decay will be observed if there is a competitive nonradiative process with different rates for different sublevels. This is a general conclusion that should not be limited to the aromatic biradicals considered here.

Registry No. D₂, 7782-39-0; m-xylene biradical, 32714-83-3; 2methyl-m-xylene biradical, 100859-21-0; 3-methyl-m-xylene biradical,

Oxidation of Small Boron Agglomerates: Formation of and Chemiluminescent Emission from BBO

T. C. Devore,[†] J. R. Woodward,[‡] and J. L. Gole*

High Temperature Laboratory, Center for Atomic and Molecular Science, and School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332 (Received: October 20, 1987; In Final Form: April 26, 1988)

A source configuration that lies intermediate to a low-pressure effusing molecular beam and a high-pressure flow device is used to generate boron cluster molecules in a highly oxidizing environment. Using this source operating in an NO_2 or N₂O oxidative environment, we generate a chemiluminescent emission spectrum, which we attribute to the asymmetric BBO molecule. The observed spectrum is characterized by a strong $\Delta v = 0$, $\Delta v = 40$ cm⁻¹ sequence grouping and a weaker Δv = +1 sequence ($\Delta \nu$ = 40 cm⁻¹), 440 cm⁻¹ to higher energy. A second sequence with $\Delta \nu \sim 142$ cm⁻¹ is also observed. Combining the 440-cm⁻¹ upper-state frequency with the 142-cm⁻¹ sequence structure implies a lower-state frequency of \sim 582 cm⁻¹ for the B-B stretch, consistent with ab initio calculation.

Introduction

Because of its high heat of combustion per kilogram, boron represents an attractive high performance fuel¹ whose use may substantially improve the performance of volume-limited vehicles. However, in order to realize this potential, both the heterogeneous gas-surface and homogeneous gas-phase boron chemistry associated with particle ignition, flame stability, and combustion efficiency must be addressed. Investigations of the combustion of boron slurries and large particles² and of boron atoms³⁻⁵ have now been reported. Unfortunately these impressive studies neglect the bridge between the combustion chemistry of boron particles and the oxidation of compounds containing a single boron atom. There is growing evidence that the clustering of reactant and product species and the reactions of these clusters may make a significant contribution to the combustion chemistry² and hence influence the ability to extract the potential energy content of boron fuels. In an assessment and investigation of this important intermediate cluster regime, it will be necessary to determine the identity and signatures of those species contributing to the combustion reactions, thus learning more about their chemical and physical properties. Recently, we reported preliminary results from the investigation of the oxidation of boron atoms and boron cluster molecules with NO_2 and $N_2O.^4$ The optical signature of a new species formed from the oxidation of boron clusters was tentatively associated with the B₂O molecule. This paper presents the results of a more complete analysis of the observed band system whose location is ideally suited for further kinetic analysis of boron cluster oxide combustion. We present evidence that the observed emission should be correlated with the molecule BBO as opposed to the thermodynamically more stable BOB.

The vaporization of mixtures of the heavier group 13 metals and M_2O_3 is known to produce M_2O molecules.⁶ The infrared spectra of Al₂O, Ga₂O, In₂O, and Tl₂O⁷ have been extensively investigated in rare gas matrices. From this work, it is known that each of the "equilibrium" generated molecules has a symmetric structure. Al₂O is linear, while the heavier compounds in this series are bent. In contrast, little is known about B_2O .

Theoretical calculations indicate that, like Al₂O, the linear symmetric structure, BOB, is the most stable configuration.⁸⁻¹⁰ The BBO structure is calculated to be less stable by $\sim 100 \text{ kJ mol}^{-1.9-10}$ However, since these calculations also show an activation barrier of $\sim 125 \text{ kJ mol}^{-1}$ for interconversion of the isomers, it is reasonable to expect that either isomer could be formed in a kinetically controlled reaction and subsequently maintained due to the high barrier to interconversion. For example, the oxidation

of B_2 , via sideways attack, forming a ringlike intermediate

₿;o

would be expected to produce the more stable B-O-B isomer. Also, since B–O–B is linear, the visible emission spectrum should show a progression in the bending mode. In contrast, end-on oxidation to give a B-B-O intermediate favors formation of the dynamically stable BBO isomer. Any progressions, if present, should be largely localized to stretching modes. Hence a vibrational analysis of the "B₂O" band can be used to indicate which

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[†]Permanent address: James Madison University, Department of Chemistry. ^{*}Present address: General Electric Lamp Division, Cleveland, OH.

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TABLE I: Deslandres Table for BBO $v_{3}' = 1$ $\nu_{3}' = 0$ v1' v_1' v1" v3' $v_{3}' = 2$ $\nu_{3}' = 3$ ν_1 v1' $\nu_1^{\prime\prime}$ v3″

isomer is formed, indirectly suggesting a mechanism by which this isomer is produced.

Experimental Section

The apparatus and procedures necessary to vaporize a high flux of cooled boron vapor have been described in detail previously.^{4,5} Briefly, the boron (Alfa 99.7%) was heated in a closed graphite crucible (~2.5 cm o.d. \times 2.5 cm high) to temperatures for which the corresponding vapor pressures of boron ranged from 13 to 135 Pa (2520–2800 K). The vapor was entrained in a precooled flow of rare gas (He or Ar, Airco 99.998%) with a pressure ranging from 13 to 400 Pa. This mixed flow intersects a flow of NO₂ (Matheson 99.5%, P = 1.3 to 13 Pa), which enters through a concentric ring injector inlet approximately 2 cm from the crucible or through a perpendicular nozzle elevated approximately 2 cm above the cooled oven assembly (~ 4 cm from the crucible). A multiple vacuum pump-valve system permits the pressure in the reaction chamber to be adjusted from 10⁻³ Pa (single collision conditions) to 500 Pa (multiple collision conditions). However, all spectra reported here were recorded under multiple collision conditions.

The spectra were obtained with a 1-m Czerny-Turner scanning spectrometer operated in first order with a Bausch and Lomb 1200 groove/mm grating blazed at 500 nm. A dry-ice-cooled EMI 9808 photomultiplier tube was used to record the spectra. The photomultiplier signals were detected with a Keithley 417 fast picoammeter whose output signal drives a Leeds and Northrup strip chart recorder. All spectra were wavelength calibrated.

Results and Discussion

As reported previously,⁴ the reaction between boron atoms and NO₂ over a wide pressure range produces emission from the A ²II state of BO and the A ²II and B ²Σ⁺ states of BO₂. However, when the argon carrier gas is precooled to dry ice temperatures to promote boron cluster formation, a new emission feature onsetting at 590 nm is observed. As the boron flux is increased, the relative intensity of this system increases substantially as it begins to dominate the spectrum.

The spectrum corresponding to the 590-nm system is depicted in Figure 1. Several features are quite apparent in this spectrum. There are two clear red degraded sequences of bands separated by approximately 440 cm⁻¹. The 615-nm feature is approximately 3 times stronger than the 590-nm feature. Two sequences are present in each band grouping. One has a spacing of ~ 42 cm⁻¹ and is most easily seen near the band origin. The second, with a spacing of ~ 142 cm⁻¹, is clearest near the band tail. The observed intensity distribution is suggestive of a transition between states that differ little in geometry.

The origin band for this transition is almost certainly the strongest band at 613.4 nm. The band at 597.4 nm is then readily assigned as the 1–0 band corresponding to an excited-state normal mode of the molecule. No other vibrational heads are obvious. One of the observed sequences almost certainly correlates with this transition; thus the estimated ground-state vibrational frequency for this mode is either 480 or 580 cm⁻¹. We have attempted to fit the observed spectrum with both frequencies. The 580-cm⁻¹ assignment gives the better fit leading to the assignments

 $B_x + NO_2 \rightarrow$



Figure 1. Observed visible emission spectrum of BBO. Progressions in the B-B stretch (here called v_3) are marked in the figure as 3^y_x . The sequence structure in a second vibration in each progression band is also indicated with the numbered tick marks.

shown in Figure 1. The Deslandres table for these assignments is given in Table I. A search for additional bands at shorter wavelengths was thwarted either because of their low intensity or their blending with bands arising from BO_2 . The search for bands to longer wavelength, hindered by low intensity, was marginally successful.

Feasible Assignment of the Emission System to BBO or OBBO. Because the observed spectrum is characterized by two distinct sequences, the emitter must be a polyatomic molecule. The conditions under which the spectrum has been excited (high boron flux, cooling to promote clustering, and low oxidant pressure) suggest that the emitter contains more than one boron atom and is likely a boron-rich molecule. The most feasible molecules that meet this criteria are B_2O and B_2O_2 . However, the larger molecules B_xO_y ($x \ge 3$; y = 1, 2) and B_2O_3 have also been considered in this analysis.

No visible spectrum has been reported for any of the B_xO_y molecules with $x \ge 2$. In an early matrix isolation experiment, Sommer et al.¹¹ reported that B_2O_3 has no observable bands in the visible spectral region and ascribed a feature at 590 nm to BO_2 . Unfortunately, however, these authors did not clearly report the complete frequency range which they examined. The infrared spectra of $B_2O_2^{11,12}$ and $B_2O_3^{11-13}$ have been observed in rare gas matrices, and ground-state vibrational frequencies are established for these molecules. Although no experimental data is available, the vibrational frequencies of the isomers of B_2O and B_2O_2 have been evaluated with quantum-chemical methods at various levels of description.^{8-10,14} From these studies, the frequencies of these

TABLE II: Calculated and Observed Frequencies for B_2O_y (y = 1-3) Vapor Molecules

mode	frequencies, cm ⁻¹							
В-О-В								
$\nu_1 (\Sigma_{\mathbf{g}}^+)$	1633.1ª	1545		(1510/1430) ^c				
ν_2 (II)	83.2			(76.90/-)				
$\nu_3 (\Sigma_u^+)$	1087.3	1002		(1005/926)				
В-В-О								
$\nu_1 (\Sigma^+)$	2092.5ª	2006 ^b		(1935/1856) ^c				
ν_2 (II)	305.3			(282/-)				
$\nu_3(\Sigma^+)$	628.4	626		(581/579)				
О-В-В-О								
$\nu_1 (\Sigma_g^+)$	2302.3ª	2222ª	2060 ^e	(2130/2055) ^c				
$\nu_2 (\Sigma_g^{\bullet+})$	630.4	628	585	(586/581)				
$\nu_3 (\Sigma_a^+)$	2089.2	2052	1897.8	(1932/1898)				
$\nu_4 (\Pi_g)$	541.9	432	410	(501/400)				
$\nu_5 (\Pi_u)$	235.5	216	213	(218/200)				
В-О-В-О								
$\nu_1 (\Sigma^+)$	2223.6ª			(2056.7) ^c				
$\nu_2 (\Sigma^+)$	1477.5			(1366.6)				
$\nu_3 (\Sigma^+)$	851. 9			(788.0)				
ν_4 (Π)	557.4			(515.5)				
ν ₅ (Π)	171.7			(158.8)				
О-В-О-В								
ν_1 (A ₁)	20	60 ^e s	ν_{6} (B ₁)	2060				
ν_2 (A ₁)	729		$\nu_7 (\mathbf{B}_1)$	1239				
ν_3 (A ₁)	5	518		454				
ν_4 (A ₁)				477				
ν ₅	4	456						

^aUnscaled calculated value from ref 10. ^bUnscaled calculated values from ref 9. ^cScaled calculated values from data obtained with a constant scaling factor (0.925). ^dUnscaled calculated values from ref 14. ^eValues calculated from force constants derived from experimental data (see ref 13, 14). ^fExperimental values from ref 12.

molecules can be reasonably estimated, as indicated in Table II.

The one clearly ascribable ground-state frequency, 580 cm^{-1} , associated with the emission system observed in this study, is in excellent agreement with an observed frequency for O-B-B-O

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and that calculated for the B-B stretch in B-B-O. It does not agree with any frequency calculated for the BOB isomer, and this compound can readily be eliminated from further consideration. The alternate ground-state frequency assignment ($\nu \sim 480 \text{ cm}^{-1}$) is in reasonable agreement with the ν_5 (A₂) mode of B₂O₃, but this molecule is eliminated from further consideration on the basis of (1) the relatively poor overall fit of the data to this alternate assignment, (2) the absorption studies of Sommer et al. in the visible spectral region, and (3) the requirement of a reasonable and consistent dynamics for molecular formation. An oftensuggested mechanism for the formation of the B₂O₃ molecule corresponds to the three-body process

$$BO + BO_2 + M \rightarrow B_2O_3 + M \tag{1}$$

In view of the observation of emission from both BO and BO₂, signaling their presence under multiple collision conditions at lower boron fluxes in the absence of significant cooling, it is difficult to rationalize how the cooling needed to induce boron clustering should be required to form B_2O_3 via the mechanism (1).

Because there is no information at present on the larger boron cluster oxides including B_3O , it is difficult to completely eliminate them from consideration. However, the emission spectrum of the B_3O molecule would be signaled by the excitation of several vibrational modes, producing a much more complex and perhaps unresolved spectral pattern. Bahn¹⁵ has noted that the combustion of boron particles in air does generate B_2O . This result suggests that the oxidation of boron clusters should also hold the potential for producing B_2O . Our results thus suggest that the molecular emitter is either B_2O or B_2O_2 .

The observed intensity distribution is suggestive of a transition between states that differ little in their geometry. The information obtained from both experiment and calculation indicates that both OBBO and BBO have linear ground states. Hence, the monitored transition is reasonably assigned as that between two linear states. For a linear-linear transition, regular sequence structure indicates that the molecules' stretching modes have been excited; the bending modes are expected to display an irregular spacing.¹⁶ Hence the $\Delta \nu = 40 \text{ cm}^{-1}$ sequence is assigned as arising from the B-O stretching mode. A careful search for bands that could be attributed to a progression in the B-O stretching frequency did not reveal features that could be readily assigned with certainty; this is probably the result of poor Frank-Condon factors.

Two weak bands were observed at 692.0 nm ($\Delta G''_{1/2} = 1970$ cm⁻¹) and 706.9 nm ($\Delta G''_{1/2} = 2155$ cm⁻¹). Neither agrees with the OB-BO symmetric stretching frequency (2060 cm⁻¹) or the OBBO asymmetric frequency (1898 cm⁻¹). The assignment of the 692-nm feature to the 3_3^2 band of the OBBO molecule seems unreasonable because the emission associated with the asymmetric mode is not expected to be as strong as that associated with the symmetric stretch. Further, we are unable to identify any bands in this sequence. The calculated frequency for the BO stretch in BBO lies between 2006⁹ and 2090 cm.^{-1 10} Noting that the calculated frequencies for B_2O_2 are ~8% high and applying a similar scaling factor, we suggest that the observed frequency should lie between 1856 and 1935 cm⁻¹. If we assign the 692-nm band as the 1_1^0 transition for the BBO molecule, the observed frequency is in reasonable agreement with the scaled calculations.

The identification of boron isotopic species might be helpful as a means of determining the identity of the observed emitter. The isotopes, their relative abundances, and the stretching frequencies expected for each are given in Table III. It would not be possible to observe isotopic structure associated with the B-B stretch in OBBO at the resolution available in this study. The isotopic B-B stretching frequencies in BBO fall into two groups ($\nu \sim 580, 600 \text{ cm}^{-1}$; Table III) separated by $\sim 20 \text{ cm}^{-1}$, which is a separation marginally large enough to be resolved for these two isotopic combinations. However, the total intensity of the

TABLE III: Expected Isotopic Frequencies (cm^{-1}) for the Streching Modes of BBO and OBBO^c

		B-B-O ^a		
mode	¹¹ B- ¹¹ B-O (0.64)	¹¹ B- ¹⁰ B-O (0.16)	¹⁰ B- ¹¹ B-O (0.16)	¹⁰ B ¹⁰ BO (0.04)
$\nu_1 (\Sigma^+)$ (B-O stretch) $\nu_2 (\Sigma^+)$ (B-B	1935 581	1995 583	1935 601	1995 603
stretch)	O-B-B-O ^b			
mode	O ¹¹ B- (0,	- ¹¹ B-O O	$^{11}B^{-10}B^{-0}$	O- ¹⁰ B- ¹⁰ B-O (0.04)
$\frac{1}{\nu_1 (\Sigma_2^+) (\text{sym B}-$	0 20	60	2103	2133

 stretch)
 ν_2 (Σ_g^+) (B-B
 585
 588
 592

 stretch)
 ν_3 (Σ_u^+) (asym B-O
 1898
 1919
 1953

 stretch)
 stretch)
 1953
 1919
 1953

^aScaled values calculated by using force constants derived from data in Table II. ^bExperimental data from ref 12 and 13. ^cAbundances are in parentheses.

higher frequency isotopic groups (Table III) is only about one-fifth (one-fourth the intensity of the stronger grouping) that of the total intensity. This low intensity prevents the identification of these bands at the resolution available in this study.

The isotope shifts in the BO stretches are larger. This is significant, for a search in the vicinity of the 692-nm band did not reveal a feature that could be identified with an isotopic BO stretch. Because of its anticipated low intensity, this result would be expected for BBO. However, the isotopic bands for OBBO should be of sufficient intensity so as to be observed in this study. Given that the assignment of the 692-nm band is correct, these results again suggest that the emitter is BBO.

The observed emission spectrum clearly demonstrates that the molecule possesses a B-B bond and that its upper and lower states have similar geometries. Although the spectrum strongly indicates that the emitter is BBO, it does not contain enough information to unequivocally eliminate OBBO from consideration. Hence, the reaction dynamics of the system were also considered as a means of suggesting the identity of the observed emitter.

Plausible Reaction Dynamics Suggesting a BBO Emitter. Two possible mechanisms can produce the observed emission. If at first, a boron atom reacts with NO₂ to form BO, this BO product can then react with a subsequent boron atom to form B_2O as follows:

$$B + NO_2 \rightarrow BO + NO$$
 (2)

$$B + BO + M \rightarrow B_2O + M (M \simeq Ar)$$
(3)

or dimerize to form B_2O_2 :

$$BO + BO + M \rightarrow B_2O_2 + M \tag{4}$$

where, based strictly on reactant concentration, the process leading to B_2O should dominate that leading to B_2O_2 . Both of these reaction sequences would be expected to produce an emitting product intensity that increases linearly with boron concentration. In a second possible reaction sequence, boron first forms a dimer or higher-order clusters. These clusters then react with NO_2 as follows:

$$\mathbf{B} + \mathbf{B} + \mathbf{M} \to \mathbf{B}_2 + \mathbf{M} \tag{5}$$

$$B_2 + NO_2 \rightarrow B_2O + NO \tag{6}$$

$$B_2O + NO_2 \rightarrow B_2O_2 + NO \tag{7}$$

For this process and further processes involving the boron clusters, the intensity is expected to increase as the square or possibly higher power of the metal flux. The behavior of the spectral emission feature with increasing metal flux is consistent with the outlined second mechanism. That is, the reaction leading to the observed emitter occurs through the oxidation of a boron molecule (which

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may be a dimer but in fact probably is a larger cluster in order to be consistent with observation).

The formation of a B_2O_2 emitter in a single reaction step can be eliminated from consideration on both thermodynamic and kinetic grounds. Further, if a multicentered process were to take place, the B_2O_2 would be constrained to formation in a bent configuration, a result inconsistent with the observed spectrum. The formation of a B_2O_2 emitter thus requires two oxidation steps. This does not seem likely under the metal-rich conditions used here. The observed system is thus assigned as arising from B_2O .

Concluding Remarks

All available data collected indicates that the 590-nm band system results from the $A \rightarrow X$ transition of BBO. While this isomer is predicted to be less stable than BOB, its formation can be rationalized on kinetic grounds. The nature of the observed spectrum indicates that the energy of reaction is largely dissipated into the stretching modes of the molecule. This strongly suggests the oxidation of the boron molecular cluster occurs through a linear intermediate, which then relaxes to give the metastable BBO structure.

If the BO frequency is $\sim 2000 \text{ cm}^{-1}$, then, based on the observed origin band sequence structure, approximately 3 eV of energy has been deposited into the B₂O molecule via the cluster reaction. This suggests that the dissociation energy for the BO bond formed in the reaction must correspond to a minimum of 6.1 eV. This should be compared to the 8.0-eV bond dissociation energy of BO.¹⁷

Finally, we should note in considering the results obtained in this study and their correlation with those of other workers^{7,15} that (1) the molecular electronic structure and (2) the excited-state manifold of the B₂O isomers differ notably. While the BBO A-X emission system lies at ~ 600 nm, extrapolation of the electronic spectroscopy⁷ established for the symmetrical isomers Al₂O-Tl₂O demonstrates that the A-X band system of BOB should lie at

much higher energy ($\lambda < 400$ nm). Further, the reactions of BOB will be distinct from those of BBO, and it is to the advantage of kineticists that the optical signatures of both isomers be established.

The homogeneous combustion chemistry of boron oxidation can take on many facets; however, there has been significant concern focused on the details of the mechanism suggested for the "high-energy content" gas-phase oxidation of BO(g) to B_2O_3 -(g).^{1-3,15} Here the key BO oxidation step in *dry atmospheres* is thought to be the rate-limiting oxidation $BO(g) + O_2(g) \rightarrow BO_2(g)$ + O(g) followed by the subsequent reaction of BO_2 with additional BO molecules, the two-step process producing $B_2O_3(g)$. While a high-energy liberating chemistry based primarily on BO(g) formation is appealing, can we be sure that gaseous BO is the prime gas-phase constituent liberated in the ignition of boron particulates? Several important gas-phase compounds released as boron combusts might be neither gas-phase BO(g) nor solid boron but rather intermediate species. Suppose that one of these species is B_2O . Can the process $B_2O(g) + O_2(g)$ compete with the two-step mechanism indicated above for B_2O_3 formation? With the data obtained in this study, some answers to this question might be forthcoming.

In conclusion, these results appear to demonstrate that the thermodynamically more stable boron cluster isomers may not be the dominant molecules that are involved in the dynamic processes influencing boron combustion reactions. Thus, in order to fully understand these processes, those reactions forming the less stable isomers must also be considered. The analysis of the spectra of those molecules generated in the present configuration can provide quantum-structural information about these species that cannot be easily obtained by using other methods. An examination of the concentration dependence provides an indication of the mechanism of reaction and the molecules that are being formed.

Acknowledgment. We acknowledge support of this research through Grants NSF-RUI-CHE-8511710 (T.C.D.) and NSF-8604471 (J.L.G.) from the National Science Foundation.

Registry No. B, 7440-42-8; NO₂, 10102-44-0; N₂O, 10024-97-2; **BBO**, 12045-60-2.

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