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Superhalogens beget Superhalogens: A case study with $(BO_2)_n$ oligomers

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Abstract

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 BO_2 as an example and the synergy 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, B_2O_4, the dimer of BO_2 has an electron affinity larger than that of the BO_2 building block. This ability of $(BO_2)_2$ and subsequent higher oligomers $(BO_2)_n$ (n = 3 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 extra-electron's charge 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 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 I, 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 X_2 (X = F, Cl, Br, and I) molecule. In this communication, we show that in contrast to halogens, dimerization of BO_2, a well-known superhalogen, does not result in lowering of the EA. In addition, the higher oligomers, $(BO_2)_n$ (n = 3 and 4) also retain their superhalogen characteristics.

More than half a century ago it was shown that PtF_6 could oxidize a 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 $MX_{(m+1)/n}$, where m is the maximal valence of the metal atom M and n is the normal valence of the electronegative atom, X (n=1 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 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 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 in 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 BO_2 as an example, we show that the electron affinities of $(BO_2)_n$ oligomers are either higher than or nearly equal to that of their building block, BO_2. Thus, like the halogen atoms, BO_2 moieties dimerize, but unlike halogen *molecules,* $(BO_2)_2$ can form superhalogen, even without the benefit of a single metal core atom.

Our choice of BO_2 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 BO_2^- are isoelectronic with CO and CO_2, respectively and are very stable. With an electron affinity of 4.46 eV [15], BO_2 can be classified as a superhalogen as it fits the formula prescribed by Gutsev and Boldyrev [4]. Recent studies [16 – 19] have shown that a single metal atom, M (M = Cu, Ag, Au, Mn, Fe) surrounded with BO_2 moieties can have electron affinities even larger than that of its superhalogen building block. Hence, these $M(BO_2)_n$ (M = Cu, Ag, Au, Mn, and Fe; $n>1$) moieties are classified as hyperhalogens. In this paper we sought the answers to the following questions: (1) would two BO_2 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 Cl_2 is smaller than that of the Cl atom? (3) How many BO_2 molecules can be combined without losing their superhalogen property? (4) Finally, does this phenomenon apply only to BO_2 or are there other systems that can also display similar property? While the answer to the first question, as expected, is yes, study of the remaining questions yielded unexpected results: Electron affinities of $(BO_2)_n$ (n=1-4) are large (greater than 4.0 eV) and mostly exceed that of BO_2!

To answer the above questions we have systematically studied the structure and energetics of $(BO_2)_n$ clusters ($n \leq 4$). The ground state geometries of neutral and anionic $(BO_2)_n$ clusters were determined by carrying out density functional theory based calculations using Gaussian09 code [20]. The hybrid gradient corrected exchange-correlation functional [21, 22] (B3LYP) along with 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, respectively. The vibrational frequencies of all the structures reported here are positive, thus these structures are confirmed to belong to 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 Figure 1 we present the equilibrium geometries of the neutral and anionic $(BO_2)_n$ (n=1-4) clusters. We note that both neutral and anionic BO_2 molecules have linear structures as has been noted before [15]. However, the situation changes when they dimerize. Both neutral and anionic BO_2 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 BO_2 dimer is an open structure (Fig.1, **2a**) with singlet spin state while the higher energy isomer is a closed cyclic structure (Fig.1, **2b**) with 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 anion. 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 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 $(BO_2)_3$ moieties again have two low-lying isomers with one being a closed ring structure with no O-O bonding while the other containing somewhat extended with O-O bonding and a BO_2 unit remaining in linear configuration. The ground state of neutral $(BO_2)_3$ 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 $(BO_2)_{3,}$ however; both these isomers are energetically degenerate, with the hexagonal ring structure preferring a triplet spin state (Fig. 1, **3a′**), while the structure with five-membered ring preferring singlet spin state (Fig. 1, **3b′**).

The geometries of neutral and anionic $(BO_2)_4$ are very similar. The building block of these geometries is the cyclic-B_3O_3 ring that is already present in the $(BO_2)_3$ structure. Each of the three B atoms in this ring is attached to one BO_2 unit, one O_2 molecule and one O atom. Note that the cyclic B_3O_3 ring is quite common in a number of boron oxygen compounds [23]. The anion is a spin-triplet while the neutral 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 $(BO_2)_n$ clusters is studied by calculating the energy it takes to fragment the cluster into a BO_2 unit and $(BO_2)_{n-1}$ cluster, namely, $\Delta E_n = -[E(BO_2)_n - E(BO_2) - E(BO_2)_{n-1}]$. Here the energies E correspond to the ground state isomers.

Our calculations show that all $(BO_2)_n$ clusters are stable against dissociation, with $\Delta E_2 = 1.87$ eV, $\Delta E_3 = 3.22$ eV, and $\Delta E_4 = 2.78$ eV. In particular, we note that $(BO_2)_3$ cluster, with the hexagonal ring structure (Fig. 1, **3a**) is thermodynamically more stable than its neighboring $(BO_2)_n$ clusters with $n = 2$ and 4. Thus, $(BO_2)_3$ can be termed as a *magic cluster*. In comparison, the neutral halogen trimers X_3 (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 X_2 unit to which an X atom is bound weakly. In fact, the energy to dissociate F_3 into F_2 and F is calculated to be only 0.03 eV, while in the case of Cl_3, the dissociation into Cl_2 dimer and Cl atom requires 0.26 eV of energy. The high stability of B_3O_6 ring is already evident in solid materials such as α and β- phases of BaB_2O_4 crystals [24]. In a recent experiment [25], the existence of B_3O_6 rings in the next generation deep-ultraviolet birefringent $Na_3Ba_2(B_3O_6)_2F$ crystal has also been reported.

The most interesting result of this study, however, is the variation in the electron detachment energies of the anionic $(BO_2)_n$ clusters and electron affinities of its corresponding neutral clusters as a function of n. The vertical detachment energy (VDE) is obtained by calculating the energy difference between the anion and neutral cluster, both at the anion's ground state geometry. 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 cases 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 II.

We now concentrate on the electron affinities of $(BO_2)_n$ clusters. We note that the EA of $(BO_2)_2$ is 4.64 eV, which is larger than the EA of BO_2, namely, 4.46 eV. This is unusual when compared to the halogen molecules, for example the EA of Cl_2 is only 2.50 eV vis-à-vis that of Cl atom, namely, 3.61 eV (Table I). The trend in Table I is consistent with the fact that the additional electron occupies the anti-bonding orbital of X-X single bond (X = F, Cl, Br and I) between the halogen molecules, which is destabilizing. As a result the EA of X_2 (X = F, Cl, Br and I) is consistently *lower* than that of the corresponding halogen atoms. However, this is not true in the case of BO_2. The higher than expected EA of BO_2 dimer is a result of extensive electron delocalization. NBO based charge analysis of $[(BO_2)_2]^-$ and its corresponding neutral species has shown that the additional electron is exclusively shared between the oxygen atoms, with a majority of charge ($-0.80e$) distributed on the terminal oxygen atoms (Fig. 1, ***2a'***), thereby resulting in an enhanced bonding interaction between the terminal oxygen and boron atoms. Structurally, this effect can be seen in the bond lengths as well; B-O_t 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 $(BO_2)_n$ (n = 3 – 4) clusters. The electron affinity of $(BO_2)_3$ is 4.24 eV and is marginally lower than the EA of BO_2, while the EA of $(BO_2)_4$ is 4.50 eV. Even though the EA of halogen dimers are lower than that of their corresponding halogen atoms, it is known that subsequent higher oligomers of halogens, X_n ($n > 2$) do have large EA values [27, 28]. Since, the EA values of *all* the $(BO_2)_n$ oligomers studied here are consistently larger than that of 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 BO_2 building unit. Thus, superhaolgens 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 $[(BO_2)_n]^-$ clusters. The experimental setup has been described in detail elsewhere [29, 30]. 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 12mm Au rod. In the tip of the Au rod a 10mm 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 from a 5mm 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 [31]. For the generation of $B_nO_m^-$ clusters, O_2 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 F_2 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 10-100 meV. The vibrational temperature of the cluster anions is estimated to be approximately room temperature.

Figure 2 displays the photoelectron spectra of BO_2^- and $(BO_2)_2^-$. The spectrum of the BO_2^- agrees well with the one published earlier by Zhai *et al.* [15]. From the spectrum of the dimer $(BO_2)_2^-$ 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 ± 0.2eV. Note that these values are in good agreement with the calculated values given in Table II. A comparison of the calculated VDE/ADE values of both isomers of $(BO_2)_2^-$ with the photoelectron spectrum indicates that both isomers (**2a′** and **2b′** in Fig. 1) are present in the cluster beam. For the larger $(BO_2)_n^-$ cluster anions, the intensity in the mass spectrum was too low to record a photoelectron spectra with this relatively high photon energy.

In summary we have shown that unlike the halogen dimers, BO_2 superhalogens yield another superhalogen upon dimerization. In fact, the electron affinity of $(BO_2)_2$ is even higher than that of BO_2. Thus, one can even regard $(BO_2)_2$ as a hyperhalogen. It is important to note that $(BO_2)_2$ 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 $(BO_2)_2$, there is no metal atom! The trend continues when more and more BO_2 moieties combine. They form polymeric structures with high electron affinities. Another unusual property of $(BO_2)_n$ clusters is that they are stable against fragmentation into small products, with $(BO_2)_3$ being the most stable in the series. This is contrary to the properties of halogen clusters. For example, X_3 (X=F, Cl) are very weakly bound with respect to X_2 and X. The question that immediately arises is whether “superhalogen begetting superhalogen” behavior and their unusual stability are unique only to BO_2? A vast class of superhalogens has been known over the past five years and we will be studying this phenomenon in detail.

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Table I. Experimental EA values of halogen atoms and their corresponding dimers [1].

Species	EA (eV)	Species	EA (eV)
F	3.40	F_2	3.12
Cl	3.61	Cl_2	2.50
Br	3.36	Br_2	2.42
I	3.06	I_2	2.52

Table II. Theoretical and experimental ADE and VDE values of $(BO_2)_n^-$ (n =1 – 4) clusters. Theoretical EA values of neutral $(BO_2)_n$ clusters are also shown. All the values are given in eV.

Species	VDE		ADE		EA
	Theo.	Expt.	Theo.	Expt.	Theo.
BO_2	4.32	4.46 ± 0.2	4.32	4.46 ± 0.2	4.32
$(BO_2)_2$	4.84 (*Iso-2a'*) 5.44 (*Iso-2b'*)	5.0 ± 0.2	4.71 (*Iso-2a'*) 4.52 (*Iso-2b'*)	4.8 ± 0.2	4.64
$(BO_2)_3$	5.06 (*Iso-3a'*) 4.44 (*Iso-3b'*)		4.75 (*Iso-3a'*) 4.25 (*Iso-3b'*)		4.24
$(BO_2)_4$	5.25		4.50		4.50

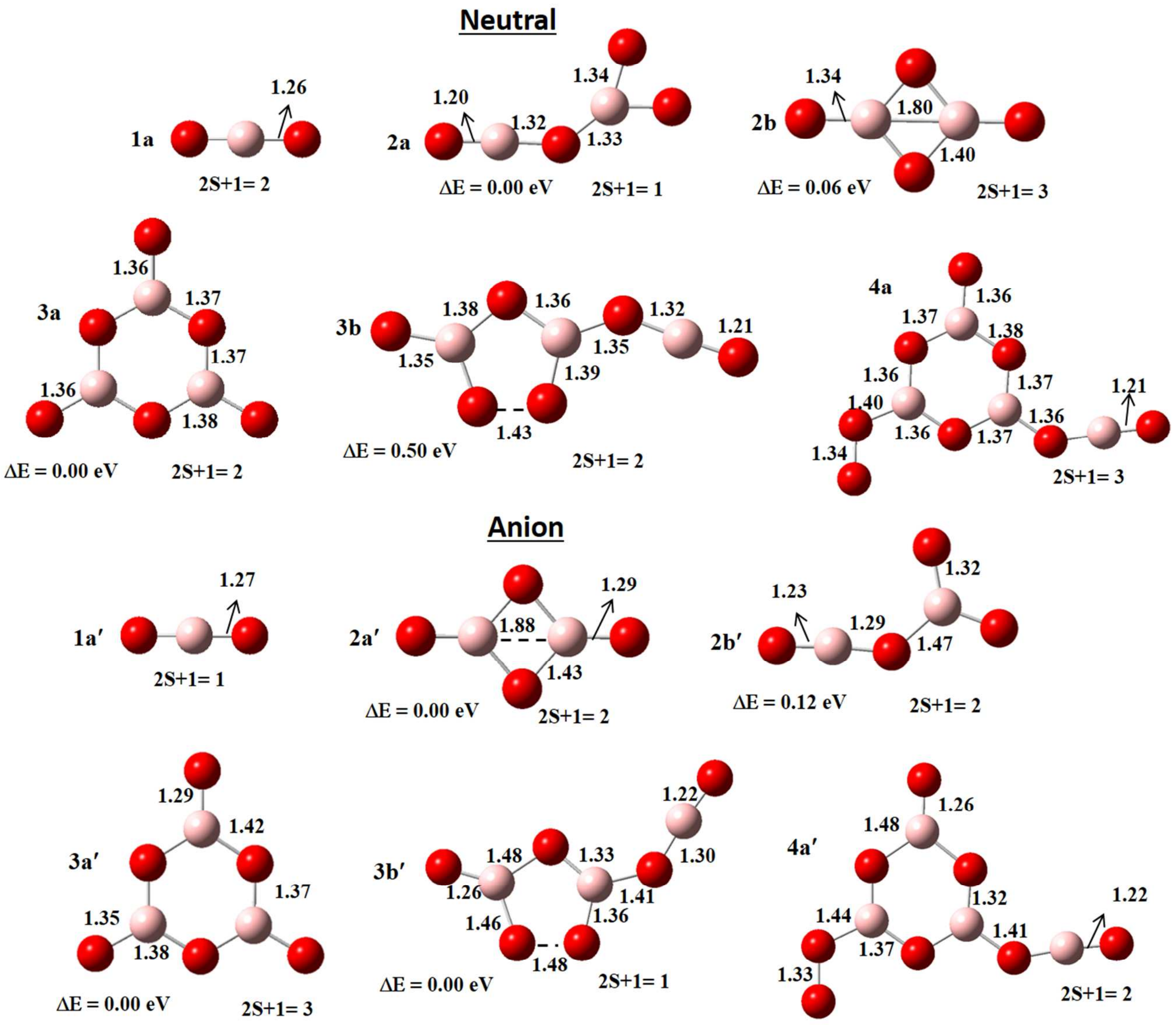

Fig. 1. The lowest energy isomers of neutral and anionic $(BO_2)_n$ (n=1-4) clusters. Bond lengths are given in Angstroms (Å). The spin multiplicities (2S+1) and the relative energies (eV) are also shown.

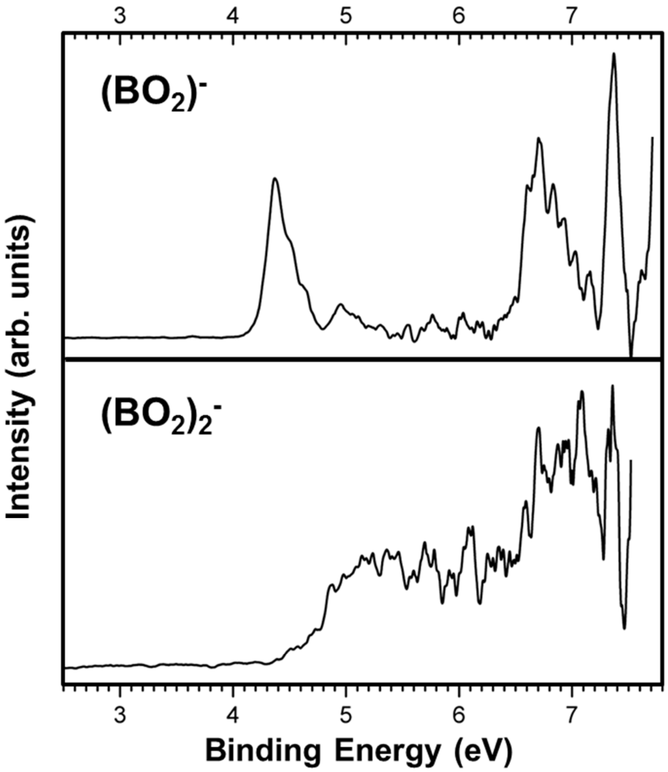

Fig. 2. Photoelectron spectra of BO_2^- and $(BO_2)_2^-$ recorded with a photon energy of 7.9 eV.