Superhalogens belong to a class of molecules that not only mimic the chemistry of halogen atoms but also possess electron affinities that are much larger than that of chlorine, the element with the highest electron affinity in the periodic table. Using \( \text{BO}_2 \) as an example and the synergism between density functional theory-based calculations and photoelectron spectroscopy experiments, we demonstrate another unusual property of superhalogens. Unlike halogens, whose ability to accept an electron falls upon dimerization, \( \text{B}_2\text{O}_4 \), the dimer of \( \text{BO}_2 \), has an electron affinity larger than that of the \( \text{BO}_2 \) building block. This ability of \( \text{(BO}_2\text{)}_2 \) and subsequent, higher oligomers \( \text{(BO}_2\text{)}_n \) \((n = 3 \text{ and } 4)\), to retain their superhalogen characteristics, can be traced to the enhanced bonding interactions between oxygen and boron atoms and due to the delocalization of the charge of the extra-electron over the terminal oxygen atoms. These results open the door to the design and synthesis of a new class of metal-free highly negative ions with potential for novel applications.

Negative ions play an important role in chemistry not only because they are the building blocks of salts, but also because they are useful in purifying air, killing molds, and serving as anti-depressants. Halogens atoms readily form negative ions and have among the highest electron affinities of any element in the periodic table. However, as shown in Table 1, when halogen atoms combine to form molecules, their electron affinities are reduced,\(^1\) *i.e.* halogens do not beget halogens. This decreasing trend is a consequence of the extra-electron occupying the antibonding orbital of \( \text{X}_2 \) \(( \text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I})\) molecule. In this communication, we show that in contrast to halogens, dimerization of \( \text{BO}_2 \), a well-known superhalogen, does not result in lowering of the EA. In addition, the higher oligomers, \( \text{(BO}_2\text{)}_n \) \((n = 3 \text{ and } 4)\) also retain their superhalogen characteristics.

<table>
<thead>
<tr>
<th>Species</th>
<th>EA (eV)</th>
<th>Species</th>
<th>EA (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>3.40</td>
<td>F(_2)</td>
<td>3.12</td>
</tr>
<tr>
<td>Cl</td>
<td>3.61</td>
<td>Cl(_2)</td>
<td>2.50</td>
</tr>
<tr>
<td>Br</td>
<td>3.36</td>
<td>Br(_2)</td>
<td>2.42</td>
</tr>
<tr>
<td>I</td>
<td>3.06</td>
<td>I(_2)</td>
<td>2.52</td>
</tr>
</tbody>
</table>

More than half a century ago it was shown that \( \text{PtF}_6 \) could oxidize a \( \text{Xe} \) atom.\(^2\) The electron affinity of this molecule was later estimated to be 6.76 eV,\(^3\) much larger than the electron affinity of any halogen atom. Gutsev and Boldyrev\(^4\) later termed such molecules as superhalogens and generalized the concept to include molecules with composition \( \text{MX}_n \text{M} \), where \( m \) is the maximal valence of the metal atom M and \( n \) is the normal valence of the electronegative atom, \( X \) \((n = 1 \text{ for halogen atoms})\).

Subsequently, several experimental studies have confirmed the existence of superhalogens consisting of simple metal atoms, such as alkalis, Mg, and Al at the core and halogen atoms on the periphery.\(^5\)–\(^7\) Considerable research conducted in recent years has shown that superhalogens not only mimic the chemistry of halogens but also can be used to promote unusual reactions,\(^8\) as a building block of energetic materials,\(^9\) as dopants to increase the electrical conductivity of polymers,\(^10\) for accessing high oxidation states of metal atoms,\(^11\) as electrolytes in rechargeable batteries,\(^12\) and in the production of organic superconductors and organic metals.\(^13\) What has not been addressed in the literature is the electron affinity of species created by combing two or more superhalogens. Will the electron affinities of these species decrease as is the case for halogen molecules or can it increase? In other words, do superhalogens beget superhalogens? In this communication we answer this question by a synergistic study using density functional theory based calculations and anion photoelectron spectroscopy experiments. By taking \( \text{BO}_2 \) as an example, we show that the electron affinities of \( \text{(BO}_2\text{)}_n \) oligomers are either higher than or nearly equal to that of their building block, \( \text{BO}_2 \).
Thus, like the halogen atoms, BO₂ moieties dimerize, but unlike halogen molecules, \((\text{BO}_2)_2\) can form a superhalogen, even without the benefit of a single metal core atom.

Our choice of BO₂ as the building unit was motivated by the special chemistry of the B atom, which is brought about by its electron deficient character and its propensity to form three-center-two-electron bonds.¹⁴ In addition, BO⁻ and BO₂⁻ are isoelectronic with CO and CO₂, respectively and are very stable. With an electron affinity of 4.46 eV,¹⁵ BO₂ can be classified as a superhalogen as it fits the formula prescribed by Gutsev and Boldyrev.⁴ Recent studies¹⁶–¹⁹ have shown that a single metal atom, \(\text{M} (\text{M} = \text{Cu, Ag, Au, Mn, Fe})\) surrounded with BO₂ moieties can have electron affinities even larger than that of its superhalogen building block. Hence, these \(\text{M(BO}_2)_n \) (\(\text{M} = \text{Cu, Ag, Au, Mn, and Fe} ; n > 1\)) moieties are classified as hyperhalogens. In this communication we sought the answers to the following questions: (1) would two BO₂ moieties dimerize, just as two halogen atoms do, to form a molecule? (2) If so, would their electron affinity be reduced since the electron affinity of a halogen molecule such as Cl₂ is smaller than that of the Cl atom? (3) How many BO₂ molecules can be combined without losing their superhalogen property? (4) Finally, does this phenomenon apply only to BO₂ or are there other systems that can also display similar properties? While the answer to the first question, as expected, is yes, study of the remaining questions yielded unexpected results: electron affinities of \((\text{BO}_2)_n \) (\(n = 1–4\)) are large (greater than 4.0 eV) and mostly exceed that of BO₂!²

To answer the above questions we have systematically studied the structure and energetics of \((\text{BO}_2)_n \) clusters \((n \leq 4)\). The ground state geometries of neutral and anionic \((\text{BO}_2)_n\) clusters were determined by carrying out density functional theory based calculations using the Gaussian 09 code.²⁰ The hybrid gradient corrected exchange–correlation functional²¹,²² (B3LYP) along with the 6-311++G(3df) basis set was employed in these calculations. The convergence for total energy and gradient were set to \(10^{-9}\) Hartree and \(10^{-4}\) Hartree Å⁻¹, respectively. The vibrational frequencies of all the structures reported here are positive, thus these structures are confirmed to belong to the minima on their corresponding potential energy surfaces. The reliability and accuracy of these computational parameters has been well established in previous studies.¹⁶–¹⁸

In Fig. 1 we present the equilibrium geometries of the neutral and anionic \((\text{BO}_2)_n \) (\(n = 1–4\)) clusters. We note that both neutral and anionic BO₂ molecules have linear structures as has been noted before.¹⁵ However, the situation changes when they dimerize. Both neutral and anionic BO₂ moieties have two close-lying isomers. The neutral isomers are separated by only 0.06 eV, but their spin multiplicities are different. The ground state of the neutral BO₂ dimer is an open structure...
(Fig. 1, 2a) with the singlet spin state while the higher energy isomer is a closed cyclic structure (Fig. 1, 2b) with the triplet spin state. The B–O bond lengths are generally same in both isomers with the exception that the terminal O atom in the ground state structure is significantly closer to the B atom, lying at a distance of 1.2 Å. The relative stability of these two isomers is reversed in the case of anions. Here, the lowest energy isomer has a closed cyclic structure (Fig. 1, 2a’) while the higher energy isomer has an open structure (Fig. 1, 2b’). Unlike the neutral state, both anionic isomers have the same spin multiplicity, namely the spin doublet. The two isomers are 0.12 eV apart. Note that the transition from the closed cyclic structure to the open structure can be achieved by breaking the bond between one of the bridging oxygen and boron atoms. The neutral and anionic (BO₂)₃ moieties again have two lowlying isomers with one being a closed ring structure with no O–O bonds while the other being somewhat extended with O–O bonds and a BO₂ unit remaining in the linear configuration. The ground state of neutral (BO₂)₃ is a hexagonal ring structure (Fig. 1, 3a) while another isomer, lying 0.5 eV higher in energy, has a five-membered ring containing an elongated O–O bond (Fig. 1, 3b). Both these isomers prefer a doublet spin state. In the case of the anionic (BO₂)₃, however, both these isomers are energetically degenerate, with the hexagonal ring structure preferring a triplet spin state (Fig. 1, 3a’), while the structure with the five-membered ring preferring the singlet spin state (Fig. 1, 3b’). The geometries of neutral and anionic (BO₂)₃ are very similar. The building block of these geometries is the cyclic-B₂O₃ ring that is already present in the (BO₂)₃ structure. Each of the three B atoms in this ring is attached to one BO₂ unit, one O₂ molecule and one O atom. That the cyclic B₂O₃ ring is quite common in a number of boron oxygen compounds. The anion is a spin-triplet while the neutral cluster is a spin-doublet. The B–O bond lengths in all of these clusters vary between 1.22 to 1.48 Å indicating the presence of both single and double bonds. The thermodynamic stability of neutral (BO₂)ₙ clusters is studied by calculating the energy it takes to fragment the cluster into a BO₃ unit and [BO₂]ₙ₋₁ cluster, namely, ΔEₙ = E[BO₂]ₙ - E[BO₂] - E[BO₂]ₙ₋₁. Here the energies E correspond to the ground state isomers. Our calculations show that all [BO₂]ₙ clusters are stable against dissociation, with ΔE₂ = 1.87 eV, ΔE₃ = 3.22 eV, and ΔE₄ = 2.78 eV. In particular, we note that the (BO₂)₃ cluster, with the hexagonal ring structure (Fig. 1, 3a), is thermodynamically more stable than its neighboring (BO₂)ₙ clusters with n = 2 and 4. Thus, (BO₂)₃ can be termed as a magic cluster. In comparison, the neutral halogen trimers X₃ (X = F and Cl) do not exhibit any such unusual stability. This is due to their structural features. The neutral halogen trimers consist of an X₃ unit to which an X atom is bound weakly. In fact, the energy required to dissociate F₃ into F₂ and F is calculated to be only 0.03 eV, while in the case of Cl₃, the dissociation into the Cl₂ dimer and Cl atom requires 0.26 eV of energy. The high stability of B₂O₆ ring is already evident in solid materials such as the α- and β-phases of Ba₂B₂O₆ crystals. In a recent experiment, the existence of B₂O₆ rings in the next generation deep-ultraviolet birefringent Na₃Ba₂(B₂O₆)₃F crystals has also been reported.

The most interesting result of this study, however, is the variation in the electron detachment energies of the anionic (BO₂)ₙ clusters and electron affinities of their corresponding neutral clusters as a function of n. The vertical detachment energy (VDE) is obtained by calculating the energy difference between the anion and the neutral cluster, both at the ground state geometry of the anion. It therefore determines the energy needed to remove an electron from the ground state of the anion without disturbing its geometry. The adiabatic detachment energy (ADE) is calculated as the energy difference between the ground state structure of the anion and structurally similar isomer of its neutral counterpart. The electron affinity (EA), on the other hand, is defined as the energy difference between the ground states of the anion and the neutral clusters. In the case where the ground state structures of anion and neutral clusters are very similar, the ADE of the anion is very close in value to that of its EA. In the photoelectron spectra, the onset (threshold) energy of the lowest electron binding energy is compared to the calculated ADE, while the VDE is taken as the binding energy of the first maximum at the lowest binding energy. The calculated electron detachment values (VDE and ADE) of anions, the calculated EA values of neutral clusters, along with the corresponding measured values of VDE and ADE are summarized in Table 2.

We now concentrate on the electron affinities of (BO₂)ₙ clusters. We note that the EA of (BO₂)₃ is 4.64 eV, which is larger than the EA of BO₂, namely, 4.46 eV. This is unusual when compared to the halogen molecules; for example, the EA of Cl₂ is only 2.50 eV. The onset (threshold) energy of the lowest electron binding energy is compared to the calculated ADE, while the VDE is taken as the binding energy of the first maximum at the lowest binding energy. The calculated electron detachment values (VDE and ADE) of anions, the calculated EA values of neutral clusters, along with the corresponding measured values of VDE and ADE are summarized in Table 2.

<table>
<thead>
<tr>
<th>Species</th>
<th>VDE</th>
<th>ADE</th>
<th>EA</th>
</tr>
</thead>
<tbody>
<tr>
<td>BO₂</td>
<td>4.32</td>
<td>4.46 ± 0.2</td>
<td>4.32</td>
</tr>
<tr>
<td>(BO₂)₂</td>
<td>4.84 (iso-2a)</td>
<td>5.0 ± 0.2</td>
<td>4.71 (iso-2a)</td>
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<tr>
<td>(BO₂)₃</td>
<td>5.44 (iso-2b)</td>
<td>5.06 (iso-3a)</td>
<td>4.24</td>
</tr>
<tr>
<td>(BO₂)₄</td>
<td>4.44 (iso-3a')</td>
<td>4.52 (iso-3a')</td>
<td>4.25</td>
</tr>
</tbody>
</table>

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and boron atoms. Structurally, this effect can be seen in the bond lengths as well; B–O bond length decreased from 1.40 Å to 1.29 Å due to the addition of the electron (Fig. 1). These effects result in higher electron binding energy. The trend, where the additional electron is mostly delocalized over the terminal oxygen atoms, continues for higher oligomers as well, thus resulting in large EA values for (BO2)n (n = 3–4) clusters. The electron affinity of [BO2]3 is 4.24 eV and is marginally lower than the EA of BO2, while the EA of [BO2]4 is 4.50 eV. Even though the EAs of halogen dimers are lower than that of their corresponding halogen atoms, it is known that the subsequent, higher oligomers of halogens, Xn (n > 2) do have large EA values.26,27 Since, the EA values of all the (BO2)n oligomers studied here are consistently larger than that of the Cl atom (3.61 eV), these clusters are classified as superhalogens. But most importantly, their EA values are either larger than or comparable to the EA of the BO2 building unit. Thus, superhalogens beget superhalogens.

In order to check if the above prediction is valid, we have carried out anion photoelectron spectroscopic experiments and determined the VDE and the EA values on [(BO2)n]− clusters. The experimental setup has been described in detail elsewhere.28,29 In short, it consists of a pulsed arc cluster ion source (PACIS), a reflectron-type time-of-flight mass spectrometer and a magnetic bottle time-of-flight electron spectrometer. For the generation of boron and boron oxide clusters the source has been modified. The lower electrode (cathode) is manufactured from a 12 mm Au rod. At the tip of the Au rod a 10 mm hole is drilled which serves as a reservoir for boron. Boron powder is pressed into this hole. The arc burns between the upper electrode made of a 5 mm Cu rod and the metal rim of the lower electrode with the boron reservoir. The same approach has been used before to generate clusters of other insulators such as sulfur with the PACIS.30 For the generation of B4O18− clusters, O2 is added to the seeding gas. The anions are mass-selected with the time-of-flight mass spectrometer. A selected bunch of anions with a defined mass are irradiated with a pulse from an F2 excimer laser. The kinetic energy of the detached photoelectrons is measured with a magnetic-bottle time-of-flight electron spectrometer. The energy resolution depends on the kinetic energy of the electrons and varies between 10 and 100 meV. The vibrational temperature of the cluster anions is estimated to be approximately room temperature.

Fig. 2 displays the photoelectron spectra of BO2− and (BO2)2−. The spectrum of the BO2− agrees well with the one published earlier by Zhai et al.15 From the spectrum of the dimer (BO2)2 the threshold energy and the vertical detachment energy can be extracted. The threshold energy is determined to be 4.8 ± 0.2 eV and the vertical electron affinity is 5.0 ± 0.2 eV. Note that these values are in good agreement with the calculated values given in Table 2. A comparison of the calculated VDE/ADE values of both isomers of (BO2)2− with the photoelectron spectrum indicates that both isomers (2a and 2b in Fig. 1) are present in the cluster beam. For the larger (BO2)3− cluster anions, the intensity of the mass spectrum was too low to record a photoelectron spectrum with this relatively high photon energy.

In summary we have shown that unlike the halogen dimers, BO2 superhalogens yield another superhalogen upon dimerization. In fact, the electron affinity of [BO2]3 is even higher than that of BO2. Thus, one can even regard (BO2)2 as a hyperhalogen. It is important to note that (BO2)2 is not a traditional hyperhalogen which is created when a metal atom with valence k is surrounded with (k + 1) superhalogens. In the case of (BO2)2, there is no metal atom! The trend continues when more and more BO2 moieties combine. They form polymeric structures with high electron affinities. Another unusual property of (BO2)n clusters is that they are stable against fragmentation into small products, with (BO2)3 being the most stable in the series. This is in contrast to the properties of halogen clusters. For example, X3 (X = F, Cl) are very weakly bound with respect to X2 and X. The question that immediately arises is whether the “superhalogen begetting superhalogen” behavior and their unusual stability are unique only to BO2? A vast class of superhalogens has been known over the past five years and we will be studying the above phenomenon in detail.

Acknowledgements

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