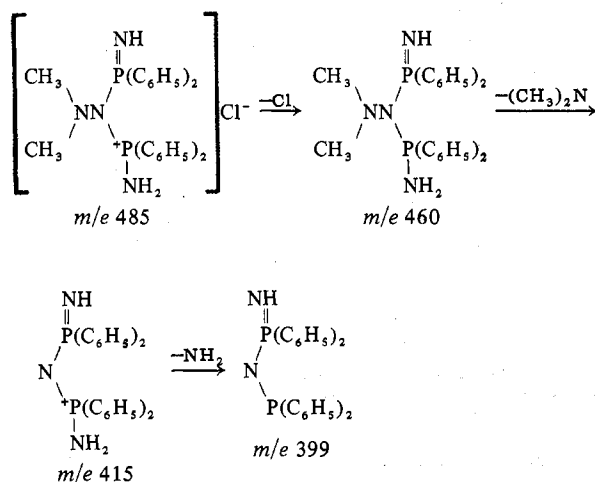


Scheme I



**Acknowledgment.** The authors wish to express their appreciation to Professor Charles Moreland for his assistance in obtaining some of the <sup>31</sup>P nmr data included in this paper.

**Supplementary Material Available.** The infrared data, Table II, and the mass spectral data, Table III, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N. W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-333.

**Registry No.** CH<sub>3</sub>CH<sub>2</sub>N[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, 2960-41-0; CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>N[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, 42998-67-4; CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>N[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, 42946-01-0; CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>N[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, 42998-68-5; C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)N[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, 42998-69-6; (+)-C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)N[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, 42998-70-9; CH<sub>3</sub>CH<sub>2</sub>-NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NPCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>, 42998-71-0; CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-NPCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>, 42998-72-1; CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NPCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-NH<sub>2</sub>, 42998-73-2; CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NPCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>, 42998-74-3; C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NPCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>, 42998-75-4; (+)-C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NPCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>, 42998-76-5; (CH<sub>3</sub>)<sub>2</sub>NNHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NPCl(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>, 42998-77-6; [CH<sub>3</sub>CH<sub>2</sub>NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>]Cl, 42998-78-7; [CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>]Cl, 42998-79-8; [CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>]Cl, 42998-80-1; [CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>]Cl, 42998-81-2; [C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>]Cl, 42998-82-3; (+)-[C<sub>6</sub>H<sub>5</sub>CH(CH<sub>3</sub>)NHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>]Cl, 42998-83-4; [(CH<sub>3</sub>)<sub>2</sub>NNHP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>]Cl, 42998-84-5.

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## Reaction of Oxygen Atoms with Diborane

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The reaction of oxygen atoms with diborane has been studied in a discharge-flow reactor using a time-of-flight mass spectrometer as a detector. When a large excess of atoms is present, the rate constant for the disappearance of diborane is  $k_2 = (4.21 \pm 2.7) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  at room temperature, with an activation energy of  $4.8 \pm 0.5 \text{ kcal mol}^{-1}$ . Under conditions of excess B<sub>2</sub>H<sub>6</sub> the reaction is considerably faster and is chemiluminescent with emission due primarily to the transition  $\text{BO}(A^2\pi) \rightarrow X(^2\Sigma, v' \leq 5)$ . The species H<sub>2</sub>O, BH<sub>2</sub>O<sub>2</sub>, and possibly BH<sub>2</sub>O are observed as products or intermediates, and the presence of OH is inferred. The B<sub>2</sub>H<sub>6</sub>-in-excess data are interpreted in terms of a chain reaction initiated by  $\text{O} + \text{B}_2\text{H}_6 \rightarrow \text{BH}_3\text{O} + \text{BH}_3$  and propagated by  $\text{BH}_3 + \text{O} \rightarrow \text{OH} + \text{BH}_2$ ;  $\text{OH} + \text{B}_2\text{H}_6 \rightarrow \text{H}_2\text{O} + \text{BH}_3 + \text{BH}_2$ . When O atoms are in excess, B<sub>2</sub>H<sub>6</sub> disappearance is controlled by the first reaction above, while O atoms are catalytically removed in the sequence  $\text{O} + \text{B}_2\text{H}_6 \rightarrow \text{BH}_3 + \text{BH}_3\text{O}$ ;  $\text{BH}_3\text{O} + \text{O} \rightarrow \text{BH}_3 + \text{O}_2$ ;  $2\text{BH}_3 \rightarrow \text{B}_2\text{H}_6$ .

### Introduction

There are several recent reviews of the chemistry of boron compounds,<sup>1-3</sup> but, perhaps surprisingly in view of the early interest in boron compounds as high-efficiency fuels, the oxidation of boron hydrides is not extensively discussed therein. Some early work by Bauer and coworkers<sup>4,5</sup> concerned borane-oxygen mixtures at the explosion limits; the behavior of such mixtures exhibited strong qualitative similarities to H<sub>2</sub>-O<sub>2</sub> mixtures. A mechanism for B<sub>2</sub>H<sub>6</sub>-O<sub>2</sub> explosions was proposed in which the chain-branching steps



(1) T. Wartik, Ed., *Advan. Chem. Ser.*, No. 32 (1961).

(2) R. T. Holtzmann, Ed., "Production of Boranes and Related Research," Academic Press, New York, N. Y., 1967.

(3) E. L. Muettterties, "The Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967.

(4) W. Roth and W. H. Bauer, "Fifth Symposium on Combustion," Reinhold, New York, N. Y., 1955, p 710.

(5) W. H. Bauer and S. E. Wiberly, *Advan. Chem. Ser.*, No. 32, 115 (1961).

are identical with those in the H<sub>2</sub>-O<sub>2</sub> reaction<sup>6</sup> if the correspondence  $\text{BH}_3 \leftrightarrow \text{H}$  be made. Although the mechanism accounts for the main features of the explosion limit behavior, no direct observation of the intermediates was reported.

The oxygen-containing compounds H<sub>2</sub>B<sub>2</sub>O<sub>3</sub> and H<sub>3</sub>B<sub>3</sub>O<sub>3</sub> have been observed in the slow oxidation of B<sub>5</sub>H<sub>9</sub>,<sup>7-9</sup> but these species, although unstable, are not sufficiently reactive to account for the explosive nature of pentaborane-oxygen mixtures. A study of the photooxidation of diborane,<sup>10</sup> initiated by flash photolysis of B<sub>2</sub>H<sub>6</sub>-O<sub>2</sub> mixtures, resulted in the conclusion that reaction 2 above is not an important step. Other significant results of this flash photolysis experiment were the spectroscopic observation

(6) B. Lewis and G. von Elbe, "Combustion, Flames, and Explosions of Gases," 2nd ed, Academic Press, New York, N. Y., 1961.

(7) E. A. Grimm and R. F. Porter, *Inorg. Chem.*, 8, 731 (1969).

(8) W. V. Brooks, C. C. Costain, and R. F. Porter, *J. Chem. Phys.*, 47, 4186 (1967).

(9) G. H. Lee, W. H. Bauer, and S. E. Wiberly, *J. Phys. Chem.*, 67, 1742 (1963).

(10) M. D. Carabine and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, 296 1 (1967).

of the reactive intermediates OH and BO<sub>2</sub>, with BO and BH appearing as well at higher temperatures.

The reaction of oxygen atoms with diborane, which for the moment we prefer to write in the less specific form



seems *a priori* quite likely to play an important role in the oxidation of diborane, whether thermal or photochemical; yet the published evidence is sparse. We have therefore undertaken a separate study of reaction 2a, under conditions which do not produce an explosion.

### Experimental Section

The apparatus used in the present study was a discharge-flow reactor; since it has been previously described<sup>11,12</sup> only a brief outline will be given here. Oxygen atoms are generated by passage of dilute (*ca.* 10% in He) molecular oxygen through a microwave discharge and then flow into a cylindrical reactor where they are mixed with diborane, usually diluted with helium. The point of mixing defines the start of the reaction, which proceeds as the mixture flows downstream. The reacting mixture is sampled by a mass spectrometer at a known distance (hence a known elapsed time) downstream from the mixing point. Thus the primary data are time-resolved mass spectra of the reacting mixture. Reactor pressure, temperature, flow rate, and mole fractions of reactants and diluent are all known and controlled. In some experiments O atoms were produced by the nitric oxide titration of active nitrogen:  $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ ; in these runs the diluent was N<sub>2</sub> rather than He.

Matheson N<sub>2</sub> (99.997%), O<sub>2</sub> (99.99%), and He (99.995%) were used without further purification. Nitric oxide (Matheson) was purified by passage through 50% aqueous KOH and anhydrous P<sub>2</sub>O<sub>5</sub> and then distilled.

Nitrogen dioxide (Matheson), used to titrate O atoms,<sup>13</sup> was mixed with O<sub>2</sub> to consume any possible NO impurity and then passed through P<sub>2</sub>O<sub>5</sub> and distilled. Diborane was extracted from an old and unidentifiable lecture bottle, condensed at -196°, pumped on to remove H<sub>2</sub>, and then passed several times through a trap at -128°. This procedure yielded diborane of at least 98% purity; the only impurities detectable by mass spectral analysis were tetraborane and pentaborane. For the runs in which the primary goal was the detection and identification of reactive intermediates, the helium carrier gas was further purified by passage through titanium sponge at 600°.

Rate measurements were performed under pseudo-first-order conditions, with at least a 10-fold excess of oxygen atoms over diborane. The peak height at *m/e* 27 was measured first with the discharge on and then with the discharge off, at about 10 randomly chosen reactor residence times. The pseudo-first-order rate constant was obtained from the slope of a plot of the logarithm of the  $[\text{B}_2\text{H}_6]_t/[\text{B}_2\text{H}_6]_0$  ratio (discharge on/discharge off) *vs.* time and converted in the usual way to a bimolecular rate constant by dividing by the concentration of O atoms.

For some experiments, also run under pseudo-first-order conditions but with diborane in excess, a different technique was used. The input flow of O atoms was held constant and the concentration of O atoms at the pinhole was measured by monitoring the *m/e* 16 peak height, as the input flow of diborane was varied. The ionizing voltage in the mass spectrometer was kept low enough to eliminate any contribution to *m/e* 16 peak height from molecular oxygen fragmentation. The slope of a plot of the logarithm of O atom concentration *vs.* diborane concentration, divided by the reactor residence time, yields the bimolecular rate constant.<sup>11</sup>

### Results and Discussion

The results of the experiments with O atoms in large excess over diborane are collected in Table I. Except as noted, the carrier gas was helium, and O atoms were produced from molecular oxygen. There is no systematic variation of the rate constant with total pressure, and this

**Table I.** Room-Temperature Rate Constants for the Reaction of O Atoms with B<sub>2</sub>H<sub>6</sub>

Reactor pressure, Torr	10 <sup>15</sup> <i>k</i> , cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>	Reactor pressure, Torr	10 <sup>15</sup> <i>k</i> , cm <sup>3</sup> molecule <sup>-1</sup> sec <sup>-1</sup>
1.0	4.56 ± 1.32 <sup>a</sup>	1.5	4.44 ± 0.35
1.0	4.64 ± 1.06	1.5	5.80 ± 0.87 <sup>b</sup>
1.0	2.27 ± 0.66	2.0	6.65 ± 1.18
1.0	6.71 ± 1.19	3.0	3.91 ± 0.32
1.5	3.54 ± 0.61	3.0	2.67 ± 0.51
1.5	4.20 ± 0.17	5.0	3.81 ± 0.35
1.5	3.54 ± 0.66	5.2	3.62 ± 0.31
1.5	3.12 ± 0.39	7.0	3.05 ± 0.27
1.5	4.75 ± 0.38	7.0	3.99 ± 0.62
1.5	3.99 ± 0.38		

<sup>a</sup> Quoted errors are standard deviations derived from linear regression analysis of the data. <sup>b</sup> N<sub>2</sub> carrier; O atoms produced by nitric oxide titration.

in turn suggests that the reaction mechanism, at least in its early stages, is not exceedingly complex.

When O atoms are produced *via* an electrical discharge in molecular oxygen, there is always the possibility that the reactive species is O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) rather than O(<sup>3</sup>P), since these species are produced in comparable concentrations.<sup>14</sup> However, when the reaction O + B<sub>2</sub>H<sub>6</sub> is run in the absence of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) (nitrogen carrier, see Table I), there is no significant change in the value of the rate constant. From this one may conclude that O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) does not react to any significant extent with diborane. This may be compared with the results of Herron and Huie, who found that O(<sup>3</sup>P) reacts at least 1000 times faster than O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) with a variety of olefinic, aromatic, and heterocyclic compounds.<sup>14</sup>

A series of runs was made at elevated temperatures, under conditions such that the total density was approximately constant at about 3.5 × 10<sup>16</sup> molecules/cm<sup>3</sup> (corresponding to 1.1 Torr at room temperature). These results are given in Table II and shown graphically in Figure 1. The activation energy, as determined from these measurements, is 4.8 ± 0.5 kcal/mol.

The numerical values of the rate constants in Table I are correct as given and need not be multiplied by a stoichiometric factor. If the measurement of B<sub>2</sub>H<sub>6</sub> disappearance is made under pseudo-first-order conditions with a large excess of O atoms and the initial slow step (eq 2a) is followed by a sequence of fast reactions consuming *n* more B<sub>2</sub>H<sub>6</sub> molecules, the usual definition of rate constant leads to the relationship  $k_{\text{obsd}} = (n + 1)k_{\text{true}}$ . The quantity (*n* + 1) is the stoichiometric factor, *i.e.*, the number of B<sub>2</sub>H<sub>6</sub> molecules consumed per O atom consumed. If, on the other hand, a sequence of faster reactions subsequently consumes more O atoms, the measurement of B<sub>2</sub>H<sub>6</sub> disappearance is unaffected and the observed rate constant is equal to the true rate constant. The latter case obtains in the O + B<sub>2</sub>H<sub>6</sub> system (*vide infra*); hence the values in Table I are correct.

The straightforward way of determining the stoichiometric factor is to measure the consumption of each reactant; an accurate determination requires that the initial concentrations of both reactants be comparable, *i.e.*, under second-order rather than pseudo-first-order conditions. Alternatively, if a pseudo-first-order rate constant can be measured under conditions of large excess of the *other* reactant, then the stoichiometric factor is given by the ratio  $k_{\text{obsd}}(\text{O in excess})/k_{\text{obsd}}(\text{B}_2\text{H}_6 \text{ in excess})$ .<sup>11</sup> Implicit in both these methods is

(11) C. W. Hand and R. H. Obenauf, Jr., *J. Phys. Chem.*, **76**, 269 (1972).

(12) C. W. Hand and R. H. Obenauf, Jr., *J. Phys. Chem.*, **76**, 2643 (1972).

(13) F. Kaufman, *Progr. React. Kinet.*, **1**, 1 (1961).

(14) J. T. Herron and R. E. Huie, *Environ. Sci. Technol.*, **4**, 685 (1970).

Table II. Temperature Dependence of the Rate Constant for  $O + B_2H_6$

$T, ^\circ K^a$	$10^{15}k, \text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$	$T, ^\circ K^a$	$10^{15}k, \text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$
300	$4.21 \pm 2.7^b$	400	$32.0 \pm 3.5$
350	$10.3 \pm 2.9$	439	$45.1 \pm 4.8$
374	$20.9 \pm 1.9$	506	$147 \pm 38$

<sup>a</sup> Temperature constant to  $\pm 5\%$  throughout the length of the reactor. <sup>b</sup> Average of room-temperature runs.

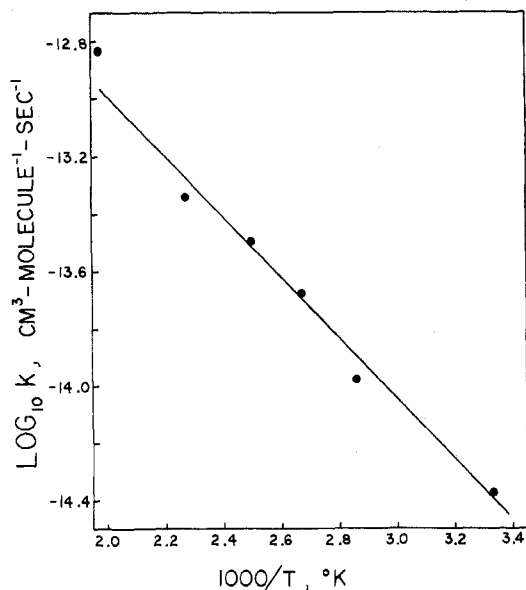


Figure 1. Variation of rate constant with temperature.

the assumption that reaction 2a is rate determining at all values of the ratio  $[B_2H_6]/[O]$ .

Both methods were attempted, with less than satisfactory results. In the direct-method reaction, conditions were set up so that the fractional consumption of O atoms was roughly equal to that of  $B_2H_6$  (thus ensuring second-order conditions) and the flow rate and fractional consumption of each reactant were measured. Three such determinations yielded values of 9, 10, and 12 for the number of O atoms consumed per diborane molecule.

Three determinations of the rate constant were made with diborane in excess and yielded values of  $1.4, 1.6,$  and  $1.7 \times 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$ ; this is more than 200 times the rate constant measured with atoms in excess and formally indicates that 200 O atoms are consumed per diborane molecule. If reaction 2a is rate determining no matter which species is present in excess, these two results should not differ by such a large factor.

Several conclusions may be drawn from these results; first, the consumption of atoms is greater than that of  $B_2H_6$ ; hence the rate constants in Table I are unambiguously defined. Second, with a large excess of atoms reaction 2a is the primary pathway for the disappearance of diborane, *i.e.*, is rate determining. In reaching this conclusion we use the fact that the reaction, under conditions of excess atoms, is pressure independent and is therefore a simple bimolecular step. Third, when diborane is present in excess, reactions other than eq 2a must account for the majority of oxygen atom consumption.

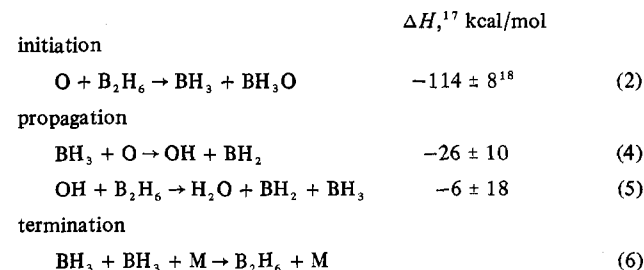
No chemiluminescence was observed when the reaction was run with atoms in excess; however, when the  $[B_2H_6]/[O]$  ratio was about 10, a soft blue glow was noted, which

increased in brightness as the  $[B_2H_6]/[O]$  ratio increased. When the ratio was increased to about 200, the chemiluminescence was sufficiently intense for spectroscopic measurement. A Heath EU-700-51 monochromator with a 1P28 photomultiplier tube was used to scan the emission spectrum over the range 290–710 nm. Sixteen emission bands were observed, of which fifteen were at wavelengths corresponding to the BO  $\alpha$  system,  $A(^2\pi) \rightarrow X(^2\Sigma)$ .<sup>15</sup> This emission has been previously observed in a similar system.<sup>16</sup> Emission was observed from levels up to  $v' = 5$  of the  $A(^2\pi)$  state, corresponding to an energy of 84.5 kcal above the ground state of BO. We cannot exclude the possibility that some excitation to the  $B(^2\Sigma)$  state is occurring as well, since much of this emission would be blocked by the Pyrex wall of our reactor.

The products of the reaction, as determined by mass spectral scans of the reacting mixture, appear at  $m/e$  ratios corresponding to the ions  $H_2O^+$ ,  $BH_2O^+$  ( $m/e$  28, 29), and  $BH_2O_2^+$  ( $m/e$  44, 45). We cannot say with certainty that the neutral species  $BH_2O$  is an intermediate in the reaction, for the ion  $BH_2O^+$  could well be due to mass spectral fragmentation from  $BH_2O_2$ . We can be more confident with respect to the observed ion  $BH_2O_2^+$ , however, and assign it as the molecular ion of the intermediate  $BH_2O_2$ . The only likely mass spectral parent for a  $BH_2O_2^+$  fragment would be boric acid,  $BH_3O_3$ . There was no trace of the  $BH_3O_3^+$  ion in the mass spectrum, even at the low (17.5 eV) ionizing voltages used. In the conventional (CEC 21-104) mass spectrum of boric acid, the  $BH_3O_3^+$  and  $BH_2O_2^+$  ions have comparable intensities at 17.5 eV.

The mechanism which governs the reaction of oxygen atoms with diborane must account for the following observations: (i) with O atoms in excess, reaction 2a is rate determining and the rate of consumption of O atoms considerably exceeds that of  $B_2H_6$ ; (ii) the reaction rate increases by some 200-fold when diborane is present in large excess; (iii) BO must be produced in a moderately energetic step, since emission is observed from  $BO(A(^2\pi), v' = 5)$ ; (iv) products and/or intermediates include  $H_2O$ ,  $BH_2O_2$ , and (possibly)  $BH_2O$ .

The great increase in the rate constant, when measured with  $B_2H_6$  in excess, is highly suggestive of a chain mechanism in which O atoms and  $B_2H_6$  are rapidly consumed. Such a mechanism is

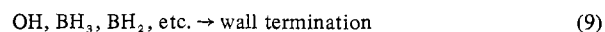


(15) R. W. B. Pearse and A. G. Gaydon, "The Identification of Molecular Spectra," Wiley, New York, N. Y., 1950.

(16) A. Fontijn and P. H. Vree, *J. Phys. Chem.*, **70**, 3377 (1966). These authors noted the chemiluminescence but did not discuss kinetics or mechanism.

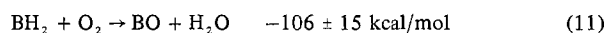
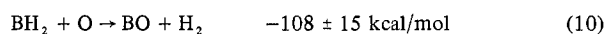
(17) Heats of reaction are calculated from heats of formation data given in *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 37 (1971).

(18) The JANAF tables of ref 17 do not list a heat of formation for  $BH_3O$ ; the approximate value of  $-70 \text{kcal/mol}$  given by R. F. Porter and S. Gupta, *J. Phys. Chem.*, **68**, 2732 (1964), was used to calculate the heat of reaction 2. The error limit is probably optimistic, but the important point is that reaction 2 is exothermic by a considerable amount.

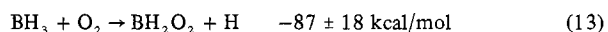
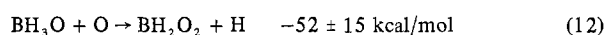


Although we were unable to obtain mass spectral confirmation of the presence of OH as an intermediate, the results of Carabine and Norrish<sup>10</sup> demonstrate its presence in the flash photolysis of O<sub>2</sub> + B<sub>2</sub>H<sub>6</sub> mixtures; it is unlikely that OH is absent from the reaction under the conditions of the present study.

The observed chemiluminescence requires that BO be produced with some 85-kcal excitation above the ground state. Reactions 10 and 11 fulfill this condition.



The observed species BH<sub>2</sub>O<sub>2</sub> could arise from either or both of the metatheses



while the possible intermediate BOH<sub>2</sub> could be the result of several reactions



etc., among which there is at present very little basis for preference.

When the reaction takes place with little B<sub>2</sub>H<sub>6</sub> present,

it is much slower, which is nonetheless consistent with the chain mechanism given above. Unless a reasonable amount of B<sub>2</sub>H<sub>6</sub> is present, the propagation steps, specifically reaction 5, cannot compete with the termination steps 6-9. The reaction can then be described more simply by reaction 2, followed by numerous steps involving various [B, H, O] species consuming O atoms and each other, but consuming little, if any, diborane. Under these conditions our measured rate constant, which describes the disappearance of B<sub>2</sub>H<sub>6</sub>, is the true bimolecular rate constant for reaction 2.

The only additional observation which must be accounted for is the greater consumption of O atoms relative to B<sub>2</sub>H<sub>6</sub>, under conditions of excess atoms. The fact that this consumption ratio is large (*ca.* 10) and not very reproducible (*vide supra*) is indicative of another chain mechanism which consumes O atoms but not B<sub>2</sub>H<sub>6</sub>, *i.e.*, a B<sub>2</sub>H<sub>6</sub>-catalyzed disappearance of O atoms. A possible reaction sequence is



for which the overall reaction is simply



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## Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine-Mercury(II) Halide Complexes<sup>1a</sup>

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Phosphorus-31 nmr results are presented for compounds of the types L<sub>2</sub>HgX<sub>2</sub> and L<sub>2</sub>Hg<sub>2</sub>X<sub>4</sub>, where L is tributylphosphine, dibutylphenylphosphine, butyldiphenylphosphine, and in several cases diethylphenylphosphine; and X is chloride, bromide, and iodide. Phosphorus-31-mercury-199 coupling constants are reported. They generally increase with the electronegativity of the halogen attached to mercury and in the order of the basicity of the phosphine, *i.e.*, (n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>P > (n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>-(C<sub>6</sub>H<sub>5</sub>)P > (n-C<sub>4</sub>H<sub>9</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P. For a particular phosphine, J<sub>P-Hg</sub> is considerably larger in the halogen-bridged dimer L<sub>2</sub>-Hg<sub>2</sub>X<sub>4</sub> than in the corresponding monomeric compound L<sub>2</sub>HgX<sub>2</sub>. J<sub>P-Hg</sub> is also generally larger as the downfield coordination chemical shift increases.

### Introduction

Phosphorus-31 nuclear magnetic resonance spectroscopy has been used extensively in recent years for the study of coordination compounds.<sup>2,3</sup> Lewis acids which have a spin = 1/2 isotope of reasonable abundance (*e.g.*, <sup>199</sup>Pt, <sup>183</sup>W, <sup>103</sup>Rh, <sup>111</sup>Cd, <sup>113</sup>Cd, etc.) are often most interesting because of the possibility of phosphorus-metal spin-spin coupling which is

generally observable for relatively inert complexes.<sup>4-7</sup> We report here a study of tertiary phosphine complexes of mercury(II) halides. Complexes of this type were definitively studied many years ago by Evans, Mann, Peiser, and Purdie,<sup>8</sup> followed by additional synthetic and physical studies.<sup>9,10</sup>

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