

Reactions of Boron Oxide and $B_nO_mH^+$ Cluster Ions with Water

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Received: June 17, 1998; In Final Form: July 27, 1998

Reactions of $B_nO_m^+$ and $B_nO_mH^+$ clusters ($n \leq 3$, $m \leq 4$) with D_2O have been studied over a collision energy range from 0.1 to 10 eV (center of mass). The reactivity and product branching are found to be highly dependent on the structure of the reactant ion. When available, the preferred site of attack is on a terminal B atom, and the chemistry is dominated by O and OD addition. Even for the most reactive clusters the peak reaction efficiency is only 5–7%, indicating the presence of a bottleneck to reaction. When the reactant has no terminal B atoms, reaction is 1 order of magnitude less efficient and appears to be dominated by attack at nonterminal B atoms. The $B_nO_mH^+$ react similarly, suggesting that the added H atom does not block the reactive sites. This is in contrast to the isoelectronic reaction with HF, where H addition decreased reactivity dramatically. The results are compared with those for related reactions, and with recent *ab initio* results. In general, theory is consistent with experiment; however, there remain a few problem species.

I. Introduction

$B_nO_mH_x$ chemistry is critical in combustion of boron, a potential high energy density fuel additive. Boron particles are coated with a $B_nO_mH_x$ layer, and the chemistry and properties of this “oxide” layer control particle ignition. In addition, achieving the theoretical energy release from boron combustion requires that $B_nO_mH_x$ species formed in combustion reactions eventually convert to $B_2O_3(l)$. The $B_nO_mH_x$ are also interesting because the bonding is unusual and there are some significant and unanticipated discrepancies between experiment and high-level theory (see below). We have reported a study of $B_nO_m^+$ and $B_nO_mH^+$ chemistry with HF,¹ of interest because HF is an important intermediate in combustion of fluorine-containing compositions. We found that HF was quite reactive with $B_nO_m^+$ but that addition of a single H atom dramatically reduced the reactivity of $B_nO_mH^+$. One result of that study was a controversy regarding the stability of the FBOH molecule. Our results required that FBOH be substantially more stable than indicated by high-level *ab initio* calculations of Page, Soto, and co-workers.²

Partly to explore possible explanations for this discrepancy, we collaborated with the Page group on a combined study of $B_nO_m^+$ structure and energetics.³ Dissociation thresholds were measured by us using collision-induced dissociation, and structures and heats of formation were calculated by Page and co-workers at the G2 *ab initio* level. For some $B_nO_m^+$ the experiments and theory were in good agreement, but for others the experimental dissociation thresholds were significantly lower. In some cases this could be rationalized by proposing that the experiments were affected by the presence of a few percent contamination by high-energy $B_nO_m^+$ isomers with lower dissociation energies. As part of the study, we calculated expected isomer concentrations using *ab initio* data as input to density of states calculations. The conclusion was that for most of the $B_nO_m^+$, the isomer contamination should be negligible. The possible exceptions were $B_2O_2^+$ and $B_3O_3^+$, where isomerization barriers (not calculated) might be large enough to stabilize some population of the high-energy linear isomers. The most serious discrepancy was found for $B_3O_4^+ \rightarrow B_2O_2^+ + BO_2$,

where the experimental threshold is more than 2 eV below that calculated from *ab initio* energetics. The discrepancy cannot be attributed to isomers, because there is no high-energy isomer likely to be stabilized in the experimental cluster source.

In this paper we present results for reaction of $B_nO_m^+$ and $B_nO_mH^+$ with D_2O . The results reveal several reaction mechanisms. In addition, the chemistry turns out to be highly sensitive to the reactant structure and thus provides a sensitive probe of isomer issues. Page and co-workers have been kind enough to fill in some of the missing thermochemical data, and we are able to make a detailed comparison of experimental and theoretical energetics. In general, the results are consistent with theory. The major exception is the HOBBO molecule, where the experiment implies substantially greater stability than the *ab initio* calculations. The relation to the earlier problem with FBOH is discussed.

II. Experimental Approach

All experiments were performed using a guided ion beam mass spectrometer, described in detail elsewhere.^{1,4} Briefly, boron oxide cluster ions are generated by 12 keV argon atom bombardment of a thoroughly degassed $^{10}B_2O_3$ sample maintained near its melting point. The nascent cluster ions are collected with a radio-frequency (rf) octapole ion guide⁵ and thermalized by $\sim 10^6$ collisions with helium buffer gas inside a labyrinthine rf ion trap. The desired cluster size is selected using a quadrupole filter, optimized to preserve the beam's narrow kinetic energy spread,⁶ and then the reactant beam is injected into another rf octapole that guides the ions through a scattering cell containing 5×10^{-5} Torr of water vapor. Pressure dependence studies indicate that this pressure is low enough that multiple collisions can be neglected. The octapole collects product ions and unreacted cluster ions, and guides them to a conventional quadrupole mass filter, where they are mass analyzed and counted.

Polycrystalline B_2O_3 was prepared for sputtering by melting it onto a stainless steel substrate and heating to 650 °C in a flowing stream of O_2 for about 4 h to remove water from the bulk. After cooling, a thin vitreous film of boron oxide results.

The oxide-coated substrate was then mounted on a heatable sputter stage in the source vacuum chamber. To remove additional water, the oxide is heated to 350–450 °C in vacuum ($\sim 10^7$ Torr) for several hours. To reduce water adsorption from the chamber background, the sample is kept near its melting point during the experiment. Even with these precautions, some B_nO_mH⁺ ions are produced, probably due to residual water contamination.

To avoid mass interferences, we used the ¹⁰B and D₂O isotopic combination. Isotopically purified ¹⁰B₂O₃ (94.11 at. % ¹⁰B) was obtained from Eagle-Pitcher. For the B_nO_m⁺ + water reactions, monitoring ¹⁰B reactant and product ions completely eliminates interference from both ¹¹B and B_nO_mH⁺ contamination. For the B_nO_mH⁺ + D₂O reaction, we have to correct for background due to contamination of the ¹⁰B_nO_mH⁺ beam by isobaric ¹¹B¹⁰B_{n-1}O_m⁺. This is straightforward, if painful, using the measured reaction cross sections for the pure ¹⁰B_nO_m⁺ clusters. The magnitude of the correction increases with number of boron atoms, and for B₃O₃H⁺, where the signal is unusually low, we were unable to obtain good corrected cross sections. We did not measure isotope effects (D or ¹⁰B) for the oxide system; however, we note that in our previous work on B_n⁺ reactions with water,⁷ no isotope effects were observed. In addition, we have occasionally compared ¹⁰B and ¹¹B effects on B_n⁺ chemistry with no significant differences found.

III. B_nO_m⁺ Structures and the Composition of Our Reactant Beam

We recently reported³ a study of B_nO_m⁺ that combined measurements from the Anderson group with high level *ab initio* calculations from the Page group. Since the resulting insight into cluster energetics, structures, and isomers is important to interpreting the present results, we will briefly summarize the main points. Boron oxide clusters tend to form linear or cyclic structures with the maximum number of BO bonds. In cases such as BO⁺, BO₂⁺, and B₂O₃⁺, only a single low-lying structure is possible: linear BO, OBO, and OBOBO, respectively. For oxygen-poor stoichiometries (B₂O⁺, B₂O₂⁺, and B₃O₃⁺) a number of low-lying isomers are possible. For example, the most stable structure for B₃O₃⁺ is linear OB-BOBO⁺. Linear BOBOBO⁺ is only ~ 0.6 eV higher in energy, and a third isomer (OB-(cyclic)BOBO) is only 1.1 eV above the ground state. For our largest oligomer, B₃O₄⁺, the ground state is linear (OBOBOBO), but there is an isomer consisting of OBO bound to a BOBO ring that is 1 eV higher in energy.

An important question, therefore, is the extent to which our experiments are affected by the high-energy isomers. To address this question, we calculated isomerization transition state energies and vibrational frequencies and used this information to model the unimolecular isomerization kinetics.³ We found that the barriers separating the *cyclic* isomers from the ground states are, in each case, too small to stabilize a significant (>0.1%) fraction of these excited isomers, as the nascent cluster ions thermalize in our collisional cooling trap. The analogous calculations for linear-to-linear isomerizations were not done. We tentatively conclude the following. For BO⁺, BO₂⁺, and B₂O₃⁺, both lack of possible isomers and agreement between calculated and experimental dissociation energies suggest that only the ground state isomer is significantly populated in our ion beam. For B₂O⁺, B₂O₂⁺, and B₃O₃⁺, it is possible that we may have a few percent contamination from *linear* excited isomers (e.g., BOBOBO⁺). This might explain why the experimental dissociation thresholds are 0.6–1 eV lower than those calculated for the ground isomers. For B₃O₄⁺ the only low-

lying isomer calculated is cyclic, and we expect that nascent cyclic isomers will be efficiently converted to the linear ground state. Nonetheless, the experimental and *ab initio* dissociation thresholds differ by about 2 eV, suggesting a real discrepancy between experiment and theory.

Chemical reactions are potentially more sensitive to isomer distributions than collision-induced dissociation. The previous study of B_nO_m⁺ chemistry with HF¹ did not shed much light on the isomer issue, because the reactivity and product branching are nearly independent of reactant structure. In contrast, the reaction with water is quite structure sensitive and provides a test of the *ab initio* structures and of the experimental isomer contamination levels.

IV. Results and Discussion

Cross sections for reaction of B_nO_m⁺ with D₂O are given in Figure 1. Analogous results for reaction of B_nO_mH⁺ with D₂O are given in Figure 2. In each figure, the total cross sections are shown as a heavy solid line. To avoid clutter, each product channel is only plotted over the collision energy range where it is significant. In previous boron and boron oxide cluster ion reactions, we have found that a few reactions dominate over the entire range of cluster sizes and collision energies. For example, in the reaction of B_n⁺ with D₂O,⁷ the dominant reaction is B_n⁺ + D₂O → B_{n-1}D⁺ + DBO, presumably driven by the high stability of the DBO product. Similarly, for B_nO_m⁺ + HF, the product distribution is dominated by elimination of FBO, FBO⁺, FBOH, and FBOH⁺ from the collision complex.¹ In both cases, these dominant reactions proceed with high efficiency.

Here, the situation is much more complicated. Despite the existence of several exoergic channels for each reactant B_nO_m⁺, total reaction efficiency is small. For the B_nO_m⁺, there are 12 different product ions and 16 different neutral products, reflecting the existence of many product combinations with similar stabilities. For B_nO_mH⁺, the branching is even more complicated. It is difficult to come up with a set of graph symbols that are consistent and at least semilegible. The symbols used are keyed to the identity of either the neutral or ionic product, depending on which seemed to be more common across the set of reactants.

A. B_nO_m⁺ + Water. Table 1 summarizes the thermochemistry for reaction of B_nO_m⁺ with water. Except where indicated, the thermochemistry is calculated with ΔH_f values from Lias et al.⁸ and from *ab initio* calculations of Page and co-workers.^{3,9,10} Virtually all ΔH_f values for boron-containing reactants and products are from theory, because experimental values are not available. For a few reactions the product energetics are unknown, and the heat of reaction values are based on estimated ΔH_f 's derived from similar species using average bond strengths. For comparison, the table also gives the energetics for collision-induced dissociation (CID) of the reactant oxide ions, based on the *ab initio* calculations.³ For the case of B₃O₄⁺, where there is a large discrepancy between theoretical and experimental CID energies, both values are given. Overall, there is good agreement between the thermochemistry and our observations. With one important exception, all reactions observed at low E_{col} are also calculated to be exoergic, and the thresholds calculated for endoergic reactions are consistent with observation.

Clearly an experiment like ours gives no direct evidence for the structure of reaction products. In some cases the structure is unambiguous; for example, OBOBO is the only likely structure for B₂O₃. In other cases several possibilities can be imagined. To calculate thermochemistry, we have to assume structures, and for want of other information, we have assumed

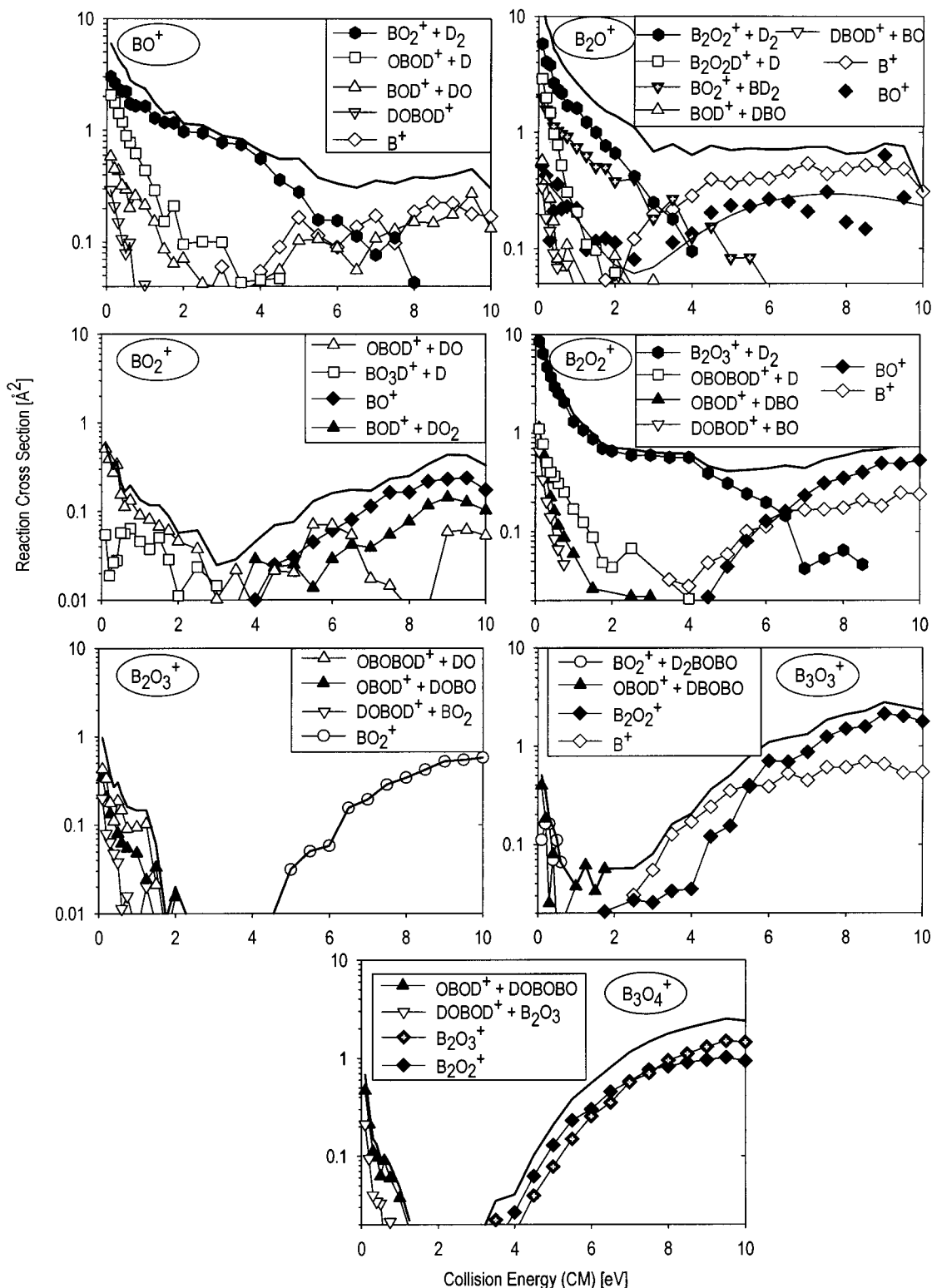


Figure 1. Cross sections for reaction of $B_nO_m^+$ with D_2O . In each frame, the total cross sections are shown as a heavy solid line.

that all species are in their most stable forms, unless otherwise indicated. In the text, tables, and figures we have sometimes used structural formulas for products to help clarify mechanistic proposals or bonding possibilities; however, it should be kept in mind that the true product structures (and reaction thermochemistry) may be different.

Reaction at High Collision Energies. For all the reactant oxides there is a cross section component that turns on at high E_{col} . This appears as a well-separated peak for the less reactive $B_nO_m^+$, and as a flattening of the E_{col} dependence and change

in product branching for the more reactive clusters. In most cases, the products observed, and their appearance energies, are similar to the fragmentation behavior observed in collision-induced dissociation (CID) with argon or xenon.³ For example, xenon CID of $B_3O_4^+$ gives rise to $B_2O_2^+ + BO_2$ and $B_2O_3^+ + BO$, with experimental threshold energies around 4.25 eV. In scattering with water the same two product ions are observed, with appearance energies similar to the experimental thresholds for Xe CID. Note, however, that the product branching ratios can be quite different for D_2O compared with the rare gases.

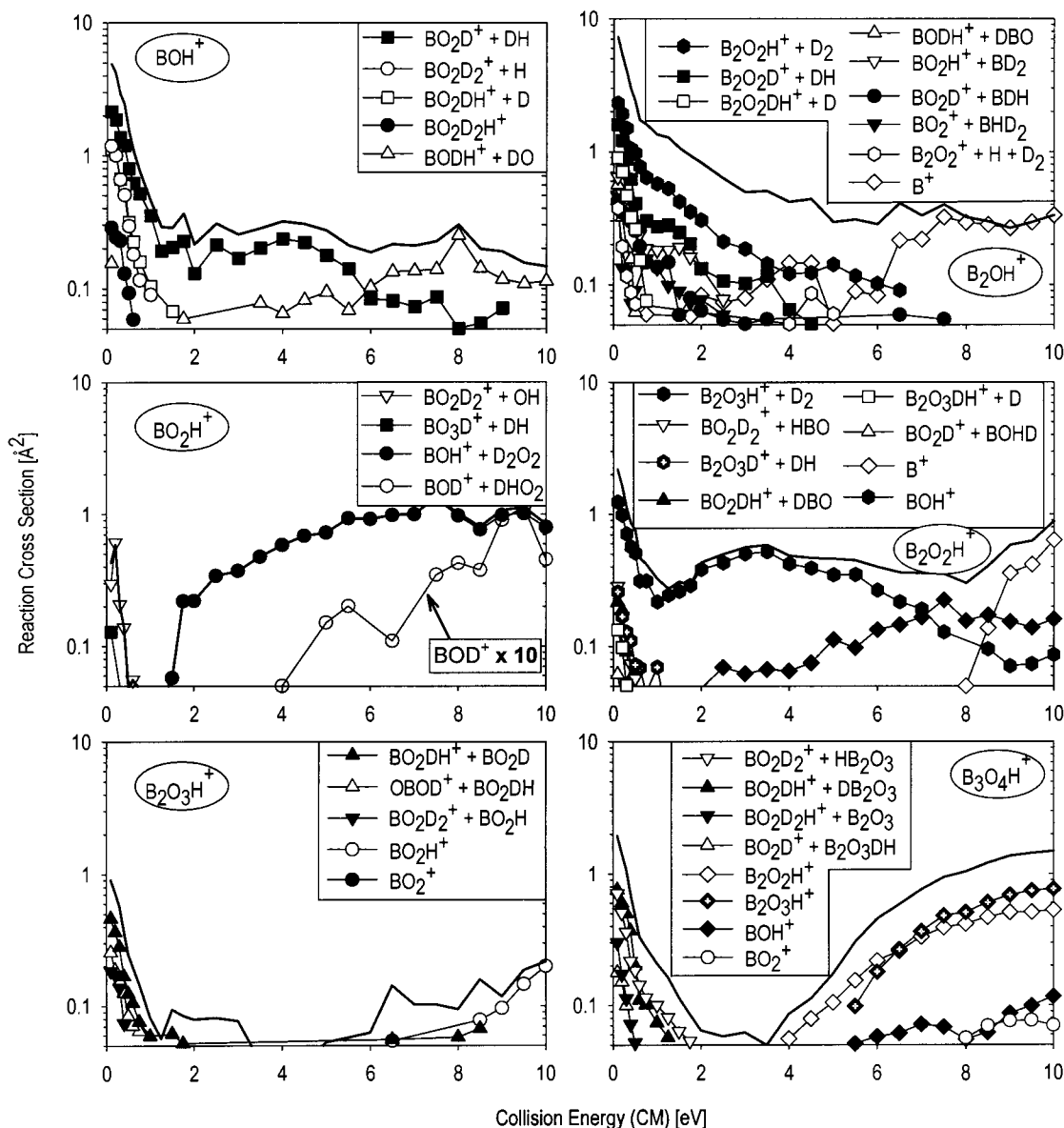


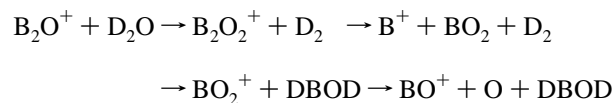
Figure 2. Cross sections for reaction of B_nO_mH⁺ with D₂O. In each frame, the total cross sections are shown as a heavy solid line.

For example, CID of B₃O₄⁺ gives B₂O₂⁺ and B₂O₃⁺ in a 3:1 ratio, while in reaction with water, the branching is ~1:1. While it is conceivable that this might reflect some change in CID dynamics, it is more likely that there is a chemical contribution to the B₂O₃⁺ signal: B₃O₄⁺ + D₂O → B₂O₃⁺ + DOBOD.

In other cases, the evidence for chemical channels at high energies is unambiguous. For example, in Xe CID of B₂O₃⁺ the lowest energy B₂O₂⁺ + O channel dominates over BO₂⁺ + BO by more than 1 order of magnitude. In contrast, reaction with D₂O at high energies generates exclusively BO₂⁺ with an appearance energy almost 2 eV lower than calculated³ for simple CID into this channel. Clearly, the BO₂⁺ signal results from the reaction B₂O₃⁺ + D₂O → BO₂⁺ + DOBOD. The appearance energy, ~4.3 eV, is consistent with the 4.13 eV threshold energy estimated using *ab initio* heats of formation. Finally, in some cases, the product ions contain atoms from both reactants. In reaction of BO⁺ and BO₂⁺ with D₂O, for example, in addition to the “fragmentation” channels, there are products like BOD⁺ and DOBO⁺.

One possible origin for the high-energy products is dissociation of nascent chemical reaction products that are too internally excited to survive. For example, in the reaction of B₂O⁺, the

appearance of the high-energy products, B⁺ and BO⁺, is coincident with the disappearance of two of the major low-energy product ions, B₂O₂⁺ and BO₂⁺. In xenon CID of B₂O₂⁺ and BO₂⁺, the dominant product ions are B⁺ and BO₂⁺, respectively. This suggests that much of the B⁺ and BO⁺ might result from the following mechanism:



In the reaction of B₂O₂⁺ with D₂O, the two high-energy product channels (B⁺ and BO⁺) also turn on as the dominant low-energy product ion (B₂O₃⁺) disappears. In this case, however, it seems unlikely that a sequential process is involved, because B₂O₃⁺ dissociates almost exclusively to B₂O₂⁺ + O. Clearly, the B⁺ and BO⁺ must result from other processes.

In summary, it appears that the high-energy scattering of B_nO_m⁺ from D₂O is dominated by chemical reactions, and possibly decomposition of primary reaction products, but there probably is also simple CID. We will focus the balance of the discussion on chemistry at low collision energies.

TABLE 1: Energetics of Observed Reactions for $B_nO_m^+$ with D_2O

reactant	products	ΔH_{rxn} (kcal/mol)	ΔH_{rxn} (eV)
BO^+	$BO_2^+ + D_2$	-11.8	-0.51
	$BO_2D^+ + D$	-44.4	-1.92
	$BOD^+ + OD$	-31.0	-1.34
	$BO_2D_2^+$	-190 ^a	-8.2 ^a
	B^+ (CID)	83.0	3.60
B_2O^+	$B_2O_2^+ + D_2$	-62.5	-2.71
	$B_2O_2D^+ + D$	-78.1	-3.39
	$BO_2^+ + BD_2$	~54	~2.3
	$BOD^+ + DBO$	-78.2	-3.39
	$DBO^+ + DBO$	-39.8	-1.72
	$BOD_2^+ + BO$	-70.7	-3.06
	$BO^+ + BOD_2$	-18.6	-0.81
	B^+ (CID >90%) ^b	43.8	1.90
	BO^+ (CID <10%) ^b	155.4	6.74
	BO_2^+	$BO_2D^+ + OD$	-18.5
$BO_3D^+ + D$		-75 ^a	-3.2 ^a
$BOD^+ + DO_2$		31.8	1.38
$BO^+ + D_2O_2$		94.8	4.1
BO^+ (CID ~90%) ^b		129.1	5.60
B^+ (CID ~10%) ^b		94.4	4.1
$B_2O_2^+$		$B_2O_3^+ + D_2$	-9.3
	$B_2O_3D^+ + D$	-49.5	-2.15
	$BO_2D^+ + DBO$	-15.0	-0.65
	$BO_2D_2^+ + BO$	-45 ^a	-2 ^a
	B^+ (CID ~90%) ^b	94.5	4.10
	BO^+ (CID ~10%) ^b	142.4	6.20
	$B_2O_3^+$	$B_2O_3D^+ + OD$	-26.1
$BO_2D^+ + BO_2D$		-22.4	-0.97
$BO_2D_2^+ + BO_2$		16 ^a	0.7 ^a
$BO_2^+ + BO_2D_2$		95.1	4.13
BO_2^+ (CID)		139.9	6.07
$B_3O_3^+$	$BO_2^+ + B_2O_2D_2$	-7 ^a	-0.3 ^a
	$BO_2D^+ + B_2O_2D$	-48 ^a	-2.1 ^a
	$B_2O_2^+ + BO_2D_2$	66.4	2.88
	$B_2O_2^+$ (CID ~5%) ^b	111.2	4.82
	B^+ (CID >90%) ^b	73.1	3.17
$B_3O_4^+$	$BO_2D^+ + B_2O_3D$	83.9	3.64
	$BO_2D_2^+ + B_2O_3$	-36 ^a	-1.6 ^a
	$B_2O_2^+$ (CID ~75%) ^b	144.9	6.28 or 4.25 ^c
	$B_2O_3^+$ (CID ~25%) ^b	149.1	6.46 or 4.25 ^c

^a Based on at least one estimated ΔH_f value—uncertainty unknown.

^b Percentages refer to branching observed in CID with inert gas targets.

^c *Ab initio* and experimental values, respectively.

Reaction at Low Collision Energy. There are two real surprises in the results presented here. Reaction efficiency is much lower than might be expected for exoergic ion–molecule reactions with no barriers. Also, product branching is not always in line with calculated reaction exoergicities. It is not possible to conclusively address these questions given the state of knowledge regarding the energetics, structures, and reactive properties of the $B_nO_m^+$ and $HB_nO_m^+$. In the discussion below we point out the interesting features, compare our results to theory by Page and co-workers, and attempt to speculate on mechanisms. The mechanistic speculations are just that, and more information from theory will be required to understand the surprising chemistry.

On the basis of reactivity at low E_{col} , the clusters can be divided into two groups. BO^+ , B_2O^+ , and $B_2O_2^+$ have total cross sections peaking near 10 \AA^2 , while the remaining clusters are about 1 order of magnitude less reactive. In all cases, reaction efficiency (the ratio of the total reaction cross section to the capture collision cross section¹¹) is relatively low, ranging from ~0.5% to ~7% at $E_{col} = 0.1 \text{ eV}$. This is despite the existence of several exoergic product channels for each $B_nO_m^+$. For the less reactive cluster ions, the efficiency also has an unusually strong dependence on collision energy. In some cases the total cross section drops by almost 2 orders of magnitude over the

E_{col} range from 0.1 to 1 eV, while the collision cross section drops by only a factor of ~5.

We believe that the best explanation for both the sharp E_{col} dependence and the low reaction efficiency is the existence of a bottleneck or tight transition state that limits reactivity. In this scenario, reaction is promoted at low energies by formation of an electrostatically-bound complex that allows time for the reactants to find the appropriate geometry or to undergo the requisite rearrangement. As collision energy is increased, the lifetime of this weakly-bound complex decreases rapidly, leading to a drop in reaction efficiency. Note that similar sharp E_{col} dependence is observed for reaction of $B_nO_m^+$ with HF ¹ and for reaction of B_n^+ with HF ,¹² CO_2 ,¹³ and water,⁷ although for those systems the reaction efficiency is much higher and the sharpness is less pronounced.

It is not clear what might give rise to a bottleneck/tight transition state. This cannot be a simple steric effect, since the $B_nO_m^+$ geometries leave all potential sites for D_2O attack readily accessible. All the major product channels are also spin-allowed. It may be that reaction occurs only for a precise reactant geometry or by a highly concerted mechanism.

To give a semiquantitative idea of the lifetimes to be expected for a weakly-bound complex, we carried out an approximate RRKM calculation¹⁴ for a medium size complex: $B_2O_2^+ - D_2O$. *Ab initio*³ vibrational frequencies and geometries were used for the $B_2O_2^+$ moiety, and experimental frequencies were used for D_2O . The $B_2O_2^+ - D_2O$ binding energy was estimated to be about 0.65 eV on the basis of an ion–dipole attractive potential, assuming a binding distance of ~2 Å. For the intermolecular low-frequency modes in the complex we guessed a set of values ranging from 50 to 100 cm^{-1} . For convenience, the transition state (TS) was assumed to be only moderately loose; i.e., the intermolecular torsions were assumed to drop in frequency by about a factor of 2 but not to the free rotor limit. Within this model, the lifetime is ~60 ns at $E_{col} = 0.1 \text{ eV}$, dropping by 3 orders of magnitude as E_{col} is increased to 0.5 eV. The magnitude of these lifetimes is highly uncertain because we do not know the true $B_2O_2^+ - D_2O$ binding energy or TS properties; however, the rapid drop in lifetime with E_{col} is consistent with the proposed mechanism.

Whenever reaction efficiencies of only 1% are observed, we need to consider the possibility that the signal might wholly or partly result from a reactive contaminant in the beam. As noted, it is possible that we have a few percent of high-energy linear isomers, at least for B_2O^+ , $B_2O_2^+$, and $B_3O_3^+$. While we cannot exclude some contribution from isomers, the following points suggest that most of the low-energy reaction is due to the ground state isomers: (1) The observed reactions are predicted to be substantially exoergic for the ground state isomers, so there is no need to invoke excited species. (2) Similar E_{col} dependence is observed for reactants where isomer contamination is likely (e.g., $B_3O_3^+$) and unlikely (e.g., $B_2O_3^+$). (3) The low-energy reactivity correlates well with the *ground state* isomer structures (next paragraph).

Both total reactivity at low E_{col} and the dominant product channels are strongly correlated with the calculated ground state isomer structure.³ The correlation of total reactivity is shown in Table 2. Reactivity is highest for B_2O^+ and $B_2O_2^+$, both of which have terminal, singly-bonded boron atoms. BO^+ also has a terminal boron atom, but doubly-bonded, and reactivity is about half that for B_2O^+ and $B_2O_2^+$. The other clusters all have only terminal oxygen atoms, and reactivity is substantially lower. The correlation is particularly interesting in light of the isomer contamination question. $B_3O_3^+$ is calculated to have the $O=$

TABLE 2: Ground State Isomer Structures, Energetics, and Low-Energy Reactivity

reactant ion	ground state structure ^a	$\Delta H_{f,298}^\circ$ ^a (kcal/mol)	σ_{TOT} (Å ²) at $E_{\text{col}} = 0.1$ eV	B _n O _m H ⁺ structure	σ_{TOT} (Å ²) for B _n O _m H ⁺ at 0.1 eV
BO ⁺	B=O	304.0	5.9	BOH ⁺ ^b	4.9
BO ₂ ⁺	O-B-O	234.4	0.3	HOBO ⁺ ^b	0.5
B ₂ O ⁺	B-O-B	286.0	12.1	BOBH ⁺ ^c	7.3
B ₂ O ₂ ⁺	B-O-B=O	165.7	11.4	HBOBO ⁺ ^c	2.4
B ₂ O ₃ ⁺	O=B-O=B-O	98.6	1.0	HOBOBO ⁺ ^b	0.9
B ₃ O ₃ ⁺	O=B-B-O-B=O	56.3	0.5		
B ₃ O ₄ ⁺	O=B-O-B-O-B=O	-46.4	1.1	HOBOBOBO ⁺ ^d	1.94

^a From Peiris et al.³ ^b From Napora and Page.⁹ ^c From Thweatt and Page.¹⁰ ^d By analogy with the calculated structures for HB₂O₃⁺ and HBO₂⁺.

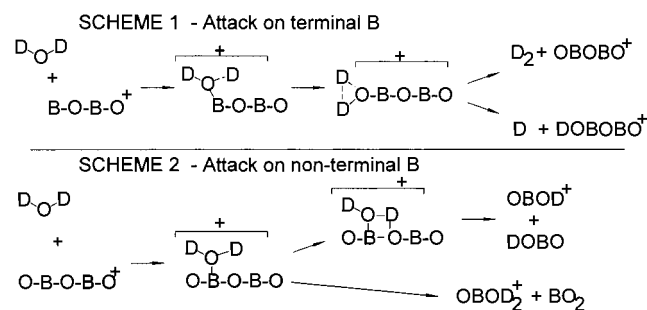
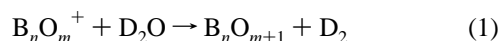


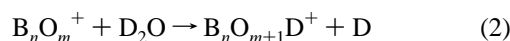
Figure 3. Possible reaction mechanisms for B_nO_m⁺ with D₂O.

B-B-O-B=O⁺ structure, with the B-O-B-O-B=O⁺ isomer 13.4 kcal/mol higher in energy. If there were significant contamination by BOBOBO⁺, we would expect increased reactivity compared to neighboring O-terminated oxides due to the singly-bonded boron termination. In addition, we would expect to see the O and OD addition reactions characteristic of the B-terminated oxides. In fact, the total reactivity of B₃O₃⁺ is very similar to both B₂O₃⁺ and B₃O₄⁺, and no signal is observed for O or OD addition. Clearly, contamination by the high-energy isomer is, at least for B₃O₃⁺, insignificant. For B₂O₂⁺, the other case where isomer contamination is most likely, the ground state BOBO isomer is reactive, and any contamination by the (presumably less reactive) OBBO isomer would make a negligible contribution to the reactivity or product branching.

The product branching in reaction with water is not simply determined by the exoergicity of the product channels. This can be seen clearly in Table 1, which lists the channels in order of the branching fraction at low E_{col} . For the B-terminated, oxygen-deficient clusters (BO⁺, B₂O⁺, and B₂O₂⁺) the dominant channel is O addition:



leaving the product oxide closer to the saturated B_nO_{n+1}⁺ stoichiometry. To a large extent, this reaction is responsible both for the enhanced reactivity of these B-terminated oxides and for the slower fall in their reactivity with increasing E_{col} . Since this channel is only seen for B-terminated reactants, it seems likely that the reaction proceeds by attack on the terminal B atom, as shown in Figure 3, scheme 1. The product channel next in importance is OD addition:



Again, this channel is only found for the B-terminated reactants, suggesting that reaction is initiated by attack on that site, as in scheme 1. For B₂O⁺ and B₂O₂⁺, there are also several channels that involve fission of the reactant oxide. These could result

from attack on the terminal B atom, followed by rearrangement and fission or possibly by attack at some other site.

One curious point is that reaction 1 dominates even though, in each case, there are more exoergic channels. In particular, reaction 2 is not only more exoergic than reaction 1, but the transition state for D elimination (reaction 2) should be looser than for D₂ elimination (reaction 1).^{15,16} If the D/D₂ elimination process was the rate-limiting step, then reaction 2 should dominate, and the fractional branching should increase with increasing energy—contrary to observation. The magnitude of the total cross section at low E_{col} indicates that there must be a bottleneck that limits reaction efficiency to <10%. The implication appears to be that the rate-limiting bottleneck is for water attack on the oxide, rather than product elimination. As already noted, it is not clear why there should be a bottleneck to attack—the reactions are highly exoergic, there is no spin restriction, and for these B-terminated oxides no rearrangement is required to give the most stable product structure.

For the O-terminated, fully-oxygenated reactants, B_nO_{n+1}⁺, the reactivity is roughly 1 order of magnitude lower than for the B-terminated oxides. For BO₂⁺ and B₂O₃⁺, D addition is an important channel, e.g., B₂O₃⁺ + D₂O → OBOBOD⁺ + OD. This is the only example of chemistry that clearly involves a terminal O atom and presumably reflects the large energy for bonding a hydrogen atom to the singly-bonded terminal O atoms in these species ($D(\text{OBO}^+-\text{H}) = 5.9$ eV, $D(\text{B}_2\text{O}_3^+-\text{H}) = 6.3$ eV⁹). This reaction could proceed by direct D addition to the terminal O atom, or possibly by D₂O attack on the adjacent B atom, followed by rearrangement and OD elimination. The absence of this channel for B₃O₄⁺ may reflect a weaker OBOBOBO⁺-D bond, attributable to the doubly-bonded terminal O atoms in B₃O₄⁺.

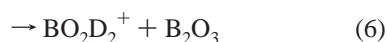
The other chemistry observed for the B_nO_{n+1}⁺ is best rationalized as attack on nonterminal B atoms. For B₂O₃⁺ and B₃O₄⁺, the reactions all involve fission of the oxide backbone, producing stable ion/neutral products such as DOBO, DOBOBO, B₂O₃, and BO₂. By analogy with the mechanism proposed for reaction of HF with B_nO_m⁺, we propose the mechanism depicted in scheme 2, Figure 3. For BO₂⁺, fission is not thermodynamically favored, but there is a small signal for BO₃D⁺ + D, corresponding to OD addition to the central B atom. The structure of the BO₃D⁺ ion is not known, but intuition suggests a 3-coordinate central boron atom.

The chemistry of B₃O₃⁺ is quite similar to that of B₂O₃⁺ or B₃O₄⁺, despite the fact that it has the same oxygen-deficient stoichiometry as BO⁺ or B₂O₂⁺. As noted, this reflects the structure of B₃O₃⁺, calculated³ to be OBBOBO⁺. Despite the fact that the O and OD addition reactions are, respectively, ~47 and ~86 kcal/mol exoergic, neither occurs. This reinforces the proposal that these reactions take place only at terminal B atom sites. Instead, what little chemistry there is occurs by insertion/fission:



Note: The structures for the neutral products are not known, and the energetics (Table 1) have been estimated by assuming bond additivity.

The only serious discrepancy between our results and the *ab initio* thermochemistry appears for B_3O_4^+ . The two reactions observed at low collision energies are, in order of decreasing importance



The structure and energetics of BO_2D_2^+ are unknown, but intuition suggests a DOBOD^+ structure, and we estimate that reaction 6 should be ~ 1.6 eV exoergic. For reaction 5, we have *ab initio* heats of formation for DOBO^+ , B_3O_4^+ , and DOBOBO ,⁹ leading to the prediction that this reaction should be ~ 3.6 eV endoergic, contrary to observation. In this case, we feel that there is a real disagreement between theory and experiment, and it probably involves both B_3O_4^+ and DOBOBO . In our combined *ab initio*/experimental study of boron oxide cations,³ the calculations predicted that B_3O_4^+ should be ~ 2.4 eV more stable than the experimental dissociation threshold. Using the experimental stability for B_3O_4^+ would lower the endoergicity of reaction 5 to 1.2 eV—still clearly inconsistent with experiment. We therefore feel that the heat of formation calculated for DOBOBO (-169.08 kcal/mol⁹) is too high by at least 1.2 eV.

This disagreement is reminiscent of one for the molecule FBOH , where our experiments¹ also suggest a heat of formation substantially lower than predicted by theory.³ Theory and experiment agree that the DOBOBO^+ cation is strongly bound ($D(\text{OBOBO}^+-\text{H}) = 6.29$ eV⁹), but the calculations predict that the neutral molecule is much more weakly bound ($D(\text{OBOBO}-\text{H}) = 1.04$ eV) than implied by the experiments. The same is true for $\text{FBOH}^+/\text{FBOH}$, and we have given a detailed discussion of this issue previously.³ As with FBOH , we have not been able to find an obvious explanation for the discrepancy, and simply note that a few problems remain in the thermochemistry of $\text{B}_n\text{O}_m\text{H}_x$. In this case, the discrepancy has significant implications for boron combustion. As noted, conversion of $\text{B}_n\text{O}_m\text{H}_x$ species produced in combustion reactions to $\text{B}_2\text{O}_3(\text{l})$ is necessary to achieve the maximum energy release. If $\text{B}_2\text{O}_3\text{H}$ is strongly bound, as experiment suggests, then this species may be difficult to dehydrogenate.

B_nO_m^+ Summary. For B_nO_m^+ , there appears to be a clear relation between reactant structure, reactivity, and product branching. Water attacks preferentially at terminal B atoms, leading to O or OD addition with moderate efficiency. For reactants with no terminal B sites, reaction is 1 order of magnitude less efficient and is mostly initiated by attack on a nonterminal B atom, leading to either addition (for BO_2^+) or fission (B_2O_3^+ , B_3O_3^+ , and B_3O_4^+). For B_3O_3^+ , the results suggest that contamination by high-energy isomers is negligible, indicating that the collisional cooling process in our source effectively anneals the reactant clusters. In general, our results are consistent with the *ab initio* calculations of Page and co-workers, but there are a few unresolved discrepancies.

B. $\text{B}_n\text{O}_m\text{H}^+$ + Water. As shown by Figure 2 and Table 2, addition of a single H atom to the reactant oxide cations has relatively little effect on total reactivity at low E_{col} . The main

exceptions are B_2OH^+ and $\text{B}_2\text{O}_2\text{H}^+$, where reactivity drops by a factor of ~ 1.7 and ~ 4.8 , respectively. We will focus the discussion on comparing the chemistry of B_nO_m^+ and $\text{B}_n\text{O}_m\text{H}^+$, with the goal of refining the reaction mechanism. In particular, the results for $\text{B}_n\text{O}_m\text{H}^+$ indicate that hydrogen migration is easy on the time scale of the collisions, at least for some reactants at low collision energies. For the hydrogenated reactants, the product thermochemistry is known too incompletely to allow construction of a table analogous to Table 1.

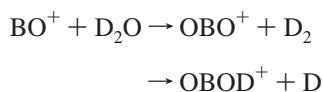
The small effect of H addition on reactivity toward water is very different from the situation in the isoelectronic reaction with HF. There, the reaction efficiencies are high for B_nO_m^+ but drop substantially for $\text{B}_n\text{O}_m\text{H}^+$. There is not a large difference in reactivity between the B- and O-terminated reactant oxides, and the products in all cases correspond to cleaving a BO from the reactant. We proposed that reaction with HF is initiated by attack on the B atom in a terminal BO group, leading to elimination of neutral or cationic FBO or FBOH, analogous to the mechanism proposed in scheme 2, Figure 3. The large effect of H addition on reactivity toward HF was taken as evidence that attachment of the H atom reduces the affinity for HF attack at the affected site.

For reaction of the bare oxide cations with D_2O , the results suggest that the preferred site of attack is on a terminal B atom, and when this is possible, the product distribution is dominated by O and OD addition (scheme 1). For BOH^+ , B_2OH^+ , and $\text{B}_2\text{O}_2\text{H}^+$, but only these, we also see O and OD addition with reasonable efficiency, suggesting that a terminal B atom site remains accessible in the hydrogenated reactants. For the B_nO_m^+ without terminal B sites, reaction occurs by attack on nonterminal B atoms (scheme 2), but with much lower efficiencies. The same reactions are seen for the analogous $\text{B}_n\text{O}_m\text{H}^+$, indicating, again, that the added H atom does not block the reactive site.

When our HF study was reported, the structures of the $\text{B}_n\text{O}_m\text{H}^+$ were mostly unknown. Recently, thanks to *ab initio* calculations of Page and co-workers,^{9,10} the situation has improved. For BO^+ , H is calculated to be strongly bonded to the O atom, yielding BOH^+ . For BO_2^+ and B_2O_3^+ , the calculated structures also have H bonded to one of the terminal O atoms: HOBO^+ and HOBBO^+ . The O–H bond formed is quite strong ($D(\text{OBO}^+-\text{H}) = 5.9$ eV, $D(\text{OBOBO}^+-\text{H}) = 6.3$ eV⁹), as might be expected from the structure of the oxide cations, each of which has a terminal, singly-bonded O atom with an unpaired electron available. For $\text{B}_3\text{O}_4\text{H}^+$, the structure is probably HOBBOBO^+ , but as noted above, there is some suggestion that the O–H bond may be weaker.

The structures are less obvious for species such as B_2OH^+ and $\text{B}_2\text{O}_2\text{H}^+$. The lowest energy structure of B_2O^+ is BOB^+ , calculated to be about 8 kcal/mol lower than BBO^+ . One could imagine three low-energy B_2OH^+ isomers: BOBH^+ , HBB^+ , and BBOH^+ . Thweatt and Page have recently calculated the energetics of these isomers¹⁰ and find that the most stable is BOBH^+ ($\Delta H_f = 214.4$ kcal/mol), followed by HBB^+ ($\Delta H_f = 228.4$), and BBOH^+ ($\Delta H_f = 257$). There are also several higher energy ring or triplet isomers. For $\text{B}_2\text{O}_2\text{H}^+$, Thweatt and Page have calculated energetics for the following isomers. The most stable is linear HBOBO^+ ($\Delta H_f = 97.1$), followed by linear OBBOH^+ ($\Delta H_f = 106.8$), planar BOBOH^+ ($\Delta H_f = 121.9$), and cyclic C_{2v} BOOBH^+ ($\Delta H_f = 123.4$).

For BO^+ , the dominant low-energy reactions are O and OD addition:



For BOH⁺, the same reactions are observed, and the cross section at low E_{col} is only slightly reduced:



The fact that reactivity and product branching are similar for BO⁺ and BOH⁺ is consistent with both reactants having the preferred terminal B atom site. A feature of the results that is difficult to explain is the preferential loss of HD, rather than D₂. Suppose, for example, that the reaction proceeds by attack on the terminal B atom, as in Figure 4, scheme 3. If the H/D atoms do not migrate freely, we would expect only D₂ loss in reaction 7 and unequal H/D loss branching in reaction 8, contrary to observation. Facile H/D migration would account for observation of both H and D elimination (reaction 8) but does not explain why D₂ elimination is not observed. Facile migration in the absence of isotope effects should give a 2:1 ratio for HD/D₂ loss.

Several factors suggest that the BOH⁺ reaction has a particularly tight bottleneck/transition state leading to products. Most obviously, we observe the BO₂D₂H⁺ adduct ion at low collision energies, implying the existence of an intermediate complex with unusually long lifetime. The binding energy of this adduct is unknown, but bond additivity using typical –BO–H bond strengths suggests a well depth relative to reactants of 4–6 eV. For an adduct with few degrees of freedom and this magnitude binding to survive the ~100 μs flight time to the mass spectrometer, there must not be any facile reaction channels. Further suggestion that the bottleneck to reaction of BOH⁺ is tight comes from the very sharp collision energy dependence found for BOH⁺, relative to BO⁺. Reaction is relatively efficient at low energies where the complex lifetime is long but falls off rapidly with decreasing lifetime (energy).

For a tight bottleneck/transition state, it is not unlikely that there could be substantial isotope effects, because the vibrational frequency distribution in the critical configuration depends strongly on the mass of the atoms being eliminated. For example, the density of states in the transition state leading to H or D elimination should be greater for H elimination, favoring H elimination. This may account for the nearly 1:1 H:D elimination branching, where the ratio would be 1:2 in the absence of isotope effects. The same reasoning also favors HD rather than D₂ elimination and this may account for the absence of significant D₂ loss. Not enough is known about the structure and frequencies of the adduct and critical configurations to attempt a quantitative calculation.

For B₂OH⁺, total reactivity at low energies is a little more than half that for B₂O⁺, consistent with one of the terminal B atom sites being blocked in the BOBH⁺ ground state structure. As expected for reaction at the remaining terminal B, both O and OD addition are observed:

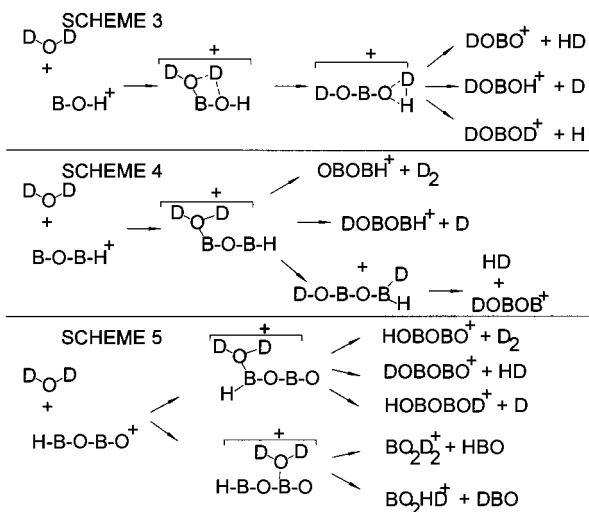
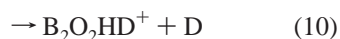


Figure 4. Possible reaction mechanisms for B_nO_mH⁺ with D₂O.

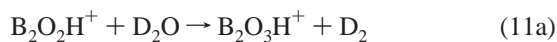
At very low energies, both (9a) and (9b) occur with nearly equal probability, but as the collision energy increases, the HD elimination branching decreases rapidly. This is consistent with reaction via an intermediate complex with sufficient lifetime to allow H and D migration. Purely combinatorial statistics for completely scrambled H/D would give a 1:2 ratio for reactions 9a and 9b. The nearly equal branching at low energies suggests that scrambling is not complete (isotope effects should favor HD loss). As the collision energy increases, the lifetime decreases rapidly and HD elimination becomes less likely, as observed. A possible mechanism is shown in scheme 4, Figure 4.

For BO₂⁺, the dominant reaction is OD addition, giving BO₃D⁺. For BO₂H⁺, the only low-energy reaction observed is nominally hydrogen addition; however, both D atoms in the D₂O end up in the BO₂D₂⁺ product ion. The reaction is, thus, actually water addition followed by OH elimination. At high collision energies, the major product observed for reaction of BO₂⁺ is BO⁺, and at least in the energy range below 5.6 eV, this must correspond to an O-abstraction reaction, yielding BO⁺ + D₂O₂. The same reaction (yielding BOH⁺ + D₂O₂) is also dominant for reaction of BO₂H⁺.

For reaction of B₂O₃⁺, several low-energy channels have roughly equal importance. For B₂O₃H⁺, the analogous reactions occur with similar cross sections, with one exception. For B₂O₃⁺, D addition/OD elimination has the largest cross section, consistent with the high stability of the DOBOBO⁺ cation.⁹ The analogous reaction for B₂O₃H⁺, yielding DOBOBOH⁺, is not observed, suggesting that the affinity for addition of a second hydrogen is substantially lower than for the first. For reaction of B₃O₄H⁺, the product distribution is analogous to that observed for reaction of B₃O₄⁺—a variety of fission products, suggesting an insertion mechanism as discussed above. There is clearly some scrambling of deuterium labels, suggesting that the reaction may proceed via an intermediate that lives long enough to allow some rearrangement.

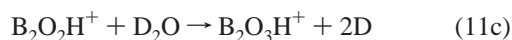
The reactant showing the largest changes upon H addition is HB₂O₂⁺, and this case is also the hardest to rationalize within our reactive site mechanism. Assuming that we have the most stable isomer, the reactant structure is predicted¹⁰ to be linear HBOBO⁺. Since the H atom is bound to the terminal boron site, we might expect this to substantially modify the chemistry, and indeed, the low-energy cross section is about a factor of 5 lower than for B₂O₂⁺. Nonetheless, the product distribution is dominated by O addition, as expected for attack at a terminal

B atom site:



One possibility is that attack at the terminal B atom site dominates, even though the H atom is bound there, as shown in scheme 5, Figure 4. The presence of H could explain the reduction in reactivity, compared to B_2O_2 , and the structure of the intermediate is certainly consistent with the observation that D_2 elimination dominates over HD elimination. There is also a small signal for OD addition that could also originate by attack at this partially blocked terminal B site. The other low energy chemistry is dominated by HBO/DBO elimination. The low efficiency of this reaction and the fact that it fissions the oxide are consistent with chemistry initiated by attack at the central B atom, as shown in Figure 4, scheme 5. Following attack on the central B atom, HBO elimination is clearly facile. It is not clear how DBO elimination occurs, and significant rearrangement would be required following attack on either the terminal or central boron atoms. It may be that proton/deuteron migration is relatively facile in the intermediates for this reactant.

One interesting observation is that the O addition cross section for $\text{B}_2\text{O}_2\text{H}^+$ has a second component that turns on at $E_{\text{col}} > \sim 1$ eV. It is not clear what gives rise to this high-energy component. An obvious possibility would be elimination of two D atoms:



but this can be ruled out on energetic grounds. Reaction 11a is calculated to be 1.47 eV exoergic, using *ab initio* heats of formation for $\text{B}_2\text{O}_2\text{H}^+$ and $\text{B}_2\text{O}_3\text{H}^+$; thus reaction 11c would be endoergic by over 3 eV. It is also possible that there might be a second reaction mechanism, with ~ 1 eV activation energy, leading to the O addition product. Note that this second, high-energy component may also be present in the O addition cross section for reaction of B_2O_2^+ . In that case the low-energy component is much larger, but there is an obvious flattening of the energy dependence at $E_{\text{col}} > \sim 1$ eV, possibly due to a second component.

$\text{B}_n\text{O}_m\text{H}^+$ Summary. The chemistry for the hydrogenated oxides is generally quite similar to that for the corresponding B_nO_m^+ . It appears that water continues to attack at terminal B atom sites when possible, leading to O and OD addition. In the absence of terminal B sites, fission products dominate, and we attribute these to attack at nonterminal B atoms, as in B_nO_{n+1} . Isotopic product branching indicates some possibility for D/H migration in the reaction intermediates.

Acknowledgment. We are grateful to Mike Page and his group for continued discussions and for providing us with structural and energetic information, prior to publication. This work was supported by the Office of Naval Research, Mechanics and Energy Conversion Division, under contract N00014-95-1-0696.

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