An Experimental and Computational Study of the Electron Affinity of Boron Oxide

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The 351 nm photoelectron spectrum of BO^- is reported. Detachment to form $^2\Sigma^+$ BO is observed, and the electron affinity of BO is determined to be 2.508 ± 0.008 eV. From the photoelectron spectra, vibrational frequencies of 1875 ± 30 cm^{-1} and 1665 ± 30 cm^{-1} are obtained for $\tilde{X}$ BO and BO^-, respectively, and the bond length in BO^- is found to be 1.236 ± 0.010 Å. The measured EA is used to derive a bond energy in BO^- of 9.39 eV. High-level molecular orbital calculations of the electron affinity are reported. The results from multiconfigurational SCF, G2, and complete basis set calculations are in good agreement with experiment.

Boron oxide is a first-row diatomic radical with well-characterized electronic structure, both experimentally and theoretically. An accurate structure for $\tilde{X}^2\Sigma^+$ BO has been determined using electronic,[1−7] microwave,[8] and ESR[9,10] spectroscopy. For this state, the bond length is 1.2049 Å,[11] and the vibrational frequency for $^{11}B^{16}O$ is 1885.69 cm^{-1}.[11] The homolytic bond energy in BO, D_0^0, is reported to be 8.34 eV.[12] Excited doublet states of BO are known, with the $A^2\Pi_i$ state lying *ca.* 24 000 cm^{-1} above the ground state.[11] The quartet states of BO have not been characterized experimentally.

Many high-level theoretical calculations have been carried out on BO. The bond lengths, vibrational frequencies, and relative energies of $\tilde{X}^2\Sigma^+$ and $A^2\Pi$ BO obtained using the coupled electron pair approximation (CEPA) were found to be in fair agreement with experimental results.[13] Marshall *et al.*[14] used UHF, UMP2, and UMP4 calculations with moderately large (up to 6-31+G*) basis sets to examine the thermochemistry and kinetics of reactions of boron atoms with O_2 and CO_2, as well as the bond energy of BO. They conclude that at least fourth-order perturbation theory is required to obtain a bond energy within 7 kcal/mol of the experimental value. The bond length and harmonic vibrational frequency calculated using multiconfigurational SCF (MCSCF) methods are found to be reasonable,[15,16] but the dissociation energy has significant error.[15] Schlegal and co-workers[17] calculated the bond energy in BO using the MP4, QCISD(T), G1, and G2 methods and obtained results similar to those of Marshall *et al.*[14] They found that the G1 and G2 methods gave predictions that agreed to within ~1 kcal/mol of the experimental values, while the MP4 and QCISD(T) calculations were less successful, giving bond energies that were too low by 7 and 13 kcal/mol, respectively. More recently, Barone[18] has examined the performance of density functional methods, specifically the Becke3LYP approach, using *ca.* 20 diatomics, including BO as part of the sample set. Using a triple-ζ basis set, he found excellent agreement between the calculated and experimental properties of boron oxide. Population and natural bond orbital analyses carried out by Knight *et al.*[10] and by Nemukhin and Weinhold[19] indicate that the singly occupied orbital in $\tilde{X}$ BO is essentially an sp hybrid localized on the boron atom. The energies of some quartet states of BO have also been calculated,[14,15] with the lowest energy quartet state calculated to lie ~6 eV higher in energy than $\tilde{X}^2\Sigma^+$ BO.

An important property of BO that has not received much attention is the electron affinity (EA). The negative ion of boron

oxide, BO^-, is a closed shell anion, isoelectronic with CO. Therefore, it would be expected to have a very high electron binding energy. The only experimental value for the EA was reported more than 25 years ago and was obtained from the equilibrium constant for the reaction $BO + Cl^- = BO^- + Cl$ over the temperature range 1623−2100 K.[20] From the equilibrium data, it was determined that the EA of BO was 18 kcal/mol lower than that of Cl, which leads to a value of 2.84 ± 0.09 eV,[21] consistent with the qualitative prediction above. This value is also consistent with the lower limit of 2.48 eV assigned by Jensen.[22] The electron affinity of BO has been recently calculated using a CI approach to be 2.97 eV.[23]

Here we report a combined experimental and computational study of the electron affinity of BO and the structure of the BO^- ion. The EA was measured using photoelectron spectroscopy of BO^- and is significantly lower than that previously reported. From the photoelectron spectrum we obtain the vibrational frequency and bond length for BO^-, and using the measured EA, we derive the bond energy. High-level molecular orbital calculations are reported, which are in agreement with the experimental findings. The electron affinity of BO is calculated to within 2 kcal/mol using MCSCF, G2, and complete basis set (CBS) methods. The angular distributions of detached photoelectrons are consistent with formation of a Σ state of the radical upon photodetachment of BO^-.

Experimental Section

A detailed description of the negative ion photoelectron spectrometer and experimental procedures has been published elsewhere.[24] Negative ions are formed in a flowing afterglow source, using helium as a buffer gas at a pressure of 0.4−0.7 Torr. Primary reactant ions such as O^- are formed from microwave discharge on a small amount of molecular oxygen, O_2, seeded in the helium. Additional ions are prepared from the reaction of O^- with neutral reagent vapors downstream in the flowing afterglow. For the present study, BO^- was prepared in three different ways. The ion was first prepared using the reaction of O^- with $BH_3-S(CH_3)_2$ or $BH_3-N(CH_3)_3$. Ion currents of 10−20 pA at *m/z* 27 (corresponding to $^{11}B^{16}O^-$) could be formed using this approach. However, the *m/z* 27 ion prepared this way was not pure BO^- and contained unidentified impurities. The impurity ions were detected as features in the photoelectron spectrum. At least two additional ions were formed in the reaction of O^- with $BH_3-S(CH_3)_2$, but one of these impurity ions could be eliminated by using $BH_3-N(CH_3)_3$.

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TABLE 1: Computational and Experimental Results for BO and BO⁻

	BO			BO⁻			BO electron affinity,[b]
method	bond length, Å	energy,[a] hartrees	frequency, cm⁻¹	bond length, Å	energy,[a] hartrees	frequency, cm⁻¹	kcal/mol
HF[c]	1.182	−99.548 51	2079	1.218	−99.600 57	1860	33.0
MP2[c]	1.212	−99.808 90	1890	1.246	−99.888 68	1693	49.2
MP4[c]	1.218	−99.821 08	1846	1.254	−99.908 82	1626	55.4
QCISD(T)[c]	1.216	−99.820 68	1847	1.246	−99.905 15	1693	53.3
Becke3LYP[c]	1.203	−100.058 87	1915	1.235	−100.154 11	1737	60.1
MCSCF[c]	1.194	−99.616 90	1946	1.245	−99.708 63	1711	57.9
G2[a]		−99.894 36			−99.988 89		59.6
CBS-Q[a]		−99.897 97			−99.991 10		58.8
CBS-APNO[a]		−100.022 29			−100.115 38		58.7
exp	1.205[c]		1885.7[d]	1.236 ± 0.010[c]		1665 ± 30[e]	57.8 ± 0.2[e]

[a] Electronic energies do not include zero-point corrections. [b] Includes a 0.3 kcal/mol correction for the difference in the zero-point energies between BO (2.7 kcal/mol) and BO⁻ (2.4 kcal/mol). [c] Quantities calculated with 6-311+G(d) basis sets. [d] Reference 11. [e] This work.

A pure beam of BO⁻ was obtained using microwave discharge on trimethoxyboroxine (**1**). Other ions formed under these conditions include BO_2^- and CH_3O^-.

1
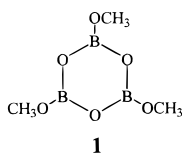
Once formed, the ions are accelerated through a nose cone with an 1 mm opening into a differentially pumped region where the beam is focused and the ions are mass selected with a Wien velocity filter ($M/\Delta M \approx 40$). After mass selection, the ion beam is crossed by the 351 nm output of an argon ion laser in the center of a buildup cavity that has been described previously.[24] The estimated power is 50−80 W. Detached electrons are energy analyzed using a hemispherical analyzer and detected using position sensitive detection. The resolution is 7−10 meV. The photoelectron spectrum depicts the number of electrons versus the electron kinetic energy (eKE). The absolute energy scale is calibrated by comparing the position of the $^3P_2 + e^-$ ← $^2P_{3/2}$ peak in the O⁻ spectrum with the known electron affinity of oxygen atom, 1.4611 eV.[25] A small energy compression factor, γ, is determined by measuring the fine structure of the tungsten spectrum, where the relative peak positions are well-known.[26] The energy scale compression is approximately 0.2%. The electron binding energy is obtained by subtracting the electron kinetic energy from the laser photon energy, 3.53119 eV.

Computational Details. Molecular orbital calculations were carried out using Gaussian94[27] on an IBM RS-6000 system. Geometries, energies, and frequencies were all calculated using a 6-311+G(d) basis set. The six orbitals used in the MCSCF calculation included 5σ, 6σ, $1\pi_x$, $2\pi_x$, $1\pi_y$, and $2\pi_y$. G2,[28] CBS-Q,[29] and CBS-APNO[30] calculations were carried out using the routines available in Gaussian94.

Results and Discussion

The 351.1 nm photoelectron spectrum of $^{11}B^{16}O^-$ is shown in Figure 1. A single feature is observed in the spectrum and is assigned to the transition from $\tilde{X}^1\Sigma$ BO⁻ to $\tilde{X}^2\Sigma^+$ BO. The origin of this band is at a binding energy of 2.508 ± 0.008 eV (57.8 ± 0.2 kcal/mol), the electron affinity of BO. This value is significantly lower than the currently accepted literature value, 2.84 ± 0.09 eV, obtained from the equilibrium constants for electron transfer between BO and Cl in the temperature range 1600−2100 K. A weak vibrational progression of 1875 ± 30 cm⁻¹ is observed, corresponding to the well-known 1885 cm⁻¹ frequency in $^{11}B^{16}O$.[11] A weak hot band is also observed in
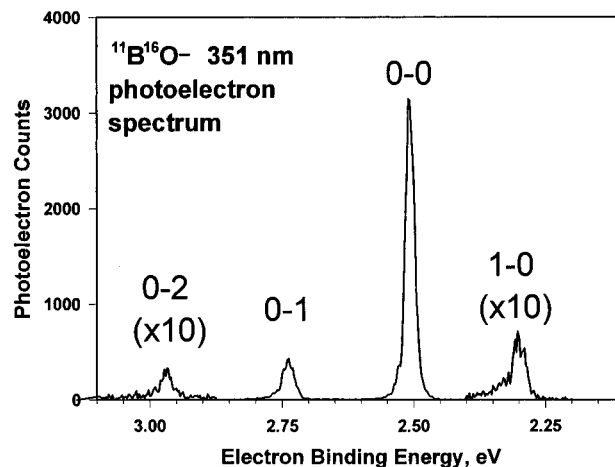

Figure 1. The 351 nm photoelectron spectrum of BO⁻ in the range of 2−3 eV electron binding energy (eBE). No other peaks were observed between 0 and 3.3 eV.

the spectrum, corresponding to anion vibrational frequency of 1665 ± 30 cm⁻¹.

The peak intensities in the vibrational progression have been modeled using a Franck−Condon fitting procedure.[24] From this analysis, we find a bond length change of 0.031 Å upon photodetachment. Using the reported bond length of 1.205 Å for $\tilde{X}$ BO, we assign a bond length of 1.236 ± 0.010 Å in BO⁻. The intensity of the hot band in the spectrum indicates an ion vibrational temperature of ∼1000 K, implying that BO⁻ is not effectively cooled by collisions with helium.

Bond Strength of BO⁻. The bond energy for formation of B + O⁻ can be calculated according to the relation shown in eq 1, where $D_0^0(BO)$ is the homolytic bond energy in BO. Using

$$D_0^0(BO^-) = D_0^0(BO) + EA(BO) - EA(O) \qquad (1)$$

a value of 8.34 ± 0.15 eV for the bond energy[12] of BO and EA(O) = 1.461 eV,[25] we find $D_0^0(BO^-) = 9.39 ± 0.15$ eV. Similarly, $D_0^0(B^--O) = 10.57 ± 0.15$ eV. Because BO⁻ is isoelectronic with N_2, it is instructive to compare the bond strengths in BO⁻ and BO with those in N_2 ($D_0^0(N_2) = 9.76$ eV)[12] and N_2^+ ($D_0^0(N_2^+) = 8.71$ eV).[12] The bonds in the boron oxide molecules are ∼0.35 eV weaker than those in the isoelectronic nitrogen species. More importantly, the *difference* in the bond energies between the closed-shell and open-shell states is the same for the two cases. Thus, we find that adding an electron to BO has the same effect on the bond energy as does adding an electron to N_2^+. However, the agreement is likely fortuitous because the bond energies do not refer to

dissociation into species with the same electronic configuration.

Angular Distributions. The spectrum shown in Figure 1 was measured with the laser polarization set to the "magic angle" ($\theta = 54.7°$) with respect to the detector, where the photoelectron signal is independent of the anisotropy parameter, β.[31−34] Spectra were also measured at $\theta = 0°$ and $\theta = 90°$, from which a value of $\beta = 1.0$ was obtained. This result indicates that the electron is detached from a σ orbital. This is consistent with what would be expected for detachment of a closed shell ion to form a radical with a singly occupied σ (or sp) orbital, as is the case for $BO^- \rightarrow BO + e^-$.

Computational Results. Calculated bond lengths, electronic energies, and vibrational frequencies for BO and BO^- are listed in the top section of Table 1. These can be compared to the experimental parameters listed in the bottom row. Of the six computational methods employed, the Becke3LYP approach provided the most accurate prediction for the bond lengths, coming to within 0.002 Å for both BO and BO^-. This is consistent with the results of Barone,[18] who found a mean absolute deviation of 0.005 Å for a set of 14 first-row diatomic molecules calculated using the Becke3LYP approach. The bond lengths calculated using the MCSCF(5,6) and MCSCF(6,6) methods for BO and BO^-, respectively, are slightly shorter than the experimental values, while the bond lengths obtained using other correlated methods, such as MP2, MP4, or QCISD(T), are long by 0.007−0.018 Å. The calculated vibrational frequencies are all in reasonable agreement with the experimental results, with the exception of those obtained at the HF level, as expected.

The calculated values for the electron affinity of BO are listed in the last column in Table 1. The computed electron affinities are the energy differences between BO and BO^- and include a 0.3 kcal/mol correction for the difference in the experimental zero-point energies. The electron affinities calculated at the MP4, QCISD(T), and Becke3LYP levels of theory are all in reasonable agreement with the experimental result, while the value obtained from the multiconfigurational approach agrees perfectly. The electron affinities calculated with the G2, CBS-Q, and CBS-APNO methods are also in very good agreement with the measured EA, with the CBS calculations giving slightly better results. All of the calculated values for the EA are much lower than the previously reported calculated value of 2.97 eV.[23]

Conclusions

The electron affinity of BO obtained from the photoelectron spectrum of BO^- is 2.508 ± 0.008 eV, significantly lower than the previously experimental value,[20,21] but is consistent with the lower limit of 2.48 eV established by Jensen.[22] The angular distributions of photodetached electrons indicates that the detachment of the BO^- ion results in formation of $\tilde{X}$ BO.

High-level *ab initio* molecular orbital calculations are in reasonable agreement with the properties of BO and BO^-. It is found that density functional calculations give highly accurate structural parameters for both BO and BO^-, while other methods give less accurate results. Reasonable values for the EA affinity were obtained at essentially all levels of theory beyond HF, with the multiconfigurational SCF, G2, and complete basis set (CBS) methods providing the best agreement with the experimental result.

Note Added in Proof. After submission of this article, we learned that Schaefer and co-workers have also carried out density functional calculations on the electron affinity of BO (Rienstra, J. C.; Schaefer, H. F., III. *J. Chem. Phys.* **1997**, *106*,

8278), with results very similar to those reported here. We thank Professor Schaefer and Jon Rienstra for sharing their results with us.

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