Communications

The Chlorination of the [Al₁₃]⁻ Cluster and the Stepwise Formation of Its Intermediate Products, [Al₁₁]⁻, [Al₉]⁻, and [Al₇]⁻: A Model Reaction for the Oxidation of Metals?**

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By allowing chlorine gas to flow over solid aluminum at temperatures above 100 °C and under standard pressure conditions, gaseous AlCl₃ is formed: $Al_{(s)} + \frac{3}{2} Cl_2 \rightarrow AlCl_{3(g)}$. The experimentally determined reaction energy is −585 kJ mol⁻¹.[1] To understand the fundamental process of dissolving of a metal in an oxidizing atmosphere—this is analogous to dissolving a metal in aqueous acid—intermediate products of individual reaction steps on the metal surface have to be identified. Because of varying surface properties, however, it is difficult to study local (microscopic) reactivity on macroscopic metal surfaces. "Naked" aluminum (Al_n) clusters, on the other hand, are well-defined molecular model compounds and as such are well-suited for such investigations. Furthermore, the reactions of [Al₁₃]⁻ with iodine and hydrogen iodide have recently attracted significant interest.[2,3]

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Here, we report our Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometric investigations on isolated [Al₁₃]⁻ clusters and their reactions with chlorine. This is the first time that it has been possible to detect the intermediate products of such reactions, in a time-resolved manner. In particular, single elementary steps of these oxidation processes were identified. Owing to the combination of experimental results and accompanying quantum-chemical calculations, a plausible mechanism for the stepwise reactive decomposition of the [Al₁₃]⁻ cluster during its reaction with chlorine will be proposed. These elementary steps revealed during the "dissolving" of "naked" metal atom clusters in the gas phase provide topologic and energetic arguments for the understanding of analogous oxidation processes taking place on the bulk metal.

After laser desorption ionization (LDI) of LiAlH₄ a homologous series of Al_n^- cluster anions was observed by mass spectrometry. Each of these mass spectra were dominated by an intense signal at m/z 350.8, the mass of [Al₁₃]⁻. The stability of these icosahedral [Al₁₃]⁻ ions with their 40 valence electrons has been discussed in the past in terms of the jellium-like shell model.[4] In the experiment described here, [Al₁₃]⁻ ions were first isolated (stored wave inverse Fourier transformation: SWIFT) in the Penning trap of a FT-ICR mass spectrometer and then cooled using argon as a collision gas.[5,6] Upon exposing these [Al₁₃]⁻ ions to a chlorine atmosphere of approximately 10⁻⁸ mbar, new signals, attributed mainly to [Al₁₁]⁻, [Al₉]⁻, and [Al₇]⁻ (Figure 1), were observed after several tens of seconds. Thus, the [Al₁₃]⁻ cluster was decomposed in a stepwise manner to smaller aluminium clusters according to the reaction sequence (1).

$$[Al_{13}]^- \xrightarrow[-2\,AlCl]{Cl_2} [Al_{11}]^- \xrightarrow[-2\,AlCl]{Cl_2} [Al_9]^- \xrightarrow[-2\,AlCl]{Cl_2} [Al_7]^- \tag{1}$$
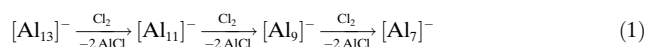
Figure 2, which is based on our experimental observations and theoretical calculations, summarizes the energetics of the stepwise reactions that form these species. In the first step, oxidation of the [Al₁₃]⁻ cluster surface proceeds to form the [Al₁₃Cl₂]⁻* intermediate product. That is during the reaction of a cluster with chlorine, two Al−Cl bonds are formed with the Al atoms of the icosahedral Al₁₂ skeleton and the Cl−Cl bond is broken. The resulting reaction energy of this step is around −450 kJ mol⁻¹, according to density functional calculations.[7,16–21] This leads to vibrational and rotational excitation energy trapped in the [Al₁₃Cl₂]⁻* cluster (symbol *) that cannot be removed by collisions at pressures around 10⁻⁸ mbar [Eq. (2a)]. This, in turn, results in the fragmenta-

$$[Al_{13}]^-_{(g)} + Cl_2 \rightarrow [Al_{13}Cl_2]^-_{(g)}$$
$$\Delta_R H^\circ_{(0\,K)} = -450 \text{ kJ mol}^{-1} \tag{2a}$$

tion of [Al₁₃Cl₂]⁻* into [Al₁₂Cl]⁻* and AlCl in the next step [Eq. (2b)]. Phase space theory[8] predicts a lifetime of several

$$[Al_{13}Cl_2]^-_{(g)} \rightarrow [Al_{12}Cl]^-_{(g)} + AlCl_{(g)}$$
$$\Delta_R H^\circ_{(0\,K)} = +195 \text{ kJ mol}^{-1} \tag{2b}$$
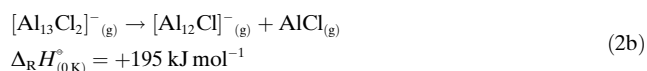
nanoseconds for [Al₁₃Cl₂]⁻*, and as a consequence, [Al₁₃Cl₂]⁻ is not detected in the experiment. In the next step, [Al₁₂Cl]⁻*
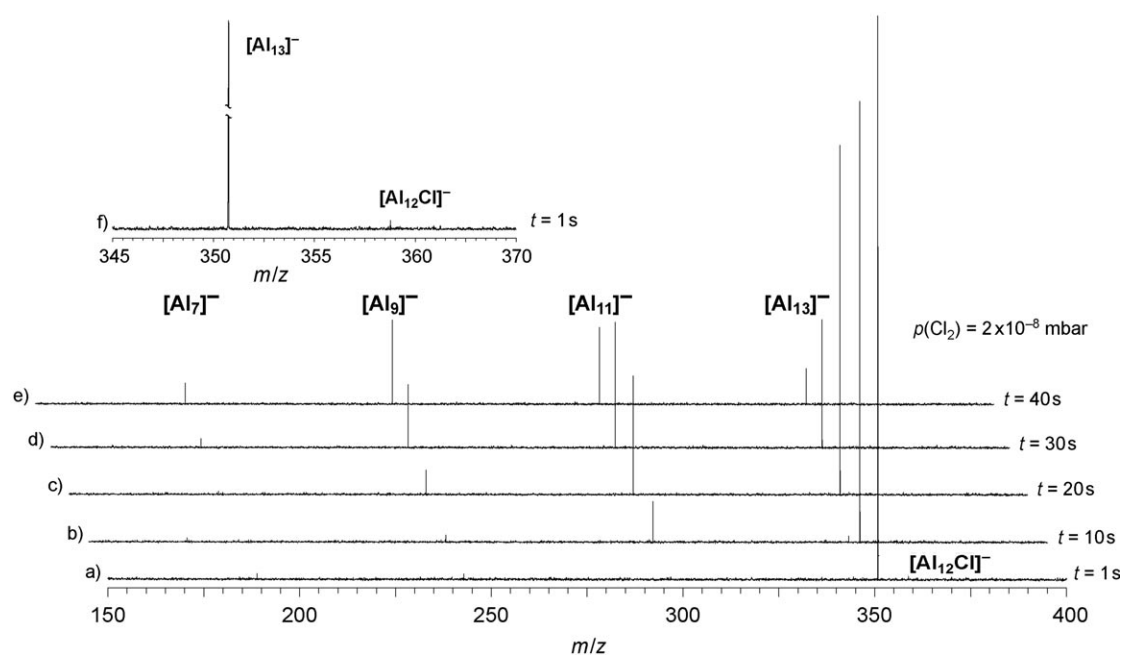
Figure 1. Typical FT-ICR mass spectrum after laser desorption ionization: at $t=0$ s $[Al_{13}]^-$ is isolated and exposed to a chlorine atmosphere (at 2×10^{-8} mbar). The decay of the $[Al_{13}]^-$ signals in favor of $[Al_{11}]^-$, $[Al_9]^-$, and $[Al_7]^-$ is presented. At $t=1$ s, $[Al_{12}Cl]^-$ can be detected in small concentrations (a, f). Every spectrum was scaled in such a way that the sum of all (integrated) signals would be 100. For clarity, Cl^- signals are not shown; for further mass spectra see the Supporting Information.

also fragments, ejecting AlCl once again and leaving $[Al_{11}]^-$ [Eq. (2c)]. For this reaction channel the lifetime of $[Al_{12}Cl]^{-*}$

$$[Al_{12}Cl]^-_{(g)} \rightarrow [Al_{11}]^-_{(g)} + AlCl_{(g)}$$
$$\Delta_R H^{\circ}_{(0\,K)} = +203 \text{ kJ mol}^{-1} \qquad (2c)$$
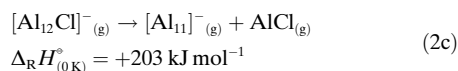
is estimated to be several tenths of a second, and indeed, this anion was observed in small amounts in our experiment (see Figure 1). By performing a double resonant experiment we showed definitively, that this intermediate step takes place, that is, when one continuously removes $[Al_{12}Cl]^-$ by radio frequency (rf) excitation, very few $[Al_{11}]^-$ will be formed.[9,10] The Langevin rate constant k_L for all ion–molecule reactions was determined to be $k_L = 0.09 \text{ s}^{-1}$ in the described pressure range.[11,12] As a consequence, an $[Al_n]^-$ cluster molecule collides with a chlorine molecule every 10 s on average, and these will react to form an $[Al_{n-2}]^-$ cluster within another 0.1 s, according to our lifetime estimations. A collisionally induced dissociation of $[Al_{13}]^-$ can be excluded, since corresponding experiments with argon as the collision gas (in the absence of chlorine) showed none of the fragmentation reactions described above.[13]

In summary, the reaction standard energy for the breakdown of $[Al_{13}]^-$ to

$[Al_{11}]^-$ due to its reaction with chlorine is -52 kJ mol^{-1}. In principle, the corresponding reactions of $[Al_{11}]^-$ and $[Al_9]^-$
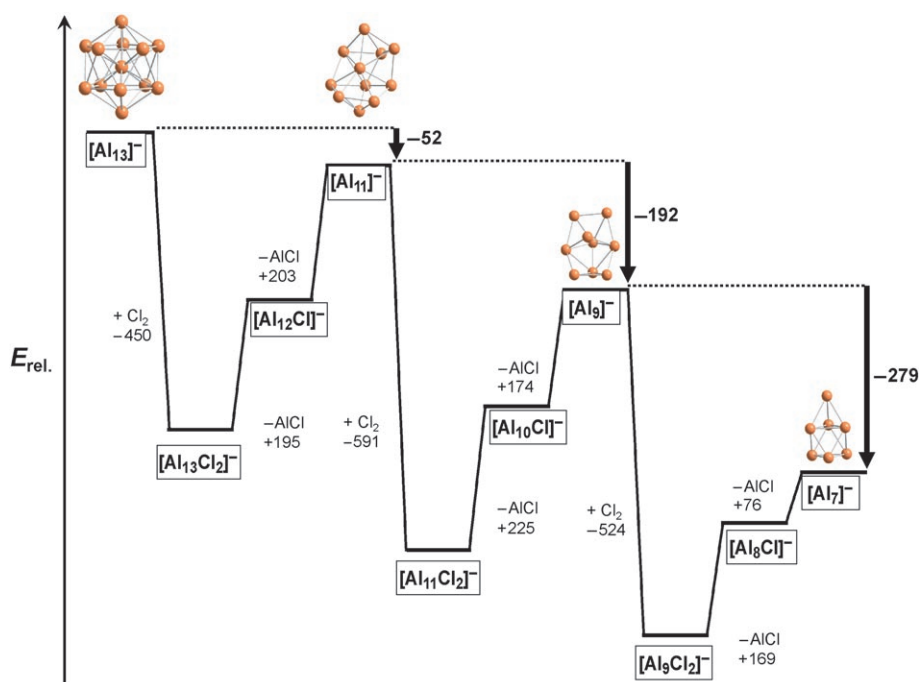
Figure 2. Schematic energy diagram for the breakdown of the cluster; the energy values are given in kJ mol^{-1}. In the first step, chlorine reacts with the surface of the $[Al_{13}]^-$ cluster to form a $[Al_{13}Cl_2]^-$ cluster, which cannot be detected in the experiment because of its short lifetime. In the second step, the spontaneous fragmentation of $[Al_{13}Cl_2]^-$ leads to the release of AlCl and the formation of $[Al_{12}Cl]^{-*}$. Subsequent release of AlCl, leads to $[Al_{11}]^-$. The breakdown of $[Al_{11}]^-$ and $[Al_9]^-$ proceeds in the same manner.

take place in the same way, but are significantly more exothermic than for $[Al_{13}]^-$ with energies of -192 kJ mol^{-1} and -279 kJ mol^{-1}, respectively. Figure 2 summarizes all of the pertinent energy balances.
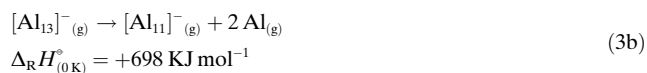
In addition to the reaction products described up to now, Cl$^-$ was always observed, even at the earliest reaction times. This was especially the case at long reaction times, and by 60 s (at a chlorine pressure of 10^{-8} mbar), Cl$^-$ was the only reaction product detected. By determining the intensities of the $[Al_{13}]^-$, $[Al_{11}]^-$, $[Al_9]^-$, $[Al_7]^-$, and Cl$^-$ signals at different times, and thus their concentrations, one can calculate the reaction rates for the individual steps in Equation (1). The exact quantitative description of the chlorination reactions of $[Al_{13}]^-$, including all subsequent and side reactions, is very complex, and it will be presented in a separate publication.[14] Here, we want to restrict ourselves to a qualitative description: essentially $[Al_n]^-$ clusters react with chlorine to give $[Al_{n-2}]^-$ at the same time releasing two AlCl molecules, that is, the resulting cluster has two less aluminum atoms. Also, in a competing reaction channel the $[Al_n]^-$ are oxidized, and Cl$^-$ is formed. Thus, on the one hand, there is the reaction progression in which $[Al_n]^-$ clusters are broken down into smaller units, while on the other hand, there are parallel oxidizing reactions of $[Al_n]^-$ clusters taking place. These latter reactions result in the formation of Cl$^-$ to one extent or another, depending on their different electron affinities.[7]

The reaction path presented here for the reactions of $[Al_n]^-$ cluster ions with chlorine, which results in the release of AlCl as the main product, is a plausible model for the corresponding reaction of bulk aluminum metal and chlorine. This conclusion is in accordance with other experiments as well: The chlorination of aluminum in matrix isolation experiments as well as in experiments on a synthetic scale showed the formation of AlCl at low chlorine pressures.[15] The reaction paths deduced from mass spectrometric investigations with $[Al_n]^-$ clusters provide a reasonable model for the primary steps during the oxidation of bulk aluminum. Below, we want to clarify this idea by a Gedanken experiment with topologic and thermodynamic arguments.

Since the topology of the $[Al_{13}]^-$ cluster with one central Al atom surrounded by twelve other Al atoms is similar to the closest packing of Al atoms in the bulk metal, this cluster is also similar with regard to its energetic behavior: To remove two Al atoms from the closest packing of bulk aluminum [Eq. (3a)] requires 654 kJ mol^{-1}, that is, double the sublimation energy. According to density functional calculations the analogous reactions of anionic and neutral Al$_{13}$ clusters [Eq. (3b) and (3c)] will require 698 and 638 kJ mol^{-1},

$$2\,Al_{(f)} \rightarrow 2\,Al_{(g)}$$
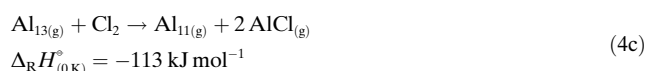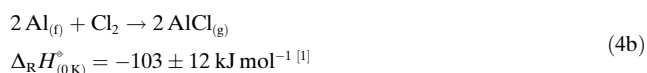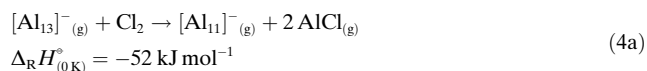$$\Delta_R H^\circ_{(0\,K)} = +654 \pm 8 \text{ kJ mol}^{-1} \tag{3a}$$

tion energy. According to density functional calculations the analogous reactions of anionic and neutral Al$_{13}$ clusters [Eq. (3b) and (3c)] will require 698 and 638 kJ mol^{-1},

$$[Al_{13}]^-_{(g)} \rightarrow [Al_{11}]^-_{(g)} + 2\,Al_{(g)}$$
$$\Delta_R H^\circ_{(0\,K)} = +698 \text{ KJ mol}^{-1} \tag{3b}$$

$$Al_{13(g)} \rightarrow Al_{11(g)} + 2\,Al_{(g)}$$
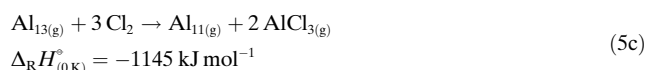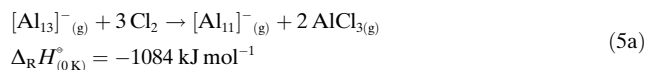$$\Delta_R H^\circ_{(0\,K)} = +638 \text{ KJ mol}^{-1} \tag{3c}$$

respectively. Although the difference in energy (60 kJ mol^{-1}) is not surprising with regard to the usual error ranges for density functional calculations (ca. 10%), the special stability of the $[Al_{13}]^-$ cluster is made clear by the significantly higher energy value for its fragmentation.

These similarities between the bulk metal and Al$_{13}$ clusters for the removal of two Al atoms [Eq. (3 a–c)] are also consequently reflected by the corresponding chlorination reactions [Eq. (4 a–c)]. The neutral as well as the investigated anionic $[Al_{13}]^-$ cluster can be considered as a well-matched model compound for investigations of primary reactions on the surface of bulk aluminum.

$$[Al_{13}]^-_{(g)} + Cl_2 \rightarrow [Al_{11}]^-_{(g)} + 2\,AlCl_{(g)}$$
$$\Delta_R H^\circ_{(0\,K)} = -52 \text{ kJ mol}^{-1} \tag{4a}$$

$$2\,Al_{(f)} + Cl_2 \rightarrow 2\,AlCl_{(g)}$$
$$\Delta_R H^\circ_{(0\,K)} = -103 \pm 12 \text{ kJ mol}^{-1} \text{[1]} \tag{4b}$$

$$Al_{13(g)} + Cl_2 \rightarrow Al_{11(g)} + 2\,AlCl_{(g)}$$
$$\Delta_R H^\circ_{(0\,K)} = -113 \text{ kJ mol}^{-1} \tag{4c}$$

When there is a high excess of chlorine, the AlCl primary product will continue to react and form AlCl$_3$. The formation of this final product of chlorination is a very exothermic reaction: $(AlCl_{(g)} + Cl_2 \rightarrow AlCl_{3(g)}$, $\Delta_R H^\circ = -534$ kJ mol^{-1} [1]$)$. Thus, the chlorination of the bulk metal aluminum must also proceed primarily by the addition of chlorine and the release of AlCl. Then, the subsequent reaction of AlCl to give AlCl$_3$ will take place with the release of reaction energy that is ten times higher (-534 kJ mol^{-1}). Consequently, the cumulative reactions [Eq. (5 a–c)], which produce AlCl$_3$ as the final product, reflect the character of $[Al_{13}]^-$ as a molecular model for the bulk metal.

$$[Al_{13}]^-_{(g)} + 3\,Cl_2 \rightarrow [Al_{11}]^-_{(g)} + 2\,AlCl_{3(g)}$$
$$\Delta_R H^\circ_{(0\,K)} = -1084 \text{ kJ mol}^{-1} \tag{5a}$$

$$2\,Al_{(f)} + 3\,Cl_2 \rightarrow 2\,AlCl_{3(g)}$$
$$\Delta_R H^\circ_{(0\,K)} -1166 \pm 6 \text{ kJ mol}^{-1} \text{[1]} \tag{5b}$$

$$Al_{13(g)} + 3\,Cl_2 \rightarrow Al_{11(g)} + 2\,AlCl_{3(g)}$$
$$\Delta_R H^\circ_{(0\,K)} = -1145 \text{ kJ mol}^{-1} \tag{5c}$$

In addition to the central breakdown reactions of $[Al_{13}]^-$ clusters to $[Al_{11}]^-$ and two AlCl, the reverse steps illustrated in Equation (6) are also relevant for understanding the

$$3\,AlCl + [Al_{11}]^- \rightarrow [Al_{13}]^- + AlCl_3 \tag{6}$$
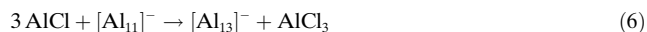
formation of metalloid clusters on a preparative scale. Therefore Equation (6) can be considered as a simplified model for a single step disproportionation, for example, of AlCl solutions ($3\,AlCl \rightarrow 2\,Al + AlCl_3$), in which metalloid Al$_n(AlR)_m$ clusters are formed as intermediates on the way finally to metallic aluminum. This consideration (in the sense of a retrosynthesis, that is, a reverse of the reaction course in Figure 2) appears to be plausible, because in contrast to the presented mass spectrometric experiments in the gas phase,

the concentration of AlCl is high in synthetically prepared AlCl solutions.[15] Here, indeed individual steps can proceed analogously to Equation (6), since this reaction is exothermic by $-467 \, \text{kJ mol}^{-1}$.

Experimental Section

The experiments were performed with an ULTIMA FT-ICR mass spectrometer (Ionspec, MALDI source), equipped with a 7.0-T magnet and a nitrogen laser (Spectra Physics, $\lambda = 337.1$ nm). Selected ions were isolated (SWIFT) and cooled down to room temperature by using argon as collision gas.[5] For the reactions, chlorine was introduced into the ICR cell with a leak valve. This typically raised the pressure from 10^{-10} mbar to 10^{-8} mbar. The reaction time was varied between 2 and 70 s.

The density functional calculations were carried out with the TURBOMOLE[16] program package, using the Becke-Perdew-86 functional (BP86).[17,18] Coulomb interactions were treated within the RI (resolution of the identity) approximation.[19,20] The grids required for the numerical integration of exchange and correlation contributions were of medium coarseness (m3[20]). The basis set was of split valence plus polarization (SVP) type.[21] To check whether the computational methods were suited for our tasks, we compared the following reactions: $AlCl_{(g)} + Cl_2 \rightarrow AlCl_{3(g)}$. The calculated reaction energy was determined to be $\Delta_R H^\circ(\text{calcd}) = -516 \, \text{kJ mol}^{-1}$. The experimental value for the reaction energy is $\Delta_R H^\circ(\text{exp}) = -534 \pm 9 \, \text{kJ mol}^{-1}$. In the past, these methods were used in a density functional study of aluminum clusters.[22] To estimate the lifetimes of the intermediate steps $[Al_{13}Cl_2]^{-*}$ and $[Al_{12}Cl]^{-*}$, phase space theory (PST) was applied.[8]

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