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Studies of chemiluminescence in boron atom reactions with O_2, SO_2, N_2O, NO_2, and H_2O_2

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Chemiluminescence has been observed in the single collision reaction of boron atoms with O_2, SO_2, N_2O, NO_2, and H_2O_2. The experiments were performed in a beam-gas apparatus using photon counting to detect the optical signals. The electronically excited $A\,^2\pi$ state of BO was observed in all the reactions. In addition, the $BO_2(A\,^2\pi_u)$ state was observed in the reaction of boron with SO_2. Cross sections for the production of electronically excited molecules were determined. These cross sections for the reactions with O_2, SO_2, N_2O, NO_2, and H_2O_2 are, respectively, 0.048, 0.0078, 0.01, 0.023, and 0.005 Å^2. In the reactions of boron with SO_2 the branching ratio was obtained for the two observed chemiluminescent reaction channels. The vibrational distributions in the electronically excited state of BO were determined in the reactions where the spectra were adequately resolved. Some implications of the results are discussed.

INTRODUCTION

The chemistry of boron has been an important and fruitful area of research for many years.[1] Most of the past work in this field, however, has been done in the context of inorganic structure studies and organic synthesis. Information about the gas phase chemistry of boron is scarce. Until a few years ago no work had been done in this area. However, there is now a growing activity in this field motivated in part by the increased interest in the fundamental chemistry of nonmetal atoms.[2-9]

The position of boron in the periodic table between metals and nonmetals makes it a good choice for such studies. In common with the alkali metals, the isolated boron atom has a single electron in its outer shell. However, unlike the metal atoms, boron shows a strong tendency toward hybridization and due to its high ionization potential its reactions are not likely to be governed by a long range electron transfer process. Thus, the gas phase chemistry of boron is expected to be characteristic of the more complex nonmetal interactions. Yet the relative simplicity of the boron atom gives one hope for observing meaningful patterns in the experimental results which will perhaps lead to the formulation of a reaction model.

In our laboratory we have developed techniques to study the various aspects of boron atom reactions. We report here studies of chemiluminescence observed in the single collision reactions of boron atoms with O_2, SO_2, N_2O, NO_2, and H_2O_2. From the detected chemiluminescence spectra we calculate the cross sections for the production of electronically excited states of product molecules and the vibrational distributions in those states. This work is a continuation and extension of our earlier experiments with O_2 and N_2O.[3]

The possible reaction pathways and the exoergicities[11] of the reactions are shown in Table I. Light from the $A\,^2\pi$ state of BO is observed in all the reactions. In addition, the reaction of boron with SO_2 produces electronically excited BO_2. In the reaction of B with H_2O_2 the electronically excited OH molecule is observed.

A number of other potentially highly exoergic reactions were studied which did not yield measurable chemiluminescence. These included reactions with CO_2, H_2O, OCS, CS_2, and several alcohols and ethers.

Chemiluminescence from boron atom reactions has also been studied recently by Green and Gole.[5] These authors studied reactions with O_2, N_2O, NO_2, O_3, and ClO_2. Under single collision conditions, chemiluminescence from reaction with O_2, N_2O, O_3, and ClO_2 was due exclusively to emission from the $A\,^2\pi$ state of BO. However, under the same conditions, in their experiments with NO_2, light from both the excited state of BO_2 as

TABLE I. Exoergicities and possible channels for the reactions.

		ΔH (eV)
$B(^2P_u) + O_2(^3\Sigma_g^-)$	$BO(X\,^2\Sigma^+) + O(^3P_2)$	-3.23
	$^*BO(A\,^2\pi) + O(^3P_2)$	-0.31
$B(^2P_u) + SO_2\,(^1A_1)$	$BO(X\,^2\Sigma^+) + SO(X\,^3\Sigma^-)$	-2.70
	$^*BO(A\,^2\pi) + SO(X\,^3\Sigma^-)$	$+0.22$
	$BO_2(X\,^2\pi_g) + S(^3P_2)$	-4.30
	$^*BO_2(A\,^2\pi_u) + S(^3P_2)$	-2.03
$B(^2P_u) + N_2O(X\,^1\Sigma^+)$	$BO(X\,^2\Sigma^+) + N_2(X\,^1\Sigma_g^+)$	-6.63
	$^*BO(A\,^2\pi) + N_2(X\,^1\Sigma_g^+)$	-3.71
	$^*BO(B\,^2\Sigma^+) + N_2(X\,^1\Sigma_g^+)$	-1.31
$B(^2P_u) + NO_2(X\,^2A_1)$	$BO(X\,^2\Sigma^+) + NO(X\,^2\pi)$	-5.20
	$^*BO(A\,^2\pi) + NO(X\,^2\pi)$	-2.28
	$BO_2(X\,^2\pi_g) + N(^4S_{3/2})$	-4.19
	$^*BO_2(A\,^2\pi_g) + N(^4S_{3/2})$	-1.92
$B(^2P_u) + H_2O_2$	$BO(X\,^2\Sigma^+) + H_2O\,(X\,^1A_1)$	-6.95
	$^*BO(A\,^2\pi) + H_2O\,(X\,^1A_1)$	-4.03
	$BO_2(X\,^2\pi_g) + H_2(X\,^1\Sigma_g^+)$	-7.56
	$^*BO_2(A\,^2\pi_u) + H_2(X\,^1\Sigma_g^+)$	-5.29
	$HBO + OH(X\,^2\pi)$	-5.14
	$^*HBO + OH(A\,^2\Sigma^+)$	-0.74
	$BOH + OH(X\,^2\pi)$	-0.22

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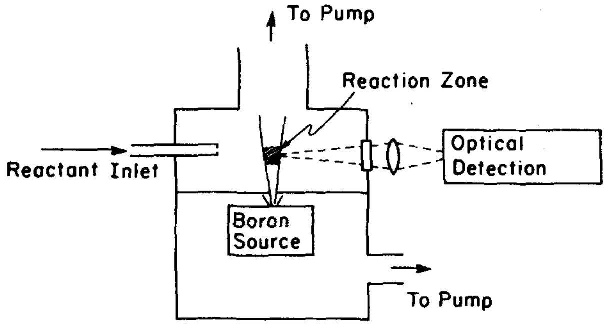

FIG. 1. Schematic diagram of the apparatus.

well as BO was observed. Under single collision conditions, we observe chemiluminescence only from excited BO. It has been suggested that the observation of bimolecular processes producing BO_2 in the experiments of Green and Gole results from a considerably higher boron beam flux in their apparatus.[10]

EXPERIMENT

The experiments were conducted in a beam–gas apparatus shown schematically in Fig. 1. Boron atoms were produced in a graphite-lined tantalum crucible heated to between 2100 and 2400 K by electron bombardment. It has been shown that thermal vaporization of boron produces an essentially monatomic gas phase.[12] The oven was insulated by three concentric tantalum heat shields and the assembly was contained in a separately pumped chamber.

The boron atoms effused from the crucible through a 2 mm hole and entered the second chamber through a 2×10 mm slit opening. The beam passed into the light shielded enclosure through a slit which formed a 2×5 mm rectangular beam. The boron density in the beam was about 1×10^9 atom cm^{-3}. The reaction zone was defined by the area of the boron beam and the vertical extent of the solid angle subtended by the detection system. The volume of this region was 0.128 cm^3. In the case of O_2, N_2O, and SO_2 the reactant gas density was measured with an ionization gauge which was calibrated using a technique described by Loriot and Moran.[13] The densities of NO_2 and H_2O_2 could not be measured with an ion gauge. Here the density was obtained from flow rate measurements which were calibrated using flow–density relationships obtained with O_2. The gas pressure in the reaction zone was in the range 10^{-5} to 10^{-3} Torr. In most cases the experiments were done at the lower end of the pressure range at less than 2×10^{-4} Torr. With differential pumping the pressure in the oven chamber was kept below 1×10^{-5} Torr. Thus, the mean free path of boron atoms was usually greater than 20 cm, which is considerably longer than the distance from the oven to the observation zone (that distance is 3 cm). Consequently, the attenuation of the boron beam was not significant and the measurements were under single collision conditions.

For each species the reactant pressure in the chamber was varied over a range sufficient to determine the region of linearity and single collision conditions. The density of the boron beam was also varied to assure linearity. In addition, various checks were performed to show that the electrons which heat the boron containing crucible did not affect the chemiluminescence measurements.

The optical detection system consisted of a 0.25 m spectrometer and a photomultiplier cooled by a refrigerator unit. The output of the photomultiplier consisted of pulses produced by individual photons. These pulses were counted by an Ortec counter unit and were converted to an analog signal which was recorded.

Optical shielding of the detection system from the boron oven was provided by a tapered tube made black by anodizing. The optical detection system was calibrated with standard light sources using the technique described by Dickson, George, and Zare.[14] The light shielding and the cooling of the photomultiplier allowed the detection of signals as low as 5 photons/s^{-1}.

RESULTS

The chemiluminescence spectra observed in the reaction of boron atoms with O_2, SO_2, N_2O, and NO_2 are shown, respectively, in Figs. 2 to 5. The spectra in Figs. 2, 3, and 5 were taken with an RCA-C31034-2 photomultiplier; the spectrum in Fig. 4 was obtained with an EM1 6256 $S(Q)$ photomultiplier. These spectra

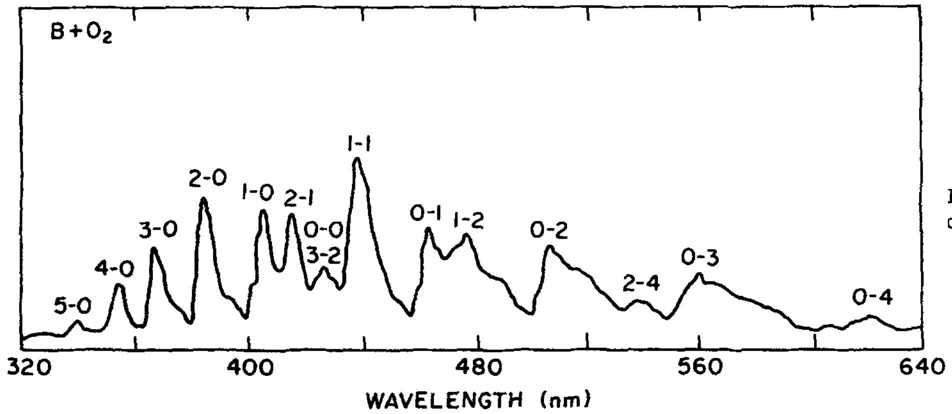

FIG. 2. Chemiluminescence spectrum observed in the $B+O_2$ reaction.

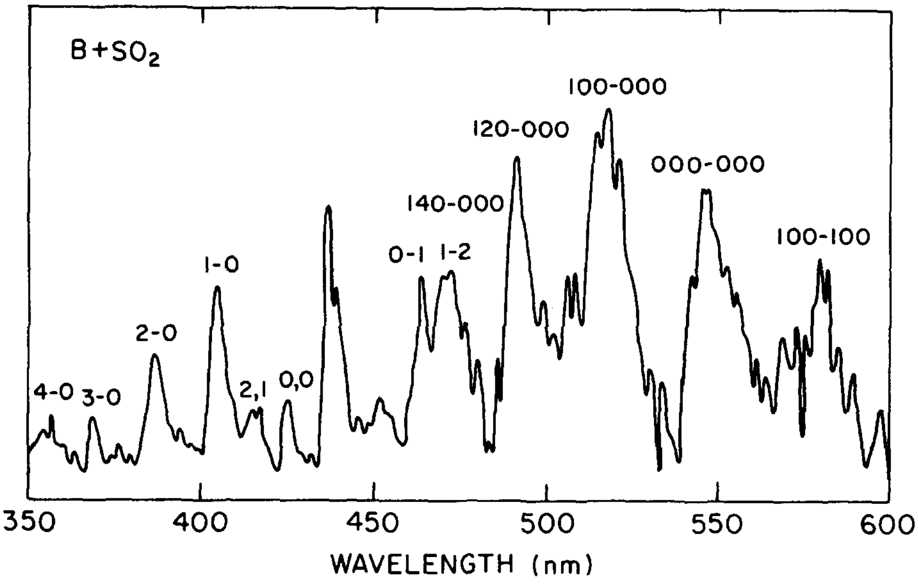

FIG. 3. Chemiluminescence spectrum observed in the $B+SO_2$ reaction.

are not corrected for the spectral response of the detection system but the thermal background produced by the boron oven has been subtracted. Below 400 nm the chemiluminescence spectrum for N_2O is similar to that of NO_2. However, because of the relatively poor signal to noise in that region, the spectrum is not shown.

With all the relevant parameters calibrated the absolute value of the cross section for the production of the excited state can also be calculated. The cross sections (σ^*) for the production of electronically excited states were obtained for all the reactions. These cross sections are shown in Table II, which also shows the total reaction cross sections (σ_T) measured in a separate flow experiment.[8]

Possible errors in the determination of the cross sections σ^* arise from the uncertainties in the photomultiplier calibration (about 50%), oxidant pressure measurements (about 20%), and the boron flux calculation (about 50%). Thus, we estimate that the accuracy of the cross section measurements is about a factor of 2.

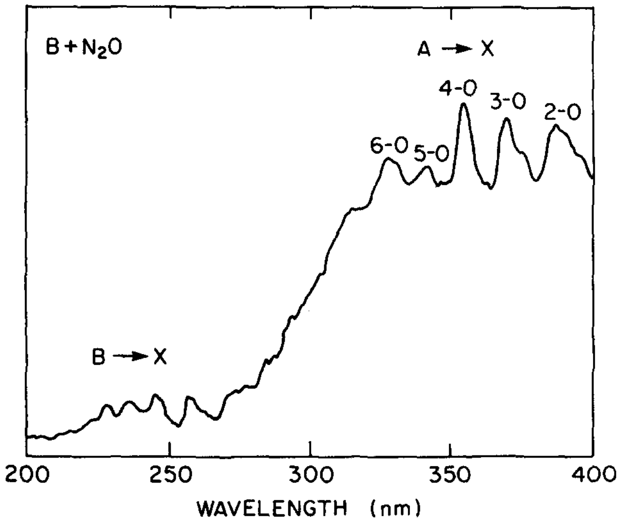

FIG. 4. Chemiluminescence spectrum observed in the $B+N_2O$ reaction.

Since the potential curves and the intensity factors for the BO molecule are well known, the nascent vibrational population distribution in the excited $A\,^2\pi$ state can be determined if the spectra are adequately resolved. The nascent vibrational population distribution and the cross sections for the production of the specific vibrational states are shown for the reactions $B+O_2$ and $B+SO_2$ in Tables III and IV, respectively. The ratio of populations is not identical to the ratio of cross sections. This is due to differences in the transition rates for the various vibrational states. The distribution in Table III is somewhat different from the data shown in our earlier publication.[3] The difference is due to the more accurate calibration of the present optical detection system.

DISCUSSION

$B+O_2$

The results for the reaction $B+O_2$ are essentially the same as observed in our earlier work and also as later reported by Hanner and Gole.[9] The spectrum clearly shows vibrational excitation of the BO $A\,^2\pi$ state up to $v=5$. As is displayed in Table III, the population distribution in the excited state is a decreasing function of vibrational number and can be approximated by a Boltzmann distribution with a vibrational temperature T_{vib} 2360 K. The total cross section for the production of the BO $A\,^2\pi$ state is 0.048 Å^2.

The energy required to reach the $v=5$ state is 3.70 eV. If the exoergicity of the reaction is 3.23 eV as shown in Table I, then the energy deficit to excite this state must be provided by the thermal energy of the reactants. Specifically, as pointed out earlier,[9] much of the kinetic energy of the boron atoms (beam temperature ~2300 K) must be utilized in the reaction channel which produces vibrationally excited BO($A^2\pi$). The near coincidence of the boron beam temperature with the

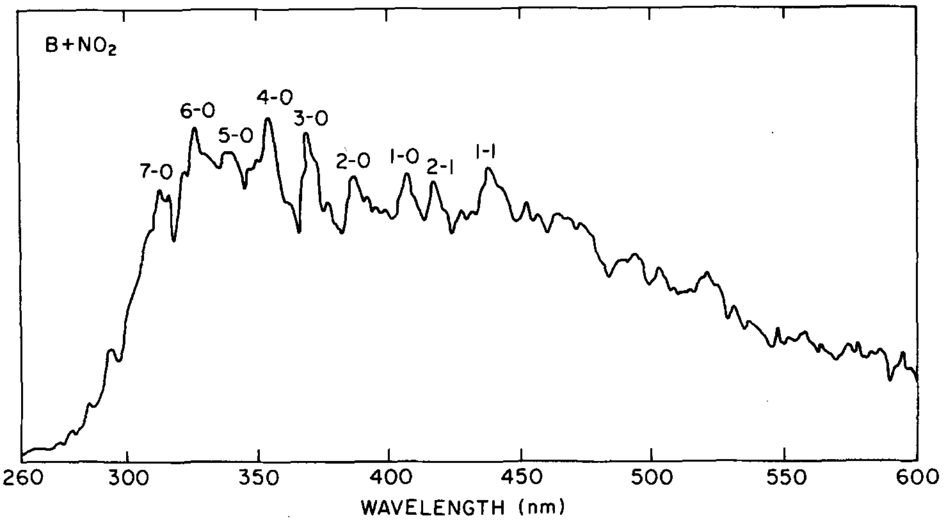

FIG. 5. Chemiluminescence spectrum observed in the $B+NO_2$ reaction.

vibrational temperature of the product BO* suggests that perhaps the translational energy is directly transferred into vibrations. On the other hand, this coincidence may be fortuitous in which case the electronically excited states are most likely produced by the boron atoms in the high velocity tail of the initial distribution.

$B+SO_2$

The chemiluminescence from the single collision reaction of boron with SO_2 clearly shows light from both the $A\,^2\pi$ state of BO and the $A\,^2\pi_u$ state of BO_2 (see Fig. 3). These two states are formed with about equal probability ($\sigma^*_{BO}=0.004$ Å^2, $\sigma^*_{BO_2}=0.0038$ Å^2).

The vibrational distribution in the $A\,^2\pi$ state of BO is shown in Table IV. As with O_2 the distribution is approximately Boltzmann, characterized by a temperature of 2280 K. Here again one must assume that part of the energy required to produce the observed states is provided by the kinetic energy of the boron atoms.

As shown in Table II, the cross section for the production of excited BO is almost exactly a factor of 10 smaller in the SO_2 reaction than in the O_2 reaction. A possible clue to this difference is obtained from energy considerations. We may postulate that the ratio of the chemiluminescence cross sections for the production of electronically excited BO is given by

$$\frac{\sigma^*_{BO}(SO_2)}{\sigma^*(O_2)} = \exp - (\Delta E/kT) ,$$

where ΔE is the difference in the exoergicity of the two reactions. This calculation yields a ratio of 0.07 which is close to our measurements.

TABLE II. Chemiluminescence and total reaction cross sections.

	Total reaction cross section σ_T (Å^2)		Chemiluminescent cross section σ^* (Å^2)
$B+O_2$	5.2	$BO(A\,^2\pi)+O(^3P_2)$	0.048
$B+SO_2$	13	$BO(A\,^2\pi)+SO(X\,^3\Sigma^-)$ $BO_2(A\,^2\pi)+S(^3P_2)$	0.004 0.0038
$B+N_2O$	0.0024	$BO(A\,^2\pi)+N_2(X\,^1\Sigma_g^+)$ $(B\,^2\Sigma^+)$	0.01 (~0.001)
$B+NO_2$		$BO(A\,^2\pi)+NO(X\,^2\pi)$	0.23
$B+H_2O_2$	5.74	$BO(A\,^2\pi)+H_2O(X\,^1A_1)$ $HBO+OH(A\,^2\Sigma^+)$	0.004 0.0008(?)

TABLE III. Vibrational distribution in the $A\,^2\pi$ state of BO ($N_{v'}$) and the production cross section ($\sigma^*_{v'}$) for the $B+O_2$ reaction.

$v'=$	0	1	2	3	4	5
$N_{v'}$	1	0.59	0.23	0.13	0.07	0.03
$\sigma^*_{v'}$ (Å^2)	0.021	0.013	0.0064	0.0040	0.0022	0.0007

TABLE IV. Vibrational distribution in the $A\,^2\pi$ state of BO ($N_{v'}$) and the production cross section $\sigma^*_{v'}$ for the B+SO_2 reaction.

v' =	0	1	2	3	4
$N_{v'}$	1	0.5	0.19	0.1	0.005
$\sigma^*_{v'}$ (Å^2)	0.0019	0.0011	0.0005	0.0003	0.0002

B+N_2O

The light emitted in the reaction of boron atoms with N_2O is in the spectral region between 2000 and 6000 Å. The main part of the spectrum is due to emission from the $A\,^2\pi$ state. The chemiluminescence below 270 nm may be due to radiation from the $B\,^2\Sigma$ state or, as suggested by Hanner and Gole,[9] its source may be higher vibrational levels of the $A\,^2\pi$ state.

The chemiluminescence cross section for this reaction is about 0.01 Å^2. The vibrational distribution in the $A\,^2\pi$ is not as clearly resolved here as it is in the reactions with O_2. This is probably due to the greater exoergicity of this reaction which leads to a higher vibrational and rotational excitation of the product BO molecule and consequently also to a more complex chemiluminescence spectrum. It was the lower resolution of the spectrum that prevented us from observing this chemiluminescence in our earlier less sensitive experiments.

The spectrum is not adequately resolved for the determination of excited state vibrational distributions. It is however evident from the spectrum in Fig. 4 that the chemiluminescence from the $A^2\pi$, $v=4$ state is greater than the emission from the neighboring states. This feature is more pronounced in the spectra observed by Hanner and Gole,[9] who attributed this to collisional V–E transfer from the vibrationally excited ground state BO, i.e., $\mathrm{BO}(X^2\Sigma^+, v''=17)+\mathrm{X} \rightarrow \mathrm{BO}(A^2\pi_{1/2}, v'=4)+\mathrm{X}$.

As shown in Table II, the chemiluminescence cross section (0.01 Å^2) is greater than the total reaction cross section by a factor of 4. A possible explanation for this discrepancy is the difference in the temperature at which these two measurements were obtained. The chemiluminescence cross sections were obtained at a boron beam temperature of 2400 K whereas the total rate coefficients were measured at room temperature. This explanation implies that the reaction of boron with N_2O is hindered by an activation energy with an upper limit of about 0.045 eV.

B+NO_2

The chemiluminescence spectrum for the B+NO_2 reaction is similar to the one obtained with N_2O except that it is shifted in energy in accord with the lower exoergicity of this reaction. However, the cross section for the production of electronically excited states is larger by about a factor of 20.

In contrast to the reactions of boron with SO_2, here chemiluminescence from electronically excited BO_2 is not observed under single collision conditions. However, chemiluminescence from the $A\,^2\pi$ state of BO_2 is observed at higher densities of NO_2 where multiple collision reactions are expected. The onset of BO_2 chemiluminescence in our system occurs at about 3×10^{-3} Torr. In this pressure range, Crumley and Gole[10] also observe BO_2 produced in large part by secondary collisions, finding that secondary processes contribute to BO_2 chemiluminescence at pressures in excess of 4×10^{-4} Torr. As the NO_2 density is raised, the BO_2 chemiluminescence increases while the BO chemiluminescence decreases, probably due to the attenuation of the boron beam. This is shown in Fig. 6, which compares the spectra observed under single and multiple collision conditions. Rate calculations show that the observed chemiluminescence from BO_2^* is consistent with the two step process (1) $\mathrm{B}+\mathrm{NO_2}\rightarrow\mathrm{BO}+\mathrm{NO}$; (2) $\mathrm{BO}+\mathrm{NO_2}\rightarrow\mathrm{BO_2^*}+\mathrm{NO}$. We estimate from our measurements that the cross section for the reaction $\mathrm{BO}+\mathrm{NO_2}\rightarrow\mathrm{BO_2^*}+\mathrm{NO}$ is equal to or less than 0.8 Å^2.

Naturally, it is of interest to consider why BO_2 is much more readily produced in the reaction with SO_2 than that with NO_2. In a previous publication DiGiuseppe

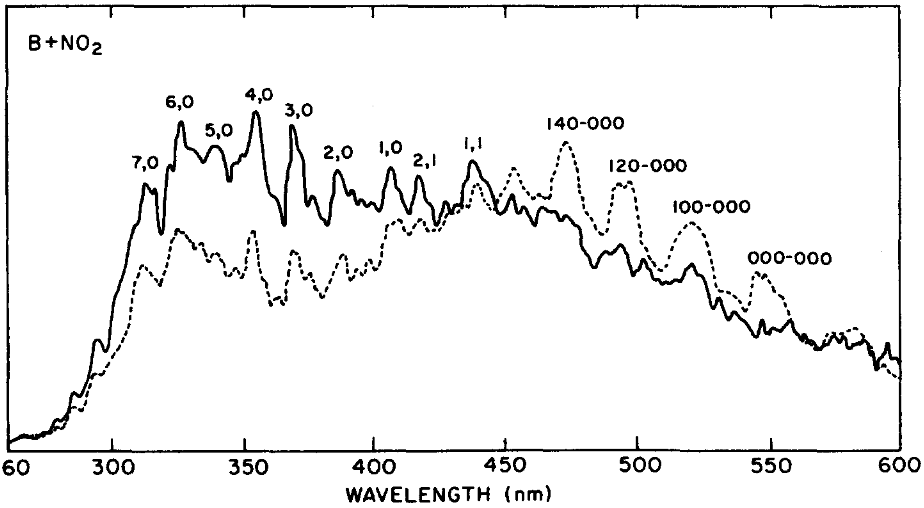

FIG. 6. Chemiluminescence spectrum observed in the B+NO_2 reaction under low reactant pressure (—) and high reactant pressure (- - - -) conditions.

and Davidovits[8] examined the possibility that the electron affinity of the molecule may be the main factor which determines its reactivity with boron. They suggested that reactions with molecules having large negative electron affinities would be blocked while the reactions of molecules with large positive electron affinities would proceed readily. The reactivities of molecules with small electron affinities (positive or negative) may fall into either category depending on the interactions within the collision complex. This approach may provide a clue here as well. Consider the collision complex consisting of boron and SO_2 or NO_2. If we assume that within this complex BO is formed first, the formation of BO_2 is then perhaps governed by the electron affinity of the other component (i.e., SO is the reaction with SO_2 and NO in the reaction with NO_2). Our experimental results are consistent with this suggestion. The electron affinity of SO is quoted[11(d)] to be greater than 1.1 eV. Thus, one would anticipate the formation of BO_2 in the reaction of boron with SO_2. On the other hand, the electron affinity of NO is close to zero[15] and therefore in the reaction with NO_2 the BO_2 channel is blocked. Certainly, more data is required to build our confidence in this picture.

$B + H_2O_2$

The signal to noise ratio in the $B + H_2O_2$ experiments is somewhat poor. Still, the production of electronically excited BO is clearly evident. Vibrational bands up to $v = 5$ are resolved. The formation of BO implies a rearrangement in which a hydrogen atom migrates from one oxygen to the other.

About 15% of the measured chemiluminescence emanates from the electronically excited $A\,^2\Sigma^+$ state of OH. Our tests indicate that the excited OH is produced by the primary reaction $B + H_2O_2$. However, the signal here is too small to establish this with complete certainty.

ACKNOWLEDGMENTS

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[11] The dissociation energies for some of the molecules involved in the boron atom reactions are not well known. The data from various sources are not always in agreement with each other. The dissociation energies for the calculations in Table I were obtained from the following sources: (a) dissociation energy for BO (8.31 eV) from 0. Manuel Uy and J. Drowort, High Temp. Sci. **2**, 293 (1970); (b) dissociation energies for OH, O_2, SO, and H_2 from G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N. J., 1950); (c) dissociation energies for N_2O, CO_2, H_2O, and SO_2 from G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1966); (d) dissociation energies for NO, H_2O_2, HBO, BOH, and BO_2 from V. I. Vedeneyev, L. v. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, *Bond Energies, Ionization Potentials, and Electronic Affinities* (Arnold, London, 1966).

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