The reaction of aluminium clusters with water: a quantum chemical investigation

Jerzy Moc
Faculty of Chemistry, Wroclaw University, F. Joliot-Curie 14, 50-383 Wroclaw, Poland
E-mail: jerzy.moc@chem.uni.wroc.pl

Abstract. The reaction of charged aluminium clusters with water in the gas phase is investigated theoretically. To this end, the doublet potential energy surface for the \( \text{Al}_n^+ + \text{H}_2\text{O} \rightarrow \text{Al}_n\text{O}^+ + \text{H}_2 \) reaction with \( n=6 \) is explored using density functional theory. The calculated reaction pathways include the initial adduct ion formation, the O-H bond activation and H\(_2\) elimination steps, and are consistent with the recent experimental report (Ref.2). The results of the current quantum-chemical study are relevant to the issues of catalytic role of the main group metal clusters and H\(_2\) generation.

1. Introduction

Recently, a series of small aluminium cluster cations \( \text{Al}_n^+ \) were detected in the mass spectrometric study of Al in helium droplets by Spence et al [1]. In another recent mass spectrometric study involving small aluminium cluster cations, Arakawa et al [2] investigated a size-dependency of the reactivity of the \( \text{Al}_n^+ \) (n=3-19) species towards water in the gas phase. Under single collision conditions, the latter authors observed the \( \text{Al}_n\text{O}^+ \) and/or \( \text{Al}_n(\text{H}_2\text{O})^+ \) clusters as major reaction products. More specifically, for \( 6 \leq n \leq 13 \), either the former or the latter species were selectively observed, while the two products were detected for \( 14 \leq n \leq 19 \). This means that the \( \text{Al}_n^+ \) cluster cations with \( n=3-5 \) were found to be unreactive towards H\(_2\)O and that aluminium hexamer (n=6) was revealed to be the smallest reactive cluster, producing \( \text{Al}_6\text{O}^+ \) and hydrogen [2]. The earlier experimental and theoretical studies of size-selective reactivity of aluminium cluster anions \( \text{Al}_n^- \) with water in the gas phase by Castleman and co-workers [3-4] demonstrated that only the relatively large cluster anions (n=16-18) reacted strongly with 2H\(_2\)O to yield \( \text{Al}_n(\text{OH})_2^- + \text{H}_2 \). The proposed mechanism [3-4] for the \( \text{Al}_n^+ + 2\text{H}_2\text{O} \) elementary reactions was the dissociative chemisorption of water molecules on the metal cluster’s neighbouring sites acting as a Lewis acid and a Lewis base, which facilitated the O-H bonds’ breakage. As noticed by Arakawa et al [2], compared to the \( \text{Al}_n^- \) cluster anions, the size range of the \( \text{Al}_n^+ \) cluster cations upon which the dissociation of water takes place (followed by the H\(_2\) release) is significantly larger. It was also suggested [2] that in the case of the \( \text{Al}_n^+ \) cations, a different mechanism for the H\(_2\)O dissociation/H\(_2\) elimination operates, which involves only one H\(_2\)O molecule for the elementary process: \( \text{Al}_n^+ + \text{H}_2\text{O} \rightarrow \text{Al}_n\text{O}^+ + \text{H}_2 \). However, the actual mechanism of the \( \text{Al}_n^+ + \text{H}_2\text{O} \) reactions in the gas phase have not been elucidated yet.

1 To whom any correspondence should be addressed.
Here, the gas-phase computational scrutiny of the mechanistic pathways of dissociation and dehydrogenation of water on the aluminium hexamer cation \( \text{Al}_6^+ \) is presented. As mentioned above, \( \text{Al}_6^+ \) is the smallest Al cluster cation proved experimentally to react with \( \text{H}_2\text{O} \) to form \( \text{H}_2 \) under thermal conditions \([2]\). It is known that in order to model adequately the gas-phase reactions of metal clusters with small molecules, an extensive probing of the underlying potential energy surfaces is indispensable \([5]\). The reported herein computational results are relevant to the issues of catalytic role of the main group metal clusters and \( \text{H}_2 \) generation.

2. Computational methods

Density functional theory using B3LYP functional \([6-7]\) and the aug-cc-pVTZ basis set \([8]\) was employed to extensively probe the potential energy surface involved in the \( \text{Al}_6^+ + \text{H}_2\text{O} \) reaction. All stationary points were subjected to frequency analysis to ensure that structures correspond to local minima (all positive eigenvalues) or transition states (TSs, one negative eigenvalue). Connectivity of the transition states with the respective local minima was assured by calculating the intrinsic reaction coordinates (IRCs) \([9]\). All the energetics discussed below has been determined at the zero-point vibrational energy (ZPE) corrected B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level. The Gaussian 09 package was employed in the calculations \([10]\).

3. Results and discussion

3.1. Reactants, initial adduct ion and products of the gas-phase reaction \( \text{Al}_6^+ + \text{H}_2\text{O} \rightarrow \text{Al}_6\text{O}^+ + \text{H}_2 \)

First, we calculated the lowest energy geometry of the bare \( \text{Al}_6^+ \) cluster cation reactant, derived from the prism-like structure and termed \( \text{R} \) (\( C_{2v}\), \( 2B_1 \)) (Figure 1). The alternative \( \text{Al}_6^+ \) geometry derived from the distorted octahedron (\( C_{2h}\), \( 2A_1g \)) (not shown) appeared to be 3.4 kcal/mol less stable at the B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ + ZPE level. Next, we predicted the structure of the species formed in the initial step of the \( \text{Al}_6^+ + \text{H}_2\text{O} \) reaction, which is the \( \text{Al}_6^+\text{•••OH}_2 \) adduct ion \( \text{COM} \) (\( C_s\), \( 2A' \)), wherein the water molecule is bound to the aluminium cluster cation through the oxygen atom (see Figure 1). The relatively short \( \text{Al} \text{•••O} \) distance of 1.97 Å in the adduct ion \( \text{COM} \) is coupled with the large binding energy of the former species of 19.4 kcal/mol relative to \( \text{Al}_6^+ + \text{H}_2\text{O} \). In other words, the formation of the initial adduct ion is a significantly exothermic step. As confirmed by the IRC following, for the two predicted paths of the \( \text{Al}_6^+ + \text{H}_2\text{O} \rightarrow \text{Al}_6\text{O}^+ + \text{H}_2 \) reaction described below, the formation of \( \text{COM} \) is a shared first step. Here, we also mention the \( \text{Al}_6\text{O}^+ \) product denoted \( \text{P} \) (\( C_{2v}\), \( 2A_1 \)), formed along with \( \text{H}_2 \). As can be seen from Figure 1, \( \text{Al}_6\text{O}^+ \) is the oxygen-bridged cluster.

3.2. PATH A

Starting from the adduct ion \( \text{COM} \), the O-H bond activation occurs via the four-centered transition state \( \text{TS1O-H} \) (\( 2A' \)) (see Figure 2). At the B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ + ZPE level, the latter transition state is calculated to lie 1.6 kcal/mol below the \( \text{Al}_6^+(\text{R}) + \text{H}_2\text{O} \) asymptote, implying a facile water molecule dissociation on the charged Al cluster (Figure 4). The resulting \( \text{Al}_6(\text{OH})^+ \) dissociation intermediate \( \text{I1} \) features the terminal Al-H bond and the O-bridged hydroxyl group, and is stabilized by 53.6 kcal/mol with respect to the \( \text{Al}_6^+(\text{R}) + \text{H}_2\text{O} \). The next step along \( \text{PATH A} \) is \( \text{H}_2 \) elimination involving transition state \( \text{TS1H}_2 \). Although \( \text{TS1H}_2 \) is predicted to lie 25 kcal/mol above \( \text{I1} \), the former species is placed 28.6 kcal/mol below \( \text{Al}_6^+ + \text{H}_2\text{O} \) (Figure 4). The \( \text{H}_2 \) elimination is followed by the formation of the weak exit channel dihydrogen complex \( \text{Al}_6\text{O}^+\ldots\text{H}_2 \) (\( \text{EXT} \)) with the concomitant rearrangement of the \( \text{Al}_6\text{O}^+ \) core. The \( \text{PATH A} \) is ended with the release of \( \text{H}_2 \). The overall \( \text{H}_2 \) elimination reaction \( \text{Al}_6^+(\text{R}) + \text{H}_2\text{O} \rightarrow \text{Al}_6\text{O}^+ \) (\( \text{P} \)) + \( \text{H}_2 \) is calculated to be exothermic by 52.4 kcal/mol (Figure 4).

3.3. PATH B

For the \( \text{Al}_6^+ + \text{H}_2\text{O} \rightarrow \text{Al}_6\text{O}^+ + \text{H}_2 \) reaction, we have identified another low energy path involving the prism-like aluminium cluster, termed \( \text{PATH B} \). With \( \text{PATH B} \) (Figure 3), the \( \text{H}_2\text{O} \) dissociation takes
place through transition state $\text{TS2O-H}$ which connects to the adduct $\text{Al}_6^{+} \cdot \text{OH}_2 (\text{COM})$ and $\text{Al}_6(\text{OH})H^+$ dissociation intermediate (I2). $\text{PATH B}$ is similar to $\text{PATH A}$ in that it leads to the $\text{Al}_6(\text{OH})H^+$ species in a barrier-less O-H bond dissociation step (at the B3LYP/aug-cc-pVTZ/B3LYP/aug-cc-pVTZ + ZPE level) (Figure 4). However, unlike I1 intermediate of $\text{PATH A}$, I2 intermediate of $\text{PATH B}$ is an ‘open-type’ species, with the terminally bound dissociated H and OH (Figure 3). We have found that the next step along $\text{PATH B}$ involves the isomerization transition state $\text{TSISO}$. According to our calculations, this is an easy interconversion with the energy barrier of 6.5 kcal/mol relative to I2, and with $\text{TSISO}$ lying 35.4 kcal/mol below the $\text{Al}_6^{+} + \text{H}_2\text{O}$ asymptote. Via transition state $\text{TSISO}$, I2 rearranges to the octahedral-like $\text{Al}_6(\text{OH})H^+$ intermediate I2-1 which features the O-bridged hydroxyl group and terminal Al-H bond.

**Figure 1.** Reactant $\text{Al}_6^{+}$ (R), initial adduct ion $\text{Al}_6^{+} \cdot \text{OH}_2$ of the gas-phase reaction of $\text{Al}_6^{+}$ with $\text{H}_2\text{O}$ (COM) and product of this reaction, $\text{Al}_6\text{O}^+$ (P) as optimized at the B3LYP/aug-cc-pVTZ level (bond distances are in Å). The R, COM and $\text{Al}_6\text{O}^+$ species are common for $\text{PATH A}$ and $\text{PATH B}$.

**Figure 2.** $\text{PATH A}$: Transition state for dissociation of the O-H bond of $\text{H}_2\text{O}$ on $\text{Al}_6^{+}$ ($\text{TSIO-H}$), $\text{Al}_6(\text{OH})H^+$ reaction intermediate (I1), transition state for $\text{H}_2$ elimination ($\text{TSIH}_2$) and $\text{Al}_6\text{O}^+ \ldots \text{H}_2$ exit channel dihydrogen complex (EX) optimized at the B3LYP/aug-cc-pVTZ level (bond distances are in Å).
Figure 3. PATH B: Transition state for dissociation of the O-H bond of H₂O on Al₆⁺ (TS₂O-H), Al₆(OH)H⁺ reaction intermediate (I₂), isomerization transition state (TSISO), Al₆(OH)H⁺ reaction intermediate (I₂-1), transition state for H₂ elimination (TS₂H₂) and Al₆O⁺...H₂ exit channel dihydrogen complex (EX) optimized at the B3LYP/aug-cc-pVTZ level (bond distances are in Å).

According to Figure 3, the latter intermediate is a starting point for the H₂ elimination step taking place through the transition state TS₂H₂. Though this TS for H₂ elimination requires overcoming an energy barrier of 19.7 kcal/mol with respect to I₂-1, it is located well below the initial reactants, i.e., by 22.4 kcal/mol (Figure 4). As was seen for PATH A, the PATH B is next continued with the formation of the exit channel dihydrogen complex Al₆O⁺...H₂ (EXT), and is ended with the H₂ expelling.

In summary, using density functional theory we have identified two low-energy paths for the gas-phase reaction of the Al₆⁺ cluster cation with H₂O molecule to yield Al₆O⁺ and H₂. Detailed reaction paths comprising the initial adduct ion formation, O-H bond dissociation and H₂ elimination major steps are described. The Al₆⁺...OH₂ initial adduct ion formation is predicted to be a significantly exothermic step (by ca. 20 kcal/mol at the B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ + ZPE computational level). The relatively deep potential well of the adduct ion along the reaction coordinate contributes to the favourable energetic location of the O-H bond dissociation transition states (related to PATH A and PATH B) with respect to the entrance channel. The overall H₂ elimination reaction is calculated to be exothermic by 52.4 kcal/mol. The calculated energy profile for the Al₆⁺ + H₂O → Al₆O⁺+ H₂ reaction with n=6 is consistent with the experimental observation [2].
Figure 4. The schematic energy profile for the $\text{Al}_6^{+} + \text{H}_2\text{O} \rightarrow \text{Al}_6\text{O}^{+} + \text{H}_2$ reaction calculated at the ZPE corrected B3LYP/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ level (note that the exit channel complex is not included).

Acknowledgement
The author acknowledges a generous support of computer time at the Wroclaw Center for Networking and Supercomputing, WCSS.

References
[1] Spence D, Latimer E, York W, Boatwright A, Feng C, Yang S and Ellis A M 2014 Int. J. Mass Spectrom. 365-366 86
[2] Arakawa M, Kohara K, Ito T and Terasaki A 2013 Eur. Phys. J D 67 80
[3] Roach P J, Woodward W H, Castleman Jr A W, Reber A C and Khanna S N 2009, Science, 323 492
[4] Reber A C, Khanna S N, Roach P J, Woodward W H and Castleman Jr A W 2010, J. Phys. Chem. A 114 6071
[5] Moc J, Musaev D G and Morokuma K 2000 J. Phys. Chem. A 104 11606
[6] Becke A D 1993 J. Chem. Phys. 98 5648
[7] Lee C, Yang W and Parr R G 1988 Phys. Rev. B 37 785
[8] Dunning T H 1989 J. Chem. Phys. 90 1007
[9] Gonzalez C and Schlegel H B 1989 J. Chem. Phys. 90 2154
[10] Frisch M J et al 2009 Gaussian 09 revision B.01 (Gaussian Inc, Wallingford, CT.)