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A Mass Spectrometric Investigation of the Low-Pressure Pyrolysis of Diborane

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Received May 11, 1970

Diborane, B_2H_6, thermally decomposes in a boron-coated Pyrex reactor over the pressure range of 5–120 mTorr into borane (BH_3), hydrogen, and boron, by a reaction which is *ca.* 0.5 order in diborane and which has an activation energy of 26 kcal/mol. The hydrogen and boron are produced by the decomposition of borane in a reaction which has an activation energy of *ca.* 10 kcal/mol. Only a small isotope effect is observed and the nature of the thermal decomposition of B_2H_6 at low pressures is dominated by strong surface effects.

A number of mass spectrometric studies of the thermal decomposition of diborane have appeared in the literature.[1–4] Most of these studies were directed toward the identification of the primary products of decomposition and the energetics involved.[5] We have expanded our original examination to try and elucidate the mechanism of the initial stages of the pyrolysis at low pressures. In contrast to the previous studies the main objective here was to provide information on the decay of BH_3. This was a necessary step in our search for conditions for the production of borane at partial pressures high enough for kinetic studies. Taken in conjunction with our concurrent studies, the results presented below are of value in understanding one aspect of the reactivity of borane.

Experimental Section

Two 3-cm^3 Pyrex glass electrically heated reactors were used in this study. In one reactor (F1) the average number of wall collisions per molecule (ν_w) is 2.8×10^4 and in the other (F2) 1.7×10^5. At room temperature a nitrogen molecule spends an average time of 0.50 sec in F1 and 3.0 sec in F2. The other details and dimensions of the reactors have been given previously. The reactors are sampled through thin-edged orifices and the pressure in the reactor is always low enough so that flow through the sampling orifice is molecular. The efflux of the reactor is collimated into a well-defined beam using a three-stage differentially pumped system of orifices and slits. The molecular beam is crossed with an electron beam and the ions produced are mass analyzed using a magnetic sector mass spectrometer. The molecular beam is mechanically modulated at *ca.* 160 Hz and only the output of the spectrometer with the same frequency and proper phase is amplified and recorded in these experiments. The modulated molecular beam technique assures unambiguous sampling as has been shown elsewhere.[7] A complete description of our present experimental apparatus is given in ref 8.

Diborane was prepared by the method of Jeffers.[9] After purification by trap to trap distillation, the diborane was stored at 77°K until use. The diborane was admitted to the reactor at room temperature through a variable leak. Reactor temperatures were varied so that any "hysteresis" in the decomposition would be observed. Sensitivity calibrations for diborane and hydrogen were made by measuring the pertinent ion intensities at a given pressure. Pressures were measured with a thermocouple gauge which was continually calibrated against a McLeod gauge for each gas. The pressures are known absolutely to ±10%. B_2D_6 was prepared in the same manner except that $NaBD_4$ was used in the preparation. The isotopic purity of the B_2D_6 was about 85% as determined from the mass spectrum.

Results

Products, Stoichiometry, and Mechanism.—Products of the decomposition of diborane were sought and identified in the manner described previously.[8] Changes in the intensities of the following ions were observed: $B_2H_x^+$ ($x = 0$–6), BH_x^+ ($x = 0$–3), and H_2^+. Selected ion intensities as a function of temperature are shown in Figure 1, for reactor F1. The ratio of the intensity of m/e 27 to the intensity of m/e 27 at 300°K (denoted as $27^+/27_0^+$) shows that decomposition sets in at about 490° K.[10] Hydrogen was the major product observed, and its production is illustrated by the increase in the m/e 2 ion intensity. Also shown in Figure 1 is the residual ion intensity of m/e 14. This is the intensity remaining after removal of the contribution due to the ion fragmentation of diborane, assuming that the latter is independent of temperature.[11] We attribute this residual intensity to the formation of borane. In these reactors, which were not designed primarily for the identification of BH_3, the concentration of BH_3 was too low to obtain accurate appearance potentials. As will be shown below, the concentration of BH_3 was about an order of magnitude less than that found in a study of BH_3CO.[12] The ratio of m/e 13 to

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(1) T. P. Fehlner and W. S. Koski, *J. Amer. Chem. Soc.*, **86**, 2733 (1964).

(2) E. J. Sinke, G. A. Pressley, Jr., A. B. Baylis, and F. E. Stafford, *J. Chem. Phys.*, **41**, 2207 (1964).

(3) A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Amer. Chem. Soc.*, **88**, 2428 (1966).

(4) J. H. Wilson and H. A. McGee, *J. Chem. Phys.*, **46**, 1444 (1967).

(5) The interpretation of the original appearance potential data[1] in terms of both BH_3 and BH_2 is incorrect. This work should have been properly reported as follows. The appearance potentials of BH_3^+ and BH_2^+ shift to lower energies on activation of the reactor by 2 and 3 eV, respectively. This shift is evidence for the formation of at least one monoborane species. This does not mean that the difference in the appearance potential of BH_3^+ from B_2H_6 and the ionization potential of BH_3 (2–3 eV) is equal to $D(H_3B{-}BH_3)$. It means only that $D(H_3B{-}BH_3) \leq 2$–3 eV. Finally, the mechanism[6] based on the active participation of BH_2 in the thermal system is no longer tenable.

(6) T. P. Fehlner, *J. Amer. Chem. Soc.*, **87**, 4200 (1965).

(7) S. N. Foner, "Advances in Atomic and Molecular Physics," Vol. 2, D. R. Bates and I. Estermann, Ed., Academic Press, New York, N. Y., 1966, p 385.

(8) T. P. Fehlner, *J. Amer. Chem. Soc.*, **90**, 4817 (1968).

(9) W. Jeffers, *Chem. Ind.* (*London*), 431 (1961).

(10) The initial decrease in this ratio is due to the increase in the average velocity of the beam molecules with increasing temperature.

(11) The intensity of m/e 14 from B_2H_6 is less than 1% of the most intense ion in the spectrum. No change in the fragmentation pattern of diborane was observed up to the decomposition temperature.

(12) T. P. Fehlner and G. W. Mappes, *J. Phys. Chem.*, **73**, 873 (1969).

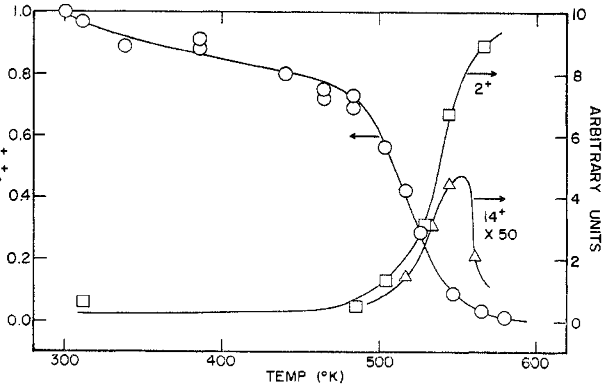

Figure 1.—Extent of reaction and product yields for diborane in reactor F1 as a function of temperature. Circles represent the normalized $B_2H_5^+$ intensity ($27^+/27_0^+$), squares the amount of H_2 (2^+) produced, and triangles the amount of BH_3 (14^+) produced.

14 was 4 ± 2 which is consistent with the value of 3 observed previously.[3,13,14] Hydrides with three and four boron atoms were sought but none was observed.

A black coating of boron was observed on the interior of the reactor. This material was analyzed on a Norelco X-ray diffractometer and showed none of the sharp lines characteristic of the several forms of crystalline boron. Lack of sufficient sample made it necessary to estimate its elemental composition from analysis of a separate material, namely, that deposited in a quartz tubular reactor under similar conditions of temperature and pressure. The latter analyzed as at least 97.4% boron and less than 1% hydrogen. It also appeared to be amorphous under the same type of X-ray analysis. Therefore it is concluded that the interior coating serving as the reaction surface is very probably pure amorphous boron. Support for this conclusion is found in a recent review[15] where it is pointed out that the thermal decomposition of boron hydrides is a good source of highly pure boron.

Calibration for hydrogen gas and diborane was carried out and the number of moles of hydrogen produced per mole of diborane lost was calculated as a function of temperature. The value obtained was 1.6 ± 0.8 (average deviation) and, although scattered, was independent of temperature, pressure, and average reactor residence time. The hydrogen mass balance is low and this may be evidence for the formation of nonvolatile higher hydrides. There are reasons, however, why the determination of H_2 is inherently less accurate than that of higher molecular weight species. First, in our spectrometer the major background peak was *m/e* 2 which resulted in poor signal to noise ratios. Second, the temperature variation of the sensitivity for H_2 was assumed to be the same as for CO and B_2H_6. Finally the low hydrogen content of the solid leads us to believe that the discrepancy in the hydrogen mass balance is not real. Calibration for BH_3 was not possible in these experiments but a relative sensitivity reported in an independent study[13] is available and allowed the calculation of the yield of this species. For reactor F1 the yield of BH_3 is *ca.* 0.6% of theoretical at 545° K. The yield in reactor F2 is less than 0.8%. Approximate upper limits on the production of higher hydrides were calculated from intensity and signal to noise considerations. We find that higher hydrides cannot account for more than 2% of the diborane lost. This means that B_5H_9, for example, cannot be present at levels higher than 1 part in 125 of the initial diborane.[16] The stoichiometry can be summarized in the equations

$$B_2H_6 \xrightarrow{0\text{–}80\%} B(s) + 3H_2$$

$$B_2H_6 \xrightarrow{0\text{–}1\%} BH_3$$

$$B_2H_6 \xrightarrow{<2\%} B_3H_x,\ B_4H_x,\ B_5H_x$$

A very simple set of reactions can be written to account for the net reaction observed

$$B_2H_6 \longrightarrow 2BH_3$$

$$BH_3 \longrightarrow B(s) + {}^3/_2H_2$$

This mechanistic scheme is not unique, but, as will be pointed out later, it is the simplest one which fits the experimental facts of this and other studies. With the above mechanism we can calculate a *b* (probability of reaction per collision) for the loss of BH_3 from the equation

$$b\nu_w = [B/(1 - B)][2(B_2H_6)/(BH_3)]$$

$$b\nu_w = 2(H_2)/3(BH_3)$$

where *B* is the fractional yield, *i.e.*, $(B_2H_6)/(B_2H_6)_0$, and ν_w is the average number of wall collisions.[17] The results of these calculations for B_2H_6 loss and H_2 formation are shown in Figure 2 at a number of temperatures. The agreement of these results with values of the same constant for the thermal decomposition of

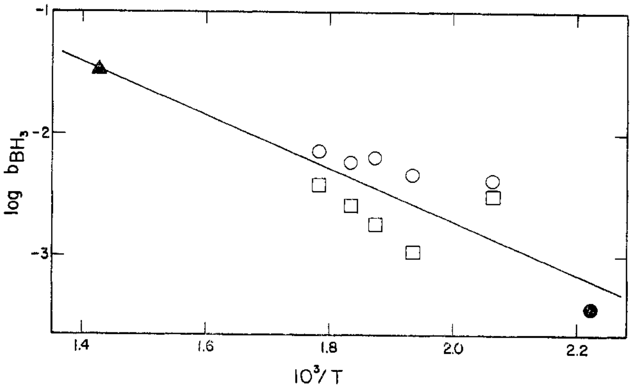

Figure 2.—Collisional efficiency for the loss of BH_3 at the walls in reactor F1 as a function of temperature. The line is the least-squares fit to all the data points. Circles are values based on B_2H_6 disappearance; squares, on H_2 formation. The solid circle is the value obtained in ref 12 and the solid triangle is the value obtained in ref 13.

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(13) G. W. Mappes and T. P. Fehlner, *J. Amer. Chem. Soc.*, **92**, 1562 (1970).

(14) O. Herstad, G. A. Pressley, Jr., and F. E. Stafford, *J. Phys. Chem.*, **74**, 874 (1970).

(15) J. G. Bower in "Progress in Boron Chemistry," Vol. 2, R. J. Brotherton and H. Steinberg, Ed., Pergamon Press, New York, N. Y., 1970, p 240.

(16) This agrees with the previous study[3] in that the pentaboranes reported were present as 1 part in 10^3 of the initial diborane or less: F. E. Stafford, private communication.

(17) See ref 12 for an explanation of this notation.

BH_3 in the borane carbonyl system[12,13] is fairly good and we take this as confirmation of the above mechanism. The combined results show that there is an appreciable activation energy of *ca.* 10 kcal for the destruction of BH_3. This observation was useful in developing a higher yield synthetic technique for the preparation of BH_3.[13]

Kinetics.—These data were treated in the fashion described in previous articles.[12,18–20] The data may be fitted to the equation

$$B/(1 - B)^n = \nu_w(g_0)^{n-1}h(T)$$

where g_0 is the initial density of collisions and $h(T)$ is a concentration independent function of temperature.[21] At a constant temperature, the yield of the reactor is examined as a function of diborane pressure and the apparent reaction order n is determined from a plot of log BP_0 *vs.* log $(1 - B)P_0$ where P_0 is the initial pressure of diborane. Representative data are shown in Figure 3 for reactor F2 at two temperatures. The least-squares slope of straight lines through the points is 0.52 at 552°K and 0.55 at 528°K. A number of runs are shown at 528°K to illustrate the day to day reproducibility of temperature and concentration measurements. For reactor F1 the order observed at 528°K was 0.77. Knowing n, $h(T)$ can be determined. The data on $h(T)$ for both reactors are plotted in an Arrhenius type form in Figure 4 on the basis of an order of 0.6. The least-squares fit to the data on protonated diborane is log $h(T) = 15.0 - 5710/T$ (molecules/cm^2)$^{0.4}$.

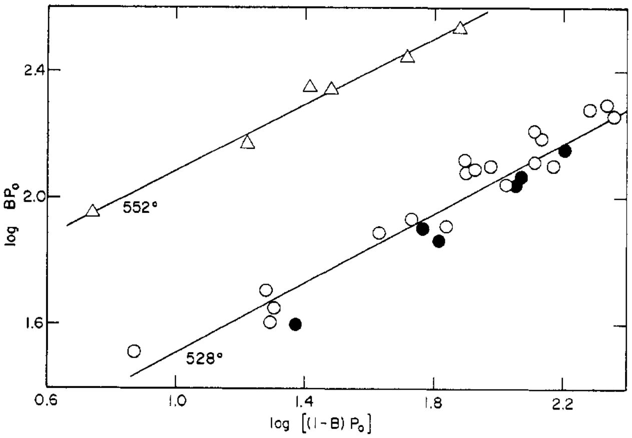

Figure 3.—Apparent-order plot for the disappearance of diborane in reactor F2. Circles refer to 528°K; triangles, to 552°K. Solid circles represent data on B_2D_6; all other points, B_2H_6.

As has been shown previously,[12] a useful diagnostic tool of the nature of the reaction occurring at very low pressures is an examination of the isotope effect. For a homogeneous unimolecular reaction at the low-pressure limit one expects to observe a large inverse statistical isotope effect. On the other hand, for a heterogeneous reaction much smaller isotope effects are expected. The results on the decomposition of B_2D_6 are shown in Figures 3 and 4. Within experimental error the rates (orders and $h(T)$'s) are equal. At best there is a small normal isotope effect. This should be compared with the large inverse isotope effect observed for the homogeneous decomposition of BH_3CO at low pressures and the small normal isotope effect observed for the decomposition of BH_3CO involving the wall.[12]

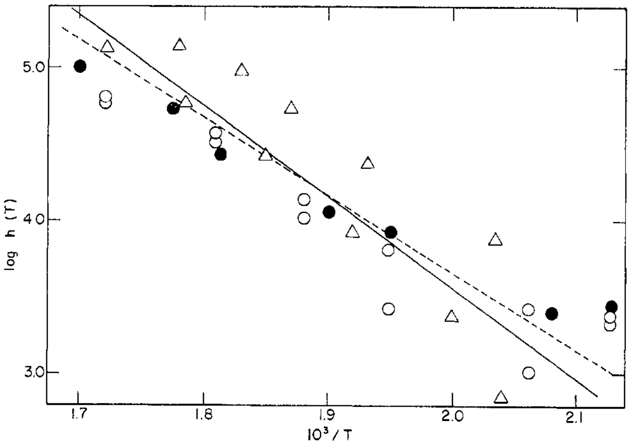

Figure 4.—Log $h(T)$ *vs.* $10^3/T$ for loss of diborane. Triangles refer to reactor F1; circles, to reactor F2. Solid circles and dotted line (least squares) represent data on B_2D_6; all other points and solid line represent B_2H_6 data.

Discussion

The observations of this study may be simply summarized. Diborane decomposes by a reaction which is less than first order in B_2H_6 and which has an apparent activation energy of 26 kcal/mol. In spite of the fact that the reaction is carried out at very low pressures, little or no isotope effect is observed. These observations strongly indicate that the reaction, under the conditions employed here, is dominated by surface interactions. The reaction order, which tends toward one with decreasing density, is indicative of a saturation phenomenon, the activation energy is too low for unimolecular dissociation, and the large inverse statistical isotope effect expected for homogeneous unimolecular decompositions at the low-pressure limit is not observed. The volatile products of the decomposition are borane and hydrogen with no measurable amounts of higher hydrides being produced. In addition, a solid deposit analyzed to be >97% boron was observed thereby effectively excluding nonvolatile higher hydrides. In terms of products, the reaction is a simple one and is consistent with the simple mechanism outlined above. However, it is possible that the direct route $B_2H_6 \rightarrow 2B(s) + 3H_2$ is important in the mechanism. If this reaction were in fact the only one leading to stable products, the formation of BH_3 would assume a minor role as the product of a side reaction. These experiments taken by themselves are not sufficient to rule out this path in a direct manner. However, consider what would obtain if, for example, both routes were equally important. Since about half of the diborane would be decomposing initially to BH_3, the true

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[18] T. P. Fehlner, *J. Amer. Chem. Soc.*, **89**, 6477 (1967); **90**, 5947 (1968).

[19] P. LeGoff, *J. Chim. Phys. Physicochim. Biol.*, **53**, 359, 369, 380 (1956).

[20] See also S. W. Benson and G. N. Spokes, *J. Amer. Chem. Soc.*, **89**, 2525 (1967).

[21] $h(T)$ is related to a reaction rate constant.[12]

values for the collisional efficiency, *b*, for loss of BH_3 would be half of our calculated values. Similar considerations hold for cases where the direct route predominates over the BH_3 route: the values for *b* become smaller as BH_3 becomes less important as an intermediate. We see, however, that by taking the BH_3 route to be the only important one, the values obtained for *b* agree quite well with values obtained in two other independent studies (Figure 2). Therefore we relegate the direct conversion of B_2H_6 to H_2 and boron to a minor role at best.

Hydrogen gas is also a product of the pyrolysis of diborane at higher pressures, lower temperatures, and longer times.[22] There is a temptation to apply the results presented here to an interpretation of the data on the overall pyrolysis under other conditions. For example, Bragg, *et al.*,[23] found that the activation energy for the rate-controlling step leading to the formation of hydrogen is *ca.* 26 kcal, which is the same as our value. In addition their first-order rate constant for the production of H_2 at 353°K, when extrapolated to 530°K, predicts our $B/(1 - B)$ for B_2H_6 at 530°K within a factor of 10. Despite this agreement it is doubtful that BH_3 is a major source of hydrogen during pyrolysis of B_2H_6 under conditions such as those used by Bragg, *et al.* There are two good reasons for this conclusion. First, in the latter study, the major boron-containing products are volatile and nonvolatile (polymer) hydrides. There is no evidence for the formation of elemental boron under conditions such as theirs. Second, in the latter type system there is a large normal isotope effect associated with the production of hydrogen.[24] Therefore, there is no direct connection between the results of this study and the results of the studies under different conditions.[22]

Our major conclusion is that there exists a fruitful area of research on the reactions of BH_3 at lower temperatures where it is less subject to the decomposition to the elements.

Acknowledgments.—This work was supported by a National Science Foundation grant, NSF-GP-6820.

[22] R. L. Hughes, I. C. Smith, and E. W. Lawless, "Production of the Boranes and Related Research," R. T. Holzmann, Ed., Academic Press, New York, N. Y., 1967, pp 116–124.

[23] J. K. Bragg, L. V. McCarty, and F. J. Norton, *J. Amer. Chem. Soc.*, **73**, 2134 (1951).

[24] R. E. Enrione and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **18**, 103 (1961).

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Rearrangement in Borane Adducts of Trimethylsilylmethylenedimethylsulfurane[1]

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Received June 2, 1970

Boron halide, borane, and trimethylboron adducts of the silyl-substituted sulfonium ylide $(CH_3)_3SiCHS(CH_3)_2$ are readily formed. The borane and alkylboron adducts rearrange at low temperature with simultaneous loss of dimethyl sulfide to give *sym*-bis(trimethylsilylmethyl)diborane and 1-(trimethylsilylmethyl)ethyldimethylborane, respectively. These rearranged products were isolated and characterized. A trimethylamine adduct with the dialkyldiborane could be converted into the asymmetrical borane cations $(CH_3)_3SiCH_2BHN(CH_3)_3py^+$ and $(CH_3)_3SiCH_2BHN(CH_3)_3P(CH_3)_3{}^+$.

Rearrangements of alkyl groups from boron to an adjacent carbon are of considerable current interest. In one class of such rearrangements there is a simultaneous migration of a base molecule, base–$CH_2BR_3 \rightarrow$ base–BR_2CH_2R. Tufariello and Lee, for example, reported the migration of an *n*-hexyl group in the reaction of trihexylborane and $(CH_3)_2SCH_2$ in solution.[3] Similar rearrangements are known to occur at higher temperature with borane adducts of phosphorus- and nitrogen-stabilized ylides.[4,5] The isolable sulfonium ylide $(CH_3)_2SCHSi(CH_3)_3$,[6] I, provides novel possibilities for the study of these rearrangements of sulfonium ylides in the absence of reactive solvent, and indeed this ylide does form some boron adducts that readily rearrange. The adduct with diborane is of particular interest in that it leads to a methyl-substituted diborane which would be difficult to prepare otherwise.

Experimental Details

Solvents used were reagent grade; tetrahydrofuran was purified by distillation form lithium aluminum hydride. Boron trichloride (Trona, electronic grade), boron trifluoride (Matheson), and diborane (Callery) were obtained commercially and used without additional purification. Boron trimethyl was prepared from boron trifluoride etherate and methylmagnesium bromide in ether according to standard directions[7] and purified by low-temperature distillation.

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[1] Presented at the 5th Midwest Regional meeting of the American Chemical Society, Kansas City, Mo., Oct 29–31, 1969.

[2] Author to whom inquiries should be addressed.

[3] J. J. Tufariello and L. T. C. Lee, *J. Amer. Chem. Soc.*, **88**, 4757 (1966).

[4] R. Köster and B. Rickborn, *ibid.*, **89**, 2782 (1967).

[5] W. K. Musker and R. O. Stevens, *Inorg. Chem.*, **8**, 255 (1969).

[6] N. E. Miller, *ibid.*, **4**, 1458 (1965).

[7] H. C. Brown, *J. Amer. Chem. Soc.*, **67**, 375 (1945).