

Are structures with Al–H bonds represented in the photoelectron spectrum of $\text{Al}_3\text{O}_4\text{H}_2^-$?

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(Received 8 February 2006; accepted 2 March 2006; published online 5 June 2006)

Photoelectron spectra of $\text{Al}_3\text{O}_4\text{H}_2^-$ clusters formed by reactions of Al_3O_3^- with water molecules have been interpreted recently in terms of dissociative absorption products with hydroxide and oxide anions that are coordinated to aluminum cations. Alternative isomers with Al–H bonds have lower energies, but barriers to hydrogen migrations that break O–H bonds and create Al–H bonds are high. *Ab initio* electron propagator calculations of the vertical electron detachment energies of the anions indicate that the species with hydrides cannot be assigned to the chief features in the photoelectron spectrum. Therefore, the previously studied dissociative absorption products are the structures that are most likely to be probed in the photoelectron spectra. © 2006 American Institute of Physics. [DOI: 10.1063/1.2189858]

INTRODUCTION

Interactions between aluminum oxide and water are pervasive in heterogeneous catalysis, corrosion, tribology, and many branches of environmental science. Chemical phenomena at interfaces between bulk Al_2O_3 and aqueous solutions are complex and therefore have stimulated a broad program of research into fundamental processes at the atomic level. Gas-phase clusters have been studied experimentally^{1–4} and theoretically^{5–7} in a search for models that capture the simplest patterns of structure and reactivity that pertain to interactions between alumina and water. These investigations were built on a foundation of work on clusters of aluminum and oxygen that established the importance of isomerism in the spectroscopic characterization of species of a given mass.^{8–14} Photoinduced isomerization in an anionic cluster, Al_3O_3^- , has been demonstrated⁸ and characterized with hole-burning techniques.⁹ The energetic order of structural isomers of a given Al_nO_m formula has been shown to differ repeatedly from that of the corresponding anions.¹² In many cases, spectra on mass-selected samples reflect the presence of two or more structures with nearly identical energies. The reactivity of these species with water molecules may now be examined with similar spectroscopic probes³ and computational tools.^{4–7}

An excellent model for aluminum oxide reactivity is provided by the Al_3O_3^- cluster, which has been shown to have two almost isoenergetic isomers known as the *book* (or *box*) and the *kite*^{11,12,14} (see Fig. 1). Recent computational studies^{5–7} focused on reactions between Al_3O_3^- clusters and water molecules and on the photoelectron spectra³ of the resulting $\text{Al}_3\text{O}_4\text{H}_2^-$ and $\text{Al}_3\text{O}_5\text{H}_4^-$ products.

Optimizations of stable structures, including anion-molecule complexes, and of transition states established the exothermicity and kinetic facility of the dissociative absorption of a water molecule by Al_3O_3^- . After the barrierless formation of $\text{Al}_3\text{O}_3^-(\text{H}_2\text{O})$ complexes, protons shift to neighboring oxides with low activation energies that do not exceed the binding energy of the anion-molecule complex. Electron propagator calculations of the vertical electron detachment energies (VEDEs) of the most stable product anion^{5,6} were in close agreement with photoelectron spectra,³ which display broad humps that are centered at ~ 2.7 and 3.8–4.0 eV. However, the unresolved vibrational structure of the $\text{Al}_3\text{O}_4\text{H}_2^-$ spectrum may conceal the presence of peaks that could belong to other isomers produced by dissociative absorption. (For example, another stable isomer is predicted to have VEDEs of 3.0 and 5.2 eV.) Studies that involved ammonia or methanol instead of water produced similar results.

Recent computational work¹⁵ has shown that $\text{Al}_x\text{O}_y\text{H}_z^-$ isomers with hydride ligands in Al–H bonds may be more stable than structures that have only hydroxide and oxide constituents. Such species may originate from oxidative additions of water molecules to aluminum oxide anions or from migrations of hydrogens that replace O–H by Al–H bonds. From these results, it is not clear whether anions with Al–H bonds are relevant to the interpretation of $\text{Al}_3\text{O}_4\text{H}_2^-$ photoelectron spectra.

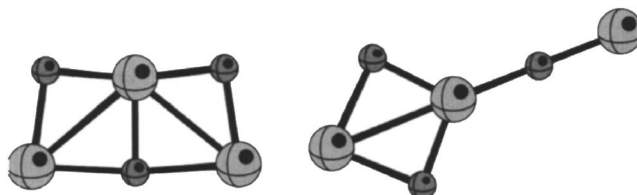


FIG. 1. Book and kite forms of Al_3O_3^- .

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In this paper, we reexamine ground state energies and structures of $\text{Al}_3\text{O}_4\text{H}_2^-$ and consider transition states which pertain to hydrogen migrations and other rearrangements. Electron propagator calculations on anion VEDEs are compared with their experimental counterparts. In combination, these results permit inferences on the species that are responsible for the observed photoelectron spectra and on the processes that produce them.

METHODS

Geometry optimizations without symmetry constraints were performed with the GAUSSIAN 03 program¹⁶ in the B3LYP/6-311+G(2d,p) approximation.^{17,18} Subsequent re-optimizations at the MP2/6-311+G(2d,p) level were carried out to verify the structures thus obtained. To locate transition states, the synchronous transit-guided quasi-Newton method¹⁹ was used. Optimized minima and transition states were confirmed with harmonic frequency analysis.

MP2 geometries were used in electron propagator²⁰ calculations of the VEDEs with the P3 approximation²¹ and the 6-311+G(2df,p) basis set.¹⁸ For every electron detachment energy calculated with the P3 method, there is a Dyson orbital φ^{Dyson} that describes the corresponding change in electronic structure,

$$\varphi^{\text{Dyson}}(x_1) = N^{-0.5} \int \psi_{\text{anion}}(x_1, x_2, x_3, \dots, x_N) \times \psi_{\text{neutral}}(x_2, x_3, x_4, \dots, x_N) dx_2 dx_3 dx_4 \cdots dx_N,$$

where x_j is the space-spin coordinate of the i th electron. The normalization integral of a given Dyson orbital is called the pole strength. Perturbative approximations such as the P3 method work best when pole strengths exceed 0.85.

Molecular pictures and Dyson orbital plots were generated, respectively, with BALL & STICK²² and MOLEKEL.²³

RESULTS

Structures

Figure 2 shows relative energies for $\text{Al}_3\text{O}_4\text{H}_2^-$ isomers, including those with hydride ligands, the previously reported dissociative adsorption products of the reaction of Al_3O_3^- isomers (book and kite) with a water molecule,^{5,6} and a newly found dissociative adsorption product. B3LYP energy differences and structures are in good agreement with MP2 results. Almost the same stability order is maintained and the largest bond distance discrepancy between these two methods is 0.015 Å. The lowest isomer (I) is a C_{2v} dihydride. This structure is closely related to the third lowest isomer of Al_3O_4^- .²⁴ The second lowest isomer (II) is a planar structure with C_s symmetry. Isomers III and VI (in the MP2 ordering) resemble the book structure of Al_3O_3^- , whereas structures VII and VIII are closely related to the kite. B3LYP Al–H bond distances are in the range of 1.58–1.61 Å. The Al–H bond distance of AlH_3 with the same model is 1.58 Å. Because of the similarity of isomer I of $\text{Al}_3\text{O}_4\text{H}_2^-$ and the third lowest isomer of Al_3O_4^- , skeletons of the other two lowest isomers of the latter anion were used as a template for investigation of alternative structures. For the lowest Al_3O_4^- isomer, which

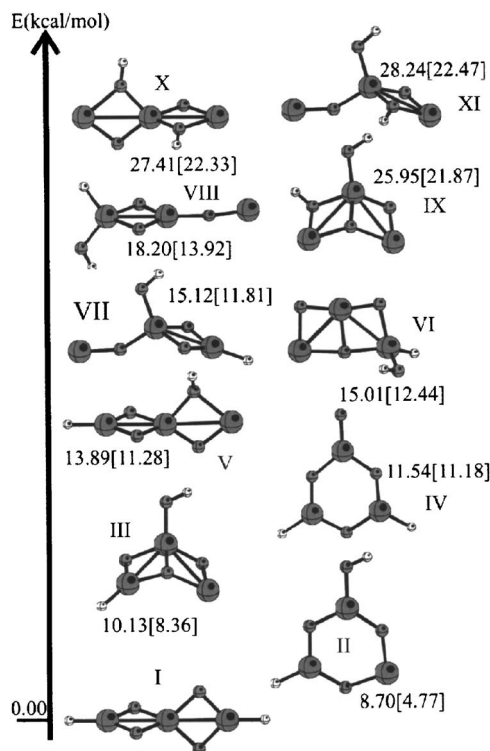


FIG. 2. MP2/6-311+G(2d,p) and B3LYP/6-311+G(2d,p) relative energies for $\text{Al}_3\text{O}_4\text{H}_2^-$ clusters. B3LYP values are in brackets.

differs from the kite form of Al_3O_3^- by an oxygen nucleus at the apex of the quadrilateral opposite to the kite's tail, addition of hydrogen nuclei to the monocoordinate Al and O atoms produces a structure that is 40 kcal/mol higher in energy than isomer I at the B3LYP/6-311+G(2d,p) level. For the second lowest Al_3O_4^- isomer, which differs from the book form of Al_3O_3^- by an oxygen coordinated to a corner Al center, placement of H nuclei at the monocoordinate O and at the dicoordinate Al leads, after optimization, to structure II.

Vertical electron detachment energies and Dyson orbitals

Table I summarizes anion VEDEs calculated with the P3 electron propagator approximation for structures I–XI. Because the pole strengths are between 0.88 and unity, this perturbative approximation is likely to be valid. Electron correlation and orbital relaxation effects cancel approximately in some cases, but in others the discrepancy between P3 and Koopmans results may exceed 1 eV. The order of final states predicted by P3 differs with respect to the Koopmans results for structures IV and VIII.

Except for the I, IV, and VIII isomers, all the first VEDEs correspond to Dyson orbitals which consist chiefly of Al 3s functions on dicoordinate Al for structures II, III, V, VI, and IX–XI or on monocoordinate Al for structure VII. For anions with two hydride ligands (I and IV), no valence electrons localized chiefly on Al centers remain and therefore the Dyson orbitals are distributed primarily over O and H centers. In the absence of hydride ligands (structures IX–XI), each anion has two VEDEs that correspond to Dyson orbitals that are concentrated on low-coordinate Al centers. The re-

TABLE I. Vertical electron detachment energies (eV) and Dyson orbital descriptions from Koopmans's theorem (KT) and P3 approximations.

Isomer	Dyson orbital ^a	KT	P3
I	O π	6.90	5.75
	O σ	7.38	6.03
	O σ	7.38	6.03
	O π	7.43	6.28
II	<i>d</i> -Al σ	1.92	1.82
	O ring σ	8.09	6.61
	O ring π	8.23	6.90
III	<i>d</i> -Al σ	2.80	2.71
	O π	7.66	6.34
	O σ	7.94	6.45
IV	O <i>p</i> ring	4.82	4.13
	O <i>p</i> π	4.69	4.15
	O <i>p</i> bond	6.28	5.54
V	<i>d</i> -Al σ	3.16	3.09
	O ring π	7.48	6.26
	O ring σ	7.83	6.47
	O <i>p</i>	7.89	6.60
VI	<i>d</i> -Al σ	3.33	3.28
	H σ	7.63	6.82
VII	Al σ tail	4.80	4.83
	O ring π	6.92	5.74
	O ring σ	7.21	5.85
	O ring π , H	8.01	6.80
VIII	O ring π	6.89	5.70
	O ring σ	7.13	5.75
	H σ	6.54	5.80
	Al σ tail	6.02	6.07
	O ring π	8.02	6.67
IX	Al σ	2.83	2.71
	Al σ	3.91	3.80
X	Al σ	3.42	3.33
	Al σ	3.64	3.60
XI	Al apex	3.05	2.97
	Al tail	5.18	5.20
	O π	7.54	6.21
	O σ	8.19	6.65

^a*d*-Al=dicoordinate aluminum.

maining cases have one hydride ligand and exhibit a single Dyson orbital that is localized on the least-coordinate Al; only for structure VIII does this orbital not correspond to the lowest VEDE. P3 corrections to Koopmans results are relatively small when the Dyson orbital is localized on Al nuclei.

Transition states

Table II displays energies for transition states which link pairs of Al₃O₄H₂⁻ minima. Except for the last case, all energy barriers correspond to the shift of a hydrogen from an oxygen atom to an adjacent aluminum. Large barriers accompany the evolution of the migrating hydrogen's character from protonic to hydridic. In contrast, a small barrier is en-

TABLE II. B3LYP/6-311+G(2*d*,*p*) energy barriers (kcal/mol) for hydrogen transfer processes and the isomerization between structures II and III.

Reactive	Product	Energy barrier
V	I	51.37
X	V	52.25
IX	II	54.81
IX	III	52.01
XI	VII	51.57
III	II	2.17

countered between structures II and III. B3LYP barriers are usually too low in comparison to results obtained with more exacting treatments of electron correlation.

DISCUSSION

In this section, the identity of the species that are represented in the photoelectron spectrum of Al₃O₄H₂⁻ is considered. The results of Fig. 2 show that the Al₃O₄H₂⁻ hydrides are more stable thermodynamically than the products of dissociative absorption of a water molecule by Al₃O₃⁻. If one considers the latter structures (IX–XI) to be kinetically favored, then isomer I can be viewed as originating sequentially from structures V and X through H migrations. Previous studies^{5,6} had not considered isomer X, which bears a close resemblance to the already encountered structure XI. Isomer II can be viewed similarly as proceeding from structure IX in a process that involves a hydrogen transfer from the corner hydroxyl group to a lateral Al atom and the formation of a six-member ring. (This process was considered in a recent study of isomers with Al–H bonds.¹⁵) The third lowest isomer (III) retains the same structure as IX except for another O to Al hydrogen shift. More complex transfer processes may link isomers IV and VI to structures with no hydride ligands. As can be seen from Table II, energy barriers for hydrogen transfer processes are very large. It is unlikely that Al₃O₄H₂⁻ structures with hydrides are formed by such pathways.

One may also consider the alternative of a one-step, oxidative addition of a water molecule to Al₃O₃⁻ to produce structures with a hydroxide and a hydride. Isomers VI and VIII could be considered to be products of such a reaction, where the water molecule approaches an Al center with a pair of valence electrons. Pathways of this type are improbable because of strong repulsions between oxygen lone pairs and the very localized pair of electrons in the noncentral Al atoms of the Al₃O₃⁻ clusters. The attack of the O of water at a central Al atom leading to the formation of the dissociative adsorption products also is preferred on electrostatic grounds.^{5,6}

The VEDEs of Table I also provide evidence on the identity of the species observed in the anion photoelectron spectrum. The second most stable isomer (II) has a VEDE of 1.82 eV, but no signal below 2.5 eV is detected in the experiment.³ Structure II therefore is not represented in the spectrum. Cluster III presents a VEDE of 2.71 eV which could be correlated with the experimental signal at 2.7–2.8 eV but for the low barrier to isomerization between

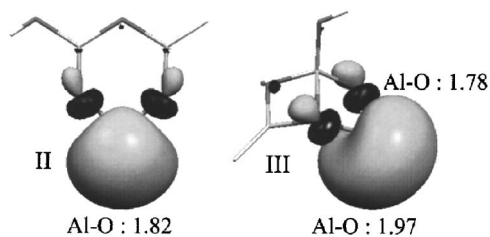


FIG. 3. Dyson orbitals for the first VEDEs of clusters II and III with Al-O bond distances (Å).

it and cluster II. Structure III must also be eliminated from consideration, for such a barrier, even if it is to be underestimated by 50%, would be surmounted frequently under the conditions of the experiment.

The difference of 0.9 eV in the first VEDEs of clusters II and III is produced by stronger overlaps between O $2p$ and Al $3s$ orbitals (see Fig. 3). The latter functions are destabilized by antibonding interactions with two O neighbors at relatively short distances in structure II, whereas only one such interaction occurs in structure III.

Some of the other hydride isomers (IV–VII) have first VEDEs which could be embedded in the broad peaks that characterize the photoelectron spectrum. The present VEDE results alone do not suffice to render these structures irrelevant to the experiment, for it is possible that they could be formed by some other pathway that has not been considered here. Other hydride structures (I and VIII) have first VEDEs which exceed the experimental photon energies. They may be present but unobserved. However, the structures with hydrides cannot account for the lowest observed VEDEs.

Given the low barriers to formation of structures IX–XI from $\text{Al}_3\text{O}_3 + \text{H}_2\text{O}$ and the high barriers that accompany H shifts that produce aluminum-hydride bonds, it is unlikely that the hydride structures contribute to the photoelectron spectrum. Measurements of higher electron binding energies of $\text{Al}_3\text{O}_4\text{H}_2^-$ enabled by more energetic photon sources may be needed to establish whether structure XI, with a VEDE of ~ 5.2 eV, is present.

CONCLUSIONS

Structures and VEDEs of the most stable $\text{Al}_3\text{O}_4\text{H}_2^-$ isomers with hydride ligands (I–VIII) have been presented. In addition, a new structure with no hydrides (X) has been studied. These results have been compared to results on two previously discovered isomers, IX and XI. Barriers to hydrogen shifts that destroy O–H bonds in favor of Al–H bonds are high. Some of the most stable hydride structures (II and III) may be eliminated from consideration because of a low predicted VEDE for structure II and a low barrier to conversion between the latter isomer and structure III. The kinetics of ion formation that precede the photoelectron experiment on $\text{Al}_3\text{O}_4\text{H}_2^-$ are likely to favor the formation of isomers IX–XI. Isomer IX's first predicted VEDE is compatible with features seen in the spectrum. Alternative methods of ion synthesis,

perhaps with precursors that contain Al–H bonds, may succeed in producing the most stable species of Fig. 2 and in facilitating their characterization through additional photoelectron spectra and *ab initio* calculations.

ACKNOWLEDGMENTS

One of the authors (A.G.-G.) would like to thank CONACYT and Posgrado en Ciencias Químicas (UNAM) for support during his research visit at Kansas State University. The National Science Foundation supported this research through Grant No. CHE-0451810 to Kansas State University. The authors would like to acknowledge Sara Jiménez Cortés and María Teresa Vázquez for technical support and DGSCA/UNAM (México) for providing computer time. This work was partially funded by DGAPA (No. IN 107399) and CONACYT-NSF (No. E120 1778/2001).

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