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Reactions of boron cluster anions: implication of site-specific chemical neutralization pathways

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Abstract

Boron cluster anions were studied in a fast-flow tube reaction apparatus. The clusters were reacted with methyl iodide, and based on comparisons with aluminum clusters, it is suggested that we have observed the formation of neutral B_nCH_3 clusters. While isotopic peak broadening and mass coincidences prohibit quantitative conclusions, analogies with previous experiments involving aluminum clusters allow us to speculate as to the nature of the neutralization process in these reactions. It is believed that the type of site-specific reactions implied here may correspond directly to the reactions observed with aluminum clusters.

Keywords: Boron clusters; Cluster reactivity

1. Introduction

Recent work on boron-based fuels has focused on small particles, where surface oxidation can prove problematic [1]. It is believed that cluster species may be tailored to resolve these issues, providing stable species that are readily converted to fuels when introduced to a flame. We recently reported on the chemical neutralization and functionalization of aluminum clusters via reaction with methyl iodide (MeI) [2], and here we present the results of similar experiments conducted with boron clusters. We also briefly discuss our recent findings on the reaction of boron cluster anions with oxygen.

While both aluminum and boron belong to group IIIA of the periodic table, their chemical properties are quite different. In the bulk phase, boron is known to exist in several allotropic forms, with B_{12} icosahedral structural units representing a persistent motif [3]. In the cluster phase, boron is again known to differ from its well-studied aluminum cousin, most notably in the tendency towards planarity exhibited by smaller clusters of bare boron [4–13]. Whereas aluminum clusters can be described by the Jellium model [14–19], assuming a spherical core potential, clusters of boron are better described by application of the Aufbau principle, appropriately accounting for molecular orbital filling. In the case of boron, curvature strain favors the formation of planar structures with delocalized π electrons above and below the atomic plane, reminiscent of conductive graphite.

Experimentally, bare boron clusters have been studied via photoelectron spectroscopy [13], collision-induced dissociation [20,21], and reaction with various gasses [22–28]. Considerable attention has been devoted to the aromatic $B_{13}{}^{+}$ cluster [29], as it was observed to exhibit enhanced stability in sequential etching reactions with water [24]. Cationic clusters of boron have been shown to follow an oxygen etching reaction pathway similar to that observed in aluminum [22]. However, boron clusters, with substantially stronger bonding than aluminum clusters, are somewhat less susceptible to fragmentation upon forming bonds with oxygen; an additive reaction pathway is therefore far more favorable for boron clusters than for those of aluminum [22]. Anderson and coworkers have summarized the results of combustion-relevant reactions in [27].

The present work focuses on anionic boron clusters, which have received little experimental (as well as little theoretical) attention. We describe the formation of neutral B_nCH_3 clusters, potentially important for combustion applications, via reaction with methyl iodide. Due to isotopic peak broadening and mass coincidences, few quantitative conclusions can be drawn. For this reason, we will rely heavily on analogy

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with aluminum, where a much more thorough understanding of the reactions described has been achieved [2,14,15]. We also suggest that the observations reported here may provide valuable insights as to the nature of the cluster–CH_3 interactions observed in the aluminum system.

2. Experiment

The fast-flow tube reaction apparatus has been described in detail elsewhere [30]. Briefly, boron clusters were produced via laser ablation of a boron target (Research and PVD Materials, 99.9999%), under a constant flow (8000 sccm) of high purity He carrier gas. The forming clusters entered the flow tube through a conical nozzle, where they were collisionally thermalized in the presence of ~0.32 Torr of He. Approximately 1-m downstream from the source, the clusters were reacted with either MeI (seeded in He) or oxygen, introduced through a reactant gas inlet (RGI). Products and reactants were then sampled through a 1-mm orifice and analyzed via quadrupole mass spectrometry. We were able to easily produce and detect clusters containing as many as 50 B atoms.

3. Results and discussion

In order to better illustrate the vast chemical differences between B_n^- and Al_n^-, we turn briefly to the clusters' reactions with oxygen. As mentioned above, reactions of boron cluster cations with oxygen have been studied previously [22]. In these experiments, the use of an isotopically pure boron target allowed for very precise peak assignments. Our target was not isotopically pure, and so mass coincidences proved prohibitive to a detailed quantitative analysis of the data. Particularly frustrating was the overlap between B_n^- and $B_{n-3}O_2^-$ peaks. While $B_nO_2^+$ species were not observed by Anderson and coworkers, our observations indicated that clusters of the type $B_nO_2^-$ represent a favored product in the oxidation of boron cluster anions. This assertion arises from the fact that, upon introduction of oxygen at the RGI, all B_n^- ($n > 22$) peaks display an increase in intensity. Obviously, such behavior is impossible if only an etching pathway (as seen with aluminum clusters) is present. While it is possible that some isomers of B_n^- do engage in an etching reaction, it is clear that the additive reaction pathway is dominant in the case of anions. Aluminum clusters, with substantially weaker binding, cannot withstand the energy absorbed via the formation of chemical bonds with oxygen [22]. Therefore, as we established in our prior work, oxidation of aluminum clusters is characterized by metal atom loss (etching), and no oxygen incorporation is observed.

While the oxygen reaction highlights the chemical differences between aluminum and boron clusters, in the reaction between B_n^- and MeI there is evidence for some chemical similarities. Fig. 1 shows the formation of I^- upon reaction.

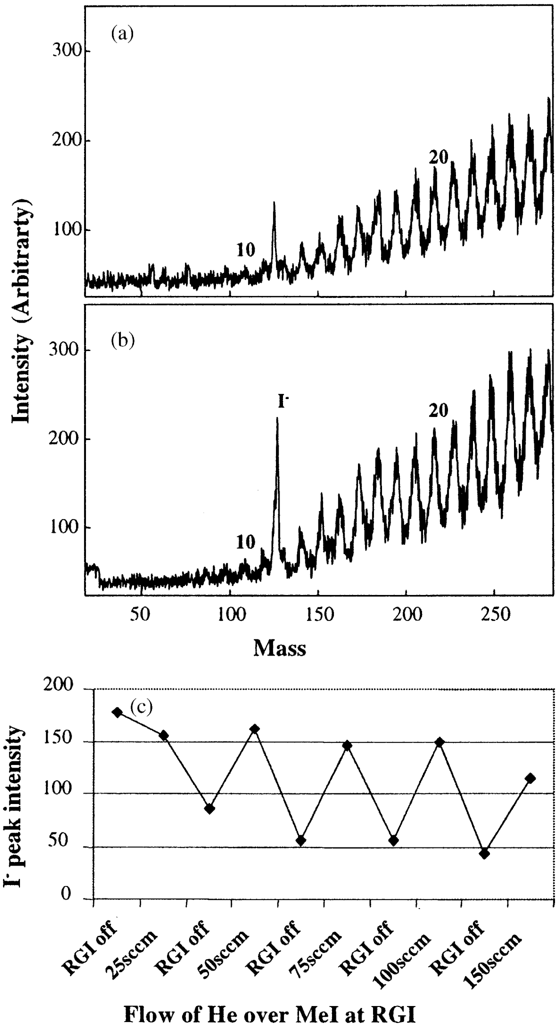

Fig. 1. Mass spectra of (a) B_n^- clusters (b) reacted with 100 sccm of He flowing over MeI. The I^- peak seen in (a) persists in the spectrum with no reactant gas due to residual MeI from prior additions sticking to the walls of the flow tube. Part (c) shows how the I^- peak consistently grows when MeI is flowing through the RGI.

In addition to the appearance of the I^- peak, clusters of the type B_nI^- were detected. This reaction channel is reminiscent of the results reported with aluminum. However, the appearance of these peaks prohibits the determination of B_n^- ($n > 12$) disappearance rates due to the very small mass separation between B_nI^- and $B_{n+12}I^-$; as in the reaction with oxygen, the breadth and proximity of neighboring peaks leads to the illusion that all B_n^- ($n > 12$) peaks grow slightly in the presence of the reactant gas.

Even for $n \leq 12$, kinetic plots were typically poor. In addition to the issues raised in reference [2], we attribute these complications to MeI contamination in the flow tube. Due to the extreme inhomogeneity of our B target's surface, and the resulting difficulties arising in the optimization of source conditions, long collection periods (~30 min) were required for each mass spectrum. Thus, to obtain reaction data, MeI was constantly fed into the flow tube for extended periods of time, and its accumulation was far more dramatic than in the previous Al experiments.

Unfortunately, no comprehensive study has been performed to provide electron affinity (EA) data for neutral boron clusters in the size range studied here [31], so we are unable to clearly derive the mechanism that leads to I^- formation. However, from available EA data of certain boron clusters, it is known that the values for ones of comparable size are greater than the corresponding aluminum clusters [13]. Hence, we find it reasonable to put forth the hypothesis that the formation of a cluster–CH_3 bond, yielding neutral B_nCH_3 clusters, allows the exothermic formation of I^-. It is unclear whether geometric or electronic properties have more of an impact on the clusters' reactivity towards MeI. In the aluminum case, inverse correlation of reactivity to EA led to the conclusion that the clusters were engaged in a covalent interaction with the CH_3 group [2]. It remains uncertain whether the covalent bond forms between a specific atom or site on the cluster surface, or between the "superatomic" valence orbital of the cluster itself.

Consideration of B_5 (the smallest cluster observed in the present experiments) and Al_5 clusters can prove instructive in the interpretation of the present data, if only in a limited way. While structurally similar, their electronic properties are known to be quite different. Boron's valence electrons delocalize over all five atoms, whereas aluminum's are concentrated over the three central atoms [13]. For $n > 6$, Al_n and B_n species have very different geometries, and of course *very* different electronic properties. It is possible that the adsorption of MeI onto the cluster surface leads to a geometric and/or electronic perturbation of the B_n^- clusters. If the interaction between the CH_3 and the boron cluster is truly similar to the interaction observed in the aluminum case, then it is reasonable to surmise that specific atoms or surface sites are involved in the bonding. The B_n^- cluster distribution is devoid of "magic" clusters. Without a spherically symmetric potential acting on the clusters' valence electrons, it is impossible to achieve superatom behavior. Therefore, the neutralization reaction would be expected to proceed through an interaction between specific surface atoms or surface sites, effectively interrupting the clusters' π-electron delocalization. While all of the similarities and differences between the reactions with Al_n^- and B_n^- cannot be completely explained, the observation of B_n^- neutralization may provide evidence that Al_n^- neutralization also proceeds through a site-specific interaction. By extension, the evidence suggests that the reactive neutralization process may actually lead to a disruption of the electron delocalization requisite for superatom behavior.

4. Conclusions

Boron cluster anions were reacted with oxygen and methyl iodide. In the case of the oxygen reaction, additive reactions were found to represent the dominant oxidation pathway. The reactions with methyl iodide revealed that a neutralization reaction is likely occurring, generating neutral B_nCH_3 clusters. As boron clusters are not superatomic by nature, the observation of this reaction is taken as evidence for cluster–CH_3 interactions arising from covalent bonding with individual atoms or surface sites. A comprehensive study of the EAs of neutral boron clusters must be performed in order to verify and understand the formation of B_nCH_3 clusters [2]. These covalently bound neutral species (like the Al_nCH_3 clusters) may be interesting as energetic materials, and thermodynamic studies are needed to asses their heats of combustion and related properties.

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