (C_{4v} and T_d) also lie energetically much higher (266 and 329 $kJ\,mol^{-1}$, respectively). Although only one band is observed for **2**, the assignment seems to be correct since five $^{16}O/^{18}O$ shifts were observed for this band which are in very good agreement with those calculated, and indicates that there are four equivalent oxygen atoms in this molecule. Moreover, this interpretation is plausible since the bands assigned to **2** appear after the formation of **1** and prior to the formation of **3**. The special bonding situation in **2** arises because in the highest singly occupied molecular orbital (SOMO; $1a_2$, Figure 3) one electron must be shared by both O_2 groups, that is, compared to neutral O_2, each O_2 group is weakened because it carries an additional 1.5 electrons. Hence **2** may not be described as $O_2^-Al^{3+}O_2^{2-}$ (that is, as hyperoxide with an additional peroxo group). Thus it appears plausible that the O–O bond in **2** is weaker and the Al–O bond stronger than in **1**.

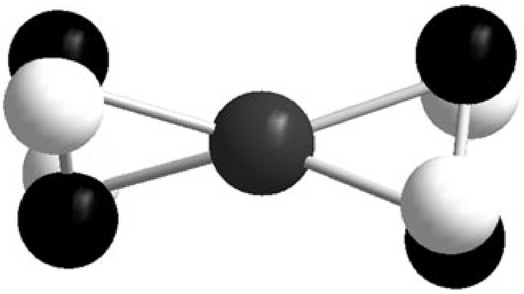

Figure 3. Graphical representation of the SOMO ($1a_2$) of $Al(O_2)_2$ (**2**).

Unlike the unusual bonding relationships in **2**, those in **3** appear analogous to the bonding relationships in the recently described $XAl(O_2)_2$ species (X = F, Cl, Br),[1] which means that in **3** there are three O_2^- groups attached to the Al^{3+} ion by interactions that are predominantly ionic in character. This situation becomes especially clear through the absence of vibrational coupling between the three O_2 vibrations, since almost identical frequencies of 1158 and 1154 cm^{-1} are calculated for the E and A_1 vibrations. In this respect, as well as with the O–O and Al–O distances and also the force constants, the expected parallels to the $XAl(O_2)_2$ species emerge. The unusual spin situation in the $XAl(O_2)_2$ compounds (triplet electronic ground states) becomes even more unusual in **3** for which a quartet ground state is found. To our knowledge this is unique for molecular compounds free of transition metals.[11] Admittedly, the energy difference between the doublet and quartet states is very small. This finding and the absence of stabilization in **3** from a Jahn–Teller distortion also provide support for an essentially ionic bonding mode. In spite of the unusual bonding situations in **1**, **2**, and **3** a consistent picture emerges for the three compounds:

The following distances and force constants were calculated for the isolated ions O_2^- and O_2^{2-}: O_2^- 135 pm, 660 $N\,m^{-1}$ and O_2^{2-} 163 pm, 190 $N\,m^{-1}$.[1] In comparison the force constants determined from the observed frequencies for

1, **2**, and **3** and the calculated distances confirm that in **1** and **3** (as with the $XAl(O_2)_2$ species) the hyperoxide ions are essentially ionically bonded to the positively charged Al centers. In **2**, in agreement with the electronic situation, the O_2 bond is clearly elongated, similar to the bond an O_2^{2-} ion. On the other hand, the Al–O bond also clearly lengthens in the order **2** < **3** < **1**, which correlates very well with the calculated Al-O_2 force constants (Table 1). These findings are illustrated in Figure 3 for the special bonding situation of compound **2**. For compound **3** and **1** this bond lengthening may be attributed to the reduced formal charge at the Al center (Al^{1+} in **1** and Al^{3+} in **3**).

The energetic ordering of the three hypervalent compounds is shown in Figure 4 and emerges from experimental thermodynamic data[12] and the quantum-mechanical results obtained in this work. Relative to 1 mol aluminum atoms, in the stepwise formation of **1**, **2**, and **3** more energy is released than for any other molecular Al_xO_y compound.[13] Nevertheless, the $Al(O_2)_n$ ($n = 1, 2, 3$) molecules described herein are certainly only obtainable in measurable quantities under matrix conditions, since the formation of alumina from $Al(O_2)_3$ is favored by 587 kJ mol^{-1}

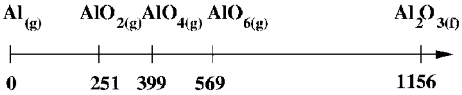

Figure 4. Energy scheme [kJ mol^{-1}] for the stepwise exothermic oxidation of Al atoms with O_2.

The results on the oxidation of aluminum atoms with excess O_2 reported herein demonstrate the complexity of such apparently trivial reactions. On the other hand, this process is an extreme situation, in the reverse case, that is, the reaction of excess aluminum atoms with few O_2 molecules is a more realistic model when it comes to the investigation of the primary products of oxidation, for example, on aluminum surfaces. This problem is at the center of current gas-phase investigations of Al_n clusters and their oxidation by O_2, reactions which are being studied with the aid of FT mass spectroscopy.[14]

Experimental section

A detailed description of the experimental construction used may be found in ref. [15]. Aluminum was evaporated in high vacuum (10^{-7} mbar) at 1400 K from a resistance-heated boron nitride cell and cocondensed with the matrix gas (Ar/O_2) for 2 h onto a copper block cooled to 10 K with a "closed cycle" cryostat (Leybold LB510). Each hour approximately 150 µg Al and 50 mmol matrix gas were evaporated. Isotope substitution experiments were carried out with $^{18}O_2$, a 1:1 mixture of $^{16}O_2/^{18}O_2$, and a 1:2:1 mixture of $^{16}O_2/^{16}O^{18}O/^{18}O_2$. The IR and Raman spectra were recorded immediately after sample deposition. The following chemicals were used in the matrix reactions: Al (Merck, 99.9999 %), Ar (Messer 99.999 %), $^{16}O_2$ (Messer 99.9998 %), $^{18}O_2$ (Linde 99.9998 %, isotopic purity 99 %).

The IR spectra were taken with Bruker (Karlsruhe) FTIR spectrometers, types 113v and 66v. DTGS and MCT detectors were used, the resolution was 1 cm^{-1}. Raman spectra were taken with a Dilor grating spectrometer, type 800. The Raman vibrations were excited with a argon ion laser (Coherent), the selected wave length was 458 nm.

The quantum-chemical DFT calculations (functional B3-LYP)[16] were carried out with the Turbomole program package.[17] The ab initio calculations were carried out at the CASSCF level with Dalton,[18] Gaussian 98[19] was used for calculation of the CCSD(T) energies. TZVPP basis sets were used for all calculations.[20]

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