

maintain the asymmetric conformation. The present data do not differentiate these possibilities.<sup>10</sup>

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### Direct Detection of the Borane Molecule and the Boryl Radical by Mass Spectrometry

Sir:

The  $BH_3$  molecule has been postulated as an intermediate in many of the pyrolysis and exchange reactions of the boron hydrides<sup>1</sup> while the  $BH_2$  radical has been postulated as an intermediate in some radiolysis reactions.<sup>2</sup> However, no direct experimental evidence of the existence of these species has been offered to date. The following is a report on their mass spectrometric detection in the pyrolysis of diborane.

The mass spectrometric method provides an elegant way to detect unstable species.<sup>3-7</sup> Basically, detection of radicals by this method involves the use of low energy electrons so that the observed current of the radical positive ion arises almost entirely from the ionization of the corresponding radical, and the contribution by dissociative ionization of molecules is small. The principles of the method are detailed in the references given.

Experimentally, samples must be removed from the reacting gas in a manner such that the unstable species are not destroyed by reactions or wall collisions. With this in mind, a special mass spectrometer having a 7-cm. radius of curvature and utilizing a quadrupole lens, wide slits, and electron-multiplier detection for maximum sensitivity was constructed. The ionizing region is open on four sides to minimize wall collisions and a small tubular quartz furnace is positioned with its exit about 5 mm. from the electron beam. The reactant diborane flows through the furnace with a contact time of about 2 msec., and the crude molecular beam issuing from the furnace is analyzed about 25  $\mu$ sec. later. Differential pumping is employed, and during a run with a pressure of about  $5 \times 10^{-4}$  torr in the furnace, the background pressure in the ionizing region is  $5 \times 10^{-7}$  torr, while in the analyzer tube and electron-multiplier sections it is  $3 \times 10^{-8}$  torr.

With diborane flowing through the reactor, the spectrometer was focused on the  $m/e = 14$ ,  $BH_3^+$ , ion peak at a low ionizing voltage. Recording the ion current as a function of the furnace temperature produced a record similar to that shown in Fig. 1a. The presence of  $BH_3$  is clearly indicated.<sup>8</sup> Examination of the  $m/e =$

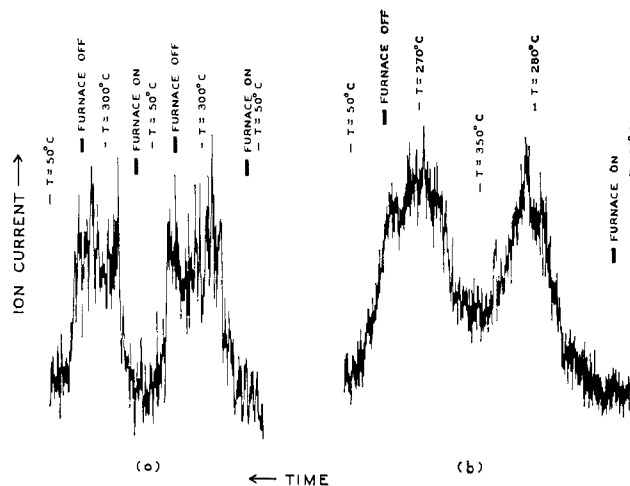


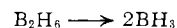
Fig. 1.—(a) Recording of the  $m/e = 14$  ion peak as a function of furnace temperature measured by a platinum:platinum-rhodium (90-10) thermocouple centered in the furnace and gas stream. An ionizing voltage of 13.0 v., ion trap current of 1  $\mu$ a. and an electron-multiplier voltage of 2000 v. were used. (b) Recording of the  $m/e = 13$  ion peak as a function of furnace temperature. An ionizing voltage of 12.5 v. was used. Other conditions were the same as (a).

13,  $BH_2^+$ , ion peak in the same manner indicates that  $BH_2$  is also present (Fig. 1b).

These experiments were completely reproducible both with pure diborane and mixtures of diborane with argon or hydrogen. Because of the basic experimental arrangement and the use of a bakeable, welded, stainless steel vacuum envelope with copper gasketed flanges, no background was observed at  $m/e = 13$  or 14 at the voltages indicated in Fig. 1. Using pure dilutant gas and examining these or other ion peaks as a function of temperature produced no change in the ion intensity even at higher ionizing voltages. Stopping the flow of diborane eliminated  $BH_3$  and  $BH_2$  production. Examination of the  $B_2H_5^+$  ion peak above its appearance potential showed an expected decrease in intensity with furnace temperature as diborane was destroyed. The  $m/e = 17$  and  $m/e = 15$  ion peaks were examined using the deuterated  $B^{11}$  compound.  $BD_3$  and  $BD_2$  were observed in the same manner eliminating the possibility that impurities are the cause of this effect.

The remaining alternative is that the temperature variation of  $BH_3^+$  and  $BH_2^+$  is being caused by the fragmentation of some other unstable species. Appearance potential measurements given below rule out the possibility that  $BH_3$  fragmentation is causing the temperature variation of the  $BH_2^+$  ion peak.  $BH_4$  was not observed and would hardly be expected to be stable at these temperatures. Simple activation energy considerations indicate that other conceivable secondary reactions would be improbable.

Our conclusion, then, is that the borane molecule and the boryl radical are definitely present in the pyrolysis of diborane. It is apparent that the initial step in the pyrolysis is a combination of the processes



A qualitative examination of the recombination of these species has been made. Addition of argon to diborane markedly decreased  $BH_3$  recombination but

(1) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(2) V. V. Subbanna, L. H. Hall, and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 1304 (1964).

(3) G. C. Eltenton, *J. Chem. Phys.*, **10**, 403 (1942); **15**, 455 (1947).

(4) J. A. Hipple and D. P. Stevenson, *Phys. Rev.*, **63**, 121 (1943).

(5) F. P. Lossing, *Ann. N. Y. Acad. Sci.*, **67**, 499 (1957).

(6) S. N. Foner and R. L. Hudson, *Advances in Chemistry Series*, No. 36, R. F. Gould, Ed., American Chemical Society, Washington, D. C., 1962, p. 34.

(7) A. J. B. Robertson, "Mass Spectrometry," John Wiley and Sons, Inc., New York, N. Y., 1954.

(8) For example of similar evidence see: S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **21**, 1608 (1953); **23**, 1364 (1955).

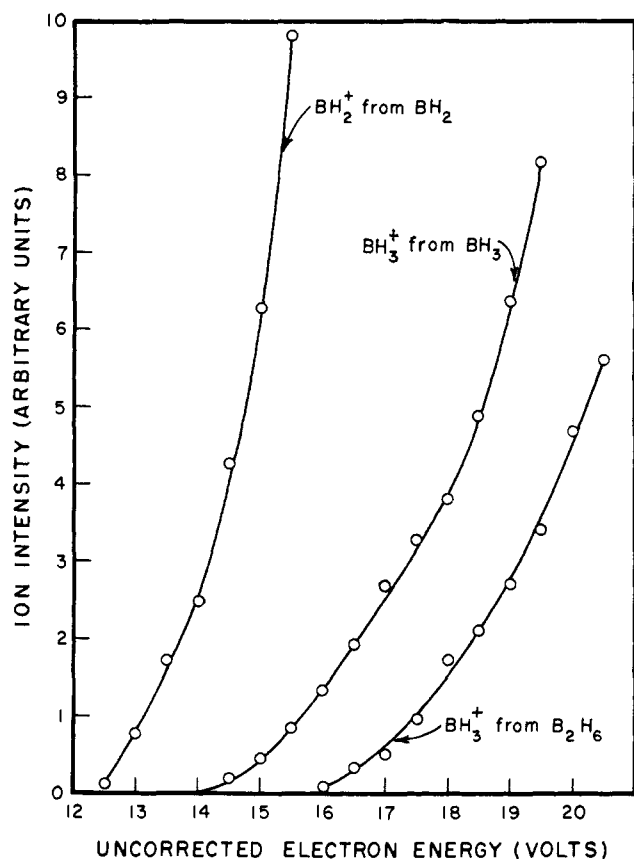


Fig. 2.—Appearance potential curves of ions from  $B_2H_6$ ,  $BH_3$ , and  $BH_2$ .

did not affect  $BH_2$ ,  $BH_4$  recombination. This is to be expected on the basis of the proposed steps if  $BH_4 \rightarrow BH_2 + H_2$  is fast.

Appearance potential measurements provided good confirmation of the results, an estimate of the relative concentration of these species, and ionization potentials. Several points are to be noted with respect to these measurements. First, maximum borane and boryl radical concentrations were obtained when over 80% of the diborane was destroyed. Thus, even at ionizing voltages high enough to produce dissociative ionization of diborane, the ion current measured was due nearly exclusively to the unstable species. Second, the abundance of  $BH_3^+$  from dissociative ionization of diborane is very small, being only 0.5% of the intensity of  $B_2H_5^+$  at 70 v. Third, the stability of the flow system allowed the rather low signal-to-noise ratio to be overcome to a large extent by making relatively long measurements at each voltage. The results are presented in Fig. 2. From these data it may be inferred that the  $BH_2$  concentration is about two to three times as large as the  $BH_3$  concentration under these conditions. A preliminary analysis of the data by plotting log ion intensity vs. voltage curves and determining the voltage shift required to match the  $BH_3^+$  ion curve from diborane gave the following ionization potentials:  $I(BH_3) = 11.4 \pm 0.2$  and  $I(BH_2) = 9.8 \pm 0.2$  e.v. using the appearance potential of  $BH_3^+$  from diborane ( $13.1 \pm 0.2$  e.v.) for calibration. This value has been determined previously<sup>9</sup> using argon as a standard and this and the appearance potential of

$BH_2^+$  ( $13.4 \pm 0.1$  e.v.) were checked in an independent measurement. The appearance potential of  $B_2H_5^+$  from diborane with the furnace on was equal to the value obtained with the furnace off.

Previously estimated values for  $I(BH_3)$  are in excellent agreement with this measured value.<sup>9,10</sup> Estimated values for  $I(BH_2)$  range between 0.5<sup>10</sup> and 1.7<sup>9</sup> e.v. lower than this measured value. Considering the assumptions made in estimates of this nature, the upper value agrees quite well with that measured.

In the usual manner,<sup>11,12</sup> simple calculations using the measured ionization potentials and appearance potentials and the known value of  $D(H-H)$  give values of  $D(BH_3-BH_3) = 1.7$  and  $D(H_2B-H) = 3.2$  e.v. Once more the agreement with previous deductions is very good.<sup>10,13</sup> Although these values are subject to the limitations of electron impact studies<sup>11,12</sup> they lend strong confirmation to the assignment of these species as  $BH_2$  and  $BH_3$ .

Two other systems have been briefly examined for  $BH_2$  and  $BH_3$ . The pyrolysis of borane carbonyl,  $BH_3CO$ , yielded  $BH_3$  and  $CO$  upon heating as might be expected. Both  $BH_2$  and  $BH_3$  were detected in the pyrolysis of tetraborane.

More detailed work is in progress and a complete report will be presented later.

**Acknowledgment.**—This work was done under the auspices of the United States Atomic Energy Commission.

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(11) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths & Co. Ltd., London, 1958.

(12) C. A. McDowell, "Methods of Experimental Physics," D. Williams, Ed., Academic Press, New York, N. Y., 1962, p. 525.

(13) M. E. Garabedian and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 176 (1964).

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### Carbonyl-Stretching Absorptions in the Pentacarbonyl Hydrides of Manganese, Technetium, and Rhenium

Sir:

A recent structure determination for  $HMn(CO)_5^2$  prompts us to report a new interpretation of its carbonyl absorptions which was originally suggested<sup>1b</sup> by results of recent studies of the pentacarbonyl halides<sup>3</sup> and structural developments on other metal hydride complexes.<sup>4</sup> These ideas apply equally well to the pentacarbonyl hydrides of Tc and Re whose absorptions<sup>5</sup>

(1) (a) Work supported by Grant No. GP 1696 from the National Science Foundation; (b) the spectral interpretation presented here is taken in a large measure from pp. 48-68 of the dissertation presented by D. K. Huggins in partial fulfillment of the requirements toward a Ph.D. at the University of California, Los Angeles, Oct., 1963.

(2) Reported by J. A. Ibers at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964 (paper no. 50, Symposium on Metal Carbonyls and Related Complexes), cf. S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2288 (1964).

(3) (a) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962); (b) I. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962).

(4) S. S. Bath and L. Vaska, *J. Am. Chem. Soc.*, **85**, 3500 (1963).

(5) (a) The maxima of the two principal bands in cyclohexane solution for the three pentacarbonyl hydrides have been reported: J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962); (b) spectra showing the principal absorptions of the pentacarbonyl hydrides in dilute solution have also been displayed previously [D. K. Huggins and H. D. Kaesz, *Can. J. Chem.*, **41**, 1250 (1963)], but the present spectra represent samples of even greater purity.

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