Interaction of water, methanol, and ammonia with $Al_xO_y^-$: A comparative theoretical study of $Al_5O_4^-$ versus $Al_3O_3^-$

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The chemical reactions of water, methanol, and ammonia with $Al_5O_4^-$ have been studied using electronic structure calculations. The chemistry of $Al_5O_4^-$ with these molecules is different from that of $Al_3O_3^-$. While $Al_3O_3^-$ dissociatively adsorbs two water molecules (and methanol), $Al_5O_4^-$ reacts with only one. In addition, $Al_5O_4^-$ does not show any reaction with ammonia while recent experimental and theoretical studies suggest that $Al_3O_3^-$ chemisorbs ammonia. These apparent differences in their chemical reactivity have been explained based on the thermodynamic stability of the corresponding reaction products and kinetic barriers associated with their formation. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2790012]

I. INTRODUCTION

The electronic structures and chemical reactions of small, nonstoichiometric aluminum oxide cluster anions ($Al_xO_y^-$) have been subjects of active research. Part of the motivation behind these studies is to understand the geometry and chemistry of the defect sites at the surface of bulk alumina using clusters as model systems. Many of these clusters have been characterized using mass spectrometry, photoelectron spectroscopy, and electronic structure calculations.[1–10] Among the hypermetallic cluster anions, $Al_3O_3^-$ and $Al_5O_4^-$ draw special attention owing to their high abundance in the observed mass spectra.[11,12] Ghanty and Davidson first proposed two almost isoenergetic structures for $Al_3O_3^-$ which were later supported by additional experiments and theoretical studies.[13–15] In a previous publication, we have assigned a near-planar ring structure as the observed isomer for $Al_5O_4^-$.[11] Besides structures, the interaction of these cluster anions with water has also been thoroughly investigated. $Al_3O_3^-$ dissociatively adsorbs two water molecules; however, it fails to bind a third one.[16,17] This is evident from the absence of any peak corresponding to $Al_3O_3 \cdot (H_2O)_3^-$ in the experimental mass spectrum.[18] Guevara-Garcia *et al.* have recently pointed out that steric factors prevent the third water molecule from dissociating on $Al_3O_3^-$.[19] In addition, both experimental and detailed theoretical studies are now available for the reaction of methanol and ammonia with $Al_3O_3^-$.[19–21] Methanol interacts with $Al_3O_3^-$ the same way water does. However, unlike the case of water and methanol, only one molecule of ammonia reacts with $Al_3O_3^-$.[20] According to Guevara-Garcia *et al.*, the relative energies of the adsorption products along the reaction pathway do not support dissociative addition of a second NH_3 molecule.[19]

In the case of $Al_5O_4^-$, although the addition of a single water molecule has been investigated in detail,[11,22] its interaction with methanol and ammonia has not been reported

thus far. Given that $Al_3O_3^-$ and $Al_5O_4^-$ correspond to stable computed structures, it will be interesting to see how $Al_5O_4^-$ interacts with these other two molecules. In fact, our results suggest that while $Al_3O_3^-$ reacts with two water molecules (and methanol), $Al_5O_4^-$ will react with only one and, unlike $Al_3O_3^-$, $Al_5O_4^-$ is not predicted to show any reaction with NH_3. In this paper, we explain the chemical behavior of $Al_5O_4^-$ in terms of the thermodynamic stability of the products formed at different stages of reaction and the associated kinetic energy barriers.

II. COMPUTATIONAL DETAILS

All the calculations reported in this study have been performed using the GAUSSIAN 03 software package.[23] Full geometry optimizations on all the molecular species have been carried out using the B3LYP hybrid density functional level of theory and the $6-311+G(3df,2p)$ basis set.[24,25] The reaction energy parameters and activation energies have been computed with the inclusion of zero-point energy corrections. All the reactants and products are true minima with all positive frequencies and the transition states are well characterized with a single imaginary frequency. The nature of the transition states are further verified by means of intrinsic reaction coordinate (IRC) scans.[26] The basis set superposition errors (BSSEs) for the molecular adducts were computed using the counterpoise (CP) method.[27] The BSSEs in such cases are computed to be less than 2 kcal/mol and have negligible impact on the final analysis. The total energy of the isolated (cluster+ligand) system is considered to be zero and this zero energy state is described as the reference level in the text.

III. RESULTS

A. Addition of water

The experimental mass spectrum for hydrated $Al_5O_4^-$ shows a peak at 217 amu, indicating the formation of $Al_5O_4 \cdot H_2O^-$.[11] However, it does not show any sign for the addition of a second water molecule. The details for the ad-

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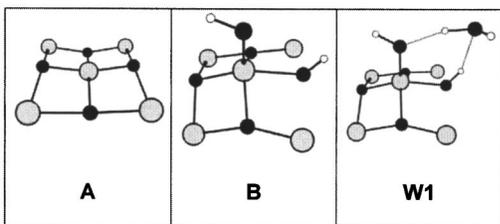
FIG. 1. Structure of bare $Al_5O_4^-$ cluster (A), monohydrated $Al_5O_4^-$ cluster (B), and H-bonded complex (W1) after addition of a second water molecule to B. Color: Al (light gray), O (black), and H (white).

dition of the first water molecule to $Al_5O_4^-$ can be found in our earlier publications.[11,22] We will examine here what prevents the species $Al_5O_4 \cdot (H_2O)_2^-$ from appearing in the mass spectrum. In the case of bare $Al_5O_4^-$, initially, water approaches the positively charged central Al atom and forms a molecular complex driven by charge-dipole-type interactions between this center and an oxygen lone pair of water. The formation of a similar complex is not possible in the case of a second water molecule. If we compare between the bare (A) and monohydrated cluster (B) ions shown in Fig. 1, the local environment around the central metal atom in the latter species is more densely populated, and prevents direct binding of H_2O to this center. However, we find alternative structures resulting from hydrogen bonding between a water molecule and cluster B. Two such H-bonded structures (W1 in Fig. 1 and W2 in Fig. 2) are presented here. In W1, the water molecule is positioned between two cluster OH groups. A somewhat similar structure has been proposed for $Al_3O_3 \cdot (H_2O)_3^-$ in Ref. 19. While water acts as a hydrogen donor in one of the H bonds, it acts as a hydrogen acceptor in the second H bond. The presence of two hydrogen bonds forms a six-membered ring in W1 and provides an additional stability of 3.8 kcal/mol compared to W2, in which a single H bond is observed between a water hydrogen and a cluster oxygen.

Dissociative adsorption of water is not possible in W1
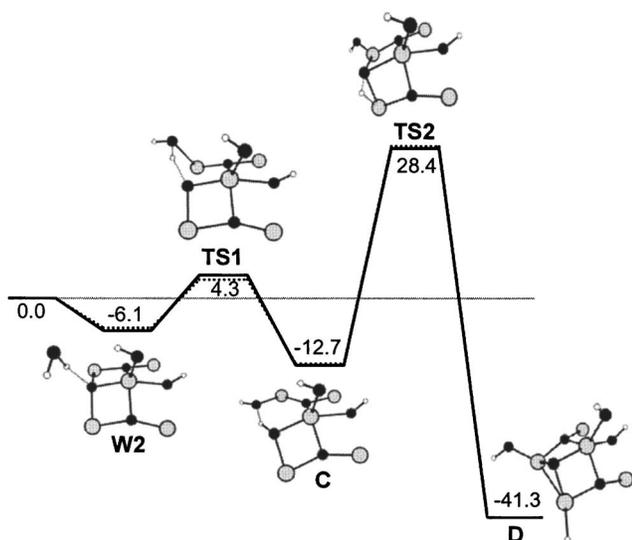
FIG. 2. Energy (kcal/mol) diagram for dissociative addition of W2. The zero energy refers to the total energy of isolated cluster (in this case, B) and H_2O.
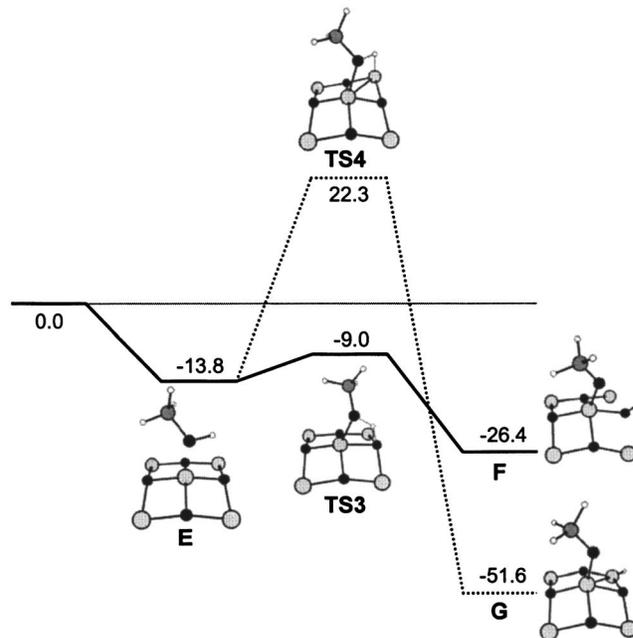
FIG. 3. Energy (kcal/mol) diagram for addition of CH_3OH to $Al_5O_4^-$. The solid line represents the formation of the hydroxide isomer while the dotted line represents the formation of the hydride isomer.

because dissociation leads to a third OH group being attached to the central Al atom in B. However, this aluminum is already pentacoordinated and the local chemical environment is too sterically crowded to accommodate an additional ligand. On the other hand, dissociation of water in W2 leads to a thermodynamically more favorable product (C), though the additional stability gained in this process is only 6.6 kcal/mol. TS1 in the potential energy diagram shown in Fig. 2 represents the transition state for this dissociative addition of water. The transition energy barrier is 4.3 kcal/mol from the reference level. This means that the reaction needs to be overall activated. An important finding from our previous work is that an isomeric structure with an Al–H bond is likely to be thermodynamically more stable but may not be energetically accessible, requiring a high kinetic barrier.[22] To consider such an isomer, we attempted a 1,2-H migration from O to the neighboring Al center in the all-hydroxy species C. Indeed, we came up with a new hydride isomer, shown as D, that is 28.6 kcal/mol more stable than C. As expected, the formation of this hydride isomer involves a very high energy transition state (TS2), unlikely to be accessible under the experimental conditions.

B. Addition of methanol

Because of their comparable pK_a values (15.5 vs 15.2), methanol interacts with $Al_5O_4^-$ in exactly the same way water does. As a result, the resulting products have similar structures and stabilities. Figure 3 shows a potential energy diagram for addition of the first CH_3OH molecule. In this diagram, E represents the initial cluster-ligand complex, TS3 is the transition state for O–H dissociation, and F is the product formed after H migration to a neighboring oxide center. Alternatively, H can migrate to a metal atom at the edge of
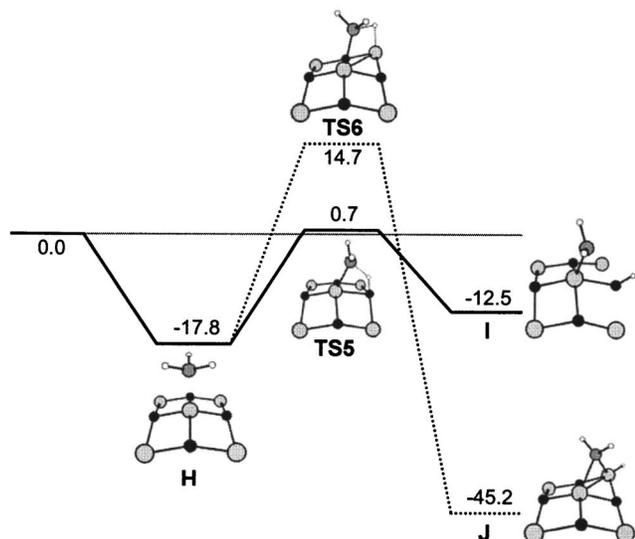
FIG. 4. Energy (kcal/mol) diagram for addition of NH_3 to $Al_5O_4^-$. The solid line represents the formation of the hydroxide isomer while the dotted line represents the formation of the hydride isomer. Note that the first reaction is endothermic.

the cluster (TS4), in which case, the product is a hydride isomer (G). For adsorption of the second methanol, the reaction energy profile is similar to that of water (shown as a dotted line in Fig. 2). Since there are no notable differences between water and methanol, we prefer not to discuss any more details.

C. Addition of ammonia

Compared to the other two ligands, ammonia is more basic and forms a strong charge-dipole complex (H) with the central Al atom in $Al_5O_4^-$. The binding energy for this complex is computed to be 17.8 kcal/mol. *Surprisingly, however, activation of a N–H bond leads to a dissociated product (I) that is significantly less stable than the initial charge-dipole complex.* Such an observation is unprecedented in the reactions of aluminum oxide cluster ions. In all previous studies, including reactions of water and methanol presented here, we see that dissociation always leads to thermodynamically more favorable states. Displayed in Fig. 4 is a potential energy diagram for ammonia reacting with $Al_5O_4^-$. The energy barrier for transition from H to I is only 0.7 kcal/mol (TS5) above the reference scale. While the amine-hydroxyl species (I) is energetically less stable than the complex H, the "hydride" isomer containing an Al–H bond (J) is 27.4 kcal/mol more stable. Again, as expected, the activation energy barrier for the corresponding transition state (TS6) is very high, 14.7 kcal/mol above the zero level.

IV. DISCUSSION

At this point, it is clear that there are three distinct minima on the potential energy surface that could be formed as products: the initial molecular complex (charge-dipole type or H bonded), the hydroxyl isomer, and the hydride isomer. Before we specifically assign which of these species are expected to form under typical experimental conditions,[11]

TABLE I. Stability of the different reaction products (ΔE) with respect to the isolated species (cluster+ligand). E_a represents activation barrier with respect to the same reference scale. Energy unit is kcal/mol.

System	ΔE	E_a	Observed
$Al_3O_3^- + H_2O$			
Complex	−14	⋯	No
OH product	−50	−13	Yes
AlH product	−67	26	No
$Al_3O_3^- + 2H_2O$			
Complex	−13	⋯	No
OH product	−29	−4	Yes
$Al_3O_3^- + 3H_2O$			
Complex	−12	⋯	No
$Al_3O_3^- + CH_3OH$			
Complex	−14	⋯	No
OH product	−48	−12	Yes
$Al_3O_3^- + 2CH_3OH$			
Complex	−13	⋯	No
OH product	−29	−5	Yes
$Al_3O_3^- + NH_3$			
Complex	−18	⋯	No
OH product	−34	−6	Yes
AlH product	−47	16	No
$Al_3O_3^- + 2NH_3$			
Complex	−6	⋯	No
OH product	−10	7	No
$Al_5O_4^- + H_2O$			
Complex	−12	⋯	No
OH product	−27	−7	Yes
AlH product	−61	10	No

we focus our attention on Table I that summarizes information about some previously studied systems. Here, ΔE refers to overall stability of a product with respect to infinitely separated reacting species (cluster+ligand). The last column in this table tells us which of these products are actually observed in the experiment. No hydride isomers have been observed so far for any of the systems. From a thermodynamic perspective, they are all exceptionally stable (on average more than 50 kcal/mol). However, high activation barriers rule out the chance of their formation. The lowest of these barriers is 10 kcal/mol and most of them are substantially larger. On the other hand, among the species that are seen experimentally, the highest activation barrier is computed to be −4 kcal/mol. This tells us that the maximum energy barrier should be somewhere in between these two extreme values (approximately less than 5 kcal/mol) for dissociation to be energetically facile. However, kinetics is not the only determining factor. Otherwise, we should have seen formation of those species that do not need to overcome a kinetic barrier, e.g., the initial molecular complexes. Thermodynamic stability of the products also needs to be considered. Note that among all the hydroxide isomers that are seen experimentally, the ($Al_5O_4^- + H_2O$) system has the lowest thermodynamic stability, which is 27 kcal/mol. Hence, we predict that a species with stability of more than 20–25 kcal/mol has a real chance to be observed in the reaction chamber. It is clear that free energy considerations will favor the separated species and explain why the molecu-

TABLE II. Computed ΔH, $T\Delta S$, and ΔG values for reactions (1) and (2) at different temperatures. Energy unit is kcal/mol.

T (K)	Reaction (1)			Reaction (2)		
	ΔH	$T\Delta S$	ΔG	ΔH	$T\Delta S$	ΔG
0	−14.8	0.0	−14.8	−25.9	0.0	−25.9
48	−15.1	−1.2	−13.9	−26.1	−1.6	−24.5
98	−15.3	−2.7	−12.6	−26.2	−3.3	−22.9
148	−15.4	−4.3	−11.1	−26.1	−5.0	−21.1
198	−15.5	−5.8	−9.7	−26.0	−6.5	−19.5
248	−15.5	−7.3	−8.2	−25.9	−8.0	−17.9
298	−15.5	−8.7	−6.8	−25.7	−9.5	−16.2
348	−15.4	−10.1	−5.3	−25.5	−10.9	−14.6
398	−15.3	−11.5	−3.8	−25.4	−12.2	−13.2
448	−15.2	−12.8	−2.4	−25.2	−13.6	−11.6
498	−15.1	−14.1	−1.0	−25.0	−14.9	−10.1
548	−15.0	−15.4	0.4	−24.8	−16.1	−8.7

lar complexes with modest binding energies are not seen experimentally. Note that the discussions made here are solely based on the density functional calculations. While a different level of theory may change the computed energies slightly, our qualitative conclusions are unlikely to change. Also, other than simple energetics, there may be additional factors that also guide the formation of a product. Nevertheless, based on the two aforesaid criteria, we will now see which of the products reported in this paper are energetically accessible.

First of all, we consider the species $Al_5O_4 \cdot (H_2O)_2^-$. While formation of D is restricted because of its high activation barrier (28.4 kcal/mol), low thermodynamic stability of W1 (−9.9 kcal/mol), W2 (−6.1 kcal/mol), and C (−12.7 kcal/mol) does not allow them to appear in the experiment. This explains the absence of any peak corresponding to $Al_5O_4 \cdot (H_2O)_2^-$ in the mass spectrum. To the best of our knowledge, no experiment has been performed so far to study interaction of methanol with the $Al_5O_4^-$ cluster. The computed energy values do not support the formation of $Al_5O_4 \cdot (CH_3OH)_2^-$. However, when one molecule of methanol reacts with $Al_5O_4^-$, the calculated energies favor the formation of the hydroxide isomer (F). The adiabatic electron binding energy of this product is predicted to be ~3.1 eV. Here, we have taken into account the fact that the computed B3LYP electron binding energies are, in general, too low by approximately 0.2 eV. It will be interesting to see if our predictions for this system are verified in future experiments. Finally, we focus on the case of ammonia. Although, the initial complex (H) has considerable stability (−17.8 kcal/mol), it is still below the benchmark set up here. We already know that the reaction that leads to the formation of the hydroxide isomer (I) is actually endothermic. As a result, it is unlikely that this species will be seen in the experiment. Finally, the high barrier precludes the possibility of formation of the hydride isomer J. Altogether, our results suggest that $Al_5O_4^-$ is unlikely to show any reaction with NH_3. This appears to be consistent with results from preliminary experimental observations.[28]

Although simple energy considerations, as considered above, provide a qualitative explanation of product formation, a more rigorous free energy analysis has also been performed to look into the effect of entropy and temperature on such reactions. The following two reactions have been considered as representative examples:

(1) $Al_5O_4^- + NH_3 \rightarrow [Al_5O_4 \cdot NH_3]^-$
      ($\Delta H_{298}^o = -15.5$ kcal/mol) and
(2) $Al_5O_4^- + CH_3OH \rightarrow [Al_5O_3(OH)OCH_3]^-$
      ($\Delta H_{298}^o = -25.7$ kcal/mol).

Reaction (1) is associated with the maximum enthalpy change where the resulting product is unlikely to be observed. On the other hand, reaction (2) is associated with the minimum enthalpy change among all the reactions where the resulting product is either observed or predicted (based on the computed results) to be observed. Note that the kinetic barriers allow both of these products to be energetically accessible. The Gibbs free energy changes (ΔG) for these two reactions are nearly linear with respect to temperature. For convenience, the computed ΔH, $T\Delta S$, and ΔG values for these two reactions at different temperatures have been listed in Table II. According to this table, the reactions are spontaneous in the forward direction at room temperature. However, above 500 K, ΔG for reaction (1) becomes positive. In contrast, ΔG for reaction (2) is still significantly negative in the vicinity of 500 K. The fact that only the product from reaction (2) is likely to be observed in the experiment suggests that the experimental condition corresponds to the clusters being at well above the room temperature. At this temperature, the ΔG's for reactions (1) and (2) will show an opposite trend. Note that the primary difference between the two reactions is that the latter is considerably more exothermic in nature. In addition, there are other factors that may prevent the formation of the molecular complexes. For example, since the experiments are actually done in the gas phase, unless the excess energy for complex formation is lost through collisions, the complex may dissociate back into the individual species.

One more question that we feel relevant to address here is why the reaction of NH_3 with $Al_5O_4^-$ is endothermic (for

hydroxide formation) while a similar reaction in $Al_3O_3^-$ is exothermic, or, for that matter, even addition of water to $Al_5O_4^-$ is exothermic. Dissociation of NH_3 in $Al_5O_4^-$ introduces significant structural rearrangement in cluster I. It weakens several Al–O bonds, especially those connected to the newly formed hydroxide center. An average increment of 0.23 Å in Al–O bond distances from H to I supports this interpretation. Although, a new Al–N covalent bond is formed in this process, the formation of this new bond (bond energy=71 kcal/mol) is not enough to compensate for the net stability lost through hydroxide formation. On the other hand, the dissociation of ammonia in $Al_3O_3^-$ does not perturb the Al–O bonds in such a significant way (less than 0.1 Å change in lengths). This explains the endothermicity of the first reaction. The dissociation of H_2O in $Al_5O_4^-$ results in a similar product (B) as I. However, in this case, the new Al–O bond (bond energy=122 kcal/mol) is strong enough to compensate for the net stability lost through hydroxide formation.

V. CONCLUSIONS

In conclusion, we have discussed the reactions of $Al_5O_4^-$ with water, methanol, and ammonia. We have shown that for a reaction product to be observed under typical experimental conditions, the thermodynamic stability of the species should be more than 20–25 kcal/mol. In addition, the activation barrier has to be less than 5 kcal/mol. Based on these sets of criteria, we see that only $Al_5O_4 \cdot ROH^-$ (R=H, CH_3) have a real chance to appear in the mass spectrum while reaction products such as $Al_5O_4 \cdot (H_2O)_2^-$, $Al_5O_4 \cdot (CH_3OH)_2^-$, and $Al_5O_4 \cdot NH_3^-$ are not expected.

We would also like to mention that $Al_5O_4 \cdot H_2O^-$ and $Al_3O_3 \cdot (H_2O)_2^-$ have similar photoelectron spectra because of their similar structures. The structure of $Al_5O_4 \cdot H_2O^-$ has been shown as B in Fig. 1. In the case of $Al_3O_3 \cdot (H_2O)_2^-$, the two monovalent Al atoms in B have been replaced by two hydrogens. This structural similarity also explains the trend that $Al_5O_4 \cdot H_2O^-$ does not react with a second water molecule while $Al_3O_3 \cdot (H_2O)_2^-$ does not react with a third water molecule.

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