

Inversion in the relative stabilities of HBO and BOH upon ionization

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Ab initio calculations of the HBO⁺→BOH⁺ potential energy surface were performed at the QCISD(T)/6-311++G(2df,2pd) level of theory. A linear ²Σ⁺+B=O-H species was found to be the global minimum for the cation although the linear ¹Σ⁺ H-B≡O isomer is the global minimum on the neutral HBO→BOH surface. Which isomer of the cation appears in various experimental circumstances depends on how the cation is produced. Ionization of ¹Σ⁺ HBO should occur near 13.2 eV and will produce the metastable linear H-B=O⁺(²Π) π-radical cation, which is 36.9 kcal/mol higher in energy than ²Σ⁺+B=O-H and is separated from ⁺B=O-H by a 36.3 kcal/mol classical barrier. Ionization of HBO with less than 37 kcal/mol of excess energy will thus yield ²Π H-B=O⁺; if the excess energy exceeds 37 kcal/mol, rearrangement to the ²Σ⁺+B=O-H σ-radical cation can occur. Production of the cation via exothermic chemical reaction will likely give the more stable ²Σ⁺+B=O-H isomer. The stability of the ²Σ⁺+B=O-H cation relative to ²Π H-B=O⁺ is due primarily to the large difference in the energies required to remove an electron from a π bonding orbital in H-B≡O or from a nonbonding boron-localized σ orbital in BOH. © 1999 American Institute of Physics. [S0021-9606(99)30307-X]

I. INTRODUCTION

The HBO and BOH isomers have been the subject of intensive *ab initio*¹⁻¹⁴ and experimental¹⁵⁻¹⁸ studies in part because solid boron and boron-based materials are favorable candidates for rocket fuels.^{19,20} It is now well established that the linear ¹Σ⁺ HBO isomer is the global minimum and that the bent ¹A' BOH isomer lies 45.0 kcal/mol higher in energy.¹⁴ Moreover, the classical energy barrier for the HBO→BOH isomerization reaction has been calculated to be 74.4 kcal/mol.¹⁴

In the ground state of the HBO isomer, the bonding involves H-B and B-O σ bonds, an oxygen-localized σ nonbonding orbital, as well as π bonds between B and O. These π bonds arise from B 2*p* and O 2*p* orbitals occupied by one electron from B and three electrons from O. Both π bonding molecular orbitals are strongly polarized toward the more electronegative oxygen atom, as a result of which their orbital energies lie only slightly below that of the O 2*p* orbital. It is for reasons that we denote this isomer H-B=O, although, as Richards *et al.* note,¹⁴ the BO bond order is likely between 2 and 3.

The BOH neutral isomer involves B-O and O-H σ bonds, a boron-localized σ nonbonding orbital, an oxygen-localized σ nonbonding orbital, and an "out-of-plane" orbital which is strongly localized on the oxygen but includes (small) contributions from the out-of-plane boron 2*p* orbital. We can thus denote this isomer as B=O-H, realizing that the extent of BO π bonding is very weak. In this isomer, the boron-localized σ nonbonding orbital is the HOMO, and the out-of-plane oxygen-dominant orbital is the next highest energy orbital.

In contrast to the situation with the neutral isomers, not

much is known about the corresponding HBO⁺ and BOH⁺ cations,²¹ even though these cations have been observed as reactants and products in mass-spectroscopic studies^{22,23} that motivated the present study. Correct interpretation of the ion-molecular reaction energies and thermochemistry in which the HBO⁺ (or BOH⁺) ion undergoes subsequent reaction with a wide variety of reagents demands that the experimentalists know both the electronic bonding nature (i.e., whether they have H-O=B⁺ σ-radical or H-B=O⁺ π-radical character) and thermodynamic energy (e.g., relative to the H-B≡O starting material) of the reactive ions. It was largely to address these issues that we have undertaken this study.

To the best of our knowledge, there are no *ab initio* calculations or spectroscopic experimental data that characterize these cations. In the JANAF Thermochemical Tables,²¹ it is assumed that HBO⁺ is the most stable isomer and that it has a ²Π ground electronic state with the following geometry parameters and vibrational frequencies: *R*(H-B)=1.19 Å, *R*(B-O)=1.25 Å, <HBO=180°, *v*₁(σ)=2559 cm⁻¹, *v*₂(π)=801 cm⁻¹, and *v*₃(σ)=1617 cm⁻¹. As we will soon show, this assumption is not correct.

The proposition that linear HBO⁺ (²Π) is the most stable cation isomer is certainly questionable because it is thought that much of the stability the neutral linear HBO relative to the bent BOH is due to the existence of the strong B≡O π-bonding in the former. Hence, to remove one electron from a π orbital of ¹Σ⁺ HBO is expected to require considerably more energy than to remove an electron from a nonbonding boron-centered orbital of bent ¹A' BOH. So, unless the ionization potential (IP) of HBO exceeds the IP of BOH by less than the BOH-HBO energy difference, the ²Π state of H-B=O⁺ will not be the lowest state of the cation. To answer such questions, we performed accurate *ab initio* calculations on HBO⁺ and BOH⁺, and we examined the po-

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TABLE I. Calculated molecular properties of the ground states of HBO and BOH.

HBO ($D_{\infty h}, {}^1\Sigma^+$)	BOH ($C_s, {}^1A'$)
QCISD(T)/6-311++G(2df,2pd)	QCISD(T)/6-311++G(2df,2pd)
$E_{\text{QCISD(T)}} = -100.550\,787$	$E_{\text{QCISD(T)}} = -100.479\,042$
$R_e(\text{H-B}) = 1.169\text{ \AA}$	$R_e(\text{B-O}) = 1.309\text{ \AA}$
$R_e(\text{B-O}) = 1.208\text{ \AA}$	$R_e(\text{O-H}) = 0.963\text{ \AA}$
	$\angle\text{BOH} = 121.1^\circ$
$\omega_1(\sigma) = 2894\text{ cm}^{-1}$	$\omega_1(a') = 3870\text{ cm}^{-1}$
$\omega_2(\sigma) = 1825\text{ cm}^{-1}$	$\omega_2(a') = 1393\text{ cm}^{-1}$
$\omega_3(\pi) = 780\text{ cm}^{-1}$	$\omega_3(a') = 616\text{ cm}^{-1}$
$T_{e\text{QCISD(T)}} = 0.0\text{ kcal/mol}$	$T_{e\text{QCISD(T)}} = 45.0\text{ kcal/mol}$
CCSD(T)/TZ2P(f,d) ^a	CCSD(T)/TZ2P(f,d) ^a
$E_{\text{CCSD(T)}} = -100.557\,490$	$E_{\text{CCSD(T)}} = -100.485\,797$
$R_e(\text{H-B}) = 1.169\text{ \AA}$	$R_e(\text{B-O}) = 1.307\text{ \AA}$
$R_e(\text{B-O}) = 1.206\text{ \AA}$	$R_e(\text{O-H}) = 0.964\text{ \AA}$
	$\angle\text{BOH} = 121.5^\circ$
$\omega_1(\sigma) = 2888\text{ cm}^{-1}$	$\omega_1(a') = 3852\text{ cm}^{-1}$
$\omega_2(\sigma) = 1831\text{ cm}^{-1}$	$\omega_2(a') = 1397\text{ cm}^{-1}$
$\omega_3(\pi) = 766\text{ cm}^{-1}$	$\omega_3(a') = 607\text{ cm}^{-1}$
$T_{e\text{CCSD(T)}} = 0.0\text{ kcal/mol}$	$T_{e\text{CCSD(T)}} = 45.0\text{ kcal/mol}$
Experiment	
$R_e(\text{H-B}) = 1.166\,67(41)\text{ \AA}^b$	
$R_e(\text{B-O}) = 1.200\,68(10)\text{ \AA}^b$	
$\nu_1(\sigma) = 2849\text{ cm}^{-1\text{ c}}$	
$\nu_2(\sigma) = 1817\text{ cm}^{-1\text{ c}}$	
$\nu_3(\pi) = 754\text{ cm}^{-1\text{ c}}$	

^aData from Ref. 14.^bData from Ref. 18.^cData from Ref. 15.tential energy surface for the HBO⁺→BOH⁺ isomerization.

II. COMPUTATIONAL METHODS

We optimized the geometries of HBO, BOH, HBO⁺, BOH⁺ and the transition state (TS) for the HBO⁺→BOH⁺ isomerization employing numerical gradients with polarized split-valence basis sets (6-311+G(2df,2pd)) at the QCISD(T) level of theory.²⁴ Results of our calculations of the neutral HBO and BOH species agree very well with the best published CCSD(T)/TZ2P(f,d) results obtained by Richards *et al.*¹⁴ as well as with the available experimental data (see Table I) and we expect the same accuracy for the cationic potential energy surfaces. The fundamental vibrational frequencies, normal coordinates, and zero-point energies (ZPE) were calculated by standard FG matrix methods. All of these calculations were carried out with the GAUSSIAN 94 program.²⁵

III. FINDINGS

A. HBO and BOH

In Table I we present results of our calculations on HBO and BOH at the QCISD(T)/6-311+G(2df,2pd) level of theory together with the earlier *ab initio* results at the CCSD(T)/TZ2P(f,d) level of theory obtained by Richards *et al.*¹⁴ and the experimental data for HBO of Kawashima *et al.*¹⁸

Our optimized bond lengths (and BOH angle) for both isomers agree with the best *ab initio* data to within 0.002 Å (0.4° for the angle) and are somewhat longer for HBO (by 0.002 Å for BH and 0.007 Å for BO) than the experimental data. The energy of the bent ¹A' BOH isomer relative to the linear ¹Σ⁺ HBO was found to be 45.0 kcal/mol at the

TABLE II. Calculated molecular properties of HBO⁺, BOH⁺, and their transition states (TS).

HBO ⁺ ($C_{\infty v}, {}^2\Pi$)	HBO ⁺ (TS1) ($C_s, {}^2A'$)	BOH ⁺ ($C_{\infty v}, {}^2\Sigma^+$)
QCISD(T)/6-311++G(2df,2pd)	QCISD(T)/6-311++G(2df,2pd)	QCISD(T)/6-311++G(2df,2pd)
$E_{\text{QCISD(T)}} = -100.064\,728$	$E_{\text{QCISD(T)}} = -100.006\,920$	$E_{\text{QCISD(T)}} = -100.123\,593$
$R_e(\text{H-B}) = 1.174\text{ \AA}$	$R_e(\text{B-O}) = 1.243\text{ \AA}$	$R_e(\text{B-O}) = 1.218\text{ \AA}$
$R_e(\text{B-O}) = 1.305\text{ \AA}$	$R_e(\text{B-H}) = 1.275\text{ \AA}$	$R_e(\text{O-H}) = 0.967\text{ \AA}$
	$\angle\text{HBO} = 85.23^\circ$	
$\omega_1(\sigma) = 2860\text{ cm}^{-1}$	$\omega_1(a') = 2221\text{ cm}^{-1}$	$\omega_1(\sigma) = 3819\text{ cm}^{-1}$
$\omega_2(\sigma) = 1463\text{ cm}^{-1}$	$\omega_2(a') = 1680\text{ cm}^{-1}$	$\omega_2(\sigma) = 1834\text{ cm}^{-1}$
$\omega_3(\pi) = 755\text{ cm}^{-1\text{ a}}$	$\omega_3(a') = 1178i\text{ cm}^{-1}$	$\omega_3(\pi) = 301\text{ cm}^{-1}$
$\omega_3''(\pi) = 679\text{ cm}^{-1\text{ a}}$		
$T_{e\text{QCISD(T)}} = 36.9\text{ kcal/mol}$	$T_{e\text{QCISD(T)}} = 73.2\text{ kcal/mol}$	$T_{e\text{QCISD(T)}} = 0.0\text{ kcal/mol}$
HBO ⁺ ($C_{\infty v}, {}^2\Sigma^+$)	HBO ⁺ (TS2) ($C_s, {}^2A''$)	BOH ⁺ ($C_{\infty v}, {}^2\Pi$)
QCISD(T)/6-311++G(2df,2pd)	QCISD(T)/6-311++G(2df,2pd)	QCISD(T)/6-311++G(2df,2pd)
$E_{\text{QCISD(T)}} = -99.999\,141$	$E_{\text{QCISD(T)}} = -99.908\,914$	$E_{\text{QCISD(T)}} = -99.968\,509$
$R_e(\text{H-B}) = 1.195\text{ \AA}$	$R_e(\text{B-O}) = 1.429\text{ \AA}$	$R_e(\text{B-O}) = 1.785\text{ \AA}$
$R_e(\text{B-O}) = 1.243\text{ \AA}$	$R_e(\text{B-H}) = 1.455\text{ \AA}$	$R_e(\text{O-H}) = 0.988\text{ \AA}$
	$\angle\text{HBO} = 56.20^\circ$	
$\omega_1(\sigma) = 2617\text{ cm}^{-1}$	$\omega_1(a') = 1791\text{ cm}^{-1}$	
$\omega_2(\sigma) = 1621\text{ cm}^{-1}$	$\omega_2(a') = 988\text{ cm}^{-1}$	
$\omega_3(\pi) = 691\text{ cm}^{-1}$	$\omega_3(a') = 1754i\text{ cm}^{-1}$	
$T_{e\text{QCISD(T)}} = 78.4\text{ kcal/mol}$	$T_{e\text{QCISD(T)}} = 134.7\text{ kcal/mol}$	$T_{e\text{QCISD(T)}} = 97.3\text{ kcal/mol}$

^aThe Renner-Teller effect causes our calculated π-vibrational frequency to be not degenerate. Therefore, as an approximation, we averaged our two frequencies to obtain $\omega_3(\pi) = 717\text{ cm}^{-1}$.

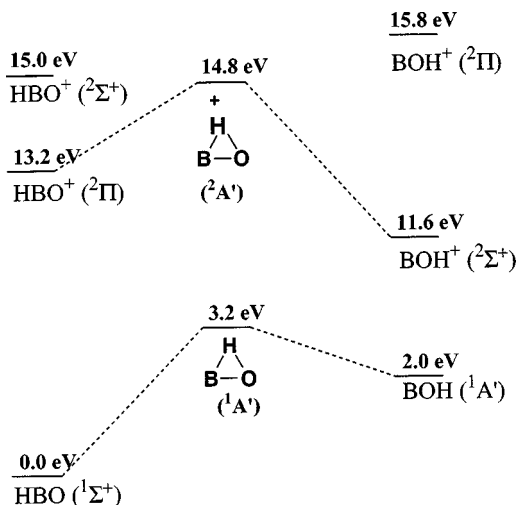


FIG. 1. Diagram of the relative stabilities of HBO, HBO⁺, BOH, BOH⁺, and (TS) structures. All data were obtained at the QCISD(T)/6-311+G(2df,2pd) level of theory, except the TS of HBO-BOH, which is at the CCSD(T)/TZ2P(f,d) level of theory (Ref. 14).

QCISD(T)/6-311+G(2df,2pd) level of theory, which is in excellent agreement with the best *ab initio* data of Richards *et al.*¹⁴ (see Table I).

B. The cations

1. HBO⁺

Linear ¹Σ⁺ HBO has a 1σ²2σ²3σ²1π⁴ valence (i.e., neglecting the O 1s² and B 1s² electrons) electronic configuration and orbital energy ordering with the 1σ, 2σ, and 3σ valence orbitals describing the BO and BH σ bonding and the oxygen-localized nonbonding electrons, while 1π are the BO π bonding orbitals. This structure has Koopmans' ionization energies of IP(1π) = 14.15 eV and IP(3σ) = 16.75 eV, with the π IP being lower because the 3σ orbital consists of a 2s-2p hybrid on the oxygen while 1π has primarily oxygen 2p character. One thus expects that the ²Π state (1σ²2σ²3σ²1π³) would be the (vertically) lowest-energy HBO⁺ cation state with the ²Σ⁺ state (1σ²2σ²3σ¹1π⁴) being the first excited state. That is indeed what we found in our subsequent more accurate calculations. The ²Π state of HBO⁺ was found to lie 13.23 eV (13.20 eV after ZPE correction) above the ¹Σ⁺ ground electronic state of HBO, with the ²Σ⁺ state lying 15.01 eV (14.97 eV after ZPE correction) above HBO (all at the QCISD(T)/6-311+G(2df,2pd) level of theory), see Fig. 1.

As one expects, detachment of an electron from the bonding 1π-MO of ¹Σ⁺ H-B≡O alters the B-O bond length and B-O vibrational frequency (see Table II). Indeed, the cation B-O bond length in the ²Π state is about 0.1 Å longer and its B-O stretching vibrational frequency is about 360 cm⁻¹ lower than in the neutral. These data indicate that π-bonding in the ²Π state of H-B≡O⁺ is indeed compromised compared to ¹Σ⁺ H-B≡O, which is why we denote this cation as H-B=O⁺.

2. BOH⁺

Within the C_s-symmetry of bent ¹A' BOH, we have a 1a'²2a'²3a'²1a''²4a'² electronic configuration with the 1a', 2a', and 3a' orbitals describing the BO and OH σ bonding and O-localized nonbonding electrons, 1a'' is the out-of-plane orbital described in Sec. III B 1 as involving very weak BO π interaction, and 4a' is the B-centered lone pair. At the Koopmans' level of theory, the two lowest IPS are IP(4a') = 10.06 eV and IP(1a'') = 16.22 eV, the latter being close to the π IP found in the H-B≡O isomer, and the former being much smaller because the 4a' orbital is centered on the less electronegative boron.

We therefore expect that the ²A' state (1a'²2a'²3a'²1a''²4a'¹) will (vertically) be substantially lower in energy than the ²A'' state (1a'²2a'²3a'²1a''¹4a'²) for the BOH⁺ cation. This state ordering is indeed what one finds upon vertical ionization, but subsequent geometry optimization of the ²A' and ²A'' states leads to linear BOH⁺ structures with the ²A' state collapsing to a ²Σ⁺ (1σ²2σ²1π⁴3σ¹) linear ⁺B=O-H state (having its unpaired electron in a B-centered 2s-2p hybrid orbital) and the ²A'' state evolving into one component of the ²Π (1σ²2σ²1π³3σ²) state of BOH⁺, with the ²Σ⁺ state being lower in energy (see Fig. 1).

3. Relative stabilities

The ²Σ⁺ state of linear ⁺B=O-H was found to be the lowest among all the cationic states of BOH⁺ and HBO⁺. The ²Π state of the BOH⁺ structure was found to lie 4.22 eV above the ²Σ⁺ state and to have a geometry corresponding to a boron atom bound weakly to ²Π OH. Unfortunately, we were not able to achieve convergence at the QCISD(T)/6-311+G(2df,2pd) level of theory to permit the frequency calculations on the ²Π excited state of BOH⁺, so we are not able to discuss this state further.

C. The HBO⁺ to BOH⁺ interconversion

Keeping in mind that linear ¹Σ⁺ H-B≡O is the global minimum on the HBO→BOH potential energy surface, although linear ²Σ⁺ ⁺B=O-H is the global minimum on the HBO⁺→BOH⁺ surface, one needs to determine the classical potential barrier on the cationic surface to make a judgment about what is likely to be experimentally observed in mass-spectrometric measurements (see Fig. 1). If a vertical ionization process begins from the HBO isomer, then ionization will occur near 13.20 eV and lead (vertically) to the ²Π state of (linear) HBO⁺. Subsequently, if the barrier to ²Σ⁺ (BOH⁺) is surmountable, the cationic system will rearrange to the lower energy ²Σ⁺ (BOH⁺).

As the linear ²Π state of HBO⁺ bends it splits into ²A' (with the hole in the 4a', nonbonding σ-MO of the cation) and ²A'' surfaces (with the hole in the 1a'', π-MO of the cation). We therefore searched for the transition states connecting to each of these symmetries. The ²A' symmetry transition state was found to be the lowest and to give the classical barrier on the ²Π (HBO⁺)→²Σ⁺ (BOH⁺) intramolecular rearrangement. This barrier was found to be 36.27 kcal/mol (33.81 kcal/mol after ZPE correction) above

${}^2\Pi$ HBO⁺, which is substantially smaller than the corresponding barrier for the HBO→BOH rearrangement. Therefore, depending on how much excess energy is deposited as the cation is made from HBO, one may end up with the temporarily stable ${}^2\Pi$ HBO⁺ cation or, after rearrangement, at the ${}^2\Sigma^+$ BOH⁺ cation.

D. Overview

In this work we have shown that ionization inverts the relative stability of HBO and BOH. For the neutral system, H-B≡O is more stable than B=O-H (by 45.0 kcal/mol) but H-B=O⁺ is less stable (by 36.9 kcal/mol) than the ⁺B=O-H isomer. One can rationalize these results in terms of the electronic structures of HBO, BOH, HBO⁺, and BOH⁺. As mentioned in the Introduction, neutral ${}^1\Sigma^+$ H-B≡O is more stable than the bent ${}^1A'$ B=O-H because of the stronger BO π -bonding in the former. To remove an electron from the π -HOMO of H-B≡O requires more energy (~13.2 eV) than to remove an electron from the nonbonding boron-localized lone pair orbital (~10 eV) of the bent ${}^1A'$ B=O-H. Moreover, when such a lone pair electron is removed from bent ${}^1A'$ B=O-H additional π -bonding is created and the stability of the resultant linear ⁺B=O-H isomer is subsequently increased. As a result of both its lower IP and the chance to form additional π -bonding, the ⁺B=O-H isomer is stabilized enough to cause it to be the global minimum on the HBO⁺→BOH⁺ potential energy surface.

These findings suggest that the π -radical cation ${}^2\Pi$ H-B=O⁺ will appear in experiments when the cation is formed by "soft" ionization of HBO. This cation isomer has its unpaired electron in a bonding π orbital. We can also infer that the more stable ${}^2\Sigma^+$ ⁺B=O-H cation, with its unpaired electron in a boron-centered nonbonding σ orbital, will be formed when the cation is created either by more severe ionization of HBO or by exothermic chemical reaction from other precursors.

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