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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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The Reaction Rates of O_2 with Closed-Shell and Open-Shell Al_x^- and Ga_x^- Clusters under Single-Collision Conditions: Experimental and Theoretical Investigations toward a Generally Valid Model for the Hindered Reactions of O_2 with Metal Atom Clusters

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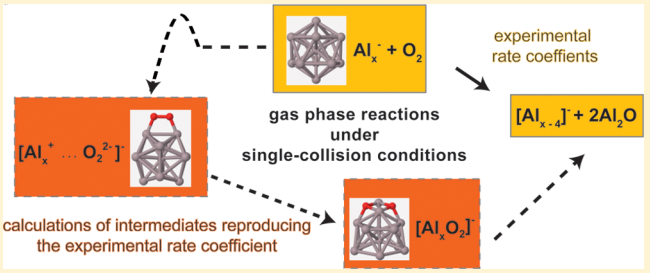
Supporting Information

ABSTRACT: In order to characterize the oxidation of metallic surfaces, the reactions of O_2 with a number of Al_x^- and, for the first time, Ga_x^- clusters as molecular models have been investigated, and the results are presented here for $x = 9-14$. The rate coefficients were determined with FT-ICR mass spectrometry under single-collision conditions at O_2 pressures of $\sim 10^{-8}$ mbar. In this way, the qualitatively known differences in the reactivities of the even- and odd-numbered clusters toward O_2 could be quantified experimentally. To obtain information about the elementary steps, we additionally performed density functional theory calculations. The results show that for both even- and odd-numbered clusters the formation of the most stable dioxide species, $[M_xO_2]^-$, proceeds via the less stable peroxo species, $[M_x^+\cdots O_2^{2-}]^-$, which contains M−O−O−M moieties. We conclude that the formation of these peroxo intermediates may be a reason for the decreased reactivity of the metal clusters toward O_2. This could be one of the main reasons why O_2 reactions with metal surfaces proceed more slowly than Cl_2 reactions with such surfaces, even though O_2 reactions with both Al metal and Al clusters are more exothermic than are reactions of Cl_2 with them. Furthermore, our results indicate that the spin-forbidden reactions of $^3O_2$ with closed-shell clusters and the spin-allowed reactions with open-shell clusters to give singlet $[M_x^+\cdots O_2^{2-}]^-$ are the root cause for the observed even/odd differences in reactivity.



INTRODUCTION

The hindered reactivity of O_2 with metal surfaces, in contrast to their fast reactions with Cl_2, is well-known in classical inorganic chemistry[1] and is based on some important differences between these reactants.

In the case of a base metal such as Al, the O_2 reaction is strongly exothermic with respect to the formation of Al_2O_3 ($2Al + {}^3/_2O_2 \rightarrow Al_2O_3$: $\Delta H_f^\circ = -1676$ kJ mol^{-1}, that is, 838 kJ per 1 mol Al), while less energy is gained in the Cl_2 reaction, where $AlCl_3$ is formed ($Al + {}^3/_2Cl_2 \rightarrow AlCl_3$: $\Delta H_f^\circ = -705$ kJ mol^{-1}).[2] Because of the high stability of Al_2O_3, it remains steadfastly on the surface of the aluminum metal, protecting it and prohibiting further oxidation of the metal. Only at high temperatures >1200 °C, where Al_2O_3 reacts with Al metal to form the low valent oxide molecule Al−O−Al, can alumina be vaporized and removed from the metal surface.[3] The formation of this linear molecule, Al−O−Al, is the essential step in the deterioration of the aluminum surface after reaction of O_2 with solid Al and, as we will see, with Al_x^- clusters:[4]

$$Al_x^- + O_2 \rightarrow Al_{x-4}^- + 2Al_2O_{(g)} \quad (1a)$$

If an excess of O_2 is applied, the Al_2O molecules are easily oxidized to solid Al_2O_3, and simultaneously a large amount of energy is gained:

$$Al_2O_{(g)} + O_{2(g)} \rightarrow Al_2O_{3(s)} \quad (1b)$$

with $\Delta_R H^\circ = -1530.5$ kJ mol^{-1}.[2] In contrast, the chlorination of Al runs at even low temperatures (>200 °C), and the reaction proceeds completely to $AlCl_3$ (or to Al_2Cl_6), which is a volatile solid compound even at these temperatures. Therefore, this reaction continues until the Al metal is consumed.[5,6]

Received: December 10, 2013
Published: February 24, 2014

   dx.doi.org/10.1021/ja4125548 | J. Am. Chem. Soc. 2014, 136, 3607−3616

Besides the thermodynamic data and experimental results, which favor a fast and complete reaction of Al metal with Cl_2 in comparison to O_2, there is a molecular-kinetic reason for the slower reaction of O_2, a stepwise transfer of four electrons from Al to O_2 via several intermediates containing AlO bonds:

$$O_2 \xrightarrow{e^\ominus} O_2^- \xrightarrow{e^\ominus} O_2^{2-} \xrightarrow{2e^\ominus} 2O^{2-}$$

(superoxo) (peroxo) (oxide)

In contrast, in the case of Cl_2 only one intermediate is possible, which contains two AlCl bonds, because every Cl_2 molecule takes two electrons to form two Cl^- anions.

The investigation of the complex reaction of O_2 molecules with metal atom surfaces was and still is a challenging problem for theory and experiment.[7] On the experimental side, it mainly had been dealt with by physicists using surface methods such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM).[7] However, the investigation of surfaces of base metals bears a fundamental difficulty. This is because the 5 eV bond energy (BE) of an Al−O bond (in an Al−O−O−Al fragment) is equivalent to the energy necessary to cleave the O−O bond in the O_2 molecule, producing two O atoms (the O_2 BE is 5.16 eV).[2] A peroxo intermediate fragment Al−O−O−Al, containing two Al−O bonds, will therefore be highly excited (5 eV excess energy) and thus O atoms can also be ejected from the surface.[8] In order to avoid such difficulties, mainly O_2 reactions with surfaces of noble metals have been investigated. There, the M−O bond energy is much smaller (e.g., for Pd−O, 2.87 eV from $PdO_{(g)}$[2] and for Pt−O, 3.28 eV[9a]), and therefore it is possible to detect intermediate fragments, for example, Pt−O−O−Pt, with microscopic methods.[9−11]

Besides the investigations of the hindered O_2 reactions with metal surfaces by using microscopic methods (AFM, STM), a further experimental approach, namely, mass spectrometric investigations of metal atom clusters and their O_2 reactions, promises to give a deeper insight into this complex reaction mechanism.

$Al_n^\pm$ clusters have been investigated in many experimental and theoretical papers during the last two decades.[6,13−16] However, only the Al_{13}^- cluster appears to be an ideal molecular model for studying reactions involving bulk metals. The surprising similarity for the chlorination of the Al_{13}^- cluster and Al metal illustrates the similar thermodynamic behavior.[12,13]

$$Al_{13}^- + 3Cl_2 \rightarrow Al_{11}^- + 2AlCl_{3(g)}$$

$$\Delta_R H = -1137 \text{ kJ mol}^{-1} \quad \text{(calcd)}$$

$$2Al_{(s)} + 3Cl_2 \rightarrow 2AlCl_{3(g)}$$

$$\Delta_R H = -1166 \text{ kJ mol}^{-1} \quad \text{(expt)}$$

However, for the observed hindered reaction of the Al_{13}^- cluster with O_2, note that also the reaction of O_2 with bulk Al is unexpectedly slow,[7,15,18] there have been given several different explanations: (1) the outstanding electronic stability of Al_{13}^- with its 40 valence electron jellium core,[17] (2) the exceptional geometry in which a central Al atom is surrounded by 12 additional Al atoms, which form an icosahedron around it, that is, a magic geometry, (3) the outstanding electron affinity (3.6 eV) of Al_{13}, which is as large as that of the atomic chlorine atom, and finally (4) the spin-forbidden reaction of triplet O_2 with the singlet Al_{13}^- species to give singlet Al_9^- and $2Al_2O$.[18−21]

It was demonstrated that isolated Al_{13}^- ions in an O_2 atmosphere of about 10^{-8} mbar in an ion cyclotron resonance (ICR) trap do not form Al_9^- species even after about 600 s.[18] In order to show that this hindered $Al_{13}^- + O_2$ reaction is not just a special case but is of general interest, we measured the rate coefficients of O_2 reactions with a number of Al_x^- clusters near the Al_{13}^- species with closed- and open-shell structure. We found slow reactions for Al_9^-, Al_{11}^-, and Al_{13}^- and comparatively fast reactions for Al_8^-, Al_{10}^-, Al_{12}^-, and Al_{14}^-. The doublet character of the last four species eliminates hindrances caused by the violation of the spin conservation rule and allows one to compare these rate coefficients with those of the spin-allowed Cl_2 reactions. In order to show the importance of this rule, O_2 reactions with $Al_{13}H^-$ (open shell) and $Al_{14}H^-$ (closed shell) are also investigated. In an ongoing investigation, we study the acceleration of the $Al_{13}^- + O_2$ reaction by increasing the collisional energy. The experimental findings and the analysis of these complex results are the subject of a further publication.[22]

To further study the general importance of the O_2 + metal reaction, we have extended our investigation to a number of Ga_x^- clusters. Though Ga is a homologue of Al, it exhibits many differences: Unexpectedly, the electronegativity (EN) of Ga, at 1.8, is higher than that of Al (1.5). Ga has seven crystalline modifications; these vary in their bond formation from covalent bonding as in the case of boron toward metallic bonding as in a real metal. The α-Ga modification, with one short Ga−Ga bond, often is called a molecular metal,[1,15] a property that is also reflected in its low melting point of 28 °C. Also, true metal structures like Ga(IV) are observed under high pressure.[15,23,24] However, the electronic behavior of naked Ga_x^- should be similar to that of Al_x^- clusters since the same number of valence electrons are involved in bonding, for example 40 in the jellium-like Ga_{13}^- cluster. Therefore, while reactions of O_2 with Ga_x^- clusters should be electronically similar to reactions with Al_x^- clusters, they are different from a thermodynamic point of view, because the Ga−O bond energy is considerably smaller than that of Al−O. The Al−O bond strength is much larger, however, than that of all noble metal−oxygen bonds, as the following comparison shows: Al−O = 5.35 eV (from Al_2O), Ga−O = 4.59 eV (from Ga_2O), and Pd−O = 2.87 eV (from $Pd{-}O_{(g)}$).[2] Accordingly, the mass spectrometric results for the Ga_x^- clusters presented here can be expected to show whether the model for the $Al_x^- + O_2$ reactions is valid for other metals that exhibit different thermodynamic properties. The different thermodynamic properties of Ga compounds in comparison to Al compounds are also reflected in procedures for forming Ga_x^- and Al_x^- clusters. While Al_x^- clusters were formed by laser desorption of solid $LiAlH_4$, Ga_x^- species can be obtained after laser irradiation of solid GaN, which will be described here for the first time.[2,25,26]

The rate coefficients presented in this work were determined by bringing either single-sized clusters or a collection of clusters with different sizes into reaction with O_2 under (nearly) single-collision conditions (10^{-8} mbar). This means that the reaction products are generally detected before a second collision with O_2 occurs. This approach is essential in order to study the single elementary steps of the reaction. In contrast, in recent flow tube experiments by other authors at about 0.5 mbar, up to 100 collisions between O_2 and a single cluster occur before the products are detected.[11] In these experiments, rate coefficients of O_2 with a large number (ca. 50) of Al_x^- clusters of different size

dx.doi.org/10.1021/ja4125548 | J. Am. Chem. Soc. 2014, 136, 3607−3616

were estimated via a data analysis based on a Monte Carlo model.[20,21]

A comparison of measured rate coefficients with predictions from kinetic theories would allow further conclusions regarding the underlying reaction mechanisms. However, the calculation of rate coefficients from first principles with molecular and transition state data from quantum chemical methods requires a reliable knowledge of barrier heights. For the reactions of $^3O_2$ with closed- and open-shell Al_x^- and Ga_x^- clusters, these calculations are complicated not only by failure of single-determinant methods but also by the existence of multiple isomeric intermediates.[27]

On the basis of our experimental results and supported by DFT calculations, we obtained evidence for a model in which the peroxo intermediate $[M_x\cdots O_2]^-$, as the earliest species along the reaction coordinate that exhibits a typical arrangement of valence electrons, plays an essential role. This peroxo intermediate is also the prominent species in a more general, hypothetical reaction scheme that is, a Gedanken experiment, which should allow predictions to be made for O_2 reaction rates of any metal atom clusters. Within this broader scheme, the oxidation of the M_x^- cluster to a M_x^+ species with simultaneous reduction of O_2 to the O_2^{2-} peroxo moiety plays the major role.[28,1]

RESULTS AND DISCUSSION

Mechanisms and Rate Coefficients. Prior to the determination of rate coefficients, we studied qualitatively the reaction pattern of all $M_{m/n}^-$ clusters (m = even-numbered; n = odd-numbered; M = Al, Ga) with O_2. The clusters were first isolated and brought to collision with oxygen at a pressure of about 4×10^{-8} mbar for several seconds. Let us consider Ga_m^- cluster anions first. For these even-numbered clusters (Ga_{10}^-–Ga_{28}^-), the following spontaneous reactions were observed.[29]

$$Ga_{10}^- + O_2 \rightarrow Ga_6^- + 2Ga_2O$$

$$Ga_{10}^- + O_2 \rightarrow Ga_5^- + Ga_2O + Ga_3O$$

$$Ga_{12}^- + O_2 \rightarrow Ga_7^- + Ga_2O + Ga_3O$$

$$Ga_{14}^- + O_2 \rightarrow Ga_{10}^- + 2Ga_2O$$

$$Ga_{16}^- + O_2 \rightarrow Ga_{12}^- + 2Ga_2O$$

$$Ga_{16}^- + O_2 \rightarrow Ga_{11}^- + Ga_2O + Ga_3O$$

$$Ga_{18}^- + O_2 \rightarrow Ga_{13}^- + Ga_2O + Ga_3O$$

$$Ga_{20}^- + O_2 \rightarrow Ga_{16}^- + 2Ga_2O$$

$$Ga_{20}^- + O_2 \rightarrow Ga_{15}^- + Ga_2O + Ga_3O$$

$$Ga_{22}^- + O_2 \rightarrow Ga_{18}^- + 2Ga_2O$$

$$Ga_{24}^- + O_2 \rightarrow Ga_{20}^- + 2Ga_2O$$

$$Ga_{26}^- + O_2 \rightarrow Ga_{22}^- + 2Ga_2O$$

$$Ga_{28}^- + O_2 \rightarrow Ga_{24}^- + 2Ga_2O$$

In contrast to all these spontaneous reactions, the odd-numbered, closed-shell Ga_n^- clusters react at least one order of magnitude more slowly with O_2, and only upper limits to the rate coefficients can be given.[30]

For the corresponding $Al_{m/n}^-$ clusters, qualitatively the analogous reactions were observed that is, spontaneous reactions for even-numbered Al_m^- clusters with formation of $Al_{(m-4)}^-$ or $Al_{(m-5)}^-$ fragments. Odd-numbered Al_n^- clusters were found to be much less reactive, Al_{13}^- and Al_9^- being nearly stable in agreement with our former observations[18] and those of Castleman et al.[21]

For the determination of rate coefficients, O_2 was admitted to the ICR cell by a manual leak valve (Varian) allowing us to maintain a constant partial pressure of 3×10^{-10} to 4×10^{-8} mbar in the cell. Note that with this method the maximum pressure was limited to $\sim 4 \times 10^{-8}$ mbar, because ion detection took place while the reaction gas (O_2) was present in the ICR cell. Rate coefficients for all $Ga_{m/n}^-$ clusters are shown in Figure 1.

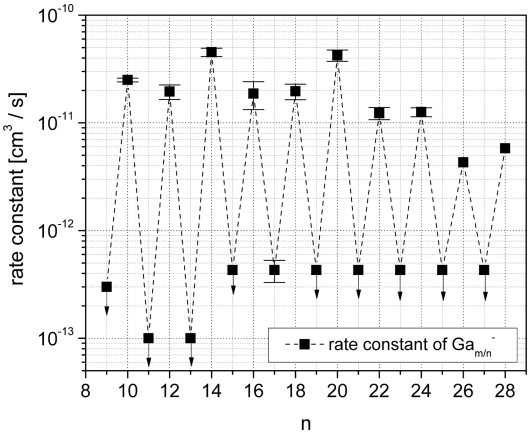


Figure 1. Measured rate coefficients for reactions of $Ga_{m/n}^-$ clusters with O_2. Error bars originate from at least two independent measurements carried out on different days. For numerical values of Ga_9^-, see Table 2.

By knowing the reaction behavior of some single-sized clusters M_n^- (see above), we were also able to study and characterize the reactivity of a whole collection of differently sized clusters (e.g., Ga_{11}^-–Ga_{28}^-) at once and to numerically fit the integrated rate equations of the consecutive reaction steps to the experimental data to obtain pseudo-first-order rate coefficients, k_i (see Supporting Information). For these calculations, the software *DetMech*[31] was used.

Since for several cluster types the rate coefficient k_i was determined by isolating the single clusters first (e.g., Ga_{10}^-, Ga_{13}^-, Ga_{22}^-, and Al_{13}^-), the reliability of the collective measurements has been confirmed because values from both measurements agree well.

In order to derive reliable reaction rates of the $M_{m/n}^-$ clusters, all ion intensities were normalized to the intensity of Ga_9^-. This is justified because (1) the rate coefficient of M_9^- with O_2 is much smaller (about a factor of 100) compared with the other (even-numbered) clusters and (2) there is no cluster that reacts to give M_9^- because for Al_{13}^- and Ga_{13}^-, even at prolonged reaction times of up to 600 s, no reaction with O_2 was observed (cf. above).

In order to generate $Al_{m/n}H^-$ clusters, the $Al_{m/n}^-$ clusters were exposed to a hydrogen atmosphere at 10^{-6} mbar for 1–3 s.[18]

Model for the Primary, Rate-Determining Step. The overall reactions of Al_x^- and Ga_x^- clusters with O_2 are exemplarily summarized for Al_x^- clusters in the following equations, which are divided into spin-forbidden (2a) and spin-allowed reactions (2b):

odd-numbered clusters

$$^1Al_n^- + {}^3O_2 \rightarrow {}^1Al_{n-4}^- + 2{}^1Al_2O \qquad (2a)$$

dx.doi.org/10.1021/ja4125548 | J. Am. Chem. Soc. 2014, 136, 3607–3616

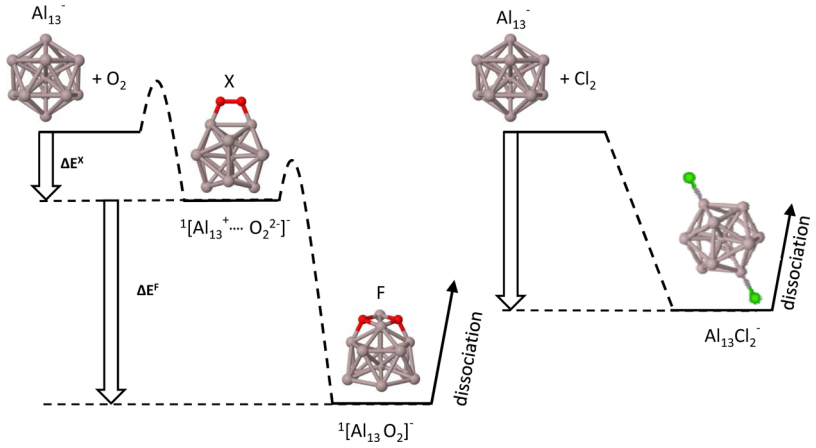


Figure 2. (left) Schematic presentation of the reaction path of an $Al_{n/m}^-$ cluster with $^3O_2$. As a spin-forbidden example, the hindered reaction of the Al_{13}^- cluster is shown: Al_{13}^- reacts via spin transition to the peroxo-bonded O_2^{2-} intermediate **X** ($^1Al_{13}^- + {}^3O_2 \rightarrow {}^1[Al_{13}^{+}\cdots O_2^{2-}]^-$) (energy gain ΔE^X) and finally to the more stable anion **F**, $^1[Al_{13}O_2]^-$ (ΔE^F) corresponding to complete oxidation of the Al_{13}^- cluster with a single O_2 molecule (cf. text). (right) Spontaneous reaction of Al_{13}^- cluster with Cl_2 to the completely oxidized $[Al_{13}Cl_2]^-$ intermediate, which rapidly decomposes to Al_{11}^- + 2AlCl.[33]

Table 1. Calculated (DFT) Values of ΔE^X and $\Delta E^X + \Delta E^F$ (eV) for the Energy Gain from the Reactants (e.g., $Ga_{13}^- + {}^3O_2$) to the Side-on Bonded Intermediate X (e.g., $[Ga_{13}^{+}\cdots O_2^{2-}]^-$) and to the Ground State F (e.g., $[Ga_{13}O_2]^-$)[a]

	Ga_9^-	Ga_{10}^-	Ga_{11}^-	Ga_{12}^-	Ga_{13}^-	Ga_{14}^-	Al_{13}^-	Al_{14}^-
$-\Delta E^X$	1.84	1.92	1.87	1.83	1.14	2.1	2.21	3.1
$-\Delta E^X + -\Delta E^F$	4.58	5.45	4.62	4.73	4.64	5.12	6.99	8.10

[a]For explanation, see Figure 2.

even-numbered clusters

$$^2Al_m^- + {}^3O_2 \rightarrow {}^2Al_{m-4}^- + 2{}^1Al_2O \qquad (2b)$$

Note, however, that this four electron reaction[32] is only the simple summarization of a very complex reaction route in which many intermediates are involved. Since quantum chemical calculations of the complex potential energy surface (PES) for the $Al_x^- + O_2$ reactions are not expected to give reliable results for transition states, we tried to develop a plausible model by correlating our measured rate coefficients with the potential energies of stable and metastable species. Additional information is gained from the different reaction rates of Al_x^- clusters with Cl_2 and with O_2 if no spin transition occurs. From our DFT calculations, it follows that the first well-defined intermediate in every $Al_{n/m}^- + O_2$ reaction is a $[Al_{n/m}^{+}\cdots O_2^{2-}]^-$ species (in the following denoted by **X**) in which a peroxo (O_2^{2-}) group is polar-bonded to the $Al_{n/m}^-$ cluster via two oxidized Al atoms (Al^+). In Figure 2, the situation is exemplified for $Al_{13}^- + O_2$, with $^1[Al_{13}^{+}\cdots O_2^{2-}]^-$ as the intermediate **X**. Note that in the following, the stabilization energy of **X** with respect to the reactants is denoted by ΔE^X. For all even-numbered Al_m^- clusters, this intermediate **X** is in a doublet state and formed without spin restrictions; for the odd-numbered clusters Al_n^-, however, **X** is in a singlet state, and a spin flip is necessary.

The peroxo moiety O_2^{2-} within these intermediates (also present in H_2O_2, for example),[1] bonded to two different metal atoms of the cluster, represents a chemically well-known situation with classical bonding,[28] which is isoelectronic to that of the F_2 molecule. Therefore, an intermediate **X** of this type can be expected to have a pronounced local minimum on the PES in accordance with our DFT results.

Thus, the $[Al_{n/m}^{+}\cdots O_2^{2-}]^-$ intermediate **X** with its local energy minimum ΔE^X (Table 1) corresponds to the first well-defined step along the reaction route, where the O_2 molecule has obtained two electrons from the $Al_{n/m}^-$ cluster. The $[Al_{n/m}^{+}\cdots O_2^{2-}]^-$ intermediate has O_2 bonded side-on, bridging between two aluminum atoms. With the transfer of two electrons, the $Al_{n/m}^-$ cluster is oxidized to an $Al_{n/m}^+$ unit, and the O−O bond distance is elongated becoming an O−O single bond in the O_2^{2-} moieties, the normal octet of electrons is maintained on each oxygen atom. This $[Al_{n/m}^{+}\cdots O_2^{2-}]^-$ intermediate reflects just the first step of the complete reaction with a four-electron transfer to two bridging O^{2-} ions of the final $[Al_{n/m}O_2]^- = [Al_{n/m}^{3+}\cdots 2O^{2-}]^-$ dioxide cluster **F** (Figure 2), which represents the global minimum.

Under high-vacuum conditions, collisional stabilization of the vibrationally excited dioxide $[Al_{n/m}O_2]^-$ cluster **F** (see Table 1) can be neglected because a low-lying decomposition channel giving $Al_{n/m-4} + 2Al_2O$ exists (Figure 3).[34] As illustrated in Figure 2 and discussed in the following, it is probably not the formation of this final, highly vibrationally excited dioxide cluster **F**, ($\Delta E^X + \Delta E^F$), that determines the overall rate constant but instead, the formation of the above-mentioned peroxo-bonded $[Al_{m/n}^{+}\cdots O_2^{2-}]^-$ intermediate **X** (Figure 2) with a much lower energy gain ΔE^X in the range of 2−3 eV. The calculated energies of the ground state **F** and the intermediate **X** of all $Al_{n/m}^-$ and $Ga_{n/m}^-$ clusters under discussion are listed in Table 1, and the corresponding structures are presented in the Supporting Information.

This conclusion is supported by our previous investigations on (spin-allowed) reactions of Al_{13}^- with Cl_2, in which Al_{11}^- and 2AlCl molecules are formed spontaneously via decomposition of the excited $[Al_{13}Cl_2]^-$ cluster and which are faster (3−6 times)[6,33] than those of the even-numbered Al_m^-/Ga_m^- clusters with O_2, which are also spin-allowed.

Despite the smaller energy gain in forming the most stable oxidized cluster (4.5 eV for $Al_{13}^- + Cl_2 \rightarrow [Al_{13}Cl_2]^-$ compared with 7 eV for $Al_{13}^- + O_2 \rightarrow [Al_{13}O_2]^-$), the overall reaction $Al_{13}^- + Cl_2$ is faster than the overall reaction $Al_{13}^- + O_2$. From this observation, we conclude that for the $Al_{m/n}^- + O_2$ reactions, a less excited intermediate is likely to exist that determines the rate

dx.doi.org/10.1021/ja4125548 | J. Am. Chem. Soc. 2014, 136, 3607−3616

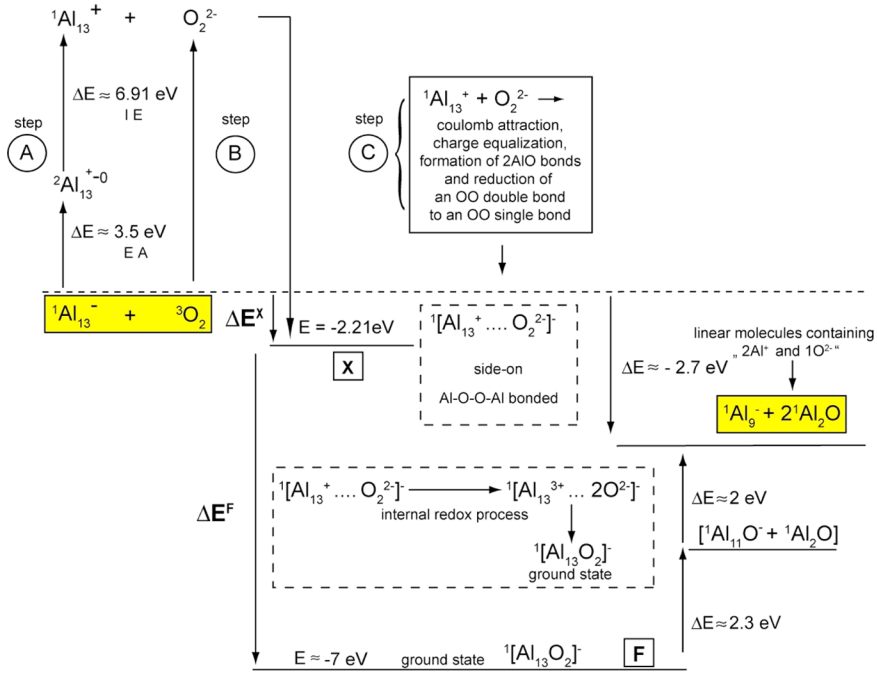


Figure 3. A schematic energy cycle of the $^1Al_{13}^- + {}^3O_2$ reaction (reactants and final products are yellow; see text). In order to understand the formation of the side-on bonded intermediate $[Al_{13}^+\cdots O_2^{2-}]^-$, **X**, (Figure 2) an alternative route via a hypothetical set of steps A, B, and C is constructed. The multistage process from the $^1[Al_{13}^+\cdots O_2^{2-}]^-$ intermediate to the ground state $^1[Al_{13}O_2]^-$, species **F**, (Figure 2) and its subsequent decomposition to the observed Al_9^- cluster is simplified. The primary reaction of the reactants proceeds via a weakly bonded charge/induced dipole complex (not shown) and a spin transition barrier (not shown) to the peroxo intermediate $[Al_{13}^+\cdots O_2^{2-}]^-$, **X**. Its energy corresponds to the value of $\Delta E^X = E(\mathbf{A}) + E(\mathbf{B}) + E(\mathbf{C})$.

Table 2. Experimentally Determined Rate Coefficients $[10^{-11}$ cm^3 s$^{-1}]$[a]

	Ga_9^-	Ga_{10}^-	Ga_{11}^-	Ga_{12}^-	Ga_{13}^-	Ga_{14}^-	Ga_{15}^-	Ga_{16}^-
	0.03[b]	2.5 ± 0.1	0.01[b]	2.0 ± 0.3	0.01[b]	4.5 ± 0.4	0.04[b]	1.9 ± 0.5
Al_8^-		Al_{10}^-		Al_{12}^-		Al_{14}^-		Al_{16}^-
8.8 ± 3.9		6.0 ± 0.6		3.0 ± 0.3		4.5 ± 0.6		4.2 ± 0.9

[a]The given error is derived from at least two independent measurements. Note that the absolute error is estimated to be on the order of ±50% and is mainly due to uncertainties of the pressure measurement. [b]Only the upper limit could be determined.

of the overall reaction. From our quantum chemical calculations, it follows that this intermediate is the peroxo species, **X**, $[Al_{m/n}^+\ldots O_2^{2-}]^-$.

On the basis of these arguments, we propose the following general model for the $Al_{m/n}^- + O_2$ reaction: The energy gain ΔE^X for the formation of the peroxo intermediate determines the overall rate of reaction. The larger the energy gain, the larger the rate coefficient. This could be a manifestation of the Evans–Polanyi principle (see e.g., ref 35). If the reaction is spin-forbidden, the rate is slowed down.

The High Reactivity of the Even-Numbered Al_m^- and Ga_m^- Clusters. In order to verify the above-mentioned model, we examined first the open-shell gallium clusters Ga_{10}^-, Ga_{12}^-, and Ga_{14}^-, for which the rate coefficients can be determined more accurately than for the similar Al_{10}^-, Al_{12}^-, and Al_{14}^- clusters. This is because the intensities and particle densities of the $Ga_{n/m}^-$ clusters are higher than those for the $Al_{n/m}^-$ clusters due to their different formation process. In any case, the reactions of even-numbered Al_m^- and Ga_m^- clusters with $^3O_2$ are spin-allowed (cf. eq 2b) and therefore can proceed spontaneously, which is confirmed by our experiments. The experimentally determined rate coefficients are displayed in Figure 1 and collected in Table 2.

Clearly, the rate coefficients increase in the sequence, $Ga_{12}^- \approx Ga_{16}^- < Ga_{10}^- < Ga_{14}^-$. Even accounting for absolute errors, the measured rate coefficients are below the Langevin limit by a factor of 20, this limit being on the order of 5×10^{-10} cm^3 s^{-1} for the $Ga_{m/n}^- + O_2$ reactions (polarizability of O_2 = 1.58×10^{-30} cm^3).[36] Obviously, the capture of O_2 by the cluster ion (ion/induced dipole interactions) is not the rate-determining step, and an energy barrier or an entropic bottleneck, in the case of the even-numbered clusters, between a weakly bound charge/induced dipole complex and the more stable $[Ga_m^+\cdots O_2^{2-}]^-$ intermediate is likely to exist. This conclusion is supported by the approximately two times faster, more exoergic O_2 reaction of Al_m^- clusters versus the analogous Ga_m^- clusters (see Table 2).[37] This is strong evidence for explaining the origin of the different rate coefficients of Al_m^- and Ga_m^- clusters. The rate-determining formation of the peroxo intermediate $^2[M_m^+\cdots O_2^{2-}]^-$ is more exoergic (ΔE^X) for the Al_m^- clusters; that is, more energy (about 1 eV) is gained for Al_{14}^- than for Ga_{14}^-. Obviously, a correlation exists between the measured rate coefficient and the calculated ΔE^X values.

Assuming a similar reaction mechanism for the different Ga_m^- clusters, the Ga_{10}^- cluster should react somewhat faster than Ga_{12}^-, and Ga_{14}^- should react significantly faster than Ga_{10}^- and Ga_{12}^-, which is in line with the experimental observation of the

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reaction rates (see preceding); that is, the Ga_{14}^- cluster exhibits the highest reactivity of all even-numbered Ga_m^- clusters because of its high exoergicity for the formation of the rate-determining peroxo intermediate, **X**, for example, 2.1 eV for $[Ga_{14}^+\cdots O_2^{2-}]^-$.

This interpretation is surprisingly supported by kinetic investigations of the O_2 reactions with alkyl radicals,[38] a completely different reaction system. As can be seen from Table 3, for both reactions (with open-shell Ga_m^- clusters and alkyl radicals), not only are the absolute rate coefficients very similar, but also a correlation is seen between the rate coefficients and the exoergicity of the association step.

Table 3. Experimental Rate Coefficients and Calculated Exoergicity for Selected $^2Ga_m^-$ + O_2 and Alkyl Radical + O_2 Reactions[a]

cluster	$k/10^{-11}$ ($cm^3\ s^{-1}$)	ΔE^X (eV)	radical[38]	$k/10^{-11}$ ($cm^3\ s^{-1}$)	−BDE (eV)
Ga_{10}^-	2.5	−1.92	primary alkyl	0.8	−1.54
Ga_{12}^-	2.0	−1.83	secondary alkyl	1.2	−1.62
Ga_{14}^-	4.5	−2.10	tertiary alkyl	2.0	−1.68

[a]BDE, bond dissociation energy of the R−O_2 bond.[38]

The Low Reactivity of Odd-Numbered Al_n^- and Ga_n^- Clusters. The fast O_2 reactions of all even-numbered Ga_m^- clusters are in contrast to the hindered reactions of the odd-numbered Ga_n^- clusters with rate coefficients below the Langevin limit by a factor of >1000 (cf. Figure 1 and Table 2). Like in the case of the Al_{13}^- and Ga_{13}^- clusters, an energy barrier has to be overcome during which the spin transition proceeds. This barrier, as with the even-numbered Ga_m^- clusters, should depend also on the stability of the peroxo intermediate **X**, for example, $[M_{13}^+\cdots O_2^{2-}]^-$. For the Ga_{13}^- cluster, the energy gain for this side-on intermediate is −1.14 eV. Furthermore, also for adjacent odd-numbered Ga_n^- clusters, the relationship between ΔE^X and the rate coefficient can be expected to apply. For Ga_9^- and Ga_{11}^-, the following ΔE^X values are calculated: −1.84 and −1.87 eV (Table 2). From these more exoergic reactions, in comparison to Ga_{13}^- (−1.14 eV), a faster reaction than for Ga_{13}^- should be expected. But unfortunately, for each of these three clusters, the rate coefficient is too small to be measured exactly under our experimental conditions; that is, only an upper limit can be given. Moreover, since the situation for the O_2 reaction with Ga_{11}^- is unexpectedly complex (see Supporting Information), one should only compare Ga_9^- and Ga_{13}^-. Specifically, Ga_{13}^- exhibits the smallest and Ga_9^- the largest upper limit, which is at least in line with our proposed correlation.

Comparison of Even- and Odd-Numbered Clusters. So far it seems as if a consistent picture can be drawn within the series of odd- and even-numbered $Al_{n/m}^-$ and $Ga_{n/m}^-$ clusters in the limited size windows, Ga_9^- to Ga_{14}^- and Al_{13}^- to Al_{14}^-. Furthermore, this picture is also valid, if one compares the slowest and the fastest reaction of an even/odd cluster pair. The ΔE^X values for the formation of the peroxo intermediates **X** of Al_{13}^- and Al_{14}^- are −2.2 and −3.1 eV, respectively. For the analogous Ga_{13}^-/Ga_{14}^- pair, the following ΔE^X values are calculated: −1.14 and −2.1 eV, respectively. In the case of the Ga clusters, an increase of a factor of ∼400 is observed for the rate coefficients (Table 2).[39]

The moderate correlation between the ΔE^X values and the rate coefficients for the M_{13}^-/M_{14}^- pair gives a first indication that there must be an additional influence, besides energy, on the reaction rate. This assumption is confirmed by the following example, for which drastically different reaction rates are observed even though the ΔE^X values are similar. As shown above, there are fast spontaneous reactions for Ga_{10}^- and Ga_{12}^- with ΔE^X values of −1.92 and −1.83 eV, respectively. Though the ΔE^X values for Ga_9^- and Ga_{11}^- (−1.84 and −1.87 eV, respectively) are in the same range, the rate coefficients for the latter ones are about 100 times slower (see Table 2).

Obviously, there is a rate-decreasing process for the odd-numbered Ga_n^- clusters, because an accelerating process for the even-numbered Ga_m^- clusters can be ruled out.[40]

The spin-forbidden transition during the slow reaction of the odd-numbered clusters (e.g., singlet Al_{13}^- with $^3O_2$ toward the singlet $^1[Al_{13}^+\cdots O_2^{2-}]^-$ intermediate) should cause an additional increase of the barrier, which in a first approximation was discussed above, as being based only on the relatively low exoergicity ΔE^X of the reaction.

Therefore, the striking difference between the rate coefficients for the even- and odd-numbered clusters gives a strong indication that the hindered $^3O_2$ reaction with closed-shell clusters is based on an additional barrier caused by the spin transition.

Can Reactivities for Size-Similar Open- And Closed-Shell Clusters Be Estimated? Besides the special effect of the spin transition, which causes a dramatic decrease of the reaction rate, there is clearly a significant correlation between the $Al_{n/m}^-/Ga_{n/m}^-$ + O_2 reaction rates of different clusters and the energy gain ΔE^X from the educts to the peroxo intermediates, which have been calculated with DFT methods. Now the question arises whether it is possible to make a simpler prediction about the reactivity of such clusters based on the ΔE^X correlation.

In order to illustrate this approach, we have developed a thermodynamic cycle leading to the peroxo intermediate **X**, which is shown in Figure 3. Using the Al_{13}^- cluster as a prominent example, the cycle involves the reactants $^1Al_{13}^-$ and $^3O_2$, which react with a ΔE^X value of −2.21 eV (Table 2) to form **X**, $^1[Al_{13}^+\cdots O^{2-}]^-$.

This model process begins with the two-step oxidation (EA + IE) of Al_{13}^- to Al_{13}^+ (**A**) and the two-step reduction of $^3O_2$ to the singlet dianion O_2^{2-} (**B**) (isoelectronic to the F_2 molecule). Subsequently, the Coulomb attraction between Al_{13}^+ and O_2^{2-} and the formation of two Al−O bonds via charge neutralization proceed, releasing energy, and finally the $^1[Al_{13}^+\cdots O_2^{2-}]^-$ intermediate, **X**, is formed (**C**). Since during this whole process[41] step **C** is nearly the same for $Al_{m/n}^-$ and $Ga_{m/n}^-$ clusters, provided they are of similar size as those discussed in this paper (e.g., Ga_9^-, Ga_{11}^-, and Ga_{13}^- or Ga_{10}^-, Ga_{12}^-, and Ga_{14}^-), the energy gain ΔE^X calculated with DFT methods should be mainly reflected by the differences in step **A**. The energy values of step **A** for some $Al_{n/m}^-$ and $Ga_{n/m}^-$ clusters have been calculated and are collected in Table 4. These values mainly determine the ΔE^X values and therefore the rate coefficients (Figure 3): The smaller the value of $E(\mathbf{A})$ = EA + IE, the more negative the value of ΔE^X, as the exoergic formation of Ga−O/Al−O bonds, step **C**, will further exceed **A**.

In the following, we will concentrate on the Ga_m^- cluster reactions. First we look at the spontaneous reactions of Ga_{10}^-, Ga_{12}^-, and Ga_{14}^-. The reaction with Ga_{14}^- exhibits the largest rate coefficient. This property of Ga_{14}^- is in line with its smallest value of $E(\mathbf{A})$ (8.57 eV), while for the slower reaction of Ga_{12}^-, the largest value of $E(\mathbf{A})$ (8.87 eV) has been obtained. Therefore, as mentioned above, the values of $E(\mathbf{A})$ for the clusters Ga_{10}^-, Ga_{12}^-, and Ga_{14}^- are in line with the observed increasing reactivity toward O_2 of these Ga_n^- clusters: $Ga_{12}^- < Ga_{10}^- < Ga_{14}^-$.

dx.doi.org/10.1021/ja4125548 | J. Am. Chem. Soc. 2014, 136, 3607−3616

Table 4. Electron Affinities (EA, eV) and Ionization Energies (IE, eV) of Neutral $Al_{m/n}$ and $Ga_{m/n}$ Clusters (n/m = 9−14) Obtained from Our DFT Calculations

	$Al_{m/n}$			$Ga_{m/n}$		
m/n	EA	IE	[EA + IE][a]	EA	IE	[EA + IE][a]
9	2.76	6.37	9.13	2.87	5.94	8.81
10	2.67	6.42	9.09	2.47	6.24	8.71
11	2.84	6.24	9.08	2.79	6.37	9.17
12	2.78	6.39	9.17	2.58	6.29	8.87
13	3.50	6.91	10.41	3.29	6.10	9.39
14	2.61	5.95	8.56	2.42	6.15	8.57

[a]This value corresponds to **A** in Figure 3.

This simple ionic model is also in line with the reactivity of the closed-shell clusters Ga_9^-, Ga_{11}^-, and Ga_{13}^-. The largest value of $E(\mathbf{A})$ is obtained as expected for Ga_{13}^-, which is in line with the lowest reactivity. The Ga_{11}^- cluster should exhibit a higher reactivity than the Ga_{13}^- cluster, and the Ga_9^- cluster should show the highest reactivity of these three species. Though the experiments result in a similar reactivity of Ga_{13}^- and Ga_{11}^- with respect to the upper limits, this rough prediction without the consideration of the spin transition for the three clusters at least seems to reflect the principal trend. Thus, within the series of even-numbered and odd-numbered clusters, the simple ionic model is in line with experiments as well as with the results of DFT calculations.

Consequences from the Predicted Reactivity Based on the Ionic Model: Spin Transition Causes an Additional Hindrance. What about the validity of this simple model if one compares even- and odd-numbered Al_x^-/Ga_x^- clusters?[42] The difference, $\Delta E(\mathbf{A})$, of the $E(\mathbf{A})$ values (Figure 3, Table 4) for Ga_{13}^- and Ga_{14}^- ($\Delta E(\mathbf{A})$ = 9.39 − 8.57 eV = 0.82 eV) corresponds to a strong increase in the O_2 reactivity from Ga_{13}^- to Ga_{14}^- by over three orders of magnitude. The acceleration of the reaction is less prominent from Ga_{11}^- to Ga_{12}^- ($\Delta E(\mathbf{A})$ = 0.3 eV) and the smallest difference is to be expected for the pair Ga_9^- to Ga_{10}^- ($\Delta E(\mathbf{A})$ = 0.1 eV). However, since even the low value of $\Delta E(\mathbf{A})$ = 0.1 eV is contrasted by an observed increase in the O_2 reactivity from Ga_9^- to Ga_{10}^- of about two orders of magnitude, there must be an additional factor that will be responsible for this large difference in the reaction rates. Furthermore, even the large $\Delta E(\mathbf{A})$ value between Ga_{13}^- and Ga_{14}^- may be not sufficient to explain the strongly different reaction rates between the slowest (Ga_{13}^-) and the fastest (Ga_{14}^-) reacting cluster alone. Consequently, there has to be a further factor that decreases the reaction rate of the odd clusters (Ga_9^-, Ga_{11}^-, Ga_{13}^-) so drastically. This contribution, as discussed above, can only be the hindered spin transition, which, for example, makes the Ga_{13}^- + O_2, as well as the Al_{13} + O_2, reaction extremely slow.

The Reactivity of $Al_{13}H^-$ and $Al_{14}H^-$ Clusters. All in all, our proposed model seems to be on solid ground. Nevertheless, we expand our discussion to two hydrogen-containing Al clusters, which already had given strong experimental indications of the essential influence of the spin conservation rule.[18,20] If one H atom is added, then also one electron is added to the cluster, and consequently, the O_2 reactivity changes dramatically. The $Al_{13}H^-$ species as an open-shell cluster is highly reactive in contrast to the inert Al_{13}^- cluster, and the $Al_{14}H^-$ closed-shell cluster is strongly unreactive in contrast to the fast reaction of Al_{14}^-. We have roughly verified this change, which has been shown experimentally for $Al_{13}H^-$ and $Al_{14}H^-$,[18] by DFT calculations. A detailed discussion would require a separate paper, since many isomers have to be included for these Al_nH^- clusters in which the H atom can easily migrate on the cluster surface.[43] Therefore, only a small number of isomers ($Al_{13}H^-/[Al_{13}H\cdots O_2]^-/Al_{13}HO_2^-$ and $Al_{14}H^-/[Al_{14}H\cdots O_2]^-/Al_{14}HO_2^-$) were considered in our calculations. As was the case in the hydrogen-free clusters, energy gains were seen when going from reactants to the intermediate **X** and again going from **X** to the final product **F**. Some results are listed in the Supporting Information, from which the following conclusion can be drawn: The ΔE^X and the ΔE^F values are similar to those of the H-free clusters Al_{13}^- and Al_{14}^-. Therefore, these results once more confirm that it is not the formation of the highly excited species **F** but instead the formation of the intermediate **X** that determines the O_2 reaction rate. Furthermore, these results are in line with the conclusion that the spin conservation rule is responsible for the different reactivity of the open-shell and the closed-shell $Al_{n/m}^-$ and $Al_{n/m}H^-$ clusters with $^3O_2$.

CONCLUSION AND OUTLOOK

In order to understand the slower reactions of Al_x^- clusters with O_2 compared with their fast reactions with Cl_2, we have investigated a number of spin-allowed and spin-forbidden O_2 reactions with Al_x^- clusters in the size neighborhood of the Al_{13}^- cluster. Furthermore, we have extended our investigations to similar Ga_x^- clusters to examine whether our results are restricted to Al or are also valid for other metal atom clusters, as well as for the oxidation of metal surfaces in general. Accordingly, rate coefficients of the reactions of O_2 with Al_x^- and Ga_x^- (x = 9−14) near the size of the exceptional M_{13}^- have been measured by FT-ICR mass spectrometry under single collision conditions, that is, subsequent fast unimolecular reactions proceed before the next collision occurs. These measurements, which quantify the even/odd properties of these clusters, in particular, the fast reaction of the even-numbered, open-shell clusters and the slow, spin-forbidden reactions of the odd-numbered, closed-shell clusters, have been complemented by DFT calculations in which we have computed the ground state energies of the reactants, the intermediates, and the products. These results provide guidelines for the discussion of the experimentally determined rate coefficients. The critical intermediate that determines the reaction rate has a normal valence bonding character, because it contains the well-known peroxo unit $(O-O)^{2-}$, which is bonded to two neighboring metal atoms on the surface of the M_x^- cluster, after it is partially oxidized to a M^+ cluster. Simultaneously, the O_2 molecule is reduced to the O_2^{2-} moiety. The energy gain, ΔE^X, during formation of this $[M_x^+\cdots O_2^{2-}]^-$ intermediate is correlated to the rate coefficient of the M_x^- + O_2 reaction. The larger ΔE^X, the larger is the rate coefficient observed (for the spin-allowed reactions). This fundamental conclusion is furthermore supported by (a) the faster O_2 reactions of the Al_x^- clusters in comparison to the Ga_x^- clusters, because the formation of Al−O bonds is more exothermic than the formation of Ga−O bonds, and (b) the spin-allowed reaction of Al_x^- clusters with Cl_2 being faster than the spin-allowed reactions with O_2. This result is in line with our model if in reactions with chlorine, the formation of the highly excited dichloride cluster $Al_xCl_2^-$ is the rate-determining step (e.g., $Al_{13}Cl_2^-$ is excited with 4.5 eV and reacts to give Al_{11}^- + 2 AlCl) and if in reactions with oxygen the intermediate **X** (e.g., $[Al_{14}^+\cdots O_2^{2-}]^-$ with 3.1 eV) represents the critical, rate-determining species.

However, the energy of this intermediate $[M_x^+\cdots O_2^{2-}]^-$ cannot, by itself, completely account for the experimental findings regarding the reactivity of similar even- and odd-numbered

dx.doi.org/10.1021/ja4125548 | J. Am. Chem. Soc. 2014, 136, 3607−3616

clusters (e.g., Ga_{13}^- and Ga_{14}^-). The spin transition during the reaction of the odd-numbered cluster causes an additional hindrance for the $^3O_2$ reaction. This conclusion has been convincingly confirmed in calculations related to the recent experimental results for the H-containing clusters $Al_{13}H^-$ and $Al_{14}H^-$. Though the ΔE^X values of the O_2 reactions with $Al_{13}H^-$ and Al_{13}^- as well as with $Al_{14}H^-$ and Al_{14}^- are very similar, the reactivity changes radically. The addition of one H atom turns spin-forbidden reactions into spin-allowed reactions and vice versa; thus rates of reactions with an even number of aluminum atoms are strongly increased, and rates of reactions with odd numbers of aluminum atoms are conversely strongly decreased.

Furthermore, we developed a model that allows us to make predictions on the trends in O_2 reactivity within a small number of similar metal atom clusters. In this simple model, the formal oxidation of the metal cluster anion, M_x^-, to the cluster cation (e.g., $Al_x^- \rightarrow Al_x^+$) determines the ΔE^X value and therefore is responsible for the differing reactivity of the clusters.

To summarize, the quantification of the rate coefficients for a small number of Al_x^- and Ga_x^- clusters in the size vicinity of the exceptional Al_{13}^-/Ga_{13}^- species in principle seems to allow a deeper insight into all reactions of O_2 with metal atom clusters and possibly also with surfaces of bulk metals;[7] that is, also small changes within the geometric structure of surfaces will change the reactivity. Therefore, our results may also be of fundamental interest for many catalytic processes on metal surfaces where the addition or substitution of a single atom can change the reactivity dramatically.

In our ongoing experiments, we plan to quantify the spin-forbidden reactions of O_2 with Al_{13}^- and Ga_{13}^- clusters via well-defined excitation of the clusters to overcome the reaction barrier during the spin transitions. These results will be published in a separate paper.[22]

EXPERIMENTAL SECTION

All experiments were carried out in a commercial FT-ICR mass spectrometer (Ion Spec, Ultima) equipped with a 7 T actively shielded magnet (Cryomagnetics, Oak Ridge, TN, USA). Since the experimental setup and methodology was described elsewhere in detail,[6,18,44−46] only the essentials are given here.

Negatively charged aluminum and gallium clusters ($Al_{m/n}^-$, $Ga_{m/n}^-$) were generated by laser desorption from $LiAlH_4$[6,44] and GaN, respectively,[25] where the commercial MALDI (matrix-assisted laser desorption/ionization) source of the FTICR-MS was used (nitrogen laser, λ = 337.1 nm, pulse energy = 300 μJ, pulse width ≈ 4 ns (FWHM)).

After cluster formation, the ions were transferred into a cylindrical ICR cell via a quadrupole ion guide. To ensure efficient ion trapping (gas assisted dynamic trapping) and translational cooling of the cluster ions, argon (Argon 6.0, basi Schöberl GmbH & Co. KG) was admitted into the cell with a pulsed valve (General Valve) at a pressure of around 1×10^{-5} mbar for ∼1 s.

For the study of ions with one particular mass-to-charge ratio (e.g., m/z = 351.77 for Al_{13}^-), the species were isolated by the SWIFT (stored waveform inverse Fourier transform) excitation technique.[47] A second thermalization step was carried out in some cases to prevent possible (re)excitation of the ions due to the isolation process and to ensure thermal conditions. Because the second thermalization step did not change the measured rate coefficient within the experimental error, we conclude that ion (re)excitation by the SWIFT method can be neglected.

QUANTUM CHEMICAL CALCULATIONS

The theoretical studies concerning the kinetics are analogous to those presented recently.[33] It should be noted that interpretation of experimentally observed rate coefficients by computations demand clear knowledge of the potential energy surface with accurate estimation of threshold energies of the various intermediates, which in turn depend on the computational method; therefore we use reaction energies as a guide to understand the reactivity of the various clusters presented here. All the calculations were performed using the generalized gradient approximation (GGA) within the framework of the DFT. The gradient-corrected exchange and correlation functionals due to Becke−Perdew were employed here.[48] Split valence basis set supplemented with polarization functions was used for all the atoms.[49] The computations were carried out using the Turbomole software.[49] In the self-consistent field (SCF) calculations, the density and energy tolerances were set to 10^{-6} e/bohr^3 and 10^{-6} hartree, respectively. In the geometry optimization, all the structural parameters were fully optimized without any symmetry constraints, with an energy convergence of 10^{-5} hartree and a maximum gradient of 10^{-4} hartree/bohr. The lowest and other higher energy isomers of all oxide clusters were obtained using an unbiased systematic structure search based on genetic algorithm method.[50,51] In this procedure, all the structures generated either through initial population or cross breeding were fully optimized without any constraints using the same methods mentioned above.

ASSOCIATED CONTENT

Supporting Information

Quantum chemical calculations, structures, and energies (eV) and further experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

This work was supported by the Karlsruhe Institute of Technology (KIT), Deutsche Forschungsgemeinschaft (DFG), and Fonds der Chemischen Industrie. This material is based in part on work supported by the Air Force Office of Scientific Research (AFOSR) under Grant Numbers, FA9550-11-1-0068 (K.H.B.) and FA9550-11-1-0171 (B.E.). K.H.B. and B.E. also thank the Defense Threat Reduction Agency (DTRA) for partial support under Grant Number HDTRA-1-12-1-007. B.K. acknowledges financial support from the BoR-RCS grant. This manuscript is dedicated to Peter Jutzi on the occasion of his 75th birthday and his outstanding contributions in main group organometallic chemistry.

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(29) The exoergic reactions of Ga_{10}^-, Ga_{12}^-, and Ga_{14}^- will be discussed in the text in more detail.
(30) Of all larger odd-numbered Ga_n^- clusters (with $Ga_n^- > Ga_7^-$), only Ga_{17}^- was found to react spontaneously with oxygen presumably because of the high stability of the Ga_{13}^- product: $Ga_{17}^- + O_2 \rightarrow Ga_{13}^- + 2Ga_2O$.
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(40) This accelerating process between the $^3O_2$ molecule and the doublet $Ga_{10}^-/Ga_{12}^-/Ga_{14}^-$ clusters might be initiated by a preorientation of the magnetic species ($^3O_2/Ga_n^-$) with a short stabilization period of the loosely bonded magnetic contact pair, which is immediately followed by a strongly exoergic step; that is, these reactions proceed spontaneously. However, this hypothesis has to be

ruled out, because the energy of a hypothetic magnetic interaction is far below the thermal energy of the interacting species.
(41) In step **C**, only Al−O/Ga−O single bonds are formed like those in the gaseous reaction products Al−O−Al and Ga−O−Ga, respectively. For these linear molecules, bond energies of 5.35 eV (Al_2O) and 4.59 eV (Ga_2O) are known from experimental data.[2,3]
(42) Our simple model is also in line with the hindered $^3O_2$ reaction of Ag_{13}^- described recently:[11] The formation of neutral Ag_{13} (EA) (see Figure 3) requires the largest energy of all Ag_n^- clusters, that is, the lowest energy ($\Delta E^X = -0.5$ eV) is gained by the formation of the end-on $[O_2Ag_{13}]^-$ cluster, and consequently the electron transfer to an O_2^- species must overcome a high barrier, which is in line with an extremely slow reaction.
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