

Primary Reaction Steps of Al_{13}^- Clusters in an HCl Atmosphere: Snapshots of the Dissolution of a Base Metal

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Abstract: Recently, the icosahedral Al_{13}^- cluster has been shown to possess some unusual characteristics due to its special stability (Bergeron, D. E.; et al. *Science* **2004**, *304*, 84–87; **2005**, *307*, 231–235). Here we present reactions of isolated Al_{13}^- clusters with hydrogen chloride, following their oxidation through the application of Fourier transform ion cyclotron resonance mass spectrometry. Due to the ultra-low-pressure conditions, the reaction time can be expanded to make one intermediate after another come into view. The following intermediates are generated sequentially, releasing AlCl and H_2 : $\text{Al}_{13}\text{HCl}^-$, Al_{12}H^- , $\text{Al}_{12}\text{H}_2\text{Cl}^-$, $\text{Al}_{11}\text{H}_2^-$, $\text{Al}_{12}\text{Cl}^-$, and Al_{11}^- . The resulting reaction scheme proves to be a molecular model for the dissolution of a metal in an acid, revealing the initial steps of a heretofore unknown fundamental heterogeneous reaction.

Introduction

Interest in bare metal atom clusters has grown in recent years, largely because they represent nanoscale intermediates between metal atoms and the bulk metal. These investigations have probed their electronic properties and chemical reactivity in search of novel properties not exhibited by the atom or bulk metal.^{1,2} In this respect, the Al_{13}^- cluster anion is remarkable for its stable electronic configuration (40 valence electrons, corresponding to a closed shell in the jellium-like shell model³) and its reactions with HI and I_2 , which have prompted it to be called a superatom.² Here we present not only a further reaction of this popular Al_{13}^- anion but also primary steps of the reaction cascade of the dissolution of this cluster in an HCl atmosphere. Furthermore, we want to show that — besides obvious differences — there are unexpected similarities between the Al_{13}^- cluster and the bulk metal and that this cluster may even be a molecular model compound for reactions of the bulk metal.

Experimental Methods

Most experiments were performed with a commercial Fourier transform ion cyclotron resonance mass spectrometer (IonSpec Hires MALDI ULTIMA FT-ICR MS), equipped with a 7.0 T magnet, and an external matrix-assisted laser desorption/ionization ion source (Ionspec), equipped with a pulsed nitrogen laser (Spectra Physics, $\lambda = 337.1$ nm). After laser desorption/ionization of lithium aluminum hydride (LiAlH_4 , rods), pure Al_n^- (lithium- and hydrogen-free) clusters were generated. Selected ions were isolated and cooled to room temperature using argon as the collision gas. For this, argon was

admitted using a pulsed valve to raise the pressure to 10^{-5} mbar for some seconds. For studying the reactions, HCl was introduced into the ICR cell with a leak valve. This typically raised the pressure from 10^{-10} mbar to 10^{-8} mbar. To initiate reactions, a sustained off-resonance radio frequency pulse at 304 305 Hz (200 Hz above the cyclotron resonant frequency of Al_{13}^-) was applied for up to 40 s.

Calculations were carried out with the density functional theory (DFT) implementation of the TURBOMOLE⁴ program package, using the Becke–Perdew 86 functional (BP86).^{5,6} Coulomb interactions were treated within the resolution of the identity (RI) approximation.^{7,8} The grids required for the numerical integration of exchange and correlation contributions were of medium coarseness (m^3). The basis set was of split-valence plus polarization (SVP) type.⁹

Results

A broad distribution of Al_n^- cluster anions (with $n = 6–25$) was detected in the FT-ICR mass spectrum after laser ablation of solid LiAlH_4 . After the pressure was increased to 10^{-8} mbar by admission of hydrogen chloride, new signals appeared that were assigned as Al_{14}H^- , Al_{15}H^- , and Al_{16}H^- . To determine the origin of the hydrogenated aluminum clusters, Al_{15}^- was isolated in the ICR cell and allowed to react with HCl. We observed that Al_{14}H^- was the only product, indicating that the reaction had proceeded as follows:



Al_{15}H^- and Al_{16}H^- were formed in the same way by reaction of Al_{16}^- and Al_{17}^- with HCl, respectively. In contrast to this,

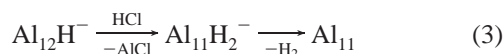
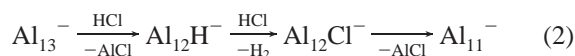
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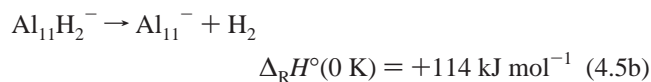
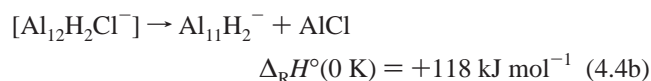
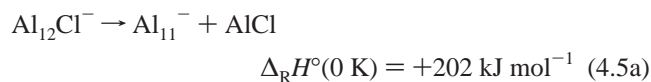
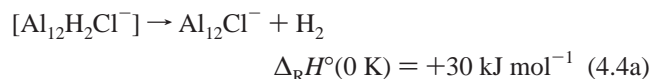
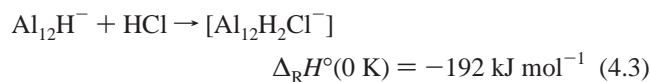
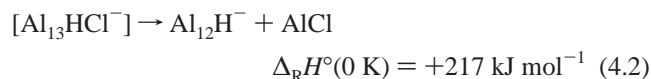
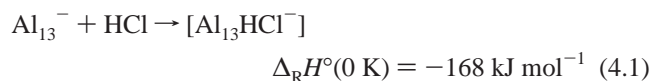
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Al_{13}^- ions did not react spontaneously in the presence of HCl; in the mass spectrum, the initial signal of isolated Al_{13}^- ions remained strong, so the proton-transfer reaction, $\text{Al}_{13}^- + \text{HCl} \rightarrow \text{Al}_{13}\text{H} + \text{Cl}^-$, can be excluded from having occurred as well.¹⁰ However, when the kinetic energy of Al_{13}^- was increased by applying a radio frequency (RF) pulse, new signals occurred that were assigned as Al_{12}H^- , $\text{Al}_{12}\text{Cl}^-$, $\text{Al}_{11}\text{H}_2^-$, and Al_{11}^- (see mass spectrum in Figure 1). When only short RF pulses (~ 5 s) were applied, the formation of Al_{12}H^- (see Figure 1b) was observed, whereas when slightly longer pulses (~ 15 s) were applied, Al_{11}^- also came clearly into view (see Figure 1c). When still more energy was supplied (through longer pulse lengths of up to 40 s), all of the reaction products shown in eq 2 appeared (see Figure 1d). To further specify the reaction pathway, we isolated Al_{12}H^- and let it react with HCl; both $\text{Al}_{12}\text{Cl}^-$ and $\text{Al}_{11}\text{H}_2^-$ resulted. When we performed a double-resonance experiment in which $\text{Al}_{12}\text{Cl}^-$ was continuously removed from the ICR cell as it was formed, $\text{Al}_{11}\text{H}_2^-$ was formed anyway, thus showing that $\text{Al}_{12}\text{Cl}^-$ and $\text{Al}_{11}\text{H}_2^-$ were formed independently. The reaction of Al_{13}^- with HCl therefore can be subdivided into two branches (eqs 2 and 3):

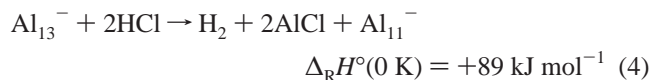


Further validation of the reaction scheme presented here was achieved via another double-resonance experiment. By removing Al_{12}H^- anions as essential intermediate species, the entire reaction cascade was disrupted.

To further elucidate these results, the reaction scheme can be subdivided into single steps. The following equations comprise all possible and necessary reaction steps for the degradation of Al_{13}^- . In each case, the reaction enthalpies have been calculated by DFT methods. These results are also presented graphically in Figure 2.



Altogether, the reaction of Al_{13}^- with HCl, going to Al_{11}^- , H_2 , and AlCl, is seen to be endothermic:



Discussion

(1) Commentary on the Experimental Results. Neither of the two intermediates, $[\text{Al}_{13}\text{HCl}]^-$ and $[\text{Al}_{12}\text{H}_2\text{Cl}]^-$, was clearly detected during these experiments. $[\text{Al}_{12}\text{H}_2\text{Cl}]^-$ was definitely not observed, while $[\text{Al}_{13}\text{HCl}]^-$ emerged in very small quantities (Figure 1d). (This fact is denoted by writing them in brackets.) The formation of an $[\text{Al}_{13}\text{HCl}]^-$ complex is postulated to be the first step during the reaction of Al_{13}^- with HCl (eq 4.1). As a consequence of ultra-low-pressure conditions, there is no bath gas to absorb its heat of formation (for $[\text{Al}_{13}\text{HCl}]^-$, $\Delta_{\text{R}}H(0 \text{ K}) = -168 \text{ kJ mol}^{-1}$ as calculated by DFT).^{4–9} Therefore, since the exothermicity of the $[\text{Al}_{13}\text{HCl}]^-$ * intermediate is so large, it is highly rotationally and vibrationally excited and thus has a very short lifetime either toward dissociation back to reactants or toward the dissociation channel shown in eq 4.2. Since the dissociation to Al_{12}H^- and AlCl (eq 4.2) was calculated to be endothermic by $+217 \text{ kJ mol}^{-1}$, this event can proceed only if additional energy is supplied, e.g., by RF excitation. If no additional energy is supplied, $[\text{Al}_{13}\text{HCl}]^-$ * can only decompose back to the educts, Al_{13}^- and HCl. This may be the reason why Al_{13}^- ions appear to be inert in an HCl atmosphere when no excitation is provided. With RF excitation, the charged reaction products of eq 4.2 are observed.¹¹

Another consequence of low-pressure conditions is that reaction channels other than those shown in eqs 4.1, 4.4a, and 4.4b can be excluded for the intermediate species $[\text{Al}_{13}\text{HCl}]^-$ and $[\text{Al}_{12}\text{H}_2\text{Cl}]^-$. The time between their collisions with HCl molecules at a pressure of 10^{-8} mbar is about 10 s on average, deduced from the Langevin ion–molecule reaction rate, where $k_{\text{L}} = 0.11 \text{ s}^{-1}$.¹² In contrast to this long period between collisions, the respective reaction decay time of some of these cluster species is very short; phase space theory (PST) predicts the lifetimes of the species produced, $[\text{Al}_{13}\text{HCl}]^-$, $[\text{Al}_{12}\text{H}_2\text{Cl}]^-$, and $\text{Al}_{12}\text{Cl}^-$, to be only some few tenths of a second.^{13,14} (The present experiments, however, show that the lifetime of $\text{Al}_{12}\text{Cl}^-$ is long enough to be detected, i.e., before the endothermic elimination step (4.5a) consumes part of its internal energy.) Considering the whole reaction cascade, those endothermic steps which lead to the products, AlCl and H_2 , are key steps in the mechanism. These steps are depicted in eqs 4.2, 4.4b, and 4.5a and in eqs 4.4a and 4.5b, where the elimination of the stable, high-temperature molecule AlCl and the generation of hydrogen

(10) Concerning the acidities of HCl and HAl_{13} , our DFT calculations indicated HAl_{13} to be a stronger proton acid than HCl in the gas phase. The reaction $\text{HCl} + \text{Al}_{13}^- \rightarrow \text{Al}_{13}\text{H} + \text{Cl}^-$ is calculated to be endothermic by $\Delta_{\text{R}}H^\circ(0 \text{ K}) = +266 \text{ kJ mol}^{-1}$ (in agreement with our experimental observation).

(11) In other words: without any external excitation, the formation of $[\text{Al}_{13}\text{HCl}]^-$ from Al_{13}^- and HCl is not observed, since the reaction back to the educts (i.e., the dissociation) is much faster than the formation of $[\text{Al}_{13}\text{HCl}]^-$. When an external excitation (RF pulse) is applied, the subsequent reaction can be lifted over the barrier, $[\text{Al}_{13}\text{HCl}]^- \rightarrow \text{Al}_{12}\text{H}^- + \text{AlCl}$ (endothermic, $+217 \text{ kJ mol}^{-1}$). The dissociation reaction of $[\text{Al}_{13}\text{HCl}]^-$ proceeds so fast that $[\text{Al}_{13}\text{HCl}]^-$ itself cannot be observed.

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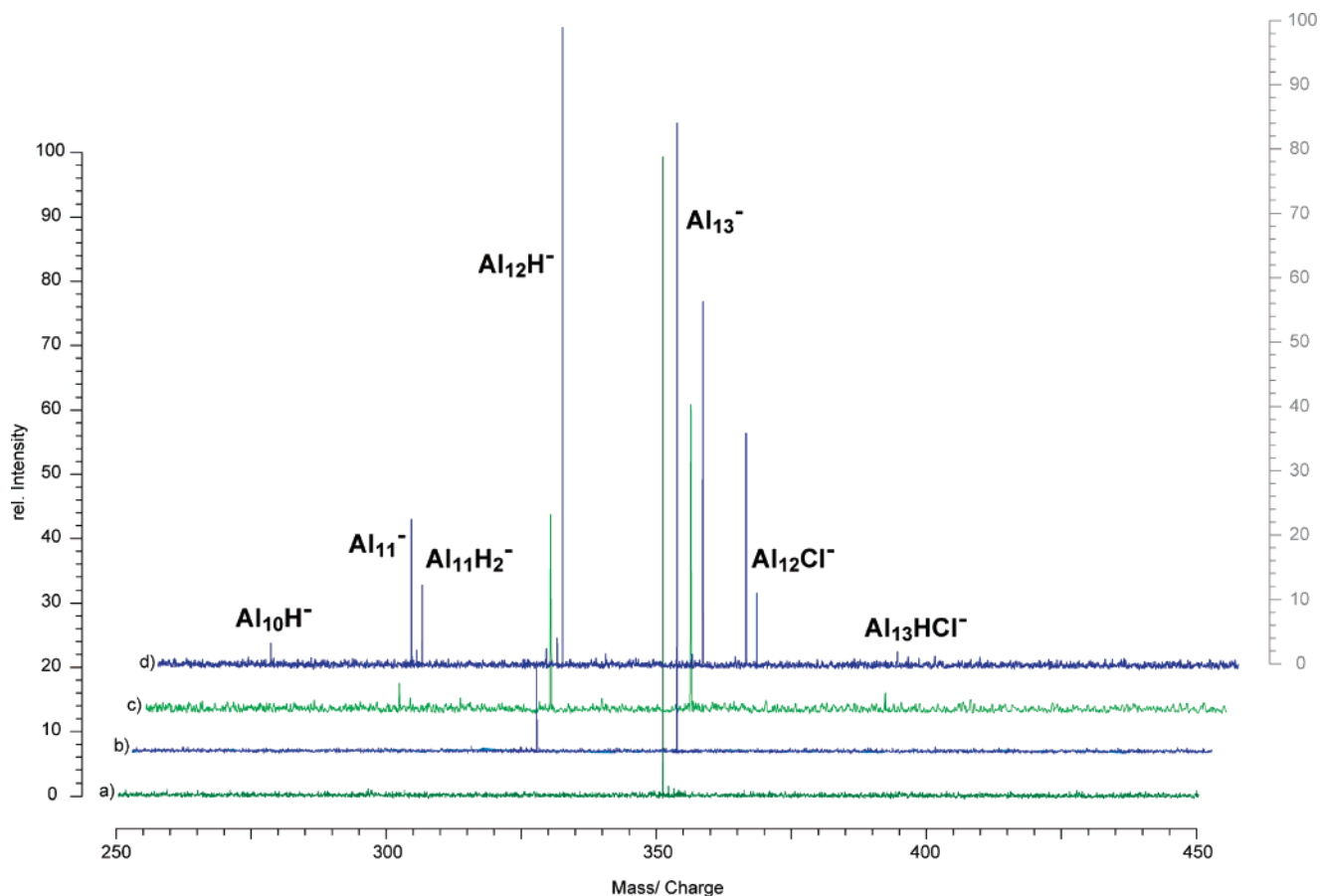


Figure 1. FT-ICR mass spectra. After laser desorption ionization of solid LiAlH_4 , Al_n^- clusters are generated. Al_{13}^- is cooled via argon collisions, isolated, and exposed to an HCl atmosphere at $\sim 10^{-8}$ mbar. (a) Without external energy supplied (RF excitation), no reaction is observed. (b) When a little energy is supplied (irradiation with RF pulse length ~ 5 s), Al_{12}H^- is found as a reaction product. (c,d) For longer RF pulse lengths, all reaction products emerge. $\text{Al}_{13}\text{HCl}^-$ is observed only in very small amounts (cf. text).

gas (H_2) are shown, respectively. The formation of hydrogen proceeds via two different elimination reactions: in eq 4.4a, Al–H and H–Cl bonds are broken and Al–Cl and H–H bonds are formed, while in eq 4.5b, two Al–H bonds are broken and one H–H bond is formed.¹⁵

All considered, the reaction of Al_{13}^- and HCl going to AlCl and Al_{11}^- is endothermic ($+89 \text{ kJ mol}^{-1}$ as estimated by DFT). Moreover, most of the elementary steps in the degradation of Al_{13}^- to Al_{11}^- (see eqs 4.1–4.5b) are themselves endothermic. Their endothermicities and the ability to control RF excitation (energy input) permits the reaction to be stopped between steps, facilitating the direct detection of intermediate species. The reaction can then be started again at will by applying appropriate RF excitation. As compared with the reactions of other aluminum cluster anion sizes and HCl, where many of the elementary steps appear to be exothermic, Al_{13}^- is a fortuitous case for mechanistic study. Its reaction pathway with HCl can be followed and mapped with fewer of the complications that might occur in other cases.

(2) Comparison to Other Results in the Literature.

Bergeron and Castleman studied reactions of aluminum clusters

with HX, where X = Cl, Br, and I.¹⁶ For reactions with HCl, they monitored the distribution of Al_n^- and Al_nCl^- clusters mass spectrometrically as a function of HCl pressure. Computational results obtained by Khanna also accompanied these experiments in order to shed light on the reaction pathways. Oxygen etching experiments were also performed.¹⁷

Here, we compare our work with these past studies. We are able to isolate Al_{13}^- (or any other cluster ion) from a mixture of Al_n^- clusters. Before HCl was admitted into the ICR cell, the isolated Al_{13}^- ions were cooled to room temperature by several argon pulses. Thus, the present work uses well-defined (mass-selected) reactants for its reactions. In Bergeron's experiment, there was no mass selection of aluminum cluster anions prior to reaction. Also, the ultra-low-pressure conditions (10^{-8} mbar) in our ICR cell make it possible to observe almost all reaction steps one after another. We calculated, that, on average, a cluster will collide with an HCl molecule every 10 s. Since Bergeron's experiments were performed in a flow tube at around 1 mbar (the HCl partial pressure was less), the collision frequency was very much higher. In addition to our ICR experiments, we also conducted crude beam-gas reactivity experiments in which a beam of laser-ablation-formed, non-mass-selected Al_n^- cluster anions was allowed to react with a

(15) The energy of $\text{Al}_{11}\text{H}_2^-$ is based on a calculation, assuming the hydrogen is covalently bound to the Al_{11}^- core. Recently, Wang et al. concluded from photoelectron studies that H_2 is physisorbed on Al_{11}^- (*J. Chem. Phys.* **2006**, *124*, 054308). Therefore, depending on the hydrogen bonds, the energetic position of $\text{Al}_{11}\text{H}_2^-$ and $\text{Al}_{12}\text{H}_2\text{Cl}^-$ in the schematic energy diagram (Figure 2) has to be shifted. However, this shift will not influence the principal conclusions.

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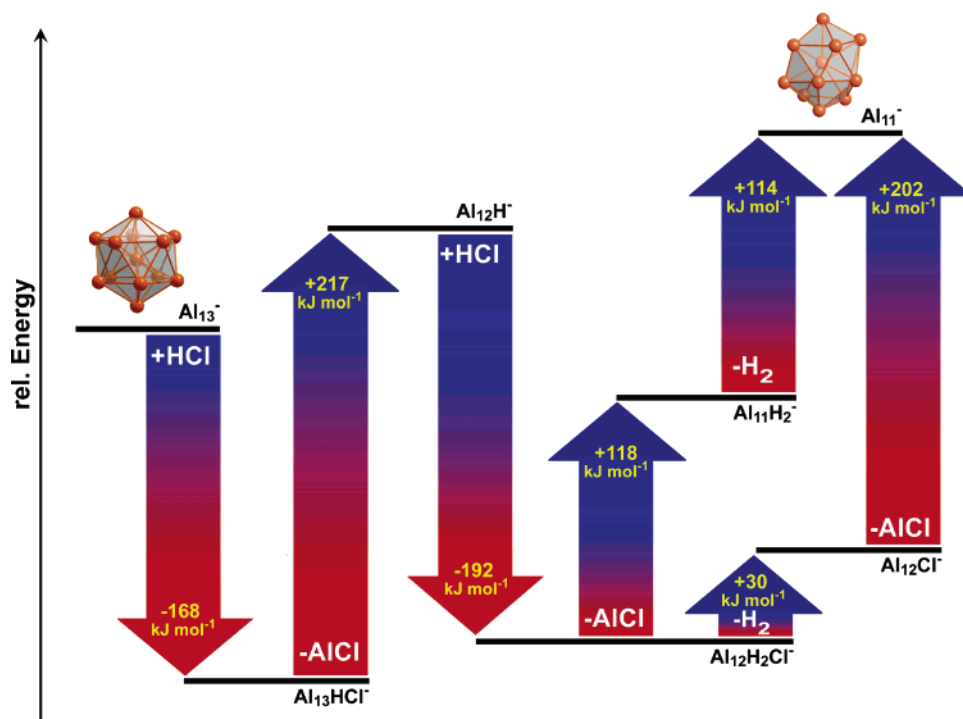
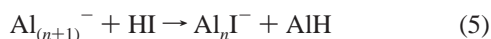


Figure 2. Schematic energy diagram. Here, all exothermic and endothermic reaction steps are visualized. Altogether, the reaction of Al_{13}^- with HCl, going to Al_{11}^- , H_2 , and AlCl , is seen to be endothermic by 89 kJ mol^{-1} . It is interesting to note that, starting from $\text{Al}_{12}\text{H}_2\text{Cl}^-$, there are two reaction channels to obtain Al_{11}^- . All energies are obtained from DFT calculations.

cloud of HCl gas ($\sim 10^{-4}$ mbar) lying in its path. While this experiment resembles Bergeron's flow tube experiment schematically, it in fact involved significantly lower pressures and shorter interaction times. Thus, each of these three experiments was carried out in a different collisional regime.

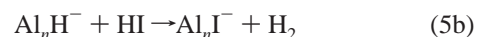
The strength of the present ICR studies lies in their ability to observe reactive intermediates directly and thus to unravel the mechanistic details of the $\text{Al}_{13}^- + \text{HCl}$ reaction. These experiments identified both Al_{12}H^- and $\text{Al}_{12}\text{Cl}^-$ as essential reactive intermediates on the way from Al_{13}^- to Al_{11}^- . [The species Al_{12}H^- has also been observed as a prominent ion in our beam-gas experiments and in the work of Ganteför and Seifert, who formed beams of it in a pulsed arc cluster ion source,¹⁸ but Al_{12}H^- was not reported as having been seen in the Bergeron work.] Together, these observations support the mechanism put forth in eqs 4.1–4.5b, and this in turn implies that AlCl is an excellent leaving group. By contrast, in the absence of HCl, we do not observe the spontaneous degradation of Al_{12}H^- into Al_{11}^- and its presumed coproduct, AlH . Thus, we find no evidence for AlH being a good leaving group.

In reactions of Al_n^- cluster anions with HI, Bergeron proposed the following mechanism for the formation of Al_nI^- :



In this case, AlH is the leaving group. Our own results for reactions of aluminum cluster anions with HI, however, suggest a different reaction scheme. Since we observe the formation of Al_nH^- under ultra-low-pressure conditions, we propose a mechanistic scheme that is analogous to that of the $\text{Al}_n^- + \text{HCl}$

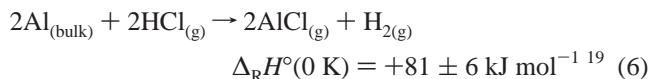
reaction. Therefore, we propose a two-step reaction pathway for the formation of Al_nI^- :



Since the reactivity of aluminum clusters is strongly dependent on the cluster size (and charge state), it is difficult to predict a general mechanism for all $\text{Al}_n^- + \text{HX}$ reactions.

Our intention has been to focus on the reactions of Al_{13}^- in an HCl atmosphere. In studying the reaction scheme that begins with Al_{13}^- and ends with Al_{11}^- , we have presented experimental evidence for a mechanism by which AlCl and hydrogen are formed as products. We next consider the extent to which our results can serve as a molecular model for the formation of AlCl and H_2 from the reaction of bulk aluminum with gaseous HCl.

(3) Interpretation and Perspectives for a Molecular Model Cycle Mechanism. The formation of AlCl from bulk aluminum and HCl is a well-known endothermic reaction in inorganic synthesis:

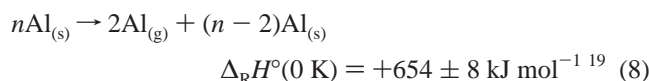
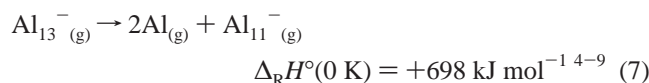


To obtain AlCl for synthetic chemistry purposes (or also for matrix isolation spectroscopy studies), high-temperature conditions ($1000 \text{ }^{\circ}\text{C}$) and low pressures (less than 10^{-3} mbar) are necessary.²⁰ Since no information is available on the mechanistic

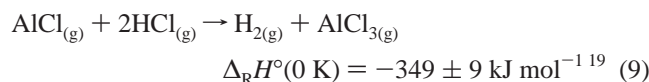
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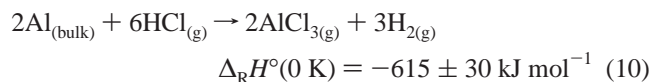
steps for this reaction, we now present arguments why Al_{13}^- can be considered as a model compound for bulk aluminum on a molecular scale. It is amazing that the formation of two AlCl molecules from the bulk reaction represented in eq 6 requires almost the same amount of energy ($+81 \text{ kJ mol}^{-1}$) as the reaction of Al_{13}^- with two HCl molecules ($+89 \text{ kJ mol}^{-1}$ by DFT). This similarity between the reactions of Al_{13}^- and of bulk aluminum with gaseous HCl seems plausible, however. The arrangement of 12 Al atoms surrounding a central Al atom is valid in both cases, and therefore, it is not surprising that the detachment of two Al atoms from an Al_{13}^- cluster or from bulk Al metal requires essentially the same amount of energy (eqs 7 and 8):^{21,22}



In large excess of HCl and under standard conditions, AlCl will react further to AlCl_3 :²³

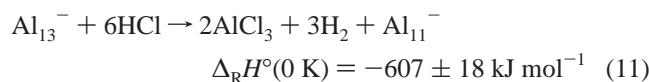


Equations 6 and 9 can be combined to give the overall reaction, eq 10:



The exceeding exothermicity of eq 9 can easily compensate for the slightly endothermic formation of AlCl (eq 6). Therefore, Al metal easily reacts in an HCl atmosphere to give AlCl_3 at temperatures of about 100°C .

Analogous thermodynamic considerations are also valid for the Al_{13}^- cluster. The combination of eqs 4 and 9 results in eq 11:



In fact, the $\Delta H^\circ(0 \text{ K})$ values of eqs 10 and 11 are essentially the same. Therefore, these results constitute an essential message: the degradation of the Al_{13}^- cluster to Al_{11}^- is a

suitable molecular model for reactions of the bulk metal. Consequently, it is now plausible to assume the same cascade of reactions for the bulk aluminum surface as for the molecular reactions of the Al_{13}^- cluster species. Also, on a bulk metal surface, the $\text{Al}-\text{Cl}$ and $\text{Al}-\text{H}$ bonds are formed in a first step, and subsequently the elimination of H_2 and AlCl and its further oxidation to AlCl_3 may complete the complex reaction cascade on the surface. However, since the final steps from AlCl to AlCl_3 have already been discussed²³ and cannot be detected by mass spectrometric techniques, the investigations presented here concentrate on the essential, thus far unknown, primary steps.

Conclusion and Outlook

Laser desorption ionization of LiAlH_4 provides a suitable method to obtain Al_n^- clusters for mass spectrometric investigations. While many Al_n^- clusters react spontaneously with HCl gas under ultra-high-vacuum conditions (10^{-8} mbar), the isolated Al_{13}^- clusters, due to their special stability, react only if additional energy is supplied. By tuning this additional energy, in combination with use of ultra-low-pressure conditions to expand the reaction time, the elementary steps of the reaction of Al_{13}^- with gaseous HCl can be detected. Finally, via thermodynamic and topological arguments, it was possible to present the most essential message of this work: the degradation of the Al_{13}^- cluster is a suitable molecular model reaction for the bulk metal.

Furthermore, but of no less fundamental interest, the results presented here may be able to give a molecular interpretation for the well-known differences between base and precious metals in an HCl atmosphere. While base metals are oxidized with the formation of the metal chloride, e.g., AlCl_3 and hydrogen, precious metals do not react with HCl . Thus, it seems plausible that the model reactions for Al_{13}^- in an HCl atmosphere should be different from primary reactions of comparable centered clusters of a precious metal like gold. In fact, thermodynamical data for $\text{Au}(\text{g})$, $\text{AuCl}(\text{g})$, $\text{AuCl}_3(\text{g})$, and Au_n clusters exhibit large uncertainties from both experiments and quantum chemical calculations.^{24–26} Consequently, these investigations, which should be seen as a challenge for the future, are a worthwhile pursuit in order to understand the fundamental differences between base and precious metals on a molecular level.

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Supporting Information Available: Results from quantum chemical calculations in comparison to experimental data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) Similarly, the comparable reaction for neutral Al_{13} clusters needs 638 kJ mol^{-1} . The difference between this value and that for eq 7 reflects the higher stability of Al_{13}^- compared to neutral Al_{13} .

(22) For such considerations, the fragmentation energies of metal clusters are often used. Bergeron et al. calculated the fragmentation energy of Al_{13}^- to be 36.51 eV , i.e., 2.8 eV per Al , or 270 kJ mol^{-1} (see ref 15). However, we think that in our case this method is not useful, since the 2.8 eV per Al atom is only an average value for the 13 Al atoms. The amount of energy needed for removing one Al from Al_n^- is highly dependent on the cluster size. This is why we restricted ourselves to the behavior of Al_{13}^- .

(23) Details of this reaction via HAlCl_2 have been discussed in a matrix isolation study: Schnöckel, H. *J. Mol. Struct.* **1978**, *50*, 275–280.

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